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OF

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A DICTIONARY

OF

APPLIED CHEMISTRY

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ABBREVIATIONS

OF THE TITLES OF JOURNALS AND BOOKS.

A.	Liebig's Annalen der Chemie.
A. a.	Annales Agronomiques.
A. Ch.	Annales de Chimie et de Physique.
P. Am. A.	Proceedings of the American Academy of Arts and Sciences.
Am.	American Chemical Journal.
Ann. M.	Annales des Mines.
Am. S.	American Journal of Science.
A. C. J.	Journal of the American Chemical Society.
Am. Ch.	American Chemist.
Am. J. Pharm.	American Journal of Pharmacy.
An.	The Analyst.
Ar. N.	Archives néerlandaises.
Ar. Ph.	Archiv der Pharmacie.
B.	Berichte der deutschen chemischen Gesellschaft.
Bl.	Bulletin de la Société chimique de Paris.
B. B.	Berliner Akademie-Berichte.
B. C.	Biedermann's Centralblatt für Agricultur-Chemie.
B. J.	Berzelius' Jahresberichte.
B. M.	Berliner Monatsberichte.
Bentl. a. T.	Bentley and Trimen. Medicinal Plants.
Bl. Ph.	Bulletin de Pharmacie.
C. S. Mem.	Memoirs of the Chemical Society of London.
C. J.	Journal of the Chemical Society of London.
C. J. Proc.	Proceedings of the Chemical Society of London.
C. N.	Chemical News.
C. R.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences —Paris.
C. C.	Chemisches Central-Blatt.
D. P. J.	Dingler's polytechnisches Journal.
Fl. a. H.	Flückiger and Hanbury. Pharmacographia 2nd Ed.
Fr.	Fresenius' Zeitschrift für analytische Chemie.
J.	Jahresbericht über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
J. A.	Jahresbericht der Agrikultur-Chemie.
J. C. T.	Jahresbericht für Chemische Technologie.
J. M.	Jahrbuch für Mineralogie.
J. Ph.	Journal de Pharmacie et de Chimie.
J. pr.	Journal für praktische Chemie.
L. V.	Landwirthschaftliche Versuchs-Stationen.
M.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
M. S.	Le Moniteur Scientifique.
N. J. P.	Neuer Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorf.
P. M.	Philosophical Magazine.
P.	Poggendorff's Annalen der Physik und Chemie.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Central-Blatt.
Ph. Centh.	Pharmaceutische Central-halle.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
R. P.	Repertorium für die Pharmacie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz. B. or *Sitz. W.*	Sitzungsberichte der K. Akademie zu Wien.
Tr.	Transactions of the Royal Society.
U.	Ure's Dictionary of Arts, Manufactures and Mines. 7th Ed.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.

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A
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APPLIED CHEMISTRY.

EAU DE COLOGNE *v.* Perfumes.

EAU DE JAVELLE. Solution of sodium hypochlorite *v. Bleach Liquor*, art. Chlorine.

EAU DE LUCE. *Aqua Luciæ.* A milky liquid containing oil of amber, alcohol, and ammonia (*v.* Amber, oil of).

EBONITE. *Sulphurised caoutchouc v.* India-rubber.

EBULLIOSCOPE. An instrument for determining the strength of spirits of wine by means of its boiling-point.

ECBOLINE *v.* Ergot of rye.

ECGONINE *v.* Vegeto-alkaloids.

E. C. POWDER *v.* Explosives.

ECHITAMINE *v.* Dita bark.

ECHITENINE *v.* Dita bark.

ECHURIN. A colouring matter obtained by adding 12 parts of nitric acid (36°B.) to a mixture of 3 parts of flavin (diamidobenzophenone) and 5 parts of picric acid, and evaporating to dryness on a water bath. Echurin is said to dye with a reddish-yellow shade (Leeds Manufacturing Co., Brooklyn, Germ. Pat. 26,186, April 4, 1883, expired August 1883).

EDULCORATION. The act of washing insoluble matter so as to remove any soluble impurity.

EFFLORESCENCE. This term is applied to two or three different phenomena, characterised by the formation of a loose pulverulent deposit on the surface of a solid body.

1. Crystallised salts are said to effloresce when they lose their water of crystallisation and fall to powder, *e.g.* normal sodium carbonate, $Na_2CO_3.5aq$.

2. The formation of a pulverulent crystalline deposit on the surface of a porous body, in consequence of the crystallisation of a salt existing in solution within its pores, or formed from materials existing therein, is also called efflorescence, *e.g.* the crystallisation of potassium nitrate on the surface of the earth or in caves, as in India, or on saltpetre plantations; of sodium sulphate and carbonate on walls; of alum on alum-slate; of ferrous sulphate on iron pyrites, &c. In all these cases the solution of the salt is drawn by capillary action to the surface of the solid body, and there crystallises in consequence of the evaporation of the water.

3. The term efflorescence is likewise applied to the effect which sometimes takes place when a saline solution is left to evaporate slowly in an open vessel. The solid salt separates in dendritic crystals just where the surface of the liquid touches the side of the vessel, and the solution, rising by capillarity between these crystals, forms a fresh crystallisation just above the first layer; and this process is continually repeated till the crystallisation thus formed extends over the edge of the vessel, and sometimes down to the table on which it stands. Sal-ammoniac and other ammonia-salts often effloresce in this manner. The effect may be prevented to a certain extent by greasing the edge of the vessel, or better, by quickly boiling the solution, or evaporating it, by heat from above (*v.* Watts' Dictionary of Chemistry).

EGG ALBUMIN *v.* Albuminoids.

EGYPTIAN BLUE. This is a blue colouring matter which was used by the Romans in the first few centuries of the Christian era, but ceased to be manufactured about the time of the invasion of the barbarians. It figures in several beautiful frescoes in the Vatican, and has also been found at Pompeii. Fouqué has discovered the composition to be that of a double silicate of calcium and copper, $CaO,CuO,4SiO_2$, devoid even of traces of alkali. The substance is crystalline, and is hardly attacked by any chemical reagents, which explains the perfect state of its preservation in the paintings for which it was employed 1,900 years ago. It may be prepared at a bright-red heat, but this temperature must not be exceeded, as it is then decomposed into cuprous oxide, *wollastonite*, and a clear light green glass. The higher the temperature the more of the latter is formed, and finally, wollastonite disappears entirely. By the old method of preparation, described by Vitruvius, fine sand and soda are intimately mixed with copper filings, then moistened with water, formed into cakes, and the latter dried. The cakes are then fused in an earthen pot until the blue colour is produced. Fouqué finds this method practicable, but uses potassium sulphate in preference to soda as a flux. He has not found it possible to replace chalk or lime by magnesia. The ancient Romans employed a large excess of silica, whilst Fouqué employs more basic mixtures, finally purifying the product with hydrochloric acid. The exquisite colour of this mineral body, the fact that it is absolutely unaffected by moisture, light, and most chemical reagents, as well as the facility and the low price of production, render it desirable that its manufacture should be again resumed (F. Fouqué, C. R. 108, 325–327, and S. C. I. 8, 291).

EGYPTIAN BROWN *v.* Pigments.

EIKONOGEN *v.* *Amido-β-naphthol sulphonic acid*, art. Naphthalene.

ELÆOPTENE. The volatile portion of an essential oil, used in contradistinction to the *stearoptene* or solid portion.

ELAÏDIC ACID $C_{18}H_{34}O_2$. A solid isomeric modification of oleic acid obtained by the action of nitrous acid upon olive oil, saponifying the glyceride (elaïdin) so formed, and decomposing the salt by hydrochloric or sulphuric acid. May also be obtained by the action of nitrous acid upon oleic acid, or by decomposing barium oleate with fuming nitric acid. M.p. 45·5. Soluble in alcohol and ether. Solutions have an acid reaction. The melted acid gradually absorbs oxygen from the air, and becomes permanently liquid. It may be distilled unchanged under diminished pressure. Heated with potash it is converted into acetate and palmitate of potassium with evolution of hydrogen:

$$C_{18}H_{34}O_2 + 2KHO = C_2H_3KO_2 + C_{16}H_{31}KO_2 + H_2.$$

Elaïdic acid dissolved in benzene, toluene, ligroïn, or chloroform, and mixed with caustic soda and shaken gives a brilliant phosphorescence (Radziszewski, A. 203, 305). Treated with dilute solution of potassium permanganate in presence of potash it is converted into a dioxystearic acid, which differs from the corresponding compound obtained from oleic acid by its lower melting-point (99·5°), and its greater solubility in alcohol and ether (A. Saytzew, B. 19, 21); *v.* Oleic acid.

Elaïdin, a solid isomeride of olein, is obtained by the action of nitrous acid upon olein, and is probably a triglyceride $C_{57}H_{104}O_6$. It melts at 32°; is nearly insoluble in alcohol, readily soluble in ether. The *Unguentum oxygenatum* and *U. citrinum* of the pharmacopœias, prepared by the action of nitric acid upon hog's lard, contain impure elaïdin.

ELALDEHYDE *v.* Aldehyde.

ELAOMARGARIC ACID $C_{17}H_{30}O_2$. An acid, melting at 41°, obtained by the saponification of eläococca oil with alcoholic potash, and decomposing the *triëläomargarin* thus formed. The glyceride when first formed is liquid, but on exposure to light gradually solidifies. Isomeric with eläostearic (m.p. 71) and eläoleic acid. Eläomargaric acid and eläostearic acid are converted into eläoleic acid when heated to 180° in sealed tubes (Cloëz, Ph. [3] 7, 756).

ELATERIN *v.* Elaterium.

ELATERITE. *Elastic bitumen, Mineral caoutchouc.* A fossil resin, somewhat resembling asphalt, found at Castleton in Derbyshire, in France, Switzerland, &c. Is a soft, flexible, elastic, and readily inflammable substance with a resinous lustre, and a dark-brown colour.

ELATERIUM. The sediment from the juice of the fruit of the *Ecbalium Elaterium* (Richard), or squirting cucumber. The British Pharmacopœia directs the employment of English grown plants (*cf.* Bentl. a. T. 115). Elaterium is a drastic purgative.

Pereira (Mat. Med. 3rd ed. 2, 1742) gives a *résumé* of the work of Braconnot, Clutterbuck, Paris, Marquart, and others on elaterium, and of the discovery of *elaterin* $C_{20}H_{28}O_5$ by Hennell (J. Roy. Inst. 1, 532) and independently by Morries (ed. Med. Surg. J. 35, 339; A. 2, 366). Good specimens of elaterium when extracted with chloroform yield 25 p.c. of elaterin which by recrystallisation is obtained as minute shining six-sided plates. The dose of elaterin is $\frac{1}{40}$ to $\frac{1}{10}$ of a grain, and to it is ascribed the whole of the physiological activity of elaterium. Elaterin is a neutral bitter compound insoluble in water, but soluble in chloroform and hot alcohol. It melts at 200° (Zwenger, A. 43, 360). If sulphuric acid be added to a solution of elaterin in melted phenol a crimson colour is produced which changes to scarlet (Lindo, C. N. 37, 35; Johannson, Fr. 24, 154). For other memoirs *v.* Power (Ph. [3] 5, 645), Flückiger a. Hanbury (Fl. a. H. 293) and Jones and Ransom (Ph. [3] 17, 217).

A. S.

ELECTROPLATING. The process of electroplating depends on the fact that when the solution of a metallic salt is decomposed by an electric current, the metal is deposited on the negative electrode or cathode, and the negative element or radicle is set free at the positive electrode or anode. If the liberated elements act chemically on the solvent or on the electrodes secondary reactions take place, thus, for example, when potassium sulphate K_2SO_4 is split up into potassium and the radicle SO_4, the metal potassium decomposes the water yielding hydrogen and caustic potash at the cathode, whilst oxygen and sulphuric acid are liberated at the anode. If copper electrodes were used in this experiment, the anode would be attacked by the SO_4 or sulphuric acid, forming copper sulphate. The appearance and the properties of a metal deposited from its solution by an electric current depend on the nature of the salt decomposed, on the strength and temperature of the solution, and on the density of the electric current.

The Daniell, Smee, Grove, or Bunsen battery, or a dynamo-machine, may be used as the source of electricity.

The liquid used in *silver-plating* consists of a solution of silver cyanide in potassium cyanide. It is prepared by dissolving pure silver in nitric acid and evaporating the acid liquid to dryness. The operation must be conducted in a glass flask or porcelain basin. The crystalline residue is dissolved in distilled water; from 3 to 5 pints of water are required for each ounce of silver. A solution of potassium cyanide in distilled water is carefully added to the silver nitrate with constant stirring, until it ceases to produce a precipitate. As silver cyanide is soluble in an excess of potassium cyanide, the addition of too much or of too little cyanide alike causes a loss of silver. 108 oz. of silver require 65 oz. of chemically pure potassium cyanide, but as commercial potassium cyanide is far from being a pure product, the percentage of pure cyanide in the commercial article must be determined by experiment before the quantity of commercial cyanide required to convert a given weight of metallic silver can be calculated. After the precipitated cyanide of silver has settled to the bottom of the vessel, the clear liquid is syphoned off and the precipitate repeatedly washed with water. It is then dissolved in a strong solution of potassium cyanide and the mixture diluted with water until it is reduced to the desired strength. Good results are obtained with liquids containing from 1½ to 4 oz. of silver per gallon, but some platers use weaker and others prefer stronger solutions.

The silver cyanide from 1 oz. of silver should be dissolved in about 2 oz. of chemically pure potassium cyanide or a proportionally larger quantity of the commercial salt. This amount of cyanide is not only sufficient to redissolve the silver cyanide, but also provides the solution with free potassium cyanide, the presence of which prevents the formation of an insoluble deposit of silver cyanide on the anode.

Plating liquid is also prepared by the battery process. A strong current is passed through a solution of potassium cyanide (4 oz. to the gallon) using a large silver anode and a small cathode. The anode is weighed from time to time and the operation is interrupted when sufficient silver has been dissolved to yield a solution containing about 1 oz. of silver per gallon. Free hydrocyanic acid may be added to increase the conductivity of the liquid by neutralising the caustic potash formed during the process. Another method is to suspend by silver wires a thick plate of silver in a solution of potassium cyanide. A porous vessel containing a clean strip of iron is placed in the solution and the surface of the liquid in the two vessels must be at the same level. The silver plate is connected with the positive and the piece of iron with the negative wire of a battery of six cells. The potassium cyanide is decomposed, and the cyanogen attacks the silver anode, forming silver cyanide which remains dissolved in the excess of potassium cyanide.

The surface of the articles to be plated is thoroughly cleansed from grease by immersion in a boiling solution of potash and rinsing in water. The subsequent treatment of the objects depends on the nature of the material of which they are composed, the object being to remove all traces of rust or oxide so that a bright surface may be exposed to the plating liquid. Britannia metal is scratch brushed with stale beer, *i.e.* brushed with bundles of fine brass wire revolving on the chuck of a lathe. Copper, brass, and German silver are pickled in hot dilute sulphuric acid (1 to 10) or in dilute nitric acid, rinsed in water, dipped in strong nitric acid sp.gr. 1·33, and finally well washed in water. The articles should not be touched with the hands after they have undergone this preliminary treatment until they are plated. In order to obtain a firmly adhering deposit of silver, the articles may be dipped in a dilute solution of pernitrate or cyanide of mercury, washed with water and at once transferred to the vat containing the plating liquid, or the use of mercury may be avoided by giving the objects a thin deposit of silver from a plating liquid containing a large excess of potassium cyanide before bringing it into the finishing liquid. This whiting or first liquid contains 2½ lbs. of potassium cyanide, 8 oz. of sodium carbonate, and 5 oz. of silver cyanide per gallon. The composition of the second or finishing solution has already been given. Articles of iron, steel, lead, zinc, or tin, may with advantage receive a thin deposit of copper before silvering.

After undergoing this preparatory treatment, the objects are transferred to the plating liquid, which is generally contained in an iron vat lined internally with wood or cement. A brass rod or tube passes round the rim of the vessel. It is connected with the positive pole of the battery or dynamo. Sheets of silver are suspended from brass bars which stretch across the vat and rest on the brass rod which runs round the vessel. The objects to be plated are suspended in the liquid by means of copper wires, which are protected by a covering of gutta-percha except at the ends. The wires are attached to another set of brass crossbars which are supported on a second brass frame connected with the negative pole of the battery. The silver plates form the anodes and the articles to be plated the cathodes. The two systems of frames and rods are isolated from each other. A mechanical contrivance is employed for giving a gentle motion to the frame from which the objects are suspended, in order that the plating liquid may be continuously agitated and its composition remain uniform throughout the vat. The articles are examined after they have been in the plating liquid for about fifteen minutes to ascertain if the deposition of silver is taking place uniformly. If this is not the case they must be scratch brushed and thoroughly cleansed before returning to the bath. When a sufficient weight of silver is deposited the current is stopped, and after a few minutes the articles are removed, washed in water and dried in hot boxwood sawdust.

The dull surface of the silver is afterwards polished, or a bright surface can be obtained by finishing the articles in a brightening liquid, *i.e.* a plating liquid to which a small quantity of a mixture of strong ammonia, carbon bisulphide, and old plating liquid is daily added. Articles from the brightening liquid must be well washed in hot water before they are dried.

Owing to the highly poisonous character of potassium cyanide and of hydrocyanic acid, it has been proposed to substitute for the ordinary plating liquid a solution of silver chloride in sodium thiosulphate (hyposulphite) or a solution of silver sulphite in potassium sulphite. Zinin (D. P. J. 1886, 259; S. C. I. 1886, 246) recommends a bath containing 6·66 grams of silver nitrate in 1,000 of water, to which 500 grams of potassium iodide are added. A weak current must be used, or free iodine will be deposited on the silver anode. Ten minutes to half an hour are usually sufficient for silvering; the objects are afterwards immersed in a bath containing 1 part by weight of potassium iodide to 4 of water, and are then ready for polishing. This bath is more expensive than the cyanide bath, but it has the advantage that any thickness of silver can be deposited.

Small articles may be silvered by simple immersion in a solution of silver nitrate, to which an excess of sodium bisulphite is added. Roseleur (C. C. 1878, 143; C. J. 1878, 538) recommends a bath prepared by gradually adding a mixture of silver chloride with eighty times its weight of cream of tartar to water boiling in a copper vessel. The articles are immersed in this boiling liquid. If the bath does not work well the articles are immersed for a few seconds in a boiling solution of silver nitrate (100), potassium cyanide (600), in water (10,000).

Better results are obtained by giving the articles a very thin coat of gold, and then covering them with a paste of the following composition:—

Silver nitrate	100
Acid potassium oxalate . .	300
Cream of tartar	300
Common salt	420
Ammonium chloride . . .	80
Water	100–150

or

Silver chloride	60
Cream of tartar	200
Common salt	300

After drying the paste is washed off in cold water. The appearance of the deposit is improved by immersion in a solution of potassium cyanide for a few seconds. The appearance of the so-called oxidised silver is produced by brushing the deposited silver with a solution of platinum chloride or by a dilute solution of ammonium sulphide.

Electro-gilding. The liquid used in electro-gilding or gold-plating can be readily prepared by the battery process by proceeding in the manner described under silver-plating. A current from three Smee's cells is passed through a hot solution containing 1 lb. of potassium cyanide in a gallon of distilled water. The electrodes consist of sheets of gold suspended by platinum wires. The operation is carried on in an earthenware, porcelain, or enamelled iron vessel. The liquid can also be prepared by dissolving 1 oz. of gold cyanide and 4 oz. of potassium cyanide in a gallon of distilled water. Some platers prefer potassium sulphocyanide or ferrocyanide to the cyanide (*v.* Ebermayer, D. P. J. 224, 631; C. J. 1878, Abstr. 178). Roseleur recommends the following mixture. Dissolve 60 parts by weight of crystallised sodium phosphate in 800 parts of hot water. Convert 1 part of gold into chloride, dissolve in 100 of water, and pour the solution into the sodium phosphate when cold. Add to the mixture 1 part of pure potassium cyanide and 10 of sodium bisulphite in 100 of water. Better results are obtained in gold-plating with a thermopile or battery than with a dynamo. The articles to be plated are thoroughly well cleaned in the manner described under silver-plating. They are then suspended in the gilding liquid by means of platinum wires, or, if they are very small, they are placed in a perforated stoneware receptacle and are connected with the negative plate of the battery. The anode consists of a gold plate, which must be equal to or larger than the surface of the articles. The solution is kept at a temperature of 90° to 130°F., and is agitated frequently. Articles of lead, tin, zinc, Britannia metal, or pewter first receive a thin deposit of copper or brass before they are brought into the gilding liquid. The colour of the gold deposited is affected by the size of the anode and the strength of the current, and it may be varied by the judicious addition of small quantities of the cyanides of silver, copper, or zinc to the plating liquid.

The gilding of cheap jewellery is often accomplished by simple immersion for less than a minute in a bath of the following composition:

Potassium phosphate . .	800
Prussic acid (1 to 8 aq.) . .	8
Gold chloride	20
Water	10,000

Deposition of copper.—The process used in the electrodeposition of copper depends on the nature of the material to be coppered. Metals like iron or zinc, which decompose acid solutions of copper salts, must receive an initial deposit from an alkaline solution; but articles of brass or German silver are easily coppered by the battery process, using a solution of copper sulphate acidified with sulphuric acid. The degree of concentration of the bath and the amount of free acid varies considerably with different operators. Some platers keep the bath saturated with copper sulphate, and add from 1 to 4 parts by weight of acid to 4 of copper sulphate. Small quantities of potassium sulphate or zinc sulphate may also be added, *e.g.* 1 oz. of zinc sulphate to each lb. of copper sulphate. The anode must be pure copper, and the cathode is suspended from copper wires. The bath is contained in a wooden vessel, with or without a lining of sheet lead. The liquid must be well stirred from time to time, so that its composition may be uniform.

Articles of iron, steel, or zinc are thoroughly scoured and cleaned by immersion in boiling caustic potash and in dilute sulphuric acid. They are washed with water and brought into an alkaline copper bath, prepared by dissolving copper sulphate in four times its weight of water. Ammonia is added to the solution until the precipitate at first produced redissolves, forming an intense blue liquid. A strong solution of potassium cyanide is added to the mixture in sufficient quantity to destroy the blue colour. This bath is used at a temperature of 120°F. Good results are also obtained by using a mixture of ammonium tartrate and copper cyanide dissolved in potassium cyanide. As these alkaline baths are more difficult to manage and are more expensive in working than the copper sulphate bath, the electric current is broken and the articles are transferred to the copper sulphate solution as soon as they have received a deposit of copper sufficient to protect them from the action of the sulphuric acid or copper sulphate in the acid bath.

F. Weil (C. R. 93, 1018; C. J. 1882, Abstr. 670) recommends the following process for the direct deposition of copper on wrought iron, cast iron, and steel. The objects are immersed in a vat containing copper sulphate, excess of caustic soda solution, and an alkaline tartrate or glycerine. The deposition may be effected in three ways: (1) by a dynamo electric machine; (2) by placing the object in the bath in contact with zinc; (3) the object in the bath is connected by a thick copper wire with zinc plates dipping into caustic soda contained in porous cells which stand in the vat.

The third method is applicable to large objects, such as lamp-posts.

Small articles of iron or steel receive a thin coating of copper by simple immersion in a solution of copper sulphate acidified with hydrochloric or sulphuric acid.

Brass can be electrolytically deposited on metallic surfaces from a solution prepared by dissolving

84 parts by weight of sodium bicarbonate
54 ,, ,, ammonium chloride
13 ,, ,, potassium cyanide
in 2,000 ,, ,, water

This solution is brought into a vat the sides of which are covered with sheets of brass and form the anode. A small sheet of brass is used for the cathode. The current is passed through the bath for one hour (*v.* J. J. Hesz, D. P. J. 235, 47; C. J. Abstr. 1880, 425).

Other brassing solutions are prepared by dissolving sulphate of copper and sulphate of zinc in the proportion of 1 to 2 parts by weight in water. Ammonia is added until the precipitate which is formed redissolves. A strong solution of potassium cyanide is next added to the mixture until the blue colour disappears. This bath is used at a temperature of 120° to 130°F. with a brass anode.

Nickel-plating. In the process of nickel-plating it is essential for the success of the operation that the objects to be plated should not only be carefully freed from grease and oxide by treatment with caustic alkali and acids (as in the case of silver plating), but, in addition to this, it is necessary that their surfaces should be thoroughly polished before they are brought into the bath. The objects are first polished with powdered lime by means of revolving drums or discs. In the case of iron and steel, the polishing is accomplished by the use of pumice stone, emery powder, and fine sand, and the operation is preceded by pickling in dilute sulphuric acid.

The articles are now suspended from hooks in hot caustic potash, rinsed in water, immersed in a warm solution of cyanide of potassium, again well washed in water, and transferred at once to the nickel bath. After treatment with potash, the articles should not be touched by the hands of the workman until they are nickelled, as the presence of even a minute quantity of grease on the surface greatly impairs the beauty of the deposit. Instead of the cyanide bath some platers prefer using a mixture of sulphuric and nitric acids containing a small quantity of soot and common salt.

Iron goods are immersed in an acid solution of copper sulphate, in order that they may receive a film of copper before they are brought into the nickelling bath.

The bath is contained in an enamelled iron vessel, or in a wooden vat lined with asphaltum. The composition of the plating liquid varies in different works, and good results are obtained in working with a warm, tolerably strong solution of nickel ammonium sulphate. Kayser (C. C. 1878, 127, and C. J. Abstr. 1878, 537) recommends a bath of nickel ammonium sulphate dissolved in 20 times its weight of water. In plating copper articles 1 part by weight of ammonium chloride is added to every 100 of nickel salt. The liquid is worked with a strong current, using a pure nickel anode, which should not be smaller than the surface to be plated. If the bath becomes acid, it must be neutralised with dilute ammonia.

Fontaine and Berly, in their work on electrolysis, also recommend a nickel ammonium sulphate bath, which should be feebly acid to litmus paper. They point out that with platinum or carbon anodes, the bath grows weaker in nickel and its acidity increases. This may be remedied by the daily addition of finely-powdered carbonate of nickel. On the other hand, with nickel anodes, the bath grows alkaline, and throws down a deposit of oxide of nickel. This has to be remedied by the occasional addition of citric acid. By using both nickel and platinum anodes in suitable proportion (to be determined by actual experiment), the bath can be kept of constant composition. The surface of the anodes should be greater than that of the objects to be plated, and the nickel anodes are best made from rolled bars. They should be arranged on each side of the piece. The best results are obtained with a dynamo machine, which should have an electro-motive force capable of varying between 1 and 8 volts. The objects should not be left in the bath when the current is not working. The deposition of the nickel should be commenced with a current of about 5 volts, but as soon as the surface of the piece is completely whitened, the intensity of the current may be reduced to 1 volt. (Fontaine recommends that the magnitude of the current should be measured by means of a galvanometer introduced into the circuit.) When a bluish-grey deposit is formed on the articles the operation is complete. The pieces are washed in cold water, then in boiling water, and are finally dried in hot sawdust.

In addition to the nickel ammonium sulphate bath, the following mixtures are also recommended (D. P. J. 211, 74, and C. J. 1874, 928):—

I. Dissolve 1,250 grams of citric acid, 500 grams ammonium chloride or sulphate, and 500 grams of ammonium nitrate in 15 litres of water. The solution is heated at 80°C., and saturated with freshly precipitated oxide of nickel. On cooling, 2½ litres of ammonia are added, and the liquid diluted up to 25 litres. 200 grams of ammonium carbonate are dissolved in the liquid, which is then filtered. The bath is worked at a temperature of 50°C.

II. (Electrician, 20, 202) 500 grams of nickel sulphate and 365 grams of neutral ammonium tartrate are dissolved in 1½ litres of water. 2½ grams of tannin dissolved in ether are added, and the mixture boiled for 15 minutes. 8½ litres of water are now added and the mixture filtered. This bath yields a white deposit of metallic nickel which is not brittle.

Cobalt can be deposited in the same manner as nickel. According to A. Gaiffe (C. R. 87, 100, and C. J. 1878, 1019), and to Becquerel (C. R. 55, 18), a white adhering deposit of metallic cobalt is obtained when a neutral solution of cobalt ammonium sulphate is used as the bath. If cobalt anodes are used the composition of the bath remains pretty constant. The addition of magnesium sulphate, chloride, or citrate, is said to be an improvement, and this improved bath has recently been patented (S. C. I. 1888, 328). The best results are obtained by working with a current density of 1 to 4 ampères per square foot in a warm bath.

Iron. Considerable difficulty has been encountered in attempts to deposit firmly adhering films of iron on copper or other metallic surfaces, as the evolution of hydrogen at the cathode in the first place interferes with the regular deposition of the iron, and, secondly, the deposit is frequently filled with cavities. The bath generally consists of a strong solution of ferrous ammonium sulphate or ferrous ammonium chloride. It can also be prepared by passing an electric current through wrought-iron electrodes immersed in a solution of 56 lbs. of ammonium carbonate dissolved in 35 gallons of water.

As ferrous salts readily oxidise on exposure to the air, the vat containing the plating liquid should be covered when not in use. The addition of a small quantity of glycerine diminishes the tendency to form basic salts. In working with the double sulphate or chloride of ammonium and iron it is very necessary to prevent the liquid becoming acid. Klein accomplishes this object by using a wrought-iron anode, several times larger than the surface of the cathode, and, moreover, the iron anode is attached to a sheet of copper. In this way a galvanic couple is established, and the anode continues to dissolve even when the current is not passing. The best results are obtained with a feeble current. By this process copper electrotypes can be faced with iron, and rendered capable of enduring a longer period of wear and tear without losing their sharpness than a copper surface.

The electrotypes must be carefully cleaned by rubbing with benzene immersion in potash, and washing in water before they are brought into the bath. After an immersion of five minutes they are washed, scrubbed, replaced in the bath for five minutes, again taken out, washed, and these operations repeated until a sufficiently thick deposit of iron has been obtained. They must now be washed carefully in boiling water, afterwards washed and brushed in cold water, and dried and rubbed with turpentine. If they are not required for immediate use, the surface may be protected from oxidation by a coat of wax or solid paraffin.

Electrodeposition of platinum.—In 1886 a patent was granted for an improvement in the deposition of platinum by electricity (S. C. I. 1887, 518). A weak solution of sodium phosphate is added to a solution of platinic chloride, and ammonium phosphate is then added to the mixture. The mixture is boiled for several hours with common salt. This bath differs in composition from that which Roseleur patented in 1847 by the substitution of common salt for sulphate of soda. A solution of platinic cyanide in potassium cyanide is also recommended for the electro-deposition of platinum. The baths should be worked at a gentle heat with moderately strong currents; they require replenishing with platinum salts from time to time.

The electrolytic deposition of certain metals is extensively practised in the arts in the process of electrotyping, in multiplying engraved copper plates, and in reproducing medallions, statuettes, &c.

In order to deposit gold, silver, or copper on a non-conducting surface, such as a casting from a medal in gutta-percha or plaster of Paris, certain expedients must be adopted for the purpose of rendering the surface of the cast capable of conducting the electric current. A conducting surface is obtained by brushing the mould carefully with finely-powdered blacklead or bronze powder, using a stiff camel-hair brush. Gore states that the admixture of 1 part of the best white bronze powder to 3 of blacklead greatly improves the conductivity of the surface, and consequently facilitates the rapid deposition of metal. In the case of plaster of Paris casts, it is well to dip them in oil or in molten wax before applying the blacklead.

Another method consists in immersing the object in a strong alcoholic solution of nitrate of silver, or in applying the silver solution to the object with a paint brush. When dry, expose the prepared object to the fumes given off by a solution of phosphorus in carbon bisulphide (to reduce the silver nitrate to metallic silver), or expose to sulphuretted hydrogen to convert the silver nitrate into sulphide.

Another method is to cover the surface of the cast with a solution of beeswax and phosphorus in carbon bisulphide. When dry, apply an aqueous solution of nitrate of silver, afterwards rinse in water and apply a dilute solution of chloride of gold. After a final rinsing in pure water the cast or mould is suspended in the plating liquid, and connected with the battery by the wire to which it is attached at the commencement of these operations. As that portion of the mould which is nearest to the anode will receive the thickest deposit, it is necessary in the case of casts containing marked depressions to arrange a system of platinum wires leading from the anode to those portions of the cast which are most distant from it. In this way uniformity in the thickness of the deposit can be secured. W. C. W.

ELEMI *v.* Resins; Oleo-resins.

ELEMI, ESSENTIAL OILS OF, *v.* Oleo-resins.

ELIQUATION or **LIQUATION.** A metallurgical term to denote the operation of separating substances by taking advantage of their different fusibilities.

ELLAGIC ACID *Bezoardic acid* $C_{14}H_6O_8$. Occurs as a constituent of certain animal concretions, in greatest quantity in those known as oriental bezoars; it also appears to exist in the bark of *Abies excelsa* (F. Strohmer, M. 2, 539-540), and can be prepared by the action of various reagents on tannic or gallic acids.

To obtain the acid from bezoars, which vary in size from that of a bean to that of an egg, the concretions are dissolved in caustic potash, care being taken not to heat the mixture and to exclude air. A current of carbon dioxide is then passed through the clear liquid. Potassium ellagate is thus precipitated as a whitish powder, which is filtered, washed, recrystallised from hot water, and decomposed by throwing it into concentrated hydrochloric acid, when the ellagic acid separates out.

When a solution of gall-nuts is exposed to the air a grey powder is deposited. On boiling this with water, dissolving the residue in potash, ellagic acid may be precipitated from the solution by the addition of a mineral acid (Chevreul).

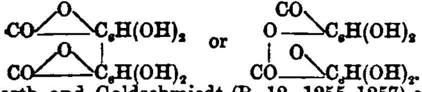
Gallic acid boiled with arsenic acid forms digallic acid. If the mass be dried and heated to 160° the arsenic acid is reduced and ellagic acid formed (H. Schiff, B. 12, 1533–1537).

The acid can also be obtained in small quantity by the action of phosphorus oxychloride on tannic acid or of the pentachloride on gallic acid, or by boiling acetyl-tannic acid with magnesia and water, and exposing the product to the air (Schiff, B. 4, 231, 967; Bl. [2] 18, 23); also by the action of iodine on tannic acid (Griessmayer), or when tannic acid is heated with dry uræmic acid (Löwe). By a modification of Löwe's process (Fr. 14, 35) ellagic acid may be prepared from divi-divi (*Cæsalpinia coriaria*). The alcoholic extract of the pods is concentrated and the residue poured into water, when the acid separates out. The filtrate is evaporated to a syrup, heated with hot water, and filtered. On washing the residue with hot alcohol tolerably pure ellagic acid is obtained (*v.* Barth and Goldschmiedt, B. 11, 846–850).

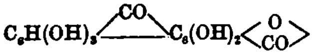
The constitution of ellagic acid is still somewhat uncertain. Schiff (B. 12, 1533–1537) gives its formula when dried in air as

$$C_6H(OH)_2COOH.C_6H(OH)_2COOH.$$

Heated to 200°–210° (B. 4, 967) it loses two molecules of water, and the resulting product ellagic anhydride, from the fact that it forms a tetracetyl derivative (Bl. 18, 23), he considers may have either the formula



Barth and Goldschmiedt (B. 12, 1255–1257) on the other hand found the loss in heating ellagic acid to be due to water of crystallisation. Below 100° the acid lost scarcely any water, and at 120° it had the composition represented by the formula $C_{14}H_6O_8$. Distilled with lime in a current of hydrogen the acid was for the most part carbonised, a little passing over unchanged. Treated according to Liebermann's method it gave a pentacetyl derivative. They further found from analysis of its sodium salt and a careful study of its reactions that it in no case behaved as an aromatic acid, and that its most probable formula was



or hexhydroxy di-phenyl ketone carbonic anhydride.

Ellagic acid is a pale yellow, light, tasteless powder consisting of microscopic prisms. On heating it is carbonised and decomposes without melting.

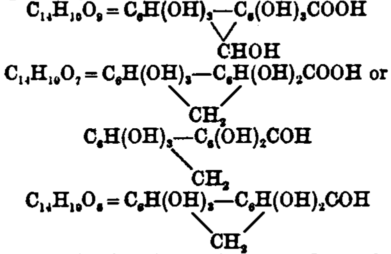
It is insoluble in water but soluble in alcohol, giving a slightly acid solution. It is dissolved by sulphuric acid and may be precipitated by adding water. Nitric acid oxidises it to oxalic acid.

With iodic acid carbon dioxide is rapidly liberated and iodine separates. Neutral ferric chloride solution is coloured greenish at first and ultimately bluish black, like ink, by ellagic acid. The solution contains ferrosoferric salts.

On fusion with caustic potash ellagic acid gives hexoxydiphenyl isomeric with the α-hexhydroxydiphenyl prepared from hydrocœrulignone by Liebermann (A. 169, 221). This body, β-hexhydroxydiphenyl, crystallises from water in colourless needles, and distilled with zinc-dust yields diphenyl. With caustic soda a third isomeride, γ-hexoxydiphenyl, is obtained. This body is almost insoluble in cold water, and may be crystallised from hot water in shining needles, becoming grey on exposure to air. By acting on ellagic acid with boiling potash the intermediate product of the reaction—hexhydroxydiphenyl-ketone $C_{12}H_8O_7$,—is produced. It crystallises from boiling water in microscopic needle-shaped prisms, and gives fluorene on distillation with zinc-dust. These bodies are distinguished by their physical properties and colour reactions with metallic salts (Barth and Goldschmiedt, B. 12, 1237–1255).

The products formed by the action of nascent hydrogen on ellagic acid vary with the time and energy of the action. With an equal quantity of sodium (as 4 p.c. amalgam) in three hours silky needles of a substance $C_{14}H_{10}O_7$ are obtained. In twenty-four hours two substances are formed, both soluble in ether. One of these sublimes in brilliant yellow needles of the formula $C_{14}H_{10}O_8$, obtained impure by Rembold (B. 8, 1494). The other, which is less soluble in cold water, has the formula $C_{14}H_{10}O_9$, and crystallises in white needles. With double the weight of sodium, and continuing the action for forty-eight hours, the γ-hexhydroxydiphenyl of Barth and Goldschmiedt (*l.c.*) was obtained. The yield was in all cases small, 2–3 p.c.

The constitutional formulæ for these bodies are probably as follows:—



When ellagic acid was heated to low redness with zinc-dust, Rembold (B. 8, 1494) obtained a colourless distillate solidifying to a laminated mass, accompanied towards the end of the reaction by a red body. The main product of the reaction he found to be a hydrocarbon $C_{14}H_{10}$, m.p. 88°, b.p. 252°, to which he gave the name ellagine. It is isomeric with phenanthrene, but is not attacked by chromic or picric acids. The red body he considered to be a polymer of ellagine.

Barth and Goldschmiedt (B. 11, 846–850) on heating ellagic acid to a barely visible red heat in a current of hydrogen obtained traces of diphenyl and a red body, but the chief product they found to be a hydrocarbon $C_{13}H_{10}$ (m.p. 113°), which, from its bromine and picric acid compounds, they showed to be identical with fluorene. The nitro- compound differed from that obtained from fluorene by Barbier; but the discrepancies are attributed to mono-nitro- compounds in Barbier's product.

By acting on gallic acid mixed with sulphuric acid with potassium permanganate, a substance $C_{14}H_{10}O_8$ was obtained which, heated with zinc-dust, yielded a hydrocarbon $C_{14}H_{10}$, identical with the ellagine of Rembold (Oser and Böcker, W. A. B. 79 [2] 148–155).

The ellagates are little known; many appear to be basic salts. Sodium ellagate $C_{14}H_4Na_2O_8$ (Wöhler and Merklim, A. 55, 133; Ernst and Zwenger, A. 159, 27) is a pale yellow crystalline powder insoluble in water, readily soluble in solutions of the alkaline hydrates. By digesting potassium ellagate in alcoholic potash the salt $C_{14}H_4K_2O_8.KHO$ is obtained. A solution of ellagic acid in potash exposed to the air deposits dull black crystals—the glaucomelanate of potassium of Wöhler and Merklim. The salt is supposed to have the formula $C_{12}H_4K_2O_7$. Barium ellagate, a basic salt, is insoluble and lemon-yellow. Lead ellagate, also basic, is an amorphous yellow precipitate, becoming olive-green on drying.

ELUTRIATION. The separation of the lighter from the heavier particles of a powder by washing and decantation.

EMBOLITE. A silver chlorobromide

$3AgCl.2AgBr$

found in Chili and Mexico. Crystallises in cubes and octahedrons, of a green or greyish green colour, with a resinous lustre, sp.gr. 5·3–5·4 (Plattner, P. 77, 134; Yorke, C. J. 4, 2).

EMERALD *v.* GLUCINUM.

EMERALD GREEN. *Hydrated chromium sesquioxide* *v.* CHROMIUM; also applied to *Schweinfurth green* (*v.* art. ARSENIC; also PIGMENTS).

EMERALD, ORIENTAL, *v.* CORUNDUM.

EMERY. (*Smirgel*, Ger.) An impure variety of corundum. Microscopic examination shows that it is a mechanical aggregate of crystalline or granular corundum and oxide of iron, chiefly in the form of magnetite. It was formerly obtained almost exclusively from Naxos, an island in the Greek archipelago, where it is found in large detached blocks in the soil, and also embedded in crystalline limestone. In consequence of deficient harbour accommodation, it is generally taken to the neighbouring island of Syra, and thence re-shipped. The lessee is bound by the Greek government to extract a minimum of 1,650 tons annually. In France the Naxos emery is still used to the exclusion of most other kinds, but in many markets the Greek emery has been largely displaced by the Turkish.

The late J. Lawrence Smith first called attention to the occurrence of emery in Asia Minor, especially at Gumach Dagh, a mountain about twelve miles east of Ephesus. It is also found near Kulah, twenty miles from Philadelphia. The Thyra mines are situated in the hills between Cosbunar and Thyra; and at the foot of this range is the Coursack mine, where a large bed of emery is now worked. At some of these localities the emery is found as loose blocks in a reddish soil, but at most of the workings it is now systematically mined by shafts and galleries. The principal workmen are Italians. The large blocks of emery are broken by sledge-hammers, but as the mineral is extremely tough it is often exposed to the action of fire and then cooled, to facilitate fracture. The broken emery is carefully picked over by hand, and sometimes not more than half is worth sending away. It is removed on camels and donkeys to the Ottoman Railway, and thence conveyed to Smyrna. From this port about 7,000 tons are annually shipped, most of it being carried as ballast in sailing vessels with light cargoes of liquorice root (*v.* Report by W. E. Stevens, American consul at Smyrna).

Emery is extensively employed in a variety of ways as an abrading agent. The mineral is crushed, sifted through wire sieves, and sorted into different degrees of fineness, known as coarse, fine, and flour; and should then be washed and elutriated. Lawrence Smith found that the effective hardness, or abrading power, is not in direct proportion to the amount of alumina in the emery, but seems rather to depend on the state of aggregation of the mineral. The following analyses are by Lawrence Smith (Am. S. 11, 366). The first column gives the effective hardness, taking that of sapphire as 100 (*v.* CORUNDUM):—

—	H	Sp.gr.	Al_2O_3	Fe_3O_4	SiO_2	CaO	H_2O
Gumach . .	47	3·82	77·82	8·62	8·13	1·80	3·11
Naxos . .	46	3·75	68·53	24·10	3·10	0·86	4·72
Samos . .	56	3·98	70·10	22·21	4·00	0·62	2·10

Analyses of the emery of Naxos, Tyre and Smyrna have been published by R. Jagnaux (Bull. Soc. Min. Fr. [7] 1884, 160).

Emery is conveniently employed in the form of 'emery cloth,' 'emery paper,' 'emery sticks,' &c., which are prepared by causing powdered emery to adhere to the glued surface of cloth and other media. 'Emery wheels' are formed by mixing the powdered mineral with some plastic or liquid vehicle, moulding the mass into a convenient shape, and then causing it to set in a solid form. The vehicle may be shellac, or artificial stone, which forms a hard cementing medium, or it may be a paste of loam and water, which is afterwards baked so as to form a coarse terra cotta.

F. W. R.

EMETINE *v.* VEGETO-ALKALOIDS.

EMODIN *v.* CASCARA SAGRADA; GLUCOSIDES; RHUBARB.

ENAMEL BLUE. *Cobalt blue* *v.* PIGMENTS.

ENAMELS are vitreous compositions, usually more or less opaque, capable of adhering by fusion to the surface of metal or of pottery. The base of the enamel is generally a colourless glass, in which are suspended particles of an opaque metallic oxide, or salt, such as stannic oxide, arsenious oxide or calcium phosphate. If these bodies be present in only small quantity, they produce an opaline glass rather than a true enamel. Opacity may also be obtained by the use of cryolite or fluor-spar. The vitreous base of most enamels is a lead-glass, but when the presence of lead is objectionable, as in enamelled vessels for culinary purposes, soda- and potash-glasses may be used. If great fusibility be required, it may be secured by the association of borates with the silicates. Colour is imparted to the enamels by the introduction of various compounds, generally metallic oxides, the use of which, in many cases, has been known from remote ages. Percy's analyses of the enamelled bricks of Babylonia (*circa* 700 B.C.) showed that a dense white was obtained by the use of stannic oxide; a rich yellow by means of antimony, apparently in the form of antimoniate of lead ('Naples yellow'); and a deep blue by copper, probably introduced as oxide but existing in the enamel as a silicate of copper and sodium. The ancient Egyptian blue enamel contains a definite silicate of copper and calcium, forming crystals remarkable for their intense pleochroism, to which Fouqué has given the name of *vestorien* (Bull. Soc. Fr. Min. [12] 1889, 36) (*v.* Egyptian blue).

The enamelling of pottery is a simple operation, since it consists in the mere fusion of an opaque glaze on to the surface of the ware. But the application of a vitreous body to a metallic surface is less easy, and it is to this process that the term 'enamelling' is sometimes restricted, while the works of art produced by enamelling on metal are themselves known as 'enamels.'

The most ancient enamels found in North-western Europe are referable to the prehistoric iron-age, and are sometimes distinguished as *neo-celtic.* But the best examples of late Celtic enamelling—such as the personal ornaments found in the Victoria Cave near Settle in Yorkshire, and the vase from a tumulus on the Bartlow Hills in Essex—represent survivals of the art in Roman times. In these ancient enamels, brilliantly-coloured opaque glass is embedded in shallow cavities in bronze: it is probable that the vitreous material was applied as a powder, mixed with a vehicle so as to form a paste, and then heated sufficiently to cause its fusion, and thus secure firm attachment to the metal.

A similar method, known as *champ levé* enamelling, was extensively employed at a much later date in Germany and at Limoges in France—a town which for centuries was the chief centre of artistic enamelling. In this process the design is traced on a plate of copper, and all the parts to be enamelled are excavated by the graver; these hollows are then filled with enamel, which is afterwards fused, and the entire surface is finally ground smooth. The design thus appears in permanent colour, each tint being defined by ridges, or areas, of metal which are the elevated parts of the original ground.

Another method of inlaid enamelling is that known as *cloisonné* work. Here the design is outlined by strips of metal, fixed to the metallic base, and the spaces between these bands are filled with enamel, which is then fused and the surface ground down. Each coloured area is, therefore, sharply separated from its neighbour by the edge of the metal fillet. Of this character were the early Byzantine enamels, which were generally executed on plates of gold. The Chinese have for many centuries been extremely skilful in this work, and the Japanese have applied a similar method to the ornamentation of porcelain.

The use of transparent enamels for the ornamentation of metal-work was introduced by the Italian goldsmiths of the thirteenth century, and afterwards became popular in France. The design was generally chased on gold or silver, and brilliant translucent enamels were applied in such a way that the varying thickness produced differences of tint.

Artistic enamelling has been largely used not only for inlaid and encrusted work but for the production of paintings on metal. The painted enamels of Limoges, introduced about 1520, were executed on slightly convex plates of copper, the subjects being generally in white and grey on a deep-violet ground. In this country, enamel painting was largely practised, by the family of Bone, during the latter part of the last and the early years of the present century. While their smaller works were executed on gold, the larger examples were on plates of copper. The copper plate, having been annealed and cleaned with dilute sulphuric acid, was coated on both sides with white enamel powder; it was then fired, and the enamelled face ground smooth. This white enamel, which was rendered so opaque by means of stannic oxide as to conceal the metal ground, was imported from Venice in the form of round cakes. The surface to be painted was further prepared by the application of a second coat of enamel, more fusible and transparent than the first; this material known to the enameller as 'flux,' was used in the form of rods and beads of white Venetian glass. Upon the fluxed surface, carefully ground smooth, the painting was executed in enamel colours, or powdered glasses mixed with an appropriate vehicle; and as it was necessary to vitrify each colour separately, a complicated subject would require several successive firings in a muffle, each liable to injure or spoil the work.

Although the difficult art of enamel painting is now rarely practised, there is a growing demand for coarse work in enamelled sheet-iron for street plates, railway notices, and other advertisements, which are generally executed in blue and white. In applying enamel to metal it is necessary to use a material which will adhere firmly to the base: at the same time it must fuse at a temperature lower than that which softens the metal, or melts the solder, if any be present. Paris has recommended as a good enamel a mixture of 130 parts of flint-glass, 20·5 of carbonate of soda, and 12 of boracic acid. Salvétat proposed to use—sand 48 parts, red lead 30, carbonate of soda 30, and boracic acid 10. It is obviously important that when enamel is used as a lining for cast-iron saucepans, stew-pans and other vessels for culinary purposes, it should be free from all ingredients which are poisonous, or may become so by contact with food. The iron should be first coated with a nearly transparent glass, and a coating of enamel then spread over this ground-layer. Raetz recommends (C. C. [3] 1878, 800) that 80 parts of powdered felspar and 25 of borax be fused together, and that the powdered mass be then mixed with 10 parts of kaolin, 6 of felspar, and 1·75 of carbonate of magnesia; this is mixed with water to a paste, which is spread over the iron, and upon this is applied a fusible powder made by fusing 37·5 parts of quartz, 27·5 of borax, 50 of stannic oxide, 15 of carbonate of soda, and 10 of saltpetre; the object thus treated is carefully dried, and then fired in a muffle-furnace. F. W. R.

ENDLICHITE *v.* VANADIUM.

ENGLISH BROWN, or **BISMARCK BROWN**, *v.* AZO- COLOURING MATTERS.

ENGLISH GREEN, or **CHROME GREEN**, *v.* CHROMIUM; PIGMENTS.

ENGLISH PINK, or **ITALIAN PINK**, *v.* PIGMENTS.

ENGLISH RED, or **VENETIAN RED**, *v.* PIGMEMTS.

ENHYDROS *v.* AGATE.

ENOSMITE *v.* RESINS.

ENSILAGE is a process of preserving green fodder for cattle. The term *silo* is applied to the pit or other depository in which the fodder (*silage*) is contained, and appears to be of Basque derivation, and originally meant a pit for storing grain. This method of preserving grass and other succulent forage crops has been in use for many years in Germany, whence the practice was carried to France, and afterwards to America. Although the German system had been fully described by Johnston in 1843 in the Transactions of the Highland Agricultural Society (new series, 9), no general notice of it was taken in these islands until 1882, when a report of the British Legation at Washington on ensilage as practised on Mr. Havemeyer's estate in New Jersey was published as a blue-book, since which time many silos, of varying forms and construction, have been made in this country. The object of all these is to exclude the air from the mass of fodder, allowing only a greater or less fermentation according to the practice of different authorities; and to this end silos have been formed (1) wholly or partly underground, (2) in the form of inclosed buildings; while in recent years silage has been largely made by building up the green fodder in the form of an ordinary stack, of which only the top is covered. Whether it be silo or stack, the principal factor is the superposition of a sufficient pressure, either by dead weight or by some mechanical system of screws, levers, or similar appliances. The changes which forage undergoes in the silo are due to fermentation, and, as may be supposed, this action varies considerably with the materials stored and with the condition of storage; as, for example, green maize undergoes principally lactic fermentation; whilst in English fodder fermentation produces alcohol, which is almost immediately converted into aldehyde. If the air has not been properly expelled from the silo, or if the fodder has been pitted in a very damp condition, the aldehyde becomes quickly converted into acetic acid.

Silage is of two kinds—viz. 'sweet' and 'sour.' Sweet silage is the result of allowing the grass to remain without pressure, and so permitting air to mingle with it until such time as a temperature of 125° to 150°F. is reached by the fermentation process; sour silage, on the other hand, results when pressure is at once applied, whereupon an acetic or lactic fermentation takes place. It appears that a temperature of about 125° is sufficient to kill the bacteria which produce acid fermentation; 'if the bacteria are killed and the silo is covered and weighted, the inclosed mass of green fodder will remain sweet and be practically preserved under the same conditions as fruits, vegetables, or meats are preserved when canned. If this be the case, it will be at once intelligible that by less packing of the fodder when put into the silo, and extending the time of filling until the temperature rises to a point fatal to the bacteria, the resulting silage will be sweet and free from acidity; while sour silage is produced by at once consolidating, covering up, and weighting the grass fodder so as to prevent the temperature rising to the point fatal to the bacteria' (A. Voelcker, Journ. Roy. Agric. Soc. 20).

Two samples of sweet silage showed only a trace of acid, not exceeding in quantity that contained in ordinary fresh meadow grass:—

—	Silage made from	
	Clover and rye grass mixed	Meadow grass
Moisture	75·80	74·40
*Albuminous compounds	2·53	2·56
Sugar and other carbo-hydrates soluble in water	1·43	2·99
Crude vegetable fibre	18·31	17·90
Mineral matter (ash)	1·93	2·15
	100·00	100·00
*Containing nitrogen	·40	·41
Volatile acids (calculated as acetic acid)	·01	·04
Non-volatile acids (calculated as lactic acid)	·01	·02

A sample of sour silage made from grass placed in a heavily weighted silo showed the following composition:—

Water	76·01
Soluble albuminous compounds	·91
Insoluble albuminous compounds	1·78
Soluble carbo-hydrates	2·87
Crude fibre	15·82
Soluble mineral matter (ash)	1·63
Insoluble mineral matter (ash)	·98
	100·00
Total nitrogen	0·43
Volatile acids (calculated as acetic acid)	0·19
Non-volatile acids (calculated as lactic acid)	1·24

This silo was provided with a tap at the bottom from which juice was drawn off from time to time. This drainage had a sp.gr. of 1·022, and contained, per imperial gallon:—

	Grains
Albuminous compounds	1,008·56
Fixed acid (lactic acid)	516·42
Volatile acids (butyric and acetic acids)	476·70
*Carbo-hydrates and amides	1,528·42
Mineral matters (ash)	1,768·20
Water	64,701·70
	70,000·00
*Containing non-albuminous nitrogen	35·84

The dry matter (dried at 100°) which was left on evaporation of its drainage contained:—

*Albuminous compounds	20·90
Lactic acid	10·71
†Carbo-hydrates and amides	31·73
Mineral matter (ash)	36·66
	100·00
*Containing nitrogen	3·34
†Containing nitrogen	·51

The subject of changes during ensilage has been very carefully investigated both at Rothamsted by Lawes and Gilbert, and at Woburn by Voelcker. The results obtained present a striking similarity, and it will suffice if one set of tables (those of Dr. Voelcker) is referred to here, although the Experiments on Ensilage conducted at Rothamsted (Lawes and Gilbert) should also be read. The silo to which these figures relate was one made at Woburn in 1886, and was of the character generally termed 'sour.' It was weighted with stones in strong elm boxes to 112 lbs. per square foot, and was unprovided with any drain. The silo was closed on July 3, and opened on December 16, the contents being 'very fair,' although 'not really fine,' meadow grass. The following are the numbers in a condensed form:—

Quality and Composition of the Grass put into Silo, and of the Silage produced.

—	Total weight	Water	Volatile acids	Non-volatile acids	Solub'e albuminoids	Inso'uble albuminoids	Digestible fibre	Woody fibre	Soluble carbo-hydrates, &c.	Soluble mineral matter	Inso'uble mineral matter	Total nitrogen	Albuminoid nitrogen	Non-albuminoid nitrogen
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Grass put in silo	32,780	23,108	—	—	47	733	3278	2670	2265	430	249	151	123	28
Silage removed	30 389	22,035	109	106	197	252	2326	2409	2254	471	230	155	73	82
Loss	2,391	1,073	+109	+106	+150	481	952	261	11	+41	19	+4	50	+54
Loss per 100 lbs. of fresh grass	7·29	3·27	+·33	+·32	+·46	1·47	2·90	·79	·03	+·12	·06	+·01	·15	+·16

The main features shown in the table are as follows: The total loss due to fermentation, evaporation, &c., in making the silage was 7·29 p.c. on the fresh grass. Of this, 3¼ p.c. consisted of water, so that the loss in dry matter was only about 4 p.c. The loss of total nitrogen when, as here, no drainage was allowed to flow away, is very slight; but the nitrogenous bodies have undergone considerable change from the albuminoid to the non-albuminoid condition, the fibre has been diminished, insoluble albuminoids have been lessened, and soluble albuminoids increased (Voelcker, A. S. J. 23, 410).

Since the nutritive value of food depends to a considerable extent on the albuminous compounds contained in it, it becomes of importance from the economic point of view to determine the quantity of such compounds in fresh green-food and in silage. Kinch found that 55 per cent. of the total nitrogen present in the silage of grass was of a non-albuminous nature, whilst in the original grass only 9 per cent. was of this form. In the case of mangold leaves Kellner found that of the total nitrogen present 27·8 per cent. in the original leaves, 45·5 per cent. in the silage, and as much as 59·7 per cent. in silage preserved in stoppered jars was non-albuminoid. Clifford Richardson examining maize silage found:—

	Per cent. total nitrogen as non-albuminoid.
Original stalks	21·2
Silage, No. 1	44·6
„ No. 2	49·6
Dried fodder	15·6
Silage from young maize	53·3
„ „ older „	47·1

These results with grass, mangolds, and maize show that in ensilage a large portion of the albuminoids are converted into non-albuminoid nitrogenous substances whilst in the ordinary drying of fodder no such change seems to take place. This is made clear by a reference to Dr. Voelcker's table given above under the heading 'Quality and Composition,' &c., where the woody fibre, as indeed the whole of the fibre, has been diminished, insoluble albuminoids are lessened, and the soluble albuminoids increased.

The application of silage as fodder and its practical effects with stock have been carefully investigated both at Rothamsted and Woburn.

V. Report on the Practice of Ensilage at Home and Abroad, Jenkins in A. S. J., new series, 20; On the Chemistry of Ensilage, Voelcker, *ibid.*; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1884–5 and 1885–6, Voelcker, A. S. J. 22; Experiments on Ensilage conducted at Crawley Mill Farm, Woburn, 1886–7, Voelcker, A. S. J. 23; articles in the Agricultural Gazette, April 27, 1885 *et seq.*, by Sir J. B. Lawes and Dr. Gilbert, reprinted in pamphlet form under the title of Experiments on Ensilage conducted at Rothamsted.

EOSIN *v.* Phthaleïns.

EPSOM SALTS. *Magnesium sulphate v.* Magnesium.

ERASINE *v.* Abietene.

ERBIUM *v.* Cerium metals.

ERECTHIDIS OIL consists of a terpene $C_{10}H_{16}$, which boils at 175° and at 18·5° has a sp.gr. of 0·838. This body absorbs a molecule of hydrochloric acid without the separation of a crystalline compound. The portion of the oil which boils above 200° also consists of a terpene (Beilstein and Wiegand, B. 15, 2854).

ERGOT OF RYE. *Spurred rye*; *Ergota*; *Secale cornutum*; *Ergot de seigle*, Fr.; *Mutterkorn*, Ger. Ergot of rye consists of the compact mycelium or spawn, the nutritive organ, of the fungus *Claviceps purpurea* (Tulasne) developed within the paleæ of the rye fruits. The same fungus grows upon the fruits of other members of the natural order Gramineæ, giving rise to less-known ergots, as, for instance, *ergot of wheat* or *ergot of oat*. The fungus is collected in the second or intermediate stage of its development, in which it remains dormant for many months. At this period it is noticeable projecting out of the heads of the rye as long, narrow, slightly arched grains of a purplish black colour and horny consistence. Ergot has been known for some three hundred years, and is an agent of great importance in medicine. Its chief action is that of a stimulant of the uterine muscles. It is employed in cases of insufficient contractile power, and as a remedy for uterine and other forms of hæmorrhage. Further botanical and historical particulars are given by Flückiger and Hanbury (Fl. a. H. 740); Pereira, Mat. Med. 3rd ed. 2, 996; Cooke, Brit. Fungi, 772; Ph. [3] 1, 702; Bentl. a. T. 303; Stoddart, Ph. [3] 10, 194; Wilson, Ph. [3] 6, 525, 545, a. 564; Parsons, Rep. United States Commissioner Agriculture, 1880, 186; Holmes, Ph. [3] 16, 684.

Ergot undergoes decomposition when kept of a kind which affects materially its physiological activity. To prevent this many methods of preservation have been suggested. These depend generally either upon removal of the oil by a solvent such as petroleum ether, or by expression, or on the addition of some substance such as ether or benzoïn which surrounds the drug with an antiseptic vapour (*v.* Gobley, J. Ph. [4] 17, 217; Ducros, Z. oesterr. Apoth. V. 1876, 8; Gionvié, Z. oesterr. Apoth. V. 1876, 126; Perret, Bull. Gen. Thérap. 1882, 202; Moss, Ph. [3] 16, 274).

Few articles of materia medica have been more studied chemically than ergot, but of the numerous more or less definite constituents which have been isolated, there are none that represent in a satisfactory manner the physiological activity of the drug, or at all events that are available to the therapeutist. Thus ergot is still administered in the form of aqueous or other extract more or less concentrated and freed from inactive constituents. Formulæ for these pharmaceutical preparations, which are liable generally to the same deteriorations on keeping as the drug itself, find their place in the various pharmacopœias. One of the most celebrated extracts of ergot, *ergotin* or *ergotine*, is that of the French pharmacist Bosjean (J. Ph. 1843, 4, 107; C. R. July 17, 1843). For examples of others *v.* Long, Med. Press Cir. 8, 435; Ronayne, Med. Press Cir. 9, 267; Squibb, Proc. Am. Pharm. Assoc. 1873, 957; Gerrard, Ph. [3] 5, 805; 13, 235; Wernich, Y.-Book Ph. 1875, 349; Carles, J. Ph. 1878, 28, 45; Active Principle of Ergot of Rye, Ph. [3] 6, 942; 7, 4; Zellhoefer, Proc. Am. Pharm. Assoc. 1877, 404; Yvon, Revue Méd. Nov. 15, 1879; Catillon, Y.-Book Ph. 1880, 305; Diehl, Ph. [3] 12, 519; Hallberg, Am. J. Pharm. 1883, 8; Conrad, Y.-Book Ph. 1883, 299; Denzel and Wacker, Ar. Ph. 22, 314; Clark, Ph. [3] 16, 521; Engelmann, Y.-Book Ph. 1887, 276.

Vauquelin in 1816 made a chemical analysis of ergot (A. Ch. 3, 337) and among other early investigators are Pettenkofer, R. P. 3, 65; Winkler (Christison on Poisons); Ludwig, Ar. Ph. [2] 114, 193; Wiggers, A. 1, 129; J. Ph. 18, 525; Chevallier, Neuest. Entd. Mat. Med. 1837, 129. The results obtained by Wiggers, which were confirmed in their main points by Chevallier, may be taken to represent those researches. That observer finds 35 p.c. of *fixed oil*, after removal of which with ether, an alcoholic extract of the residue is prepared, which, after evaporation and washing of the residue with water, leaves 1¼ p.c. of a very active resinous substance to which the name *ergotine* was applied. *Fungin* occurs to the extent of 46 p.c. and the chief remaining constituents estimated are *gum*, *sugar* and *phosphates*. Starch is said to be altogether absent.

About the year 1865, Wenzell (Vierteljahresschrift prakt. Pharm. 14, 18) announced the discovery of three new compounds obtained from ergot: two amorphous alkaloids, *ergotine* and *ecboline*, and a volatile acid with which they are combined, *ergotic acid*. Ecboline is active physiologically. This ergotine must not be confused either with pharmaceutical preparations such as Bosjean's ergotine or with indefinite substances like Wigger's ergotine. Wenzell obtained the two alkaloids from an aqueous extract of ergot, after first freeing it from acids giving insoluble lead compounds. Ecboline comes down first by treatment with mercuric chloride, and then ergotine is precipitated as phosphomolybdate, and from these combinations the free alkaloids are obtained. Both are soluble in water and alcohol, but insoluble in ether and chloroform. They are distinguished from each other by the different solubility of their mercuric chloride compounds and by their behaviour towards other alkaloidal reagents. The research of Wenzell was confirmed and extended by Manassewitz (P. Z. 6, 387); Hermann (Vierteljahresschrift prakt. Pharm. 18, 481; N. R. P. 20, 283), and Ganser (Ar. Ph. 144, 195; N. R. P. 20, 301). Manassewitz analysed ergotine.

Hermann, who further examined oil of ergot, notes that it is a non-drying oil and consists essentially of *triolein* and *tripalmitin* together with traces of *butyric* and *acetic acids*. The physiological activity of the oil is due entirely to resinous constituents with which it is usually contaminated. Oil of ergot has been recently studied by Shoemaker (Ph. [3] 11, 717) and Dietrich (Pharm. Z. 27, 264), and in 1869 Ludwig (Ar. Ph. 1869, 137, 36) found it to contain a compound supposed to be *cholesterin*. Tanret has, however, shown (C. R. 108, 98) that this substance may be distinguished by several reactions from cholesterin. He names it *ergosterin*. It crystallises from alcohol in nacreous plates or needles, having the composition $C_{26}H_{40}O_{2},H_{2}O$. They lose a molecule of water at 110°, melt at 154°, and boil at 185° (20 mm.). Ergosterin contains one alcoholic OH, replaceable by alkyl radicles. Most observers find *lactic acid* in ergot, and crystalline lactates have not unfrequently been mistaken for alkaloidal or other active constituents. Evidence of *leucine* has also been noticed. Hermann found ergot *ash* to consist of:—NaCl 1·51, K_2O 30·06, Na_2O 0·65, CaO 1·38, MgO 4·88, Al_2O_3 0·59, Fe_2O_3 0·86, MnO 0·26, P_2O_5 45·12, SiO_2 14·67 = 99·98. Ganser maintains that the *ammonia* and *trimethylamine* derived from ergot do not exist as such in the drug, but are the result of the breaking up of nitrogenous constituents under the influence of heat and alkali. Ergot sugar is *mycose*, and is extracted by 80 p.c. alcohol (Mitscherlich, A. 106, 15; Müntz, J. 1873, 829). Aqueous extract of ergot contains 3·2 p.c. *albumen*, but the total percentage of albuminoids is much higher, for the drug contains some 3 p.c. of nitrogen (Fl. a. H.). Blumberg (Ph. [3] 9, 23, 66), who has recently reinvestigated the two alkaloids of Wenzell, finds them exceedingly difficult to free from admixed lactates. According to this observer both are without physiological action on frogs, and in their chemical behaviour they are so nearly identical that he regards them as one and the same compound, more or less admixed with impurities.

Another attempt to isolate an active constituent from ergot was made by Buchheim (Ar. Ph. 1875, 7, 32), who ascribes the physiological action to a *kind of gelatin* formed by the mycelium of the fungus from the gluten of the rye. Compare also Squibb (Proc. Am. Pharm. Assoc. 1873, 957).

Tanret in 1875 (C. R. 81, 896; 86, 888; A. Ch. [5] 17, 493; J. Ph. 26, 320) announced the discovery in ergot of an active crystalline alkaloid, *ergotinine*, a specimen of which was sent to London a few years later. To obtain ergotinine the drug is extracted with 86 p.c. alcohol. The residue, after removal of the spirit by distillation, separates into three parts, a fatty layer, an aqueous extract, and a resinous precipitate. The precipitate and the fatty layer are treated with ether and the ethereal solution is shaken with dilute sulphuric acid, which takes up the alkaloid as sulphate. After purification ergotinine is a strongly alkaline crystalline solid, insoluble in water but soluble in alcohol, ether, and chloroform, the alcoholic solution exhibiting a green fluorescence. The yield of alkaloid is about 0·1 p.c. It undergoes rapid decomposition when exposed in the free state to the air. When fresh it gives with concentrated sulphuric acid a yellowish passing into an intense violet-blue colour. Heated with potash methylamine is formed. The individuality of ergotinine having been questioned by Dragendorff and Podwissotzky (Ph. [3] 6, 1001), and by Blumberg (Ph. [3] 9, 598), Tanret in further communications maintains his original statements (J. Ph. 23, 17; 24, 263; 26, 320; C. R. 86, 888; Ph. [3] 9, 707). Compare also Chahbazian (Med. Times Gaz. 1882, 624). Tanret finds also a crystalline *camphorlike compound* in ergot which melts at 165°, boils at 209°, and is insoluble in water but soluble in alcohol and chloroform.

A further examination of ergot has been conducted by Dragendorff and his pupils (Dragendorff a. Podwissotzky, Ph. [3] 6, 1001; N. J. P. 1877, 39; Podwissotzky, Y.-Book Ph. 1884, 87; Blumberg, Ph. [3] 9, 23, 66, 147 a. 598). By treating aqueous extract of ergot with 40–45 p.c. alcohol a precipitate is obtained of a slimy colloïdal substance, *scleromucin*. This body is neither an alkaloid nor a glucoside, and though it contains nitrogen it gives no reaction for albumen. It is physiologically active, but is not suited for use in medicine on account of its sparing solubility, when dried, in water. The filtrate from scleromucin gives on addition of 90 p.c. alcohol a further precipitate of 2–3 p.c. of a colloïdal substance which forms weak combinations with bases. This compound, *sclerotic acid*, is physiologically active and is recommended for therapeutical application. It is now an article of commerce and has been employed in 0·03 to 0·045 gram doses subcutaneously. It is not an alkaloid or a glucoside, and gives no reaction for albumen though containing 4·2 p.c. of nitrogen. The filtrate from sclerotic acid contains the alkaloid or alkaloids of Wenzell. After treating ergot with a solution of tartaric acid, alcohol extracts several compounds which precipitate on standing. The first of these is the red colouring matter of ergot, *scleroerythrin*. It is insoluble in water but soluble in alcohol. Associated with it is another colouring matter, *scleroiodin*, likewise insoluble in water, but distinguished from scleroerythrin by insolubility in alcohol after it has been once isolated. Scleroerythrin seems to be related to anthraquinone and alizarin. It occurs only in minute quantity, and is associated with two other substances. When an alcoholic solution of crude scleroerythrin is treated with lime water, all the scleroerythrin precipitates as an insoluble calcium compound, leaving the compounds *picrosclerotin* and *fuscosclerotic acid* in solution. If this solution be acidulated with sulphuric acid and agitated with ether, fuscosclerotic acid is taken up by the ether, and from the residue picrosclerotin may be obtained. The former is a yellowish-brown acid, and the latter a bitter alkaloid, which is poisonous to frogs, and in its chemical behaviour with concentrated sulphuric acid gives a violet-blue colour reaction resembling that of Tanret's ergotinine. A similar reaction is given by scleroiodin. After the removal of these compounds from ergot, which has been treated with tartaric acid, ether extracts a body in tabular citron-yellow crystals, *scleroxanthin*, together with colourless needles of *sclerocrystalline*. The former appears to be merely a hydrate of the latter. Both are without physiological action when administered to frogs. All these compounds were analysed, but their state of purity was not sufficient to warrant the derivation of formulæ from the numbers obtained.

The recent announcement by Kobert (C. C. 1885, 66) of three new compounds in ergot, *ergotic* and *sphacelic acids* and *cornutine*, is questioned by Tanret (J. Ph. 1885, 11, 309).

Ergotismus or ergot-poisoning has occurred from time to time owing to the use of flour contaminated with ergot, and on this account a chemical examination of flour or bread for ergot is sometimes required. The methods employed depend chiefly on the recognition of the colouring matter of the fungus (*v.* Boettger, C. C. [3] 2, 624; E. Hoffmann, Pharm. Z. 23, 576, 726, and 742; Stoddart, Ph. [3] 10, 194; Wolff, Pharm. Z. 23, 532, and 694; Petri, Fr. 18, 211; Poehl, B. 16, 1975; Palm, Fr. 22, 319).

A. S.

ERGOTIC ACID *v.* Ergot of rye.

ERGOTINE *v.* Ergot of rye; also Vegeto-alkaloids.

ERGOTININE *v.* Ergot of rye; also Vegeto-alkaloids.

ERICINOL *v.* Ericolin; Ledum palustre (Linn.).

ERICOLIN is found in several plants belonging to the order *Ericaceæ*, especially in the herb of the marsh wild rosemary, *Ledum palustre* (Rochleder and Schwarz, A. 84, 368), less abundantly in the common heath or ling, *Calluna vulgaris* (Rochleder, *ib.* 354), in *Rhododendron ferrugineum* (Schwarz, *ib.* 361), and in the red bearberry, *Arctostaphylcs uva ursi* (Kawalier, Sitz. W. 9, 29).

To prepare it from *L. palustre* the chopped leaves are thrown into boiling water and boiled for several hours. The filtrate obtained after adding basic lead acetate to the liquid is evaporated in a retort to one-third of its bulk. In Thal's modification of this process (B. 16, 1502*a*) the liquid is concentrated *in vacuo*, the separated lead salt filtered off, and the liquid freed from lead by hydrogen sulphide. The filtrate is then evaporated to a syrup and the ericolin dissolved out by anhydrous ether-alcohol. The substance left on evaporating this solvent is repeatedly dissolved in a mixture of ether and alcohol till it no longer leaves any residue (Rochleder and Schwarz).

On heating the mother liquor obtained in the preparation of arbutin from the leaves of red bearberry with dilute hydrochloric or sulphuric acid, ericolin is deposited as a resinous precipitate, which may be purified by solution in alcohol and precipitation by water (Kawalier).

Rochleder and Schwarz, after deducting 10·6 p.c. ash, found ericolin to contain 51·71 p.c. carbon and 7·19 hydrogen, whence they deduced its formula to be $C_{34}H_{56}O_{21}$ (51·00 C and 7·00 H).

Thal (*l.c.*), after separating an admixed substance (containing 57·5 p.c. carbon and 7·29 hydrogen), which was insoluble in ether-alcohol from ericolin, assigned to the latter body the formula $C_{26}H_{21}O_3$, but subsequently altered it to $C_{26}H_{30}O_3$ to suit the decomposition equations of the substance. Ericolin, as prepared by Thal, is a brown-yellow, odourless, hygroscopic bitter substance decomposed even below 100°. It is decomposed by water. By extracting successively with benzene, chloroform, and a mixture of ether and alcohol, different substances go into solution; it appears that the ericolin is thus broken up into a sugar and ericinol. With dilute sulphuric acid warmed to 100° a sugar and a resinous brown-yellow viscid mass, hydroericinol, are produced. An analysis of the latter body gave numbers corresponding with the formula $x(C_6H_{12}O_2)$, subsequently modified to $x(C_5H_{10}O_2)$.

The equations representing these decompositions are as follows:

$$\underset{\text{Ericolin}}{C_{26}H_{30}O_3} + 4H_2O = C_6H_{12}O_6 + \underset{\text{Ericinol}}{C_{20}H_{26}O}$$

$$C_{20}H_{26}O + 7H_2O = \underset{\text{Hydroericinol}}{2(C_{10}H_{20}O_4)}$$

Thal also isolated ericolin from *Calluna vulgaris* and recognised it by the smell of ericinol in many *Ericaceæ* and *Vaccinieæ*.

ERIGERON CANADENSE is an oil consisting of a terpene boiling at 176°, sp.gr. 0·8464. It absorbs two molecules of hydrochloric acid to form a solid dihydrochloride $C_{10}H_{16}.2HCl$, melting at 47°–48° (Beilstein and Wiegand, B. 15, 2854).

ERUCIC ACID $C_{22}H_{42}O_2$. A homologue of acrylic acid obtained together with oleic acid by the saponification of the fixed oil of white mustard. It was found together with benic acid by Goldschmiedt (Sitz. W. 70, 451) in the oil expressed from black mustard, and by Fitz (B. 4, 442) in the fat oil of grape seeds. It is best obtained by saponifying rape oil (from *Brassica campestris*) with alcoholic potash, distilling off the alcohol and dissolving the acid liberated on the addition of sulphuric acid in three times its volume of 95 p.c. alcohol; on cooling to 0° crystals of erucic acid separate out in an almost pure condition (Reimer and Will, B. 19, 3320).

Erucic acid crystallises in colourless needles, m.p. 34°. Heated with phosphorus oxychloride it forms an anhydride $C_{44}H_{82}O_3$, an oil which may be crystallised in a freezing mixture. By treatment with nitrous acid, or better by warming erucic acid with dilute nitric acid to the melting-point and then adding sodium nitrite, erucidic acid (brassic acid, brassidic acid) is produced. This acid stands to erucic acid in the same relation as elaïdic to oleic acid. Fused with potash erucic acid yields aradic (arachidic) and acetic acids. With hydriodic acid and amorphous phosphorus it is converted into an acid probably isomeric with benic acid (Goldschmiedt, *l.c.*). When bromine is added to erucic acid under water a di-bromide $C_{22}H_{12}Br_2O_2$ is produced. It crystallises from alcohol in small white nodular crystals, m.p. 42°–43°, and is reduced to erucic acid by sodium amalgam in alcoholic solution. Its barium and lead salts $(C_{22}H_{41}Br_2O_2)_2Ba$ and $(C_{22}H_{11}Br_2O_2)_2Pb$ are white, viscid, easily decomposable precipitates (Otto, A. 127, 182; 135, 226). Erucic acid di-bromide heated in sealed tubes to about 145° for 7–8 hours, with 4 or 5 mol. potassium hydrate in alcoholic solution yields the potassium salts of benolic acid, $C_{22}H_{40}O_2(=C_{22}H_{42}Br_2O_2-2HBr)$. At ordinary temperatures only 1 mol. of hydrobromic acid is abstracted by potash in alcoholic solution; monobromerucic acid $C_{22}H_{11}Br.O_2$ is formed, with rise of temperature and separation of potassium bromide. On diluting the solution with water and adding hydrochloric acid, the acid separates as an oil which soon solidifies. It melts at 33°–34° and remains liquid for a long time. It is heavier than water and insoluble therein, but dissolves readily in alcohol and ether. It unites with bromine, forming a di-bromide

$$C_{22}H_{41}BrO_2.Br_2,$$

which melts at 31°–32° and forms amorphous viscid salts. With alcoholic potash the dibromide loses hydrobromic acid, but whether dibromerucic acid or monobrombenolic acid is then produced is still undecided. The formation of one or other of those bodies depends on the number of molecules of hydrobromic acid removed.

When erucic acid dibromide is triturated with water and a large excess of silver oxide, and the mass is heated for several hours till it turns brown and hydrobromic acid is eliminated, on boiling with water a yellow oil separates which is a mixture of liquid oxyerucic acid $C_{22}H_{42}O_3$ and di-oxybenic acid $C_{22}H_{44}O_4$. The latter partially crystallises out on long standing. For complete separation the washed oil is saponified with baryta water; the precipitate is exhausted with ether and the dissolved barium oxyerucate is decomposed by hydrochloric acid. The oxyerucic acid which separates as a colourless oil is purified from alcohol. It is viscid, lighter than water, insoluble therein, but miscible in all proportions with alcohol and ether. Its salts $C_{22}H_{41}O_3M^1$. are amorphous. All excepting those of the alkali metals and barium are insoluble in water. Oxyerucic acid may also be formed from monobromerucic acid by the action of silver oxide. Boiled with potash ley it is converted into di-oxybenic acid (Hausknecht, A. 163, 40). Sodium erucate $C_{22}H_{41}NaO_2$ is soluble in alcohol and gives precipitates of lead and barium erucates on the addition of an alcoholic solution of the acetates of these metals. The silver salt is a curdy precipitate which becomes coloured on exposure to light.

Ethyl erucate $C_{22}H_{41}(C_2H_5)O_2$ is a colourless oil boiling above 360° without decomposition. The amide $C_{22}H_{41}O(NH_2)$, m.p. 84° and the anilide m.p. 55° are crystalline bodies readily soluble in ether and benzene, sparingly soluble in alcohol (Reimer and Will, *l.c.*).

ERUCIN. A crystalline body said to exist in white mustard seed. It is insoluble in water, sparingly soluble in alcohol, easily in ether and in oils (Simon, P. 64, 593).

Di-erucin $C_3H_5OH(C_{22}H_{41}O_2)_2$. When rape oil is allowed to stand for a long time a yellowish tallow-like deposit is frequently found in the casks. This, by repeated solution in ether and subsequent addition of alcohol may be obtained in silky needles. Di-erucin melts at 47° and is readily soluble in ether and light petroleum, insoluble in cold but soluble in hot alcohol. A tri-erucin could not be separated from rape oil (Reimer and Will, *l.c.*).

ERYTHRIN. *Erythric acid, Erythrinic acid* $C_{20}H_{22}O_{10}$. An ethereal salt of erythrol and orsellinic acid; is a constituent of most lichens from which archil is prepared. Erythrin was discovered by Heeren (S. 59, 313) in *Roccella tinctoria*, from which lichen and several others of the same genus it may be extracted by boiling water, or better with milk of lime.

The method employed by Stenhouse to prepare this substance from *R. fuciformis* (C. J. [2] 5, 222) is as follows. Three pounds of the lichen are macerated for 20 minutes in a milk of lime, made by slaking ½ lb. of lime in 3 gallons of water. After three macerations the lichen is completely exhausted. These weak lime liquors are used instead of milk of lime to exhaust fresh quantities of the lichen, whilst the first and strongest liquor is rapidly filtered through bag-filters, 6 inches wide and 6 feet long. The clear liquor as it passes through is immediately precipitated by hydrochloric acid, as prolonged contact with the lime decomposes part of the erythrin. The precipitated erythrin is collected on bag-filters and after the greater portion of the mother liquors has been removed, it is freed from hydrochloric acid and calcium chloride by stirring it up once or twice with a considerable quantity of water, and again collecting.

The experiments of De Luynes (A. Ch. [4] 2, 385), Menschutkin (Bl. [2] 2, 424), and Hesse (A. 139, 22) have confirmed the view first put forward by Berthelot, that erythrin is the diorsellinic ester, and picroerythrin, one of its decomposition products, the mono-orsellinic ester of erythrol.

$$\underset{\text{Erythrol}}{C_4H_6(HO)_4} \qquad \underset{\text{Picroerythrin}}{C_4H_6(HO)_3(C_8H_7O_4)}$$

$$\underset{\text{Erythrin}}{C_4H_6(HO)_2(C_8H_7O_4)_2.}$$

Air-dried erythrin retains 6 p.c. water $=2C_{20}H_{22}O_{10}.3H_2O$ which is partly given off over sulphuric acid, and completely at 100°, the lead salt $(C_{20}H_{19}O_{10})_2Pb_3.3H_2O$ and bromerythrin $(C_{20}H_{19}Br_3O_{10})_2.3H_2O$ (Hesse, J. 1866, 658). Erythrin is a white crystalline solid, m.p. 137° (Hesse), destitute of taste and odour, sparingly soluble in water (1 pt. in about 240 of boiling water) but easily soluble in alcohol, ether, and alkalis. Above 200° it is decomposed, yielding carbon dioxide and orcinol ($C_7H_8O_2$). Boiled with water or with alkalis it is resolved into picroerythrin and orsellinic acid.

$$C_4H_6(HO)_2(C_8H_7O_4)_2 + H_2O$$
$$= C_8H_8O_4 + C_4H_6(HO)_3C_8H_7O_4.$$

On further boiling the orsellinic acid is decomposed into orcinol and carbon dioxide; the picroerythrin may also be broken up into erythrol and a further quantity of orsellinic acid.

On boiling with absolute alcohol, picroerythrin and ethyl orsellinate are formed. If the alcohol contains water, orcinol and carbon dioxide are produced in addition from the action of the water on the erythrin:

$$C_4H_6(HO)_2(C_8H_7O_4)_2 + C_2H_5OH$$
$$= C_4H_6(HO)_3.C_8H_7O_4 + C_8H_7(C_2H_5)O_4$$
$$C_4H_6(HO)_2(C_8H_7O_4)_2 + H_2O$$
$$= C_4H_6(HO)_3C_8H_7O_4 + C_7H_8O_2 + CO_2$$

Ether has no action on erythrin (1 pt. dissolves in 328 of ether at 20°). Amyl alcohol on boiling exerts a similar action to ethyl alcohol.

Strong sulphuric acid dissolves erythrin in the cold, and decomposes it on heating. Hydrochloric acid dissolves it on boiling. Nitric acid dissolves it in the cold without evolution of nitrous fumes, forming a substance soluble in alcohol and precipitated by water; no oxalic acid is produced.

On heating erythrin with nitric acid nitrous fumes are evolved. Bromine converts erythrin dissolved in water into a yellow resin. When the erythrin is covered with ether containing water and bromine is slowly added, tri-brom-erythrin $2(C_{20}H_{19}Br_3O_{10})3H_2O$ is formed in white crystalline spherules, nearly insoluble in cold water, soluble in alcohol, slightly soluble in cold ether. The alcoholic solution is acid, gives a white precipitate with lead acetate, purple with a small quantity of ferric chloride, brown-red with a larger quantity; sodium hypochlorite imparts to it a transient blood-red colour. Boiled with alcohol it is resolved into ethyl dibrom-orsellinate and bromopicro-erythrin. Tri-bromerythrin cakes together a little above 100°C., melts to a colourless frothy mass at 139°, and at a higher temperature gives off acid vapours and burns away (Hesse, A. 117, 310; *ibid.* 139, 32).

Chlorine decomposes erythrin suspended in water, dissolving a considerable portion and forming a yellow resinous substance.

Erythrin reacts as a very weak and unstable acid. With potash, soda, lime, and magnesia, it forms salts having an alkaline reaction, and which are decomposed on heating. Carbon dioxide precipitates erythrin from their solutions if freshly made; after a few days no precipitate is formed.

An alcoholic solution of erythric acid is not precipitated by silver nitrate, but on adding ammonia a white precipitate is formed which soon becomes black and produces a specular deposit of silver. Chloride of gold is not altered by boiling with an alcoholic solution of erythrin. Ferric chloride imparts to the solution a deep purple tint which ammonia changes to yellow, without precipitation, unless the solution is boiled. The alcoholic solution is not precipitated by neutral lead acetate, but with basic acetate it yields a copious precipitate.

Picroerythrin $C_{12}H_{16}O_7$ is produced by the action of boiling water or milk of lime on erythrin. It can be obtained pure by the method given by Hesse (A. 139, 22). Erythrin is boiled with amyl alcohol. When the decomposition is complete, the excess of amyl alcohol is distilled off, and amyl orsellinate gradually separates as a colourless oil. Filtered from this at 40° the liquid deposits white silky efflorescent needles of picroerythrin $C_{12}H_{16}O_7.3H_2O$.

Picroerythrin is a bitter substance, sparingly soluble in cold but readily in boiling water, forming a slightly acid solution. It is unaltered by prolonged boiling with water, and is not etherified by alcohol. It dissolves in cold alkalis, and its ammoniacal solution speedily becomes reddish in contact with air. Boiled with baryta it is broken up into carbon dioxide, orcinol, and erythrol. Its aqueous solution gives no precipitate with neutral lead acetate, but with basic acetate a copious precipitate is produced. It gradually reduces gold chloride, but not silver nitrate, even on boiling, unless ammonia be added. The solution acquires a fine purple tint with ferric chloride.

β-erythrin $C_{21}H_{24}O_{10}$, the homologue of erythrin, was discovered by Menschutkin (Bl. [2] 2, 424; J. 1864, 548). It is prepared by the action of lime water on some varieties of *Roccella fuciformis*. It is a white crystalline powder, m.p. 115°–116° (Lamparter, A. 184, 243). Soluble in alcohol and ether, with violent evolution of carbon dioxide, nearly insoluble in water.

Boiled with water orsellinic acid and β-picroerythrin are produced, with alcohol the latter body and ethyl orsellinate. β-erythrin is coloured transiently red by chloride of lime, and its solution in ammonia forms an easily reducible precipitate with silver nitrate. It gives with basic lead acetate, a gelatinous precipitate.

β-picroerythrin $C_{13}H_{18}O_{10}$ produced by the action of water or alcohol on β-erythrin, crystallises in needles, very soluble in water and alcohol, sparingly soluble in ether. Its aqueous solution is slightly acid, and gives a red colour with chloride of lime. It dissolves also in ammonia, and the solution forms with basic lead acetate a white precipitate, and with silver nitrate a reddish precipitate, which deposits metallic silver on warming. Boiled with baryta water it is resolved into carbon dioxide, erythrol, and β-orcinol (Menschutkin).

ERYTHRITE. *Cobalt bloom v.* COBALT.

ERYTHROBENZIN. A synonym for *Fuchsin* or *Magenta v.* TRIPHENYLMETHANE COLOURING MATTERS.

ERYTHRODEXTRIN is a dextrin produced by the action of diastase or dilute boiling sulphuric acid on starch. It is nearly insoluble in water, is coloured red by iodine, whether it be solid or in solution, and is readily produced from soluble starch by the smallest possible quantity of diastase (Musculus and Gruber, C. R. 86, 1459). Brown and Heron (C. J. 1879, 596) consider that soluble starch $10(C_{12}H_{20}O_{10})$ is broken up by diastase into one molecule of maltose and one of α-erythrodextrin, water being taken up, and that the α-erythrodextrin is further decomposed into maltose and β-erythrodextrin. In this way the destruction of the starch proceeds with the formation of seven achroodextrins till only maltose is left. They also are of opinion, from the fact that the formation of maltose always accompanies that of the erythrodextrin, that this body, the α-dextrin of O'Sullivan (C. J. 1879, 170) and Bondonneau (C. R. 81, 972, 1210), is one of the ordinary transformation products of the degradation of soluble starch, and not merely an isomeride of that body.

Musculus and Gruber (Bl. 30, 54) consider that the starch, under the action of diastase, is converted into the soluble modification $50·66(C_{12}H_{20}O_{10})$, and this, by the assumption of water, into maltose and erythrodextrin. The specific rotation of this body is more pronounced, and its reducing action on alkaline cupric solutions less powerful than those of the achroodextrins into which it is converted previous to the final production of maltose. The experiments of Herzfeld (B. C. 1880, 847, and the fact observed by Bondonneau that maltose and maltodextrin can be produced by the action of diastase on dextrin free from starch, go some way to refute the view held by Musculus and others, that the starch molecule is decomposed into dextrin on the one hand, and into maltose on the other. It is also worthy of note that the red colour with iodine, so characteristic of erythro-dextrin, was obtained with a mixture of an achroodextrin and a ½ p.c. solution of soluble starch (Musculus and Meyer, H. 4, 451).

ERYTHROETIN *v.* RHUBARB.

ERYTHROL. *Erythromannite, Erythrite, Phycite, Pseudorcin, Eryglucin*

$$C_4H_{10}O_4 = C_4H_6(HO)_4.$$

This tetratomic alcohol exists in the alga *Protococcus vulgaris*, and is produced by boiling erythrin or picroerythrin, or the ethyl salts obtained from any of the varieties of *Roccella tinctoria* with excess of baryta of lime.

The extract of *Lecanora Montagnei* obtained with milk of lime, is boiled down in an open pan to about one-third or one-fourth its volume, the lime is precipitated by carbon dioxide, and the filtered solution evaporated to a syrup on the water-bath. The syrup consists mainly of orcinol and erythrol mixed with a considerable quantity of resin and red colouring matter. The orcinol and the greater part of the colouring matter may be extracted with cold ether; or the syrup may be mixed with three times its volume of strong alcohol, from which, after a time, the erythrol separates in small crystals. These are collected on a cloth filter, pressed, washed with cold strong alcohol, and recrystallised twice or thrice from hot alcohol.

Erythrol is prepared from *Protococcus vulgaris* by boiling the alga for some hours with water. The filtered and decolourised solution is then evaporated to a syrup, precipitated with alcohol or basic lead acetate, and the filtrate left to crystallise. Or, 1 lb. of *P. vulgaris* is digested at a temperature of 50°-100° with 2 lbs. of alcohol, the liquid decanted, the green residue strongly pressed, the liquid then filtered, and the alcohol distilled to one half. The erythrol mother liquor, which is deposited on cooling, separates when the liquid is again heated into two layers, and the alcohol at the same time evaporates. The lower of these layers, which is much less coloured than the upper, yields on evaporation a crystalline mass, saturated with a black syrup. On pressing this between fine linen and washing with very cold water, the erythrol may be recrystallised from a hot aqueous solution (Lamy, A. Ch. [3] 35, 138; 51, 232).

From erythrin, which is a di-orsellinate of erythrol, erythrol may be obtained by heating it for about two hours at 150° in a closed iron vessel with a quantity of milk of lime somewhat less than sufficient to decompose it; the exclusion of air prevents the formation of a large quantity of resinous matter. The liquid filtered from calcium carbonate, on evaporation at a gentle heat deposits orcinol in fine crystals, and the mother liquors on further evaporation yield a crystalline mass of orcinol and erythrol, from which the former is extracted by ether (*v.* De Luynes, C. R. 56, 803). Stenhouse (C. J. [2] 5, 222) dissolves the erythrin in a slight excess of milk of lime, boils for half an hour in a vessel with a long condensing tube, to exclude air, precipitates the lime in the resulting solution with carbon dioxide, or (on a large scale) by exact neutralisation with dilute sulphuric acid, and evaporates the filtered solution to dryness. On digesting the residue for twenty to thirty minutes with a mixture of benzene, toluene, &c. (b.p. 110°-150°) in a metallic vessel provided with a condenser, an undissolved portion is left free from orcinol, which on evaporation and filtering from resin &c. deposits crystals of erythrol. These may be purified by washing with cold alcohol, pressing, and recrystallising once or twice from hot water.

Erythrol crystallises in large, colourless, transparent quadratic prisms having an adamantine lustre. Observed faces: $P . \infty P \infty, \frac{3P3}{2}$. Inclination of $P:P = 123° 43'$; $P:\infty P \infty = 109° 29'$; $3P3:\infty P \infty = 138° 42'$ (Miller). Sp.gr. 1·452–1·449 (Schröder, B. 12, 561). It melts at 112°, and volatilises partly undecomposed (Lamy); at 120° (Hesse, A. 117, 327); at 126° (Liebermann, B. 17, 873), and may be cooled far below its melting-point without solidifying. It boils at 329°-331° (uncor.) under ordinary pressures, and at 294°-296° under 200 mm. (Liebermann).

It is optically inactive (Lamy), and has no action on litmus. Its taste is sweet, but less so than that of orcinol, and it is not fermentable by yeast. It is very readily soluble in water, its heat of solution being at 18°-5·2° cal., and at 9°-5·12 cal. (Colson, C. R. 104, 113), sparingly in cold alcohol and insoluble in ether. It does not lose water below 100°, and does not precipitate neutral or basic lead acetate, copper salts, or ammonia nitrate of lead (Stenhouse).

Erythrol is not altered by ammonia, by bromine, or by chloride of lime. Heated to 260° with solid potassium hydrate it yields oxalic and acetic acids with evolution of hydrogen. With fuming hydrochloric acid it gives secondary butyl iodide $C_4H_8.HI$. A concentrated aqueous solution of erythrol in contact with platinum black absorbs oxygen so quickly that the mass becomes red-hot; with a dilute solution the action is more gradual and erythrolic acid $C_3H_4(OH)_2COOH$ is produced (De Luynes, Sell. Bl. [2] 5, 384). By oxidising a warm solution of erythrol with fuming nitric acid, the same acid is generated (Lamparter, A. 134, 243).

With dilute nitric acid, oxalic acid, tartaric acid, and a large quantity of hydrocyanic acid are produced, and with chromic acid and potassium permanganate, or with chromic mixture, formic acid, carbon dioxide, and oxalic acid are obtained (Przybytek, Bl. [2] 35, 108).

E. Fischer and J. Tafel (B. 20, 1088) by the oxidation of erythrol with dilute nitric acid procured a substance which reduced Fehling's solution and which formed with phenyl hydrazine a crystalline body $C_{16}H_{18}N_4O_2$, m.p. 166°-167°, sparingly soluble in water, more readily in ether and benzene. By dissolving powdered erythrol in small quantities at a time in fuming nitric acid, keeping the solution cool and mixing it with a weight of sulphuric acid equal to, or rather more than the nitric acid used, Stenhouse obtained a crystalline mass, which, washed with cold water and recrystallised from hot alcohol, gave large shining laminæ, m.p. 61° of butinetetranitrate (tetranitrate of erythrol, nitro-erythrol $C_4H_6(O.NO_2)_4$. This body takes fire when strongly heated, and when perfectly dry and mixed with sand it detonates under the hammer.

When erythrol is dissolved in sulphuric acid (1 part of erythrol to 20-30 of concentrated sulphuric acid) and the mixture heated to 60°-70°, the compound $C_8H_{11}O_2(SO_4H)_3$ is produced which forms salts with metals. The general formula of the salts is $M''_3(C_8H_{11}S_3O_{14})_2$. Those of calcium and barium take up six, and that of lead, twelve, molecules of water of crystallisation (Hesse, A. 117, 329).

Erythrol dissolves easily in chlorosulphonic acid (sulphuric monochloride) forming acid butine tetrasulphate (erythrol tetrasulphuric acid $(C_4H_6(SO_4H)_4$, which crystallises in snow-white masses consisting of small prisms. It is decomposed by water with regeneration of erythrol. Its potassium salt $C_4H_6(SO_4K)_4 + 4H_2O$ is formed by neutralising a well-cooled aqueous solution with potash. The salt is sparingly soluble in cold, readily in hot water. The barium and lead salts are obtained on heating a solution of the potassium salt in the water bath, with barium chloride and lead acetate respectively (P. Claësson, J. pr. [2] 20, 1-34).

By heating erythrol for about 100 hours with 12-15 parts concentrated hydrochloric acid, De Luynes (A. Ch. [4] 2, 385; J. 1864, 497) obtained erythrol di-chlor-hydrin $C_4H_6(OH)_2Cl_2$. By raising the temperature to 120°-130° the result is more quickly attained, or the compound may be produced by heating erythrol to 120°–130° in a current of hydrochloric acid (Przybytek, B. 14, 2072). It melts at 124°–125° (m.p. 145° De Luynes).

Butine tetrachloride $C_4H_6Cl_4$ is produced by the action of phosphorus pentachloride on erythrol. It melts at 73° and crystallises in prisms (Henninger, Bl. 34, 194, Bell, B. 12, 1271). By acting on erythrol dichlorhydrin with a mixture of nitric and sulphuric acids, di-nitro-dichlorhydrin $C_4H_6(Cl_2)(NO_2)_2O_2$, m.p. 60°, is obtained (Champion).

Erythrol dibromhydrin $C_4H_6(Br_2)(OH)_2$ is formed by heating erythrol with a saturated solution of hydrobromic acid for 3 hours at 100° in a sealed tube. It is insoluble in water and melts at 130° (Champion, C. R. 73, 114). When this body is put into a mixture of fuming nitric acid and concentrated sulphuric acid, and the solution after a time is poured into cold water, a flaky precipitate of dinitrodibromhydrin, $C_4H_6(Br_2)(NO_2)O_2$, m.p. 75°, is produced. It does not detonate under the hammer (Champion). Phosphorus pentabromide converts erythrol into the compound $C_4H_6Br_4$, m.p. 112° identical with the crotonyline tetrabromide of Henninger (Colson, C. R. 104, 113).

By the action of bromine on erythrol in sealed tubes heated to 175°, Colson (*l.c.*) obtained a liquid which he considers has probably the formula $CBr_2.CHBr.CHBr.CH_2Br$ and a solid isomeric with the liquid, melting at 167°–169° to which he assigns the symmetrical formula

$$CHBr_2.CHBr.CHBr.CHBr_2.$$

When erythrol is boiled for 6 hours with two and a half times its weight of formic acid, and the excess of acid distilled off, a crystalline residue consisting of various formins—salts of erythrol in which one or more pairs of OH-groups are replaced by formyl—is obtained. Tetraformin $C_4H_6(H.COO)_4$ is thus obtained in silky needles melting at 150° and decomposed by hot water. On distilling the mixture of formins at 250°, carbon monoxide, carbon dioxide, and crotinyline are evolved and a liquid passes over consisting of water, formic acid, crotonaldehyde and two other substances, viz. crotonylene glycol $C_4H_6(OH)_2$ and a liquid (C_4H_6O), b.p. 67°, for which Henninger proposes the name dihydrofurfurane. The reaction also gives rise to the first anhydride of erythrol $C_4H_8O_3$ (Henninger, C. R. 98, 149).

The second anhydride of erythrol $C_4H_6O_2$, was prepared by Przybytek (B. 17, 1091) by the action of potash on erythrol dichlorhydrin. It is a colourless mobile volatile liquid, b.p. 138°. The sp.gr. at 0° is 1·1322. It combines with water, acids, and ammonia. Water slowly converts it into erythrol, and hydrochloric acid into the original dichlorhydrin. It forms compounds with hydrocyanic acid and aniline. Its constitutional formula is

$$\underbrace{CH_2\;.\;CH}_{O}.\underbrace{CH\;.\;CH_2}_{O}.$$

When heated with anhydrous barium oxide for three days at 200°–220° the anhydride yields furfuran; when heated with phosphorus pentasulphide it gives thiophen. A solid polymer of the anhydride is produced during the reaction (Przibytek, J. R. 1886, 123°–124°). Thiophen, impure, may be obtained from erythrol itself by distilling it with phosphorus pentasulphide and sand (Paal and Tafel, B. 18, 188).

Oxalins corresponding to the formins of erythrol are formed on heating erythrol with oxalic acid (Lorin). By acting on erythrol with nitroalizarin in presence of sugar and sulphuric acid, beautiful colouring matters soluble in alcohol are obtained (Brunner, B. 15, 174).

By subjecting erythrol to the action of a mixed ferment from cowdung, two molecules of the alcohol are resolved into one of butyric acid and one of succinic acid, water and hydrogen being eliminated. With hay-water butyric and acetic acids with traces of alcohol and formic acid are produced, together with succinic acid in much less quantity than in the preceding fermentation. The erythrol seems to be decomposed in different ways by the two ferments, succinic acid in the one case, and volatile acids in the other, being the main products of the change (Fitz, B. 11, 1890; B. 12, 474).

ERYTHROLEÏNIC ACID *v.* ARCHIL.

ERYTHROPHLEÏNE is an alkaloid occurring in the bark of *Erythrophlœum guineense*. It is an active poison, and may be obtained from the bark by treating the alcoholic extract, evaporated to small bulk, with warm water, evaporating the aqueous extract at a low temperature, and rendering it alkaline with ammonia or sodium carbonate. On extracting with acetic ether and evaporating the resulting solution, the base is left. It is slightly soluble in ether, benzene, and chloroform, but dissolves in water, ethyl acetate, amyl alcohol, and ordinary alcohol. It forms salts with acids, and its chloride forms a double salt with platinic chloride. Its solutions exhibit the following reactions:

Picric acid: yellow-green precipitate.

Iodine in potassium iodide: reddish-yellow precipitate.

Iodide of mercury and potassium: white precipitate.

Iodide of bismuth and cadmium: flocculent white precipitate.

Potassium bichromate: yellowish precipitate.

Mercuric chloride: white precipitate.

Auric chloride: whitish precipitate.

Palladium chloride: white precipitate.

In contact with manganese dioxide and sulphuric acid, a violet colour, less intense than that produced by strychnine under the same circumstances, is obtained. It soon changes to dirty brown. With acids and alkalis, in boiling, erythrophleïne splits up into erythrophleïc acid and a volatile base, manconine.

Erythrophleïne acts on the system like a mixture of digitaline and picrotoxine. Erythrophleïc acid has no marked action. Manconine behaves like nicotine and pyridine.

Gallois and Hardy (Bl. [2] 26, 39), Harnack and Zabrocki (B. 15 [2] 2623), Harnack (B. 16, 87).

ERYTHROSIN. The potash or soda salt of tetraiodofluoresceïn obtained by iodising fluoresceïn in an aqueous or alkaline solution

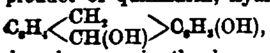
$$C_{20}H_6O_5I_4M_2.$$

Known also as Erythrosin B, Pyrosin B, Iodeosin Dianthine B, Eosin J, &c.

ERYTHROSIN G. The potash or soda salt of Diiodofluoresceïn $C_{20}H_8O_5I_2M_2$, obtained by Nölting in 1875 by iodising fluoresceïn with iodine and iodic acid, or by iodine chloride and alkali.

ERYTHROXYANTHRAQUINONE $C_{14}H_8O_3$ is produced, along with an isomeric hydroxyanthraquinone, by the action of phthalic anhydride on phenol, in presence of sulphuric acid. $C_8H_4O_3 + C_6H_6O = H_2O + C_{14}H_8O_3$. Salicylic acid, anisol, and even asinic acid behave in the same way as phenol. The two hydroxyanthraquinones are separated by boiling with water and barium carbonates; erythroxyanthraquinone is unaltered by this treatment, whereas in the case of the isomer a soluble barium compound is formed.

Erythroxyanthraquinone may also be prepared from amido-anthraquinone, dissolved in acetic acid to which a little sulphuric acid has been added, by adding potassium nitrite till the solution becomes yellow. After a short time, on adding water and boiling, yellow flakes of erythroxyanthraquinone separate, and increase as the acetic acid evaporates. The body may be recrystallised from alcohol (Roemer, B. 15, 1786). Erythroxyanthraquinone crystallises from alcohol in groups of pomegranate-yellow needles, more soluble in hot than in cold alcohol. It melts at 173°-180° (Baeyer and Caro), at 190° (Liebermann), at 191° (Roemer). It begins to sublime at 150°, and condenses to form fine needles, reddish-yellow in colour, like alizarin. It is almost insoluble in dilute ammonia, and only slightly soluble in strong ammonia. With lime or baryta-water it gives a dark-red, almost insoluble lake, decomposable by carbon dioxide. The absorption spectrum of a sulphuric acid solution of erythroxyanthraquinone differs from that of its isomeride, hydroxyanthraquinone; the latter body is also more easily converted into alizarin by fusion with caustic potash than the former (Baeyer and Caro, B. 7, 968).

The constitution of erythroxyanthraquinone has been established by Liebermann (B. 10, 611; 11, 1611), who synthesised it from a reduction product of quinizarin, hydroxyhydroanthranol,  $C_6H_4\Big\langle{}^{CH_2}_{CH(OH)}\Big\rangle C_6H_3(OH)$, in which the hydroxyl group in the benzene nucleus occupies the ortho- position. Frande (B. 12, 237) was also able to show that in methylhydroxyanthraquinone, a derivative of ordinary hydroxyanthraquinone, the hydroxyl group was in the para- position, and hence, in the isomeric erythroxyanthraquinone, the hydroxyl group must be in the ortho- position with regard to the ketone group. Erythroxyanthraquinone is therefore *o*-hydroxyanthraquinone *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

ESCHEL *v.* COBALT.

ESPARTO, *Macrochloa* and *Stipa tenacissima*, Endogen. This grass is a native of Spain, Portugal, Greece, and North Africa. It is largely used as a raw material for paper-making, having been introduced into this country by Routledge. For this purpose it possesses many advantages, as it grows abundantly without cultivation, is easily harvested, yields a large percentage of cellulose of high quality with comparatively simple treatment.

Of the various kinds known to commerce, such as Spanish, Tripoli, Arzen, Oran, Sfax, Gabes, &c., the first-named is preferred by paper-makers, as it yields more and better fibre. It therefore commands a higher price.

To give some idea of the importance of esparto as a paper-making material, it may be mentioned that the annual imports into the United Kingdom are between two and three hundred thousand tons.

It is also used for the purpose of making coarse mats and ropes (*v.* Spon's Enc. of the Industrial Arts).

Esparto arrives in this country firmly pressed into bales. The first operation which it undergoes in the paper mill is that of 'dry-picking,' in contradistinction to a subsequent process known as 'wet-picking.' The grass is spread out on tables covered with coarse wire cloth, and any root-ends, weeds, &c., which may have found their way into the bales through imperfect gathering are picked out. Any sand or dirt escapes through the wire cloth. The removal of dirt can be more completely effected by machinery. For this purpose the grass is fed into a mechanical duster or willow, where it receives a violent shaking, the dirt being loosened and removed. The cleaned esparto is then fed into 'vomiting' boilers, where it is treated with caustic soda solution at pressures varying from 10 to 40 lbs. per sq. in. for from 3 to 5 hours. The amount of soda required is about 17 lbs. of 60 p.c. caustic soda per cwt., but it varies with the quality of the grass, the form of boiler, the pressure at which it is boiled, and the time allowed. When the boiling is completed, the liquor is run away, evaporated to dryness and ignited, and the alkali recovered in the form of carbonate. This is dissolved in water, converted into caustic by means of lime, and is again available for use.

The boiled grass is washed once or twice in the boiler, and is then subjected to the 'wet-picking' process, whereby any unboiled portions are removed. The process is being gradually abandoned in favour of what is known as the 'presse-pâte' system, which consists in purifying the pulp by passing it when bleached through a series of strainers and knotters. It is then made into a coarse web of pulp on the 'presse-pâte,' which may be described as a paper machine without the drying cylinders.

The subsequent treatment of esparto does not differ essentially from that of other fibres, and need not be particularly described.

The ultimate fibres of esparto vary in length from 3·5 to 0·5 mm., the mean being about 1·5; the mean diameter is 0·012 mm.

The fibres possess, owing to their fineness and their tendency to curl, considerable 'felting' properties. Paper made from esparto is soft to the touch, 'bulks' well, and at the same time is strong.

Esparto cellulose can be recognised in a paper by the fact that when boiled with a solution of aniline sulphate a rose-pink colour is developed. A similar colour is produced with straw cellulose, but of a paler shade. They can be distinguished by the size and shape of the peculiar serrated cuticular cells which are to be seen when the celluloses are examined under the microscope.

Moreover, esparto pulp always contains a number of the fine hairs which line the inner surface of the glabrous leaf, and which serve to distinguish it from straw.

The chemical characteristics of esparto are those of the ligno-celluloses and the pecto-celluloses, the latter predominating.

Its composition is shown by the following analyses (Hugo Müller):

	Spanish	African
Cellulose	48·25	45·80
Fat and wax	2·07	2·62
Aqueous extract	10·19	9·81
Lignin and pectous substances	26·39	29·30
Ash	3·72	3·67
Water	9·38	8·80
	100·00	100·00

ESTRAMADURITE *v.* Calcium.

ETHYL COMPOUNDS *Ethyl*

$C_2H_5 = CH_3 - CH_2$

is a univalent basylous radicle not known in the free state, the body $C_4H_{10} = (C_2H_5)_2$ which was named ethyl (afterwards diethyl) by its discoverer, Frankland (C. J. 2, 263), being now regarded as butane.

Ethyl acetamide *v. Ethylamine.*

Ethyl acetate *v.* under Acetic acid.

Ethyl alcohol *v.* Alcohol.

Ethyl boride $(C_2H_5)_3B$. *Triethyl boride, Borethyl*; b.p. 95°. Sp.gr. $\frac{23^\circ}{}$ = ·696. V.D. = 3·40 at 132° = 3·598; at 101·6° = 3·76; calc. = 3·399. From action of $Zn(C_2H_5)_2$ upon $(C_2H_5)_3BO_3$, or from BCl_3 and $Zn(C_2H_5)_2$ (Frankland, Tr. 1862, 167; Pr. 1876, 25, 165).

A spontaneously inflammable, colourless liquid burning with green flame, decomposed by HCl, evolving C_2H_6, and forming $B(C_2H_5)_2Cl$. Is slowly decomposed by water, and destroyed by HNO_3, with formation of boric acid. Absorbs NH_3, forming an oily liquid $NH_3B(C_2H_5)_3$ of an aromatic odour, which is fairly stable even in contact with O. $B(C_2H_5)_3$ absorbs O and forms $B(C_2H_5)_3O_2$, b.p. 125°. This, by the action of water, yields ethylboric acid $B(C_2H_5)(OH)_2$, a crystalline solid resembling naphthalene in appearance; can be sublimed at 40°, has a sweet taste, and acid action, but does not combine with bases. By action of $Zn(C_2H_5)_2$ upon this body we get $B(C_2H_5)(OC_2H_5)_2$ and $B(OC_2H_5)_3$ b.p. 112°; V.D. (dissoc.) 2·78. By further action of $Zn(C_2H_5)_2$ upon ethylboric acid we get $B(C_2H_5)_2OC_2H_5$ b.p. 102°; V.D. = 3·914. Water converts this into $B(C_2H_5)_2OH$, a spontaneously inflammable liquid which absorbs oxygen, yielding $BC_2H_5OC_2H_5OH$, m.p. 8°.

Ethyl bromide C_2H_5Br. *Hydrobromic,* or *Bromhydric ether*, b.p. 38·37 (Regnault, J. 1863, 70); b.p. 40·7° at 57 mm. (Pierre); sp.gr. $\frac{15^\circ}{}$ = 1·4189 (Mendeléeff); $\frac{0^\circ}{}$ = 1·4733 (Pierre); $\frac{13·5^\circ}{}$ = 1·4685; crit. temp. = 236° (Pawlewski, B. 16, 2633).

Preparation.—1. By action of P and Br upon alcohol (Serullas, A. Ch. 34, 99). 40 parts red P and 160 parts absolute alcohol are slowly mixed with 100 parts Br, kept cool until all action is over; the mixture is then distilled, and the distillate purified by washing with water and rectification (Personne, C. R. 52, 468). 2. Absolute alcohol is heated with Br and distilled, and the distillate is freed from excess of Br by washing with KOH and a second distillation (Löwig, A. 3, 288).—3. 4 parts KBr and 5 parts of a mixture of 2 parts H_2SO_4 and 1 part alcohol of 96 p.c. are distilled, and distillate purified as above (De Vrij, J. 1857, 441).—4. C_2H_4 in presence of $AlBr_3$ combines with HBr to form C_2H_5Br (Gustavson, J. R. 16, 95).

Is a colourless liquid having a sweetish taste, with burning after-taste. Its vapour possesses anæsthetic properties (Robin, C. R. 34, 649). Is slightly soluble in water, and miscible with alcohol and ether. The vapour is decomposed by heat, yielding C_2H_4 and HBr, or, if the temperature be higher, C is deposited (Löwig). Burns in air with a green flame, evolving HBr. By introduction of Cl we get 2 isomeric bodies of the composition C_2H_4ClBr b.p. 84·5° and 106°, and 3 isomers of composition $C_2H_3Cl_2Br$ b.p. 137°, 151°, and 160° (Lescœur, Bl. 29, 483). By action of Br we get (1) $CH_2Br.CH_2Br$, (2) $CH_3.CHBr_2$, (3) $CH_2Br.CHBr_2$, and (4) $CH_2Br.CBr_3$ (Tawildarow, A. 176, 12). By action of Br and P upon alcohol we get, further, $C_2H_4Br_2$ b.p. 160°, $C_2H_3Br_3$ b.p. 180°, $C_2H_2Br_4$ b.p. 196°–200° (Bertrand, Finot, Bl. 34, 28); *v. Ethylene bromide.*

With ammonia it yields $N(C_2H_5)H_3Br$, and with ethylamine, diethylammonium bromide $N(C_2H_5)_2H_2Br$; similarly, with diethylamine, it yields $N(C_2H_5)_3HBr$. $AlBr_3$ has no action in the cold, but, on heating, decomposes C_2H_5Br, yielding HBr, hydrocarbons and a compound of the composition $C_4H_8.AlBr_3$ (Gustavson, J. R. 16, 102).

Ethyl chloride C_2H_5Cl. *Chlorhydric* or *Hydrochloric ether* b.p. 12·5° (Regnault, J. 1863, 67); sp.gr. $\frac{0^\circ}{}$ = ·9214; $\frac{8^\circ}{}$ = ·9176; $\frac{0^\circ}{}$ = ·920 (Pierre); = at b.p. ·851 (Ramsay, C. J. 35, 470); S.V. 75·8 (Kopp). (Robiquet and Colin, A. Ch. [2] 1, 348; Regnault, A. Ch. 71, 355; Kuhlman, A. 33, 108; Löwig, P. 14, 346; Gm. 7, 367; Gerh. 11, 308).

From alcohol by the action of S_2Cl_2 or metallic chlorides (Rouelle [1759]); from alcohol and HCl (Basse [1801]). Composition first ascertained by Robiquet and Colin. Also formed by action of Cl upon C_2H_6 (Darling, A. 150, 216), and of HCl upon ether in sealed tubes (Berthelot).

The action of HCl upon alcohol gives a very poor yield of C_2H_5Cl unless $ZnCl_2$ is added to the alcohol before passing in HCl (Groves, C. J. 1874, 636). Krüger (J. pr. [2] 14, 193) recommends that a mixture of 1 part of $ZnCl_2$ in 82 parts of alcohol should be saturated with HCl gas in the cold, and then heated to boiling-point. HCl being passed in during distillation, a reflux condenser stops the alcohol vapour, and the C_2H_5Cl passes on and is collected in a well-cooled receiver. The $ZnCl_2$ is said to act by abstracting water from the alcohol, and the nascent C_2H_4 combines with HCl to form C_2H_5Cl.

The formation of C_2H_5Cl in this process is partly due to the action of HCl upon alcohol, and partly to the union of this nascent C_2H_4 with HCl (Schorlemmer, C. J. 1875, 308); this view is sustained by the fact that, if amyl alcohol be thus treated, both primary and secondary amyl alcohol are produced, and the latter can only be formed from the radical C_5H_{10}. Ethyl chloride is also formed by the action of PCl_5 upon alcohol, and also, to some extent, by the action of Cl upon alcohol. Hence the formation of ethyl chloride in the manufacture of chloral.

It is a colourless mobile liquid which does not freeze at −29°; has a pungent ethereal smell, and a sweetish taste, and burns with a green-edged flame, evolving HCl. It is sparingly soluble in water, but mixes readily with alcohol and ether. It dissolves phosphorus, sulphur, fats, oils, and many resins. It combines with many metallic chlorides—*e.g.* $SbCl_3$, Fe_2Cl_6—to form crystalline compounds.

It is used in medicine like ether, but, on account of its volatility, it is mixed with an equal volume of alcohol, and is then known as "'alcoholised muriatic ether' P.B. It is decomposed at a red heat into C_2H_4 and HCl; at higher temperatures carbon separates, and CH_4, H, and HCl are set free. Strong HNO_3, when boiling, liberates HCl and forms $C_2H_5NO_3$ in small quantity (Thenard, Boullay). SO_3 absorbs it, forming $SO_3.C_2H_5Cl$, a fuming liquid b.p. 130°—probably the three isomers $C_2H_5O.SO_2.Cl$, $CH_2Cl.CH_2.SO_2.OH$, and $CH_2(OH).CH_2SO_2.Cl$ (Purgold, Z. 1868, 669; B. 6, 502). When vapour of C_2H_5Cl is passed through boiling H_2SO_4, HCl is evolved (Thenard), also C_2H_4 and SO_2 (Boullay). When the vapour is led through a tube containing heated soda-lime, a mixture of CH_4 and H is evolved, and $NaC_2H_3O_2$ and Na_2CO_3 are formed (L. Meyer, A. 139, 282), while, according to Dumas and Stas, C_2H_4 and NaCl are formed. On $AgNO_3$ C_2H_5Cl has no action until after prolonged contact, but even after some months only a very small quantity of AgCl is formed (Thenard, Boullay); but AgCl is rapidly thrown down when C_2H_5Cl is heated with a sol. of $AgNO_3$ to 100° in sealed tubes (G. C. Foster).

NH_3 has only a slight action at ordinary temperatures, but on heating a mixture of NH_3 and C_2H_5Cl ammonia and ethylene are formed, and a deposit of NH_4Cl is noticed (Dumas and Stas, A. Ch. 73, 154). When a mixture of ethereal NH_3 and C_2H_5Cl is exposed to sunlight, crystals of ethylamine hydrochlorate separate (Stas, K. 1, 455). When heated with alcoholic NH_3 to 100° in sealed tubes, $NH_3C_2H_5Cl$ is also produced, together with traces of $NH_2(C_2H_5)_2Cl$ and $N(C_2H)_4Cl$ (Groves, C. J. 13, 331). KOH slowly removes Cl from C_2H_5Cl, yielding (in aqueous sol.) alcohol and KCl. Alcoholic KOH and C_2H_5Cl heated to 100° in sealed tube deposits KCl and forms $(C_2H_5)_2O$ (Balard, A. Ch. [3] 12, 302). Passed into heated sol. of K_2S, sulphide of ethyl is formed; with alcoholic KHS mercaptan is formed (Regnault).

Chlorine derivatives of ethyl chloride.—(Regnault, A. Ch. [2] 71, 355; Beilstein, A. 113, 110; Geuther, J. 1870, 436; Z. 1871, 147; Stadel, Z. 1871, 513; B. 6, 1403; A. 195, 182). Cl has no action upon C_2H_5Cl in the dark, but acts slowly in diffuse light, and rapidly in sunlight, forming $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 (Regnault).

Dichlorethane, $C_2H_4Cl_2$.

1. *u-Dichlorethane*, CH_3CHCl_2, *v. Ethylidene chloride.*

2. *s-Dichlorethane* $CH_2Cl.CH_2Cl$ *v. Ethylene chloride.*

Trichlorethane $C_2H_3Cl_3$.

1. *Chlorethylene chloride* $CH_2Cl.CHCl_2$, b.p. 115° (Pierre, A. 80, 127); 113·7° at 760 mm. (Städel, B. 15, 2563); 113°·5–114° at 753·2 (Schiff, A. 220·97); sp.gr. $\frac{0^\circ}{\ }$ 1·4223 (P.); $\frac{9\cdot4^\circ}{4^\circ} = 1\cdot14577$; $\frac{113\cdot5^\circ}{4^\circ} = 1\cdot2945$ (Schiff); $\frac{25\cdot6^\circ}{0^\circ} = 1\cdot4406$ $\mu_A = 1\cdot4719$ at 22°; $R_\infty = 42\cdot26$ (Kanonnikow), from C_2H_3Cl and PCl_5 (Regnault, A. Ch. [2] 69, 151).

2. *Ethenyl trichloride* $CH_3.CCl_3$, b.p. 74·5° (Geuther, J. 1880, 435), 74·1° at 760 mm. (Städel, B, 15, 2563); sp.gr. $\frac{0^\circ}{\ } = 1\cdot3465$ (Pierre, A. 80, 127), $\frac{16^\circ}{\ } = 1\cdot372$ (Regnault, A. 33, 317), $\frac{0^\circ}{\ } = 1\cdot3657$, $\frac{26^\circ}{4^\circ} = 1\cdot3249$; $\mu_A = 1\cdot4199$ at 21°; $R_\infty = 42\cdot0$ (Kanonnikow): by the chlorination of ethyl chloride (Regnault, A. 33, 317). Decomposed by sodium alcoholate, giving $C_2H_2ClOC_2H_5$ and $C_2H_4O_2$.

Tetrachlorethane $C_2H_2Cl_4$.

1. *u*-$CH_2Cl.CCl_3$, b.p. 135° (Regnault, A. Ch. [2] 69, 162), 138·6° (Pierre, A. 80, 130), 135·1° cor. (Geuther, Brockhoff, J. 1873, 317); sp.gr. $\frac{0^\circ}{\ } = 1\cdot6116$ (P.), $\frac{19^\circ}{\ } = 1\cdot576$ (R.), $\frac{0^\circ}{\ } = 1\cdot5825$, $\frac{26^\circ}{\ } = 1\cdot5424$; μ_A at $t^\circ = 1\cdot4772 - 0\cdot000437t$, $R_\infty = 50\cdot72$ (Kanonnikow). Formed by chlorination of ethyl chloride (Laurent, A. 22, 292); or action of Cl upon $CH_2Cl.CHCl_2$ (Regnault). Decomposed by sodium alcoholate into $C_2HCl_2.OC_2H_5$ and $CH_2(OC_2H_5)CO_2Na$.

2. *s*-$CHCl_2.CHCl_2$, b.p. 147° cor.; sp.gr. $\frac{0^\circ}{\ } = 1\cdot614$; $\frac{24\cdot3^\circ}{\ } = 1\cdot578$ (Paterno, Pisati, J. 1871, 508) $\frac{0^\circ}{\ } = 1\cdot6258$; $\frac{26^\circ}{0^\circ} = 1\cdot5897$; μ_A at $t^\circ = 1\cdot4905 - 0\cdot000433t$; $R_\infty = 50\cdot6$ (Kanonnikow). From C_2H_2 and $SbCl_5$ (Berthelot, Jungfleisch, A. Suppl. 7, 254), from dichloraldehyde and PCl_5 (Paterno, Pisati); by long heating yields HCl and C_6Cl_6.

Pentachlorethane $CHCl_2.CCl_3$, b.p. 159·1° cor.; 161·7° at 760 mm. (Städel); m.p. −18°; sp.gr. $\frac{0^\circ}{\ } = 1\cdot7089$; $\frac{10\cdot15^\circ}{4^\circ} = 1\cdot6926$ (Thorpe, C. J. 37, 192); $\mu_A = 1\cdot4871$ at 25·1°; $R_\infty = 59\cdot05$ (Kanonnikow). By action of chlorine upon C_2H_5Cl, also from C_2HCl_3O and PCl_5 (Paterno, A. 151, 117).

Hexachlorethane $CCl_3.CCl_3$ *v. Carbon trichloride*, art. CARBON.

Ethyl cyanate $CN.OC_2H_5$, *Cyanetholine*; sp.gr. $\frac{15}{\ } = 1\cdot127$; decomposed by heating; by passing CNCl into C_2H_5ONa in absolute alcohol (Cloëz, C. R., 44, 428; A. 102, 355); from CNBr and absolute alcohol and ether (Ponomarew, B. 15, 515; Mulder, R. 1, 210; 2, 133), 3 parts Na are dissolved in a mixture of 58 parts alcohol and 116 parts ether and a solution of 19 parts CNBr dissolved in 70 parts ether added, the mixture after filtering is distilled on the water-bath, to the residue 86 parts of water are added and the precipitated oil washed with water (Mulder, R. 3, 306).

It is a colourless liquid, insoluble in water, miscible with alcohol and ether, split up by KOH into C_2H_5OH and KCNO, by action of HCl splits up into C_2H_5Cl and $H_3C_3N_3O_3$ (Gal, B. 6, 439).

Ethyl iso-cyanate, *Ethyl carbimide*, $C_2H_5.NCO$, b.p. 60° (Wurtz, A. Ch. [3] 42, 43); sp.gr. ·8981 (W.). By action of KCNO upon $KC_2H_5SO_4$ at 180–250°. Distillate is a mixture of the cyanate (iso-cyanate) and the iso-cyanurate, which can easily be separated by distillation. Ethyl carbimide is a mobile liquid with a suffocating smell. It is converted by water, ammonia, or the amines into ethylated ureas. It is decomposed by KOH into ethylamine and potassium carbonate.

$CO_2C_2H_5NCO + 2KOH = K_2CO_3 + N(C_2H_5)H_2$. (Wurtz).

HCl led into $C_2H_5N.CO$ yields ethyl carbonyl ammonium chloride $N(C_2H_5)CO.HCl$ b.p. 95° (Habich and Limpricht, A. 109, 107), b.p. 108–112° (Gal, Bl. 6, 435), a strongly-smelling liquid whose vapour excites tears; decomposed by water into CO_2 and $N(C_2H_5)H_3Cl$.

A similar compound with HBr is known b.p. 118–122° (Gal).

Ethyl cyanide or **Propionitrile** C_2H_5CN (Pelouze, A. 10, 249; Frankland and Kolbe, A. 65, 269; C. J. 1, 60; Dumas, Malaguti and Leblanc, A. 74, 329); b.p. 98·1° cor. (Engler, A. 133, 153); 97·08° cor. (Thorpe, C. J. 37, 205); 97°–97·2° at 757·1 mm. (Schiff, B. 19, 567); sp.gr. $\frac{0^\circ}{} = \cdot 8010$, $\frac{73\cdot 6^\circ}{4^\circ} = \cdot 7938$ (Thorpe), $\frac{97^\circ}{4^\circ} = \cdot 7015$ (S.); H.C. (as vap.) at 18° = 471·450 cal. (Thomsen, Th. 4, 129).

From $Ba(C_2H_5SO_4)_2$ and KCN (P.), from cyanogen chloride and $Zn(C_2H_5)_2$ (Gal, Z. 1868, 252), from $Zn(C_2H_5)_2$ and $(CN)_2$ (Frankland and Graham, C. J. 37, 740).

Preparation.—By heating C_2H_5I with pure KCN and alcohol to 180°; C_2H_5Cl dissolved in three times its weight of alcohol is heated with KCN to 100° or 150° (Rossi, A. 159, 79). C_2H_5I is heated with KCN in closed tubes to 180° and the product distilled, and the distillate is freed from excess of C_2H_5I by means of a solution of $CaCl_2$, upon which the C_2H_5CN swims, while the heavier C_2H_5I sinks to the bottom (Williamson, P. M. [4] 2, 205; Gautier, A. Ch. [4] 17, 180).

It is a mobile colourless liquid with an agreeable odour, soluble in water from which $CaCl_2$ or NaCl causes it to separate. V.D. = 1·928. It combines with the hydracids, *e.g.*, HCl; the product C_2H_5NHCl forms monoclinic prisms soluble in water and melting at 121° (Gautier). Chlorine combines with C_3H_5N to form dichlorpropionitrile $C_3H_3Cl_2N = CH_3.CCl_2.CN$, a liquid body b.p. 103–107°, which polymerises on standing to a solid $(C_3H_3Cl_2N)_3$. By distillation of KCN with $KC_2H_5SO_4$ Gautier obtained a liquid, b.p. 79°, of the composition $C_3H_5N.3C_2H_6O$ miscible with water and volatile only with dissociation. Propionitrile also forms compounds with metallic chlorides and with cyanogen chloride. $C_3H_5N.CNCl$ is a liquid decomposed by water; b.p. 60–68° (Hencke, A. 106, 280).

A compound $2(C_2H_5.CN)Pt(CN)_2.2H_2O$ is formed as reddish needles by the action of HCl upon $Pt(CN)_2$ in absolute alcohol (Than, A. 107, 315). Propionitrile is decomposed by KOH yielding potassium propionate

$$C_2H_5CN + KOH + H_2O = \left\{\begin{matrix}C_2H_5\\COKO\end{matrix}\right. + NH_3.$$

Dilute H_2SO_4 yields propionic acid and $(NH_4)_2SO_4$ and also, according to Meyer (J. pr. 67, 147), ethylammonium sulphate.

By the action of metallic potassium upon C_2H_5CN we get $KCN.C_2H_6$ and cyanethine $C_9H_{15}N_3(=(CH_3)_3C_6H_2N.(NH).NH^2\,?)$ (Frankland and Kolbe, C. J. 1, 60).

Ethyl cyanurate $(C_2H_5OCN)_3$; m.p. 29° (Mulder, B. 15, 70; R. 2, 133); b.p. 275° (Claesson, J. pr. [2] 33, 131), separates from crude ethyl cyanate (M.); by passing $(CN)_2$ into a mixture of dry C_2H_5NaO and absolute ether (Ponomarew, B. 18, 3265); also, together with isocyanurate by the action of $Ag_3C_3N_3O_3$ upon C_2H_5I in the cold (P.); an oily liquid soluble in alcohol, ether, $CHCl_3$ and CS_2; 100 parts cold H_2O dissolve 7 parts of $(C_2H_5OCN)_3$, the aqueous solution gives with Nessler's reagent a heavy precipitate.

Ethyl cyanurate is decomposed by HCl with formation of $(HCNO)_3$; with Br forms unstable yellow needles $(CNOC_2H_3Br_2)_3$. A hydrate $(C_2H_5.CNO)_3 + 12H_2O$ separates as long needles from the aqueous solution on standing at 0° (Mulder, R. 1, 203).

$(C_2H_5.CNO)_3HgCl_2$, needles insoluble in water, soluble in alcohol and ether, separates when two constituents are warmed together in dilute aqueous solution (Ponomarew, B. 18, 3265).

Ethyl iso-cyanurate

$$C_9H_{15}N_3O_3 = C_3N_3O_3(C_2H_5)_3;$$

m.p. 95°, 85° (Habich and Limpricht, A. 109, 102); b.p. 276° (H. and L.): by action of KCNO or $K_3C_3N_3O_3$ upon $KC_2H_5SO_4$ (Wurtz), or by heating $Ag_2HC_3N_3O_3$ or $Ag_3C_3N_3O_3$ with C_2H_5I to 120° (H. and L.). Also by action of $K_2HC_3N_3O_3$ upon C_2H_5I at 150–200° (Ponomarew, B. 18, 3271). By heating the compound of ethyl carbimide with HCl or HBr, in a tube to 100° we get HCl or HBr and $(C_2H_5)_3C_3N_3O_3$ (Gal, A. 137, 127). It forms rhombic prisms (Rammelsberg, J. 1857, 273) fairly soluble in hot water, soluble in alcohol and in acids.

Not acted upon by NH_3, but with KOH yields $N(C_2H_5)H_2$ and K_2CO_3; by action of warm baryta water CO_2 and tri-ethyl biuret

$$C_2H_5.N(CONHC_2H_5)_2$$

are formed. By action of C_2H_5NaO we get $C_2H_4.N.C_2H_5.H_2$, triethyl guanidine $C_7H_{17}N_3$ and triethyl biuret $C_2H_5N(CONHC_2H_5)_2$ (Hofmann, J. 1861, 516).

Diethyl cyanuric acid $H(C_2H_5)_2O_3N_3C_3$; m.p. above 200°, though partly sublimed with decomposition at that temperature. Formed by warming $(C_2H_5OCN)_3$ with $Ba(OH)_2$ on a water-bath (Ponomarew, B. 18, 3267); the mixture is diluted with water, filtered, saturated with CO_2, and evaporated; the free acid is prepared from the lead salt by means of H_2S. Is a crystalline powder slightly soluble in cold water and alcohol, insoluble in ether. $Ba((C_2H_5)_2C_3N_3O_3)_2$ crystallises from hot aqueous solutions with $3H_2O$; from dilute solutions in microscopic needles with $12H_2O$. By action of pure C_2H_5I upon the lead salt we get triethyl cyanurate (m.p. 29°) (*v. supra*), but if the C_2H_5I contains free I, the product contains also the ethyl isocyanurate (m.p. 95°).

Ethyl ferrocyanide. By action of gaseous HCl upon an alcoholic solution of $K_4Fe(CN)_6$ crystals containing $(C_2H_5)_4Fe(CN)_6 + 2C_2H_5Cl + 6H_2O$ separate (Buff, A. 91, 253). These are decomposed and turned blue by action of air, and by keeping over lime lose their water of crystallisation. If to a solution in alcohol, ether be added crystalline scales of $(C_2H_5)_4Fe(CN)_6 + 6H_2O$ are thrown down, from which all the water can be extracted by standing over lime.

Ethyl fluoride C_2H_5F. Reinsch (J. pr. 19, 314) obtained by action of CaF_2 and H_2SO_4 upon

C_2H_5HO a colourless ethereal liquid with a smell like horse-radish; it burnt in air, but was not obtained pure enough for analysis. A gas was obtained by heating $C_2H_5.HSO_4$ with KF.HF. by Fremy (A. 92, 247).

Ethyl formamide $NC_2H_5.COH.H$; b.p. 199°; sp.gr. $\frac{21^{\circ}}{} = \cdot952$. By distilling an aqueous solution of $N.C_2H_5.H_2.CHO_2$: separates from distillate upon addition of KOH (Linneman). By action of $NC_2H_5.H_2$ upon C_2H_5ClO (Hofmann, B. 5, 247); a thick colourless liquid.

Ethyl formate $C_2H_5.CO_2H$. B.p. 54·4° at 760 mm.; sp.gr. $\frac{0^{\circ}}{4^{\circ}} = \cdot9376$; b.p. 53·4°–53·6° at 754·5 mm.; sp.gr. $\frac{53\cdot4^{\circ}}{4^{\circ}} = \cdot8731$ (R. Schiff, A. 220, 106). Capillarity constant at boiling-point, $a^2 = 4\cdot528$ (Schiff, A. 223, 75). H.C. p. 388 cal. (Berthelot, Ogier).

By distilling a mixture of 6 parts alcohol (90 p.c.), 7 parts sodium formate and 10 parts conc. H_2SO_4 (Liebig); by distilling a mixture of ethyl oxalate with oxalic acid (Löwig, J. 1861, 599); by heating a mixture of glycerine, oxalic acid, and alcohol in a reflux condenser, and then distilling (Lorin, Bl. 5, 12). On the large scale a mixture of 9 parts of starch and 29 parts of MnO_2 (of 85 p.c.) is heated with 28 parts of H_2SO_4, 5 parts H_2O, and 15 parts of alcohol (85 p.c.) (Stinde, D. P. J. 181, 402).

A mobile colourless liquid with a pleasant aromatic smell; is used for flavouring arrack and rum; is decomposed by water, for which it has strong affinity. Sodium or C_2H_5NaO decomposes it into CO and alcohol (Geuther, Z. 1868, 655). Cl forms with it in sunlight *dichlorethyl formate* $C_2H_3Cl_2CO_2H$, which is a colourless oily liquid, decomposed on heating, and which by action of alkalis is decomposed into acetic, formic, and hydrochloric acids. By further action of Cl in sunlight *perchlorethyl formate* $C_2Cl_5CO_2Cl$; b.p. 200°; sp.gr. $\frac{18^{\circ}}{}$ 1·705, identical with *perchlormethyl acetate*, $CCl_3.CO_2.CCl_3$, is formed (Cloëz, A. Ch. [3] 17, 297).

Ethyl hydrate *v.* ALCOHOL.

Ethyl hydride, *Ethane*, *Dimethyl*, C_2H_5H (Frankland and Kolbe, C. J. 1, 60). Gas, sp.gr. 1·036, condensed at 4° and 46 atmospheres pressure (Cailletet, J. 1877, 68). S. at $t^{\circ} = \frac{9\cdot4556 - \cdot35324t + \cdot006278t^2}{100}$ (Schickendatz, A. 109, 116) $= \frac{8\cdot710 - \cdot33242t + \cdot00603t^2}{100}$ (Bunsen). S. (alcohol) = 1·5 (Berthelot, J. 1867, 344); H.C. p. 373·3 cal. (Th.), = 389·3 (Berthelot, A. Ch. [5] 23, 180, 227); H.F. (from amorphous C) = 11·7 cal. (B.); occurs in crude petroleum.

Pittsburg gas consists of ethane mixed with a little CH_4 and CO_2, and is used for smelting and lighting purposes.

By action of K upon C_2H_5CN, also by action of water upon $Zn(C_2H_5)_2$ (Frankland and Kolbe, C. J. 3, 338); by action of Zn upon C_2H_5I in presence of water; by electrolysis of acetic acid or acetates. $2CH_3COOH = C_2H_6 + 2CO_2 + H_2$, the C_2H_6 and CO_2 coming from the positive electrode (Kolbe, A. 69, 279), by heating 9 parts of C_2H_5I with 2·6 parts of $AlCl_3$ to 140° or 150° (Köhnlein, B. 16, 562) by action of $Hg(C_2H_5)_2$ upon H_2SO_4 (Schorlemmer, A. 132, 234), by heating an excess of BaO_2 with acetic anhydride and sand

$$2(C_2H_3O)_2O + BaO_2$$
$$= C_2H_6 + 2CO_2 + Ba(C_2H_3O_2)_2$$

(Schützenberger, Z. 1865, 703). It can also be prepared by the action of nascent H (from ZnCu couple or Zn dust) upon a mixture of C_2H_5I and C_2H_5OH (Sabanejeff, B. 9, 810).

Ethyl iodide C_2H_5I (Gay-Lussac, A. Ch. [1] 91, 89; Serullas, A. Ch. [2] 25, 323 and 42, 119; Frankland, C. J. 2, 263; 3, 32); b.p. 72·34° (Linnemann, A. 160, 204), b.p. 71·3° (Andrews), 71·6° (Frankland); sp.gr. $\frac{14\cdot5^{\circ}}{} = 1\cdot9444$ (L.), $\frac{0^{\circ}}{} = 1\cdot9755$ (Pierre), $\frac{15^{\circ}}{} = 1\cdot9309$ (Mendeléeff); V.D. = 5·417 (Marchand).

From alcohol and HI (Gay-Lussac); from alcohol, iodine, and phosphorus (Serullas). Personne (C. R. 42, 468) suggested the use of red P, and according to Beilstein (A. 126, 250), 1 part red P and 5 parts of alcohol (90 p.c.) are placed in a retort, and 10 parts of iodine slowly added. After twenty-four hours the C_2H_5I is distilled off, washed with NaOH sol. and with water, and dried over $CaCl_2$. The residue consists chiefly of ethyl phosphoric acid, hence the use of excess of alcohol. If the alcohol and I are well mixed first, and the P be added gradually 6·7 parts of I are said to be enough.

C_2H_5I is a colourless, pleasantly smelling liquid, almost insoluble in water, but miscible with alcohol and ether. It precipitates silver from its solutions in the cold, easily forms double compounds with silver salts, metals, and ammonia. Br displaces the I, and forms C_2H_5Br; Cl forms C_2H_5Cl (Dumas, Stas, A. 35, 162). ICl forms C_2H_5Cl and I_2. HCl has no action, but, on the contrary, C_2H_5Cl is decomposed by HI into C_2H_5I and HCl (Lieben, Z. 1868, 712). By action of HI at 150° ethane and iodine are formed. HNO_3 also causes the separation of I (Marchand, J. pr. 33, 186). Metallic Ag abstracts I, and leaves diethyl $(C_2H_5)_2$. By heating with water to 150° we get alcohol (Reynoso, J. 1856, 567); with excess of alcohol yields ether and some C_2H_4 (Lieben, Rossi, A. 158, 166). Is gradually turned brown by exposure to light, owing to formation of free I and liberation of butane (Frankland, C. J. 3, 322). In presence of mercury the reaction is much more rapid owing to combination of the liberated I with Hg. Is used largely for the preparation of other ethyl compounds.

Ethyl mercaptan *v. Ethyl sulphydrate.*

Ethyl nitrate $C_2H_5NO_3$, *Nitric ether*, b.p. 86·3° at 728·4 mm.; sp.gr. $\frac{0^{\circ}}{} = 1\cdot1322$, $\frac{15\cdot5^{\circ}}{} = 1\cdot1123$ (Kopp, A. 98, 367); H.F.p. = 40,780; H.F.v. = 38,750; H.C. = 325,690 (Th. 4, 214). Obtained from alcohol by the action of nitric acid in presence of some substance which will destroy nitrous acid, *e.g.* urea (Millon, A. Ch. [3] 8, 233).

Preparation.—400 grams of pure nitric acid (sp.gr. 1·40, previously heated with 1 p.c. of urea in order to destroy lower oxides of nitrogen) are mixed with 300 grams absolute alcohol and 100 grams of urea nitrate, and distilled; when half the liquid has distilled off a mixture of 400 grams of nitric acid and 300 grams of alcohol is allowed to drop into the retort and the distillation continued (Lossen, A. Suppl. 6, 220).

Silver nitrate, heated with ethyl iodide (or bromide) and alcohol, yields, not ethyl nitrate, but the nitrite, together with aldehyde (Bertrand, Bl. 33, 566).

Ethyl nitrate is a colourless liquid with pleasant odour and taste; almost insoluble in water, but miscible with alcohol and ether. Ammonia forms ethylamine nitrate; nascent hydrogen yields hydroxylamine and other bases (Lossen). Sulphuretted hydrogen yields mercaptan (Kopp, A. 64, 320). Alcoholic potash decomposes it with separation of crystals of potassium nitrate.

Ethyl nitride *v. Ethylamine.*

Ethyl nitrite $C_2H_5NO_2$, *Nitrous ether*; b.p. 16·4° (Liebig), 17° (Mohr, J. 1854, 561; Brown, Ph. 15, 400), 17·5° (Dunstan and Dymond, Ph. 18, 861); sp.gr. $\frac{15{\cdot}5^\circ}{} = {\cdot}900$ (Br.); $\frac{0^\circ}{0^\circ} = {\cdot}917$ (D. and D.); H.F.p. = 30,610; H.F.v. = 28,870 (Th. 4, 217).

This body was discovered in 1681 by Kunkel. Obtained from alcohol by action of nitric acid, especially in presence of some oxidisable matter, *e.g.* copper.

Preparation.—500 grams of potassium nitrite and 1 litre alcohol (45 p.c.) are mixed and cooled by means of ice; a mixture of sulphuric acid (500 grams), water (500 grams), and alcohol (500 grams) is then slowly dropped in, the heat produced volatilises the ether, which is condensed in an efficient condenser (Feldhaus, A. 126, 71). Dunstan and Dymond (*l.c.*) recommend that 34·5 grams sodium nitrite in 120 grams water be slowly mixed with a mixture of 13·5 grams of sulphuric acid with 32 grams alcohol and about 75 c.c. water kept cool by ice. The ethyl nitrite separates out as a layer floating on the surface. As thus prepared the liquid contains only traces of alcohol, from which it is freed by shaking with water.

Ethyl nitrite is a mobile liquid with a pleasant ethereal smell and taste, liable to undergo decomposition, especially in presence of water. It can be preserved if mixed with alcohol and a small quantity of glycerin. It is decomposed by sulphides in accordance with the following equation: $C_2H_5NO_2 + 3H_2S = NH_3 + C_2H_6O + H_2O + 3S$ (Kopp, A. 64, 321).

It is slightly soluble in water and miscible with alcohol. Mixed with alcohol it constitutes the 'sweet spirit of nitre,' *spiritus ætheris nitrosi*, of the British Pharmacopœia, which is thus prepared: 1 pint of rectified spirit is mixed with 2 fluid ounces of sulphuric acid and 2½ ounces of nitric acid. The mixture is run into a retort containing 2 ounces of fine copper wire. 12 ounces are distilled off at 77°. ½ ounce more of nitric acid is then added, and 3 ounces more are distilled off. The distillate is then mixed with 2 pints of rectified spirit.

Ethyl oxide, $(C_2H_5)_2O$, *Ether, Ethylic ether, Vinic ether,* formerly called *Sulphuric ether, Phosphoric ether,* &c., according to the acid used in its preparation; b.p. 34·97° (Regnault), 34·6° at 762 mm. (Schiff, A. 220, 332), 34·9° (Kopp); sp.gr. $\frac{0^\circ}{} = {\cdot}7360$; $\frac{17{\cdot}5^\circ}{} = {\cdot}7185$ (Hager), $\frac{34{\cdot}6^\circ}{4^\circ} = {\cdot}6950$ (Schiff), $\frac{15^\circ}{} = {\cdot}7024$. $\frac{25^\circ}{25^\circ} = {\cdot}7099$; $\frac{15^\circ}{15^\circ} = {\cdot}7201$ (Perkin, C. J. 45, 474). M.M. = 4·777 at 20°. Freezes at −129° to a crystalline mass, which melts at −117·4° (Olzewski, M. 5, 128). Capillarity constant at b.p. $a^2 = 4{\cdot}521$ (Schiff). S. at 17·5° = 8.

The preparation of ether from alcohol and sulphuric acid was first described by Valerius Cordus (1540), and the method of making this 'oleum vitrioli dulce' was published in 1552 by Conrad Gessner. Frobenius, 1730, named it sulphuric ether. Val. Rose (Scher. J. 4, 253) showed that it contained no sulphur, but its composition was first made out by Saussure (G. A. (1808) 29, 132) and also by Dumas and Boullay (A. Ch. [2] 36, 294). Its constitution was first studied by Liebig (A. 60, 31; 23, 39) and Regnault (A. Ch. [2] 71, 352). Williamson in 1850-51 (B. A. 1850, 65, and P. M. [3] 37, 350) established the views now held as to its constitution and formation.

Formation.—From alcohol, by action of phosphoric or arsenic acid (Boullay, G. A. (1818) 44, 270); by action of boron fluoride (Desfosses, A. Ch. [2] 36, 294); of $ZnCl_2$ (Masson, A. 31, 63); of $SnCl_4$, and other metallic chlorides (Kuhlmann, A. 33, 97, 192). From alcohol by heating with dry NH_4Cl to 260°–400° (Berthelot, A. 88, 110). From C_2H_5NaO and C_2H_5I (Williamson). From alcohol and HCl, HBr, or HI at 200° to 240°, or by heating alcohol with $ZnCl_2$, $SnCl_4$, $HgCl_2$, $CaCl_2$, $MgSO_4$, or chrome alum to 300° (Reynoso, A. Ch. [3] 48, 385).

$$C_2H_5OH + HCl = C_2H_5Cl + H_2O$$

and $C_2H_5Cl + C_2H_5OH = (C_2H_5)_2O + HCl$. Also from C_2H_5Br or C_2H_5I and HgO (Reynoso), or from C_2H_5I and Na_2O (Green, Bl. 29, 458).

The continuous method now adopted is due to Boullay (J. Ph. 1, 97), and the true explanation of the action was first given by Williamson (*l.c.*). The alcohol and sulphuric acid first form $C_2H_5HSO_4$ and H_2O, and then by the action of $C_2H_5HSO_4$ upon more alcohol $(C_2H_5)_2O$ and H_2SO_4 are formed. That this is true Williamson proved by using amyl sulphuric acid and ethyl alcohol when amyl-ethyl ether was produced.

Preparation.—Boullay's method is usually employed. A mixture of 9 parts H_2SO_4 with 5 parts of alcohol (90 p.c.) is placed in a retort, and alcohol is slowly dropped in and the temperature is maintained between 130° and 140°. An iron retort lined with lead is usually employed, and the ordinary mercurial thermometer, which is of course liable to fracture, is replaced by a bulbed tube containing some non-drying oil. The tube is then either exhausted by the air-pump, and hermetically sealed, or its open end is closed by a plug of cotton-wool, and two marks are made on the tube corresponding to positions of the surface of the oil at 130° and 140° respectively. In order to avoid risk of explosion by contact of the vapour with direct flame, coils of lead tubing, conveying superheated steam or the vapour of some liquid of high boiling-point (*e.g.* coal-tar phenol), are used as a source of heat. The distillate is treated with milk of lime or sol. of soda in order to remove the SO_2 which is always simultaneously formed. It is then rectified in an apparatus devised by Mohr, which consists of a still from which the vapour is led through a vessel kept at 38° by warm water. Here the alcohol and water vapours are condensed, and the ether passes over, and is condensed in an efficient condenser.

By means of an apparatus devised by Soubeiran, ether can be prepared in a fairly pure state by one operation. A mixture of about 30 lbs. of H_2SO_4 with 20 lbs. of alcohol of 85 p.c. is heated rapidly to 130° in a copper still, to the bottom of which two tubes convey alcohol from a tinned copper reservoir. The neck of the retort (which is of lead) is connected with the first condenser, which is a copper vessel kept warm by allowing the waste water from the worm tub (where the ether is condensed) to flow over the outside of it. Here the steam and vapour of alcohol are condensed, and the liquid formed can be drawn off from below by means of a stopcock. The ether vapour then passes on to the purifier, which consists of a vessel filled with wood charcoal saturated with a solution of caustic soda, which not only removes the SO_2, but also absorbs the oil of wine. The pure ether passes on, and is condensed in a well-cooled worm.

In the preparation of ether the temperature of the mixture must be maintained between 130°-140°. The greatest yield of ether is obtained at 140°-145°; below this temperature the yield is less, and above this much SO_2 is evolved (Prescott, Norton, Am. 6, 243). The last traces of water and alcohol are got rid of by shaking with $CaCl_2$. Lieben (A. Suppl. 7, 218) recommends shaking with 20 or 30 separate small quantities of water, and the ether is then redistilled over sodium or phosphoric oxide.

Ethylic ether is apt to contain varying quantities of vinyl alcohol, formed partly during its preparation and partly by the action of atmospheric oxygen with simultaneous formation of hydrogen peroxide, which reacts upon the ether with production of a further quantity of vinyl alcohol

$$(1)\quad \begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\!\!>\!O + O_3 = \begin{matrix}CH_2CHOH\\CH_2CHOH\end{matrix} + \left.\begin{matrix}HO\\HO\end{matrix}\right\}.$$

$$(2)\qquad 3\left\{\begin{matrix}CH_3CH_2\\CH_3CH_2\end{matrix}\right.\!\!>\!O + 9H_2O_2$$

$$= \begin{matrix}3CH_2CHOH\\3CH_2CHOH\end{matrix} + 12H_2O + O_3.$$

The vinyl alcohol may be removed by repeatedly shaking the ether with water or treatment with bromine, phenylhydrazin, or caustic potash (Poleck and Thümmel, B. 22, 2863).

At 17·5° 12 parts of water dissolve 1 part of ether, and 35 parts of ether dissolve 1 part of water; 100 parts of absolute ether dissolve at 12° 2 vols. of water (Napier, Bl. 29, 129).

If ether be shaken with an equal volume of CS_2 a turbidity is produced if water be present.

Decompositions.—Pt black, CrO_3 or HNO_3 oxidise ether to acetic acid; ozone produces ethyl peroxide. By oxidation under the influence of a spiral of Pt wire there is formed a body melting at 51° and crystallising in rhombic prisms. This is decomposed by ammonia with formation of O, CH_2O, and a small quantity of CH_2O_2; it also gives the reaction for H_2O_2 (Legler, A. 217, 382). When ozonised oxygen is passed into ether a solution is obtained containing $C_2H_2O_4$, $C_2H_4O_2$ and H_2O_2, also a small quantity of CH_2O_2 (A. W. Wright). Ether combines with H_2SO_4 to form $C_2H_5HSO_4$; by action of SO_3 we first get $(C_2H_5)_2SO_4$, but by excess of SO_3, $C_2H_5HS_2O_7$, and a small quantity of a body of the composition $CH_2(SO_3C_2H_5)_2$ are formed. When ether is heated with water and a small quantity of H_2SO_4 to 150-180° alcohol is formed (Erlenmeyer, Z. 1868, 343). According to Lieben (A. 165, 136) the reaction goes on, though very slowly, without H_2SO_4, and at the ordinary temperature. Ether combines easily with HI and yields C_2H_5I (Silva, B. 8, 903), and is decomposed by heating with zinc-dust into C_2H_4 and water (Jahn, M. 1, 675).

A hydrate $(C_2H_5)_2O.2H_2O$ is known; it is a solid body which only exists below −3°·5, and is obtained by the rapid evaporation of aqueous ether on filter paper (Tanret, Bl. 30, 505, also C. R. 87, 765). Ether bromide $(C_2H_5)_2O.Br_2$ formed by action of dry bromine, is an oil which solidifies below 0° to red plates which melt at 22°, liquefy in air, and are decomposed by heating with water at 70° or 80° into HBr, C_2H_5Br, bromal, and a body which boils at 175°, soluble in water and of the composition $C_4H_5Br_3O_2$ (Schützenberger, A. 167, 86).

Ether combines with various metallic salts and forms crystalline bodies, *e.g.* $BeCl_2 2(C_2H_5)_2O$, large prisms (Atterberg, B. 9, 856), $HgBr_2.3(C_2H_5)_2O$ (Nicklès, J. 1861, 200), $AlBr_3.(C_2H_5)_2O$ (N.). $TiCl_4\ (C_2H_5)_2O$, crystalline, m.p. 42-45°; b.p. 118° to 120°, decomposes into $TiCl_3\ (OC_2H_5)$ (Bedson, A. 180, 236; C. J. [1876], 1, 311).

Properties.—A colourless very mobile liquid with pleasant smell. Volatilises very quickly, and by so doing produces great cold. Vapour tension at −20° = 67·49 mm.; at 0° = 182·34 mm.; at 10° = 286·4 mm.; at 20° = 433·2; at 30° = 636·3 mm. It is extremely inflammable, and its vapour, which is very heavy, forms an explosive mixture with air. Ether is very soluble in concentrated HCl solution (Draper, C. N. 35, 87). It is miscible with almost all organic liquids, and with liquid CO_2. It is a good solvent for resins, fats, alkaloids, &c., and sulphur and phosphorus dissolve in it to a small extent. It also dissolves I, and many salts, *e.g.* Fe_2Cl_6, $HgCl_2$, $PtCl_4$, and many gases, notably ammonia.

Its vapour when inhaled produces insensibility (Faraday, 1818), and it is used as an anæsthetic in surgery. It is also occasionally used in surgery for producing local anæsthesia; this is done by directing a spray of ether upon the skin, when the extreme cold produced by evaporation produces complete insensibility.

It is also used as a solvent in the preparation of collodion, in the extraction of tannic acids, of several alkaloids, &c.

Ethyl peroxide $(C_2H_5)_4O_3$, produced by leading dry ozone into absolute ether (Berthelot, Bl. 36, 72), is a thick syrup which does not solidify at −40°, is partially volatile on heating, but easily explodes, is miscible with water, by which it is decomposed into C_2H_5OH and H_2O_2.

Substitution Products of Ether.

Chlorine acts violently upon ether, setting fire to it, and liberating carbon (Cruikshank). If the ether be kept cool by ice, and in the dark, substitution products are obtained. The Cl replaces the H atom by atom from one ethyl group first, in the following order $C\underset{2}{H}\underset{3}{H}\underset{4}{H}C\underset{1}{H}\underset{5}{H}OC_2H_5$ (Lieben, A. 111, 121; 146, 180; Abelganz, 164, 197; Jacobsen, B. 4, 215; also Liebig, A. 1, 220; Malaguti, A. Ch. [2] 70, 338; [3] 16, 5).

Monochlorether *Monochlorethyl oxide*

$CH_3CClHOC_2H_5$,

b.p. 97–98°; by the chlorination of ether (Lieben); by saturating a mixture of aldehyde and alcohol with HCl (Frapolli, Wurtz, A. 108, 226), by the action of PCl_5 upon acetal (Bachmann, A. 218, 39). It is decomposed by H_2SO_4 into HCl, C_2H_4O and C_2H_5OH. C_2H_5NaO forms NaCl and acetal, water decomposes it into HCl, aldehyde and alcohol (Laatsch, A. 218, 36).

Dichlorether *Dichlorethyl oxide*

$CH_2ClCHClOC_2H_5$,

b.p. 140–145°, sp.gr. $\frac{23^\circ}{}$ 1·174; by action of Cl upon ether (Malaguti, A. 32, 15); by action of HCl upon a mixture of chloraldehyde and C_2H_5OH (Natterer, M. 5, 496); by action of Cl upon chloracetal (N).

Dichlorether is decomposed on heating in a tube into C_2H_5Cl and other products. C_2H_5ONa forms first *chloracetal* $CH_2ClCH(OC_2H_5)_2$. By heating with excess of C_2H_5ONa in sealed tubes *ethyl glycol acetal* $CH_2(OC_2H_5)CH(OC_2H_5)_2$ is formed. In ethereal solution $Zn(C_2H_5)_2$ yields *ethyl chlorether* $CH_2Cl.CH(C_2H_5)OC_2H_5$, b.p. 141°; sp.gr. $\frac{0^\circ}{}$ = ·9735. With excess of $Zn(C_2H_5)_2$ we get $CH_2(C_2H_5)CH(C_2H_5)OC_2H_5$ [(b.p. 131°·4 at 749·6, sp.gr. $\frac{0^\circ}{}$ = ·7865 (Lieben, A. 178, 14).] Strong caustic potash forms alcohol, a body $C_8H_{16}Cl_2O_3$, a little glycollic acid and two isomeric bodies of the composition $C_4H_9ClO_2$ (Abelganz, A. 164, 218); α—$C_4H_9ClO_2$, *chloraldehyde alcoholate* $CH_2Cl.CHOH.O.C_2H_5$, b.p. 93–95°; and β. $C_4H_9ClO_2$ *oxychlorether* $CH_2OH.CHCl.O.C_2H_5$, also formed by chlorination of ether (Jacobsen, B. 4, 217), b.p. 151–155°.

Trichlorether $CHCl_2CHClOC_2H_5$, b.p. 167° to 168°; by the action of PCl_5 upon dichloracetal $CHCl_2CH(OC_2H_5)_2$ (Krey, J. 1876, 475), decomposed by heating with C_2H_5ONa yielding *dichloracetal.*

Tetrachlorether $CCl_3CHClOC_2H_5$, b.p. 189°·7 at 758·7 mm.; sp.gr. $\frac{0^\circ}{}$ = 1·4379; $\frac{15\cdot2}{}$ = 1·4182; formed by action of Cl upon monochlorether in contact with I (Wurtz, Vogt, Z. 1871, 679), or of chloral alcoholate, $CCl_3CHOH.O.C_2H_5$ upon PCl_5 (Henry, B. 101, 435; Paterno, Pisati, J. 1872, 303). A liquid with a camphorlike smell, decomposed by heating with water into C_2H_5OH, HCl and chloral. Alcoholic KOH forms with it *trichlorvinyl ethyl ether* $CCl_2.CCl.OC_2H_5$.

Pentachlorether. Two isomers:

(1) $CCl_3.CCl_2OC_2H_5$, b.p. 190–210° with decomp.; sp.gr. 1·645 (Jacobsen, B. 4, 217), by action of Cl upon trichlorvinyl ethyl ether (*v. supra*) (Busch, B. 11, 445).

(2) $CCl_3.CHCl.O.CH_2.CH_2Cl$, b.p. 235°; sp.gr. $\frac{8^\circ}{}$ = 1·577. By action of PCl_5 on a compound of chloral and glycol hydrochlorate

$CCl_3CH(OH)OCH_2CH_2Cl$

(Henry, B. 7, 763).

Hexachlorether $CHCl_2.CHCl.O.CHCl.CHCl_2$, b.p. 250° by action of PCl_5 upon dichloraldehyde saturated with HCl (Paterno, Pisati, J. 1871, 508).

Octochlorether $C_4H_2Cl_8O$ from aldehyde hydrochlorate and Cl in sunlight (Roth, B. 8, 1017). Camphorlike smelling, volatile crystals.

Perchlorether $(C_2Cl_5)_2O$ (Regnault, A. 34, 27); sp.gr. $\frac{14\cdot5}{}$ = 1·900 (Malaguti, A. Ch. [3] 16, 4); the ultimate product of the action of Cl upon ether in sunlight, is a solid, forming orthorhombic scales m.p. 69°, which possess a smell like that of camphor. Decomposed by heating to 300° into C_2Cl_6 and $CCl_3.COCl$; with K_2S yields chloroxethose $(C_2Cl_3)_2O$, with liberation of S (Malaguti, A. Ch. [3] 16, 19). This body is a liquid, b.p. 210°; sp.gr. $\frac{21^\circ}{}$ = 1·652, which combines with Cl in sunlight to form $(C_2Cl_5)_2O$, or with Br yielding $(C_2Cl_3Br_2)_2O$.

Ethylates. Bodies formed from alcohol by the replacement of the hydrogen of the OH group by metals or other radicles *v.* ALCOHOL.

Ethyl pentasulphide *v. Ethyl sulphide.*

Ethyl phosphates.

1. *Normal ethyl phosphate* $(C_2H_5)_3PO_4$, b.p. 215°; sp.gr. $\frac{12^\circ}{}$ = 1·072. By action of heat on lead diethyl phosphate $Pb(C_2H_5)_4(PO_4)_2$ (Vōgeli, A. 69, 190); from C_2H_5I and Ag_3PO_4 (Clermont, A. Ch. [3] 42, 330); from $POCl_3$ and C_2H_5ONa (Limpricht, A. 134, 347); from P_2O_5 and absolute alcohol (Carius, A. 137, 121). Colourless liquid, miscible and slowly decomposed by water forming diethyl phosphoric acid.

2. *Diethyl phosphoric acid* $(C_2H_5)_2HPO_4$, a syrupy liquid obtained by action of P_2O_5 upon alcohol. It is a monobasic acid and forms well-marked salts, *e.g.* $Ca((C_2H_5)_2PO_4)_2$ crystalline needles; $Pb[(C_2H_5)_2PO_4]_2$ needles, m.p. 180°, soluble in water.

3. *Ethyl phosphoric acid* $H_2(C_2H_5)PO_4$, an oily liquid decomposed by heating, evolving $(C_2H_5)_2O$, C_2H_5OH and C_2H_4. Equal parts of alcohol (90 p.c.) and syrupy H_3PO_4 are heated to 60° or 80°, diluted with water and neutralised with $BaCO_3$, filtered, the Ba salt allowed to crystallise, and then decomposed by H_2SO_4 (Pelouze, A. Ch. [2] 52, 37).

Also produced by action of P_2O_5 upon ether or alcohol or of syrupy H_3PO_4 upon ether (Vōgeli, J. 1847–48, 694). Forms crystalline salts with the metals; of these the lead salt is least soluble.

Ethyl phosphide *v.* PHOSPHORUS, ORGANIC BASES OF.

Ethyl phosphites.

1. *Triethyl phosphite* $(C_2H_5)_3PO_3$, b.p. 191° (or 188° in stream of H); sp.gr. $\frac{15\cdot5^\circ}{}$ = 1·075 (Railton, C. J. 7, 216); from PCl_3 and alcohol or sodium ethylate (Railton).

An ethereal-smelling liquid which absorbs O and which is converted by PCl_5 into

$PO(OC_2H_5)Cl_2$, PCl_3 and C_2H_5Cl

(Geuther, Herzt, J. 1876, 207).

2. *Ethyl-phosphorous acid* $H_2(C_2H_5)PO_3$, very unstable syrupy liquid, obtained by action of PCl_3 upon weak alcohol (Wurtz, A. Ch. [3] 16, 218). The salts do not crystallise well, but are more stable than the acid.

Chloride of ethyl-phosphorous acid $C_2H_5POCl_2$ b.p. 117·5° cor.; sp.gr. $\frac{0^\circ}{4^\circ}$ = 1·30526 (Thorpe, C. J. 37, 346); from PCl_3 and C_2H_5OH (Menschutkin, A. 139, 343), decomposed by water into HCl, C_2H_5OH and H_3PO_3; also by heating to 165° into C_2H_5Cl, P, PCl_3, and P_2O_3 (Chambon, J. 1876, 205).

Diethyl pyro-phosphorous acid is not known, but the zinc salt $(C_2H_5)_2P_2O_5Zn$ is produced when $Zn(C_2H_5)_2$ is heated with P_2O_5 to 140° (Dilling, Z. 1867, 266).

Ethyl selenic acid $C_2H_5.H.SeO_4$, very unstable, produced from H_2SeO_4 and C_2H_5OH (Fabian, A. Suppl. 1, 244). The salts are also unstable, the most permanent being the strontium salt; they can be crystallised with the ethyl-sulphuric acid salts.

Ethyl selenhydrate, *Selenium mercaptan* C_2H_5HSe; b.p. about 100°, not obtained pure, heavier than and insoluble in water. A nauseous-smelling liquid which combines easily with HgO (Wöhler, Siemens, A. 61, 360).

Ethyl selenide, *Selenethyl* $(C_2H_5)_2Se$, b.p. 108°; discovered by Löwig (P. 37, 552). By action of K_2Se upon $(C_2H_5)_2C_2O_4$ (L.); by action of $KC_2H_5SO_4$ upon K_2Se (Joy, A. 86, 35; Rathke, A. 152, 210); the crude product is then distilled again with KOH, $C_2H_5HSO_4$ and a small piece of P or S (Pieverling, A. 185, 331; B. 9, 1469). A colourless mobile liquid with a not unpleasant smell, is insoluble in water, acts as a base, HCl precipitates from a solution in dilute HNO_3 an oily liquid $(C_2H_5)_2SeCl_2$. This chloride gives with aqueous NH_3 a crystalline oxychloride $[(C_2H_5)_2Se]_2OCl_2.(C_2H_5)_2Se$. Combines with C_2H_5I to form crystalline $(C_2H_5)_3SeI$ (Pieverling). This is a white substance resembling Epsom salts in appearance. The $(C_2H_5)_2SeCl_2$ forms double salts with several metallic chlorides, *e.g.* $[(C_2H_5)_2SeCl_2]_2PtCl_4$, monoclinic crystals (Schimper, J. 1877, 315).

Ethyl diselenide $(C_2H_5)_2Se_2$, b.p. 186°, formed as a by-product in the preparation of $(C_2H_5)_2Se$, was first obtained by Wöhler and Dean (A. 97, 1); from $KC_2H_5SO_4$ and K_2Se_2 (Rathke, A. 152, 212); has a most intensely disagreeable smell and acts as a poison (Pieverling). A solution in dilute HNO_3 gives with HCl monoclinic crystals of $(C_2H_5)_2Se_2O_2(OH)_2Cl_2$ which are soluble in water, and are reduced by SO_2 to ethyl diselenide.

Ethyl sulphates.

Mono-ethyl sulphates $C_2H_5HSO_4$ (*Ethyl-sulphuric acid*; *sulphethylic acid*; *sulphovinic acid*). Sp.gr. $\frac{16^\circ}{} = 1{\cdot}316$.

First noticed by Dabit (Crell's Ann. [1802] 1, 394); and again by Sertuerner (Gilb. Ann. 60,53; 64, 67 [1818–1820]) (see also Heeren, P. 7, 193; Hennel, Tr. 1826, 240; 1828, 365; Serullas, A. Ch. [2] 39, 153; Liebig and Wöhler, P. 22, 487; Liebig, A. 9, 17, 32; 13, 32, 38; Dumas and Boullay, A. Ch. [2] 36, 300).

Formed by action of sulphuric acid upon alcohol (Dabit, Sertuerner, Serullas); also by absorption of ethylene in sulphuric acid (Hennel; Berthelot, A. Ch. [3] 43, 385); by heating ether with strong H_2SO_4 (Hennel; Magnus, P. 27, 386); from S_2Cl_2 and alcohol (Heusser, A. 151, 249); from $SO_3.HCl$ and alcohol in the cold (on heating, this gives $C_2H_5O.SO_2.Cl$, Claesson, J. pr. [2] 19, 245).

Preparation.—A mixture of equal parts of absolute alcohol and strong sulphuric acid is heated for four hours on the water-bath; by this treatment 59 p.c. of the H_2SO_4 used is converted into mono-ethyl sulphate (Berthelot, Bl. 19, 295). By using 3 mols. alcohol and 1 molecule H_2SO_4 (*i.e.* 3 to 2 by weight) 77 p.c. of the sulphuric acid is utilised (Claesson, J. pr. [2] 19, 246). The mixture is diluted with water and neutralised with lead or barium carbonate, filtered, evaporated to crystallisation, the crystals dissolved in water and the acid set free by means of H_2SO_4, or, in case of lead carbonate being used, by means of H_2S. The precipitated $BaSO_4$, $PbSO_4$ or PbS is removed by filtration and the liquid evaporated *in vacuo* over sulphuric acid. Mono-ethyl sulphate is a syrupy liquid very soluble in water, soluble also in alcohol but insoluble in ether.

Heated with water, yields alcohol and sulphuric acid; on heating with alcohol to 140° ether and H_2SO_4 are formed. Oxidising agents *e.g.* MnO_2 or K_2CrO_4 give aldehyde (Jacquemin and Lies Bodard, J. 1857, 345). The salts are very soluble in water and can be heated in dilute solutions without decomposition, though in strong solution, or by prolonged heating, they are decomposed with formation of alcohol, a sulphate, and free H_2SO_4. This decomposition may be diminished by the addition of an alkaline hydrate or carbonate. By dry distillation the salts yield 'heavy oil of wine,' a liquid containing diethyl sulphate and olefines. HCl gas yields C_2H_5Cl and a metallic sulphate (Köhler, B. 19, 11, 1929).

Salts (*v.* Marchand, P. 32, 456; 41, 595). $LiC_2H_5SO_4+H_2O$; $NaC_2H_5SO_4+H_2O$; $KC_2H_5SO_4$, crystallises in anhydrous monoclinic plates, sol. in ·8 pts. H_2O at 17° (Schabus, J. 1854, 560; Marignac, J. 1855, 608). $Mg(C_2H_5SO_4)_2+4H_2O$; $Ca(C_2H_5SO_4)_2+2H_2O$, forms monoclinic laminæ, soluble in ·8 pts. water at 17° (M.);

$$Ba(C_2H_5SO_4)_2+2H_2O,$$

monoclinic plates, sp.gr. $\frac{21^\circ{\cdot}7}{}$ 2·080 sol. in ·92 pts. of water at 17°(M.); $Pb.(C_2H_5SO_4)_2+2H_2O$, large rhombic tables — $Pb(C_2H_5SO_4)_2+PbO$ amorph., sol. in ·54 pts. H_2O at 17°.

Chloride of ethyl sulphuric acid $Cl.C_2H_5.SO_3$, b.p. 151°–154° (cor.) (Claesson, J. pr. [2] 19, 248), with slight decomp.; 93°–95° at 100 mm. (Müller, B. 6, 227). From C_2H_5Cl and SO_3, together with isomers (*v.* under *Ethyl chloride*, p. 21); by dropping SO_2Cl_2 into alcohol (not *vice versâ*; diethyl sulphate is then formed) (Behrend, J. pr. [2] 15, 28); from a salt of ethyl sulphuric acid and PCl_5 (Purgold, B. 6, 505); from ethyl chloroformate $C_2H_5.CO_2.Cl$ and fuming sulphuric acid (Wilm, B. 6, 505). By passing C_2H_4 into HSO_3Cl; $SO_3H.C_2H_4.SO_2Cl$ is also produced (Müller, B. 6, 227).

A liquid with an irritating smell, exciting tears, and decomposed by contact with water into HCl,H_2SO_4 and alcohol. When the chloride is added to methyl alcohol or ethyl alcohol, ethyl sulphuric acid and CH_3Cl or C_2H_5Cl are produced; with amyl alcohol, amyl sulphuric acid and ethyl chloride are formed (Müller). If, on the other hand, absolute alcohol is dropped into the chloride, diethyl sulphate is produced (Claesson).

Bromethyl sulphuric acid

$$CH_2Br.CH_2.OSO_2OH(?)$$

from ethylene bromide and SO_3 (Wroblewski, Z. 1868, 563). The barium salt is anhydrous and is decomposed by continued heating with water, with separation of $BaSO_4$ and formation of glycol (Beilstein and Wiegand, B. 15, 1370). An isomeric body $CH_3.CHBr.OSO_2.OH$(?) is formed by acting upon ethylene bromide with Ag_2SO_4 and water (B. and W.), the barium salt is very soluble in water and its solution decomposes on warming into $BaSO_4$, HBr, and glycol.

Diethyl sulphate $(C_2H_5)_2SO_4$; sp.gr. $\frac{19^{\circ}}{}$ = 1·1837 (Claesson, J. pr. [2] 19, 257); b.p. 208° (with decomp.), 113·5° at 31 mm.; 118° at 40 mm.; 120·5° at 45 mm. (Villiers, Bl. 34, 26); m.p. about $-24·5°$ (V.); occurs in 'heavy oil of wine.' Formed by leading SO_3 vapour into absolute ether (Wetherill, A. 66, 117); in small quantity by distillation of $C_2H_5HSO_4$; by dropping alcohol into chloride of ethyl sulphuric acid $C_2H_5O.SO_2.Cl$, or by action of H_2SO_4 upon alcohol (Claesson); from Ag_2SO_4 and C_2H_5I (Stempnewsky, B. 11, 514). A mixture of 1 vol. absolute alcohol and 2 vols. H_2SO_4 is distilled slowly *in vacuo* (Villiers). Absolute alcohol is mixed with Nordhausen sulphuric acid, the ether separated by means of $CHCl_3$, and the product distilled *in vacuo* (Claesson and Lundvall, B. 13, 1699).

Is an oily liquid, with an odour like that of peppermint; insoluble in water, and slowly decomposed by that liquid even in the cold; when heated with water yields alcohol H_2SO_4 and $C_2H_5HSO_4$. Heated with alcohol forms ether and $C_2H_5HSO_4$; warm baryta water forms alcohol and $Ba(C_2H_5SO_4)_2$ (Villiers). In solution in benzene it is converted by NH_3 into the ethyl sulphates of NH_4, $NH_3(C_2H_5)$ and $N(C_2H_5)_4$.

Dibromo-diethyl sulphate $(CH_2Br.CH_2)_2SO_4$; by action of ethylene bromide upon Ag_2SO_4 in presence of benzene (Beilstein and Wiegand, A. 15, 1369); a heavy oil insoluble in water, soluble in benzene and ether, decomposed on heating. Heated with water yields bromide of ethyl sulphuric acid, and finally HBr, H_2SO_4, and glycol.

Ethyl sulphites.

Mono-ethyl sulphite

$$C_2H_5HSO_3 = C_2H_5O.SO.OH,$$

ethyl sulphurous acid, *hyposulphethylic acid.* The potassium salt $KC_2H_5SO_3$ is obtained from diethyl sulphite and KOH sol. (Warlitz, A. 143, 75); it forms crystalline laminæ and is very unstable. By treatment with PCl_5, diethyl sulphite yields the *chloride of ethyl sulphurous acid* $Cl.SO.OC_2H_5$, which boils at 122°, is decomposed by water into HCl,SO_2 and alcohol, and gives by further action of PCl_5 at 180° thionyl chloride, C_2H_5Cl and $POCl_3$ (Michaelis and Schumann, B. 7, 1074). Ethyl sulphurous acid is isomeric with ethyl sulphonic acid $C_2H_5.SO_2.OH$ (*q. v.*).

Diethyl sulphite $C_2H_5O.SO.OC_2H_5$; sp.gr. $\frac{0^{\circ}}{}$ 1·1063 (Carius, J. pr. [2] 2, 279); b.p. 161·3°; from alcohol and S_2Cl_2: 18 parts of absolute alcohol are mixed with 50 parts of S_2Cl_2, previously warmed to 60°; the mixture is kept at this temperature for an hour, and then distilled; the portion boiling above 150° is redistilled (Warlitz, A. 143, 74).

A colourless liquid, with mint-like odour, miscible with alcohol and ether; insoluble in water. Decomposed by water; with PCl_5 yields a chloride C_2H_5OSOCl, which on distillation splits up into C_2H_5Cl and SO_2 (Geuther, A. 224, 223; Michaelis and Wagner, B. 7, 1074). Decomposes at 200° into SO_2 and ether (Prinz, A. 223, 374); is also split up by heating with $SOCl_2$ to 120° into SO_2 and C_2H_5Cl (Geuther).

Ethyl sulphydrate C_2H_5HS. *Mercaptan*, *Ethyl mercaptan*, b.p. 36·2° (Nasini, B. 15, 2882); sp.gr. $\frac{20^{\circ}}{4^{\circ}}$ = ·83907 (N.) $\frac{21^{\circ}}{}$ = ·835. By distilling $Ba(C_2H_5SO_4)_2$ with $Ba(HS)_2$ (Zeise, A. 11, 1); by action of KHS upon C_2H_5Cl (Regnault, A. Ch. [2] 71, 390); by heating absolute alcohol saturated with SO_2 in a sealed tube, there are also formed $HC_2H_5SO_4$, $(C_2H_5)_2O$ and free H_2SO_4 (Endemann, A. 140, 336); from P_2S_5 and alcohol (Kekulé, A. 90, 310). It is best prepared by saturating a solution of KOH (sp.gr. 1·3) with H_2S, mixing with a solution of $Ca(C_2H_5HSO_4)_2$ (also of sp.gr. 1·3) and distilling on water bath (Liebig, A. 11, 14); according to Claesson (J. pr. [2] 15, 193) $(C_2H_5)_2S$ is also formed; NaC_2H_5S is prepared from the product of this action, the alcoholic solution evaporated to dryness, the $(C_2H_5)_2S$ removed by means of benzene and the C_2H_5NaS decomposed by dilute H_2SO_4.

Is a colourless liquid with a penetrating garlic-like smell, slightly soluble in water, from which it crystallises on evaporation as

$$C_2H_5HS.18H_2O, \text{ m.p. } 12^{\circ} \text{ (Claesson).}$$

Br gives the following reaction

$$C_2H_5HS + 3Br = C_2H_5Br + HBr + BrS$$

(Friedel, Ladenburg, A. 145, 189). HNO_3 forms $C_2H_5SO_2.SC_2H_5$, or if the acid be stronger, ethyl sulphonic acid.

It forms crystalline compounds with $SiCl_4$ (Demarçay, Bl. [2] 20, 127). It absorbs NO forming a dark-red solution.

The hydrogen of mercaptan is replaceable by metals forming mercaptides, *e.g.* C_2H_5KS, $-Hg(C_2H_5S)_2$, transparent plates, m.p. 76–77° (Otto, B. 13, 1290; 15, 125) very slightly soluble in cold alcohol, soluble in 12–15 parts hot alcohol (Liebig, A. 11, 17); $Pb(C_2H_5S)_2$ yellow precipitate formed when $Pb(C_2H_3O_2)_2$ and C_2H_5HS are mixed in alcoholic solutions. $As(C_2H_5S)_3$ a foul-smelling oil formed from $AsCl_3$ and C_2H_5NaS, decomposed by heat into As and $(C_2H_5)_2S_2$.—$Pt(C_2H_5S)_2$ pale yellow precipitate decomposed with ignition by air (Zeise).

Ethyl sulphide $(C_2H_5)_2S$; b.p. 91° (Pierre, J. 1851, 51); 91·9° at 754·7 mm. (Beckmann, J. pr. [2] 17, 451); 92·2°–93° cor. at 754 mm. (Nasini, B. 15, 2882); sp.gr. $\frac{0^{\circ}}{}$ = ·8367 (Pierre); $\frac{20^{\circ}}{4^{\circ}}$ = ·83676 (N.); from K_2S and C_2H_5Cl (Regnault, A. Ch. [2] 71, 387); from $Zn(C_2H_5)_2$ and $SOCl_2$ (Gauhe, A. 143, 266); from KHS and $KC_2H_5SO_4$ in alcohol (Hobson, C. J. 10, 56); also from P_2S_5 and $(C_2H_5)_2O$ (Beckmann).

It is a colourless liquid with strong garlic-like smell, insoluble in water. Chlorine acts upon it in the dark, forming substitution products, (1) $(C_2H_3Cl_2)_2S$, yellow liquid, b.p. 167–172°, sp.gr. $\frac{12^{\circ}}{}$ = 1·547; (2) $(C_2H_2Cl_3)_2S$, b.p. 189–192°, sp.gr. $\frac{13·5^{\circ}}{}$ = 1·219; (3) $(C_2HCl_4)_2S$, b.p. 217–222°. By prolonged action of chlorina C_2Cl_6 is formed and possibly $(C_2Cl_5)_2S$ (Riche, A. Ch. [3] 43, 283; A. 92, 358). $(C_2H_2Cl_3)_2S$ also results from action of chlorine upon $(C_2H_3Cl_2)_2S$ which can be obtained from C_2H_4 and Cl_2S_2 (Guthrie, A. 116, 241). Bromine forms $(C_2H_5)_2SBr_2$, a yellowish-red unstable body which by the action of KI yields $(C_2H_5)_2SI_2$, a black liquid (Rathke, A. 152, 214).

Ethyl sulphide combines with many metallic chlorides to form crystalline compounds, *e.g.* $(C_2H_5)_2S.HgCl_2$, white crystals soluble in alcohol and ether, m.p. 90°. $(C_2H_5)_2SHgI_2$ yellow needles, m.p. 110°. $2(C_2H_5)_2S.TiCl_4$ dark-red crystals (Demarçay).

Nitric acid (of sp.gr. 1·2) forms *ethyl sulphoxide* or *diethyl sulphine oxide* $(C_2H_5)_2SO$, a soluble oily liquid, solid at low temperatures and decomposed by heating. Fuming nitric acid converts this into *diethyl sulphone* $(C_2H_5)_2SO_2$; b.p. 248°; m.p. 70–72° (Oefele, A. 127, 370; 132, 88); R_∞ = 47·53 (Kanonnikow, J. R. 15, 451); also formed from $Pb(C_2H_5)_4$ and SO_2 (Frankland and Lawrance, C. J. 35, 244), also from $(C_2H_5)_2S$ and a solution of $KMnO_4$ (O.). Rhombic plates soluble in 6·4 parts water at 16°.

Triethyl sulphine $(C_2H_5)_3S$ forms compounds in which it plays the part of a univalent radicle.

$(C_2H_5)_3SI$ from $(C_2H_5)_2S$, C_2H_5I and H_2O (Oefele, A. 132, 82); from HI and $(C_2H_5)_2S$ or HI and C_2H_5HS, or C_2H_5I and C_2H_5HS (Cahours, A. 135, 352; 136, 151); forms rhombic plates of disagreeable odour and soluble in water. By action of Ag_2O yields *triethyl sulphine hydrate* $(C_2H_5)_3SOH$, a strong base; displaces NH_3 and has caustic action on the skin; it forms a crystalline deliquescent mass, which unites with acids to form deliquescent salts which form double compounds with many metallic salts, *e.g.* $PtCl_4.2(C_2H_5)_3SCl$ dark-reddish prisms soluble at 20°·7 in 30 parts of water (Dehn, A. Suppl. 4, 90; Jörgensen, J. pr. [2] 6, 82; Kraut, A. 210, 321).

When $(C_2H_5)_2S$ is heated with CH_3I *diethyl-methyl-sulphine iodide* $(C_2H_5)_2CH_3SI$, an unstable non-crystalline body, is formed from which other salts can be obtained; the chloride $(C_2H_5)_2CH_3SCl$ forms many double salts (Krüger, J. pr. [2] 14, 195). An isomeric body, *ethyl-methyl-ethyl sulphine iodide*, is also known (Krüger) which is crystalline; it is prepared from $C_2H_5CH_3S$ and C_2H_5I.

Ethyl disulphide $(C_2H_5)_2S_2$; b.p. 152·8°–153·4°, cor. at 730 mm. (Nasini, B. 15, 2882); sp.gr. $\frac{20^\circ}{4^\circ}$ = ·99267 (N.); by distillation of $KC_2H_5SO_4$ with K_2S_2 and water (Zeise, A. 11, 1; Morin, A. 32, 267; Löwig, Kopp, A. 35, 345; Cahours, A. 61, 98). By action of I upon a slight excess of a solution of C_2H_5NaS (Kekulé, Linnemann, A. 123, 279), by action of S upon C_2H_5SNa (Böttger, A. 223, 348).

A colourless liquid with garlic-like smell, very slightly soluble in water; with dilute HNO_3 gives $(C_2H_5)_2S_2O_2$, an oily liquid, which may be regarded as the ethyl salt of ethyl thiosulphonic acid $C_2H_5SO_2SC_2H_5$.

Ethyl trisulphide $(C_2H_5)_2S_3$, from K_2S_3 and $KC_2H_5SO_4$ (Cahours, Bl. [2] 25, 184); also from $(C_2H_5)_2S_2$ and S (H. Müller); a colourless liquid, with unpleasant smell.

Ethyl tetrasulphide $(C_2H_5)_2S_4$, from S_2Cl_2 and C_2H_5HS (Claesson, J. pr. [2] 15, 214); a heavy oily liquid, with disagreeable odour.

Ethyl pentasulphide $(C_2H_5)_2S_5$, by heating $(C_2H_5)_2S_4$ and S to 150°; a tough elastic solid.

Ethyl sulphinic acid $C_2H_5HSO_2$; by action of $Zn(C_2H_5)_2$ upon SO_2 (Wischin, A. 139, 364; Hobson, C. J. 10, 58): the sodium salt is produced by oxidation of sodium mercaptide by dry oxygen (Claesson, J. pr. [2] 15, 199). The free acid is a syrupy liquid with a sweet taste; by action of HNO_3 yields ethyl sulphonic acid and $C_4H_{11}NS_2O_5$ [$=(C_2H_5SO_2)_2NO$], crystals, m.p. 81·5°, very slightly soluble in water (Zuckschwerdt, A. 174, 308). Forms salts, of which $NaC_2H_5SO_2$ crystallises from alcohol in anhydrous crystals (C.); the lead salt was prepared from $Pb(C_2H_5)_4$ and SO_2 by Frankland and Lawrance (C. J. 35, 244).

Ethyl sulphonic acid

$$C_2H_5HSO_3 = C_2H_5.SO_2.OH$$

by the oxidation of C_2H_5HS by HNO_3 (Löwig and Weidmann, P. 49, 329; Kopp, A. 35, 346); by oxidation of C_2H_5CNS or of $(C_2H_5)_2S_2$ (Muspratt, C. J. 1, 45); from C_2H_5I and K_2SO_3 (Graebe, A. 146, 37). The acid is a crystalline deliquescent body; by action of ICl_3 at 150°, we get dichlorethyl sulphonic acid; excess of ICl_3 gives C_2Cl_6 (Spring and Wessinger, B. 15, 445); unites with bases to form salts.

Ethyl sulphonate

$$(C_2H_5)_2SO_3 = C_2H_5SO_2OC_2H_5;$$

b.p. 213·4° cor.; sp.gr. $\frac{0^\circ}{0}$ = 1·1712 $\frac{20^\circ}{4^\circ}$ = 1·1452° (Nasini, B. 15, 2884); by action of ethyl sulphonic chloride $C_2H_5SO_2Cl$ and C_2H_5NaO (Carius, J. 1870, 726; J. pr. [2] 2, 262), also from C_2H_5I and Ag_2SO_3.

Ethyl sulphonic chloride $C_2H_5SO_2Cl$; b.p. 177·5° cor. (Carius), 171° (Otto, B. 15, 122); sp.gr. $\frac{22{\cdot}5^\circ}{}$ = 1·357° (C.); by action of PCl_5 on $NaC_2H_5SO_3$ (Gerhardt and Chancel, C. R. 35, 690); by action of Cl upon ethyl oxysulphide (S. and W., *l.c.*). Colourless liquid with unpleasant smell.

Ethyl thiocyanate C_2H_5SCN; b.p. 141°–142° (Meyer, A. 171, 47), 146° cor. (Buff, B. 1, 206), sp.gr. $\frac{0^\circ}{}$ = 1·033, $\frac{19^\circ}{}$ = 1·0126, $\frac{146^\circ}{}$ = ·8698 (B.); by action of KCNS upon $KC_2H_5SO_4$ (Cahours, A. Ch. [3] 18, 264; A. 61, 95), from C_2H_5Cl and KCNS (Löwig, P. 67, 101).

A mobile liquid with unpleasant odour, insoluble in water, miscible with alcohol and ether; by action of sodium forms NaCN and $(C_2H_5)_2S$ (Hofmann, B. 1, 184); by heating with solution of KOH yields $(C_2H_5)_2S_2$, KCN, and KCNO (Brüning, A. 104, 198), with alcoholic KOH, forms $(C_2H_5)_2S_2$, CO_2, NH_3, but no KCNS (Löwig), but with alcoholic KHS yields C_2H_5HS and KCNS (L.). By action of aqueous NH_3 at 100° it yields $(C_2H_5)_2S_2$, NH_4CN, urea, oxalic acid, and other products (Kremer, J. 1858, 401; Jeanjean, J. 1862, 364). By passing Cl into it there results $(CNCl)_3$ and a liquid $C_2H_5SCl_3$; b.p. 134–135° (James, J. pr. [2] 30, 316). A chlorine substitution product C_2H_4ClSCN was obtained by James (J. pr. [2] 20, 352) by heating C_2H_4ClBr with KCNS and alcohol; an oil heavier than water, with unpleasant smell; b.p. 202°–203°; m.p. below −20°.

Ethyl thiocyanate forms compounds with HCl, HBr, and HI (Henry, J. 1868, 652; Glutz, A. 153, 312).

Ethyl isothiocyanate C_2H_5NCS (L.), *Ethyl-thiocarbimide, mustard oil*; b.p. 134°, sp.gr. $\frac{0^\circ}{}$ = 1·0192, $\frac{22^\circ}{}$ = ·9972°, $\frac{133{\cdot}2^\circ}{}$ = ·8763° (Buff, B. 1, 206); by action of C_2H_5NCO upon P_2S_5 (Michael and Palmer, Am. 6, 259), also in very small quantity when $Hg(CNS)_2$ is heated with C_2H_5I (Michael, Am. 1, 417), also by heating $CSCl_2$ and $(C_2H_5)NH_2$ (Rathke, A. 167, 211). A solution of ethylamine in alcohol is treated with CS_2, when crystals of ethyl ammonium ethyl thiocarbamate separate out, $2C_2H_5H_2N + CS_2 = NHC_2H_5CS.SNH_3C_2H_5$. A solution of this body is then treated with $HgCl_2$, when the mercury compound is precipitated.

$$2NH(C_2H_5)CS_2N.(C_2H_5)H_3 + HgCl_2$$
$$= (C_2H_5)H_3NCl + [NH(C_2H_5)CS_2]_2Hg.$$

On distilling, this body yields the mustard oil, HgS and H_2S (Hofmann, B. 1, 171; 2, 452); is a liquid with very disagreeable smell, and in contact with the skin produces a burning sensation (Hofmann, B. 1, 26); with absolute alcohol forms monothioethyl urethane

$$N(C_2H_5)HCSOC_2H_5,$$

a liquid, b.p. 204–208°; with aldehyde ammonia forms a body which crystallises in needles (m.p. 118–119°), and having the composition $C_{14}H_{31}N_3S_2O_2$,

$$2C_2H_5NCS + 4C_2H_4O.NH_3$$
$$= C_{14}H_{31}N_3S_2O_2 + NH_3 + 2H_2O$$

(Schiff, B. 9, 573). This body is soluble in alcohol and ether, and in hot water.

Ethyl thiophene $C_4H_3SC_2H_5$; b.p. 132–134°, (cor.) sp.gr. $\frac{24^\circ}{} = \cdot 990$; by action of C_2H_5Br and Na upon C_4H_3IS (Meyer and Kreis, B. 17, 1560).

Ethyl telluride $(C_2H_5)_2Te$, *tellurethyl*; b.p. 98° (Heeren, J. 1861, 565), from K_2Te and $KC_2H_5SO_4$ (Wöhler, A. 84, 69; 35, 111; Mallet, C. J. 5, 71). A heavy, viscid, reddish-yellow liquid, with a very unpleasant smell, burns in air with blue flame, evolving fumes of TeO_2; hardly soluble in water, and oxidised by exposure to air; is poisonous. HNO_3 forms $(C_2H_5)_2TeHNO_3$ (monoclinic prisms). Strong HCl precipitates the oily compound $(C_2H_5)_2TeCl_2$ from a solution of the nitrate; ammonia converts this into $[(C_2H_5)_2Te]_2Cl_2O$ (hexagonal prisms), which, when treated with Ag_2SO_4 yields $[(C_2H_5)Te]_2.H_2SO_4$ (colourless prisms). By action of Ag_2O upon a solution of the chloride, $(C_2H_5)_2TeO$ is produced, which on concentration decomposes.

Ethyl ditelluride $(C_2H_5)_2Te_2$ is said to be formed in the preparation of $(C_2H_5)_2Te$, and to be a dark-red liquid, with high boiling-point. When $(C_2H_5)_2Te$ is acted upon by C_2H_5I, *triethyl tellurium iodide*, $(C_2H_5)_3TeI$, is formed, m.p. 90–92° (Cahours, Bl. [2] 4, 40), which crystallises in yellow prisms.

ETHYLAMINES.

Bodies in which one or more atoms of H in NH_3 are replaced by C_2H_5.

Ethylamine $C_2H_5.NH_2$; b.p. 18·7°, sp.gr. $\frac{8^\circ}{-} = \cdot 6964$, $\frac{2^\circ}{-} = \cdot 708$ (Hofmann, B. 22, 699); H.C. = 408·5 cal. (Berthelot, A. Ch. [5] 23, 244); from ethyl carbimide and KOH (Wurtz, A. 71, 330; also C. R. 28, 223); from C_2H_5Br and NH_3 (Hofmann, A. 74, 159); by the putrefaction of yeast and of flour (Hesse, J. 1857, 403; Sullivan, J. 1858, 231), by heating alcohol with NH_4Cl to 300° (Berthelot, A. Ch. [3] 38, 63); by action of nascent H upon acetonitrile (Mendius, A. 121, 142). It is also produced in the dry distillation of the residues from beet-root in sugar manufacture (Duvillier and Buisine, A. Ch. [5] 23, 317), by action of $KC_2H_5SO_4$ upon alcoholic NH_3 at 120° (Erlenmeyer and Carl, J. 1875, 617).

Preparation. — (1) 1 vol. of nitric ether $C_2H_5NO_3$ is treated with 3 vols. of alcoholic ammonia for 12 hours at 100°; the free bases are separated from the NH_3 by neutralising with H_2SO_4 or HCl and extracting with alcohol; the sulphates or chlorides are then decomposed by NaOH and the free bases combined with picric acid and crystallised. The picrate of $(C_2H_5)_3N$ separates first, in yellow needles, then the $C_2H_5NH_2$ salt in brown prisms; the picrates are then separated and decomposed by HCl, and the bases liberated by KOH (Carey Lea, C. N. 5, 118).

(2) Crude C_2H_5Cl, from manufacture of chloral, is heated for an hour with 3 times its volume of alcohol (95 p.c.), previously saturated with ammonia, in an iron vessel heated by a water-bath. On cooling, the NH_4Cl is filtered off, and the remainder distilled until free from NH_3 and alcohol, the residue (hydrochlorates of mono-, di-, and triethylamine, mixed with a little NH_4Cl) is treated with a strong solution of NaOH, and the liquid drawn off and dried by means of solid NaOH; it consists of a mixture of the three bases; ethyl oxalate is then added, and the $(C_2H_5)_3N$, which is unacted upon, is distilled off; the residue consists of a mixture of solid *diethyl oxamide* $C_2O_2(NHC_2H_5)_2$ and liquid *diethyl oxamic ethyl ether* $C_2O_2N(C_2H_5)_2OC_2H_5$, which are separated and the diethyl oxamide decomposed, after recrystallising from hot water, with KOH. $C_2O_2(NHC_2H_5)_2 + 2KOH = 2C_2H_5NH_2 + K_2C_2O_4$ (Hofmann, B. 3, 109, 776; also Duvillier and Buisine, C. R. 88, 31).

Properties.—Is a mobile liquid, with strong ammoniacal odour, is strongly caustic, and has an alkaline reaction; burns with yellow flame, is miscible in all proportions with water, displaces NH_3 from its salts, and, like ammonia, precipitates metallic hydrates and oxides from salts. It, however, dissolves the hydrates of Al (Wurtz), Au, and Ru (Carey Lea), and does not dissolve those of Cd, Ni, and Co. The chloride is decomposed on distillation into $C_2H_5H_2N$, $(C_2H_5)_2HN$, NH_3, C_2H_4, and C_2H_5Cl (Fileti and Piccini, B. 12, 1508). CrO_3 oxidises ethylamine to aldehyde and N (Carstanjen, J. 1862, 330).

Salts (*v.* Wurtz, A. 76, 329).—$(C_2H_5).NH_2.HCl$, deliquescent plates, m.p. 76–80°; b.p. 315–320° (with decomposition). Molec. Refract. 35·97 (calc. 35·95) (Kanonnikow, J. pr. [2] 31, 347). Soluble in alcohol. Prepared by heating 1 vol. of C_2H_5Cl with 3 vols. alcoholic ammonia to 100° (Groves, C. J. 13, 331). $C_2H_5H_2N.HgCl_2$, by action of alcoholic $HgCl_2$ on alcoholic $C_2H_5.H_2N$; a crystalline precipitate soluble in hot HCl solution. With excess of $HgCl_2$ in aqueous solution a white precipitate $2C_2H_5H_2N.HgCl_2 + 2HgO$ is thrown down; by heating $C_2H_5H_2N$ with excess of $HgCl_2$ a yellow precipitate $ClHg.OHg.NH.C_2H_5$ separates, while a crystallisable compound $ClHg.NH.C_2H_5$ remains in solution (Köhler, B. 12, 2308). $2C_2H_5NH_2.PtCl_2$ yellow powder, combines with $(C_2H_5)NH_2$ and forms $4C_2H_5NH_2.PtCl_2.2H_2O$ colourless crystals soluble in water.

$(C_2H_5.NH_2HCl)_2.PtCl_4$, orange yellow, flat rhombohedrons (Weltzien, A. 93, 272), hexagonal rhombohedrons (Topsoë, J. 1883, 619); sp.gr. $\frac{19^\circ}{4^\circ}$

= 2·255 (Clarke, B. 12, 1399). $C_2H_5.NH_2.HCl.AuCl_3$ golden yellow monoclinic prisms soluble in water (T.).

$(C_2H_5NH_2)_2H_2SO_4$ deliquescent body soluble in alcohol, forms double salts with other sulphates, *e.g.* ethyl-ammonium alum

$(C_2H_5NH_2)_2.H_2SO_4 + Al_2(SO_4)_3 + 24H_2O$

octahedral crystals soluble at 25° in 6·89 parts of water.

Substitution Products of Ethylamine.

Dichlorethylamine, ethylated chloride of nitrogen, $C_2H_5.NCl_2$; b.p. 88–89° at 762 mm.; sp.gr. $\frac{15^\circ}{}$ = 1·230; by passing Cl through aqueous $C_2H_5NH_2$ (Wurtz, C. R. 11, 810), prepared by distilling a mixture of $C_2H_5NH_3Cl$ with 2⅓ times its weight of bleaching powder and a little water (Tscherniak, B. 9, 146), a yellow oily liquid with a penetrating smell, insoluble in water and acids, decomposes on long standing into HCl, NH_4Cl, $C_2H_5NH_3Cl$, $CHCl_3$, C_2H_3N, and C_2H_5Cl (Köhler, B. 12, 1870). The pure substance keeps unchanged for long periods under water (Tscherniak, B. 12, 2129). Alkalis decompose it into acetic acid and NH_3; behaves towards many bodies as free Cl. $Zn(C_2H_5)_2$ forms $(C_2H_5)_3N$ and $ZnCl_2$.

Di-iodoethylamine $C_2H_5NI_2$ and *dibromoethylamine* $C_2H_5NBr_2$ are formed similarly; the former is a dark-blue liquid (Wurtz).

Diethylamine $(C_2H_5)_2NH$; m.p. −40° (Hofmann, B. 22, 699); b.p. 57·5° (Hofmann, A. 73, 91); 55·5° at 759 mm. (Oudemans, R. 1, 59); sp.gr. $\frac{0^\circ}{}$ = ·7262; $\frac{15^\circ}{}$ = ·7107 (H., B. 22, 699). From NH_3 and C_2H_5I (Hofmann), or NH_3 and $C_2H_5NO_3$ (Lea, J. 1861, 493). Prepared by the action of KOH upon the $C_2O_2N(C_2H_5)_2OC_2H_5$ obtained in manufacture of ethylamine (*q. v.*).

Also by action of very dilute NaOH solution upon $[(C_2H_5)_2N(NO)]_2H_2SO_4$ (Kopp, B. 8, 622).

Is a colourless, inflammable liquid with strong ammoniacal smell, very soluble in water; is a strong base and acts like $C_2H_5NH_2$ except that it does not dissolve $Zn(OH)_2$ (Carey Lea). The nitrate decomposes suddenly at 170° and yields *nitrosodiethylamine* $(C_2H_5)_2NNO$ (Franchimont, R. 2, 95); the chloride $(C_2H_5)_2NH.HCl$ forms non-deliquescent plates; m.p. 99–100° (F.) 215–217° (Wallach, A. 214, 275); b.p. 320–330° (W.), and combines with many metallic chlorides, *e.g.* $[(C_2H_5)_2NHHCl]_2PtCl_4$ orange yellow monoclinic crystals (Topsoë, J. 1883, 619).

Nitrosodiethylamine $(C_2H_5)_2NNO$; b.p. 176·9° (cor.); sp.gr. $\frac{17\cdot5^\circ}{}$ = ·951 V.D. = 3·36 (calc. = 3·53) (Knecht, B. 10, 979); by distilling neutral solution of $(C_2H_5)_2NHHCl$ with a concentrated solution of KNO_2 (Geuther, A. 128, 251; J. 1871, 695); a yellow oil with aromatic smell, decomposed by HCl into $(C_2H_5)_2NH$ and HNO_2. Alcoholic KOH at 140° forms NH_3 and $(C_2H_5).NH_2$. Na amalgam forms N_2O and $(C_2H_5)_2NH$.

Triethylamine $(C_2H_5)_3N$; b.p. 89–89·5° at 736·5 mm. (Brühl, A. 200, 186), 89–90° at 767·8 mm. (Hofmann); sp.gr. $\frac{15^\circ}{}$ = ·735 (Hofmann, B. 22, 700); critical temperature 267·1° (Pawlewski, B. 16, 2633), remains liquid at −75° under 10 mm. pressure (H.). By the action of NH_3 upon C_2H_5I (Hofmann, A. 73, 91), or upon $C_2H_5NO_3$ (Carey Lea).

Preparation.—Crude ethylamine (from C_2H_5Cl and NH_3) in alcoholic solution is treated with C_2H_5Cl (Duvillier and Buisine), or by distillation of $(C_2H_5)_4N.OH$.

Properties.—An oily liquid with strong ammoniacal smell, slightly soluble in water; strong base. On strongly heating its salts $(C_2H_5)_3N$ is destroyed with formation of a little $(C_2H_5)_2N.NO$ (Geuther, Z. 1886, 513).

Its chloride forms feathery non-deliquescent scales, and combines with many metallic salts to form double compounds. $(C_2H_5)_3N.HNO_3$; m.p. 98–99° (Franchimont, R. 2, 339).

Tetra-ethylammonium compounds, Tetraethylium $(C_2H_5)_4N$.

Tetra-ethylammonium hydrate $(C_2H_5)_4N.OH$, formed from the iodide $(C_2H_5)_4NI$ by the action of Ag_2O. It forms very deliquescent needles which eagerly absorb CO_2, is a strong base, displaces NH_3, precipitates metallic hydroxides, and gives a blue solution with sugar and $CuSO_4$, is decomposed by dry distillation, forming ethylamine, ethylene, and H_2O; when heated with C_2H_5I gives $(C_2H_5)_4I$ and alcohol.

Salts.—$(C_2H_5)_4NCl$, forms deliquescent crystals, and yields many double salts, *e.g.*,

$[(C_2H_5)_4NCl.]_2HgCl_2$

tetragonal crystals; $(C_2H_5)_4NCl.HgCl_2$ triclinic crystals (Topsoë, J. 1883, 620); $[(C_2H_5)_4NCl]_2PtCl_4$ orange yellow, crystalline (monoclinic (T.)); difficultly soluble in water, almost insoluble in alcohol; $(C_2H_5)_4NBr_3$ light-orange needles, m.p. 78°; combines with Br to form an unstable pentabromide (Marquart, B. 3, 284); gives with alcoholic I solution a precipitate of $(C_2H_5)_4NI_3$, quadratic prisms (Weltzien, B. 91, 33); the moniodide $(C_2H_5)_4NI$ forms large crystals soluble in cold water and in alcohol, insoluble in ether; sp.gr. 1·559 (Schröder, B. 12, 562). Many other salts have been prepared (Classen, J. 1864, 420; J. pr. 93, 446).

Ethyl hydroxylamine $C_2H_5O.NH_2$; b.p. 68°; sp.gr. $\frac{7\cdot5^\circ}{}$ = ·883 (Gürke, A. 205, 277); by the action of HCl upon benzoyl ethyl-hydroxylamine ethyl ether $C_6H_5CO.NC_2H_5.OC_2H_5$, or upon the ethyl ether of benzaldoxime $C_7H_6{:}N.OC_2H_5$ (Lossen and Zanni, A. 182, 223).

A strongly-smelling inflammable liquid, miscible with water, alcohol, and ether; gives with $AgNO_3$ a white precipitate which, on heating, is changed to metallic silver; with acids forms salts, *e.g.*, $C_2H_7NO.H.Cl$, scaly plates; m.p. 128°; decomposed by heating with HCl to 150° into C_2H_5Cl, NH_3OHCl, and NH_4Cl; unites with $PtCl_4$ to form $(C_2H_7NO.HCl)_2PtCl_4$; prismatic crystals, soluble in water and in absolute alcohol (Lossen and Zanni). The sulphate $(C_2H_7NO)H_2SO_4$ crystallises with difficulty, and also is soluble in water and in alcohol.

Diethyl hydroxylamine $NHC_2H_5.OC_2H_5$. The hydrochlorate, $C_4H_{11}NOHCl$ is obtained by the action of Sn and HCl upon $C_2H_5NO_3$ (Lossen, A. Suppl. 6, 238); the salts are more soluble in water than those of hydroxylamine; the free base is a syrupy liquid soluble in water, and with strong basic properties.

$C_4H_{11}NO.HCl$ syrup—$(C_4H_{11}NO.HCl)_2PtCl_4$ orange-yellow plates soluble in warm alcohol and in water.

Mixed ethyl bases.

Triethyl methyl ammonium $N(C_2H_5)_3CH_3$— forms salts, *e.g.* $N(C_2H_5)CH_3I$, which are obtained by action of $N(C_2H_5)_3$ upon the corresponding salt of CH_3 (Hofmann, A. 78, 277) (for *Salts*, *v.* Topsoë, J. 1883, 620). The picrate melts at 267-268° (Lossen, A. 181, 374).

Diethyl dimethyl ammonium $N(C_2H_5)_2(CH_3)_2$. The iodide can be obtained from $N(CH_3)_2H$ and C_2H_5I, or from $N(C_2H_5)_2H$ and CH_3I (*v.* Meyer and Lecco, A. 180, 177) (for *Salts*, *v.* Topsoë, *l.c.*). The picrate melts at 285-287° (Lossen, A. 181, 374).

Ethyl trimethyl ammonium $NC_2H_5(CH_3)_3$, the iodide is formed from $(CH_3)_3N$ and C_2H_5I (Müller, A. 108, 1) (for *Salts*, *v.* Topsoë). The picrate melts at 299-300° (Lossen).

Triethyl propyl ammonium $(N(C_2H_5)_3C_3H_7$ forms an iodide which crystallises in large needles (Mendius, A. 121, 136).

Diethyl isoamylamine $N(C_2H_5)_2C_5H_{11}$, b.p. 154°; from the distillation of $N(C_2H_5)_3C_5H_{11}OH$ *q. v.* (Hofmann); $[N(C_2H_5)_2C_5H_{11}HCl]_2PtCl_4$ yellow needles.

Triethylisoamyl ammonium $N(C_2H_5)_3C_5H_{11}$. The iodide is formed by the action of $N(C_2H_5)_3$ upon $C_5H_{11}I$ (Hofmann, C. J. 4, 313; A. 78, 279); the hydrate decomposes on heating as follows: $C_5H_{11}(C_2H_5)_3N.OH = NC_5H_{11}(C_2H_5)_2 + C_2H_4 + H_2O$

Diethyl methyl isoamyl ammonium $N(C_2H_5)_2CH_3.C_5H_{11}$ the iodide is formed from $N(C_2H_5)_2C_5H_{11}$ and CH_3I (Hofmann).

Ethyl-methyl-amylamine $N.C_2H_5.CH_3.C_5H_{11}$, b.p. 135, is obtained by distillation of the hydrate of preceding radicle (Hofmann).

Ethyl acetamide $NH.C_2H_5C_2H_3O$, b.p. 205°, sp.gr. $\frac{4{\cdot}5^{\circ}}{} = {\cdot}942$ (Wurtz); from ethyl acetate and ethylamine (Wurtz, A. Ch. [3] 30, 491; C. R. 36, 180; A. 76, 334) or from C_2H_5NC and $HC_2H_3O_2$ (W. 88, 315); a liquid which, by action of Cl yields *chlorethyl acetamide* $NCl.C_2H_3O.C_2H_5$ (Norton, Tcherniak, Bl. 30, 106; C. R. 86, 1409), an oily unstable liquid slightly soluble in water.

Diethyl acetamide $N(C_2H_5)_2C_2H_3O$, b.p. 185°-186°; sp.gr. $\frac{8{\cdot}5^{\circ}}{} = {\cdot}9248$ (Wallach, A. 214, 235).

Ethyl diacetamide $NC_2H_5(C_2H_3O)_2$; b.p. 185-192° (Wurtz); sp.gr. $\frac{20^{\circ}}{} = 1{\cdot}0092$ (W.); by heating propionitrile with $(C_2H_3O)_2O$ to 200° (Wurtz, A. Ch. [3] 42, 43).

Ethyl hydrazines.

1. *Ethyl hydrazine* $C_2H_5HN.NH_2$; b.p. 99°·5 at 709 mm., is prepared by reducing nitrosodiethyl urea $N(C_2H_5)H.CON(NO)C_2H_5$ by means of zinc-dust and acetic acid; this yields ethyl hydrazine urea (semi-carbazide) $NC_2H_5H.CO.N(NH_2)C_2H_5$ and this by action of HCl forms $C_2H_5HN.NH_2$, CO_2 and $C_2H_5NH_2$; by passing in HCl the chloride separates out which is then decomposed by strong KOH solution and solid KOH, and the resulting oily liquid distilled over BaO (Fischer, A. 199, 287).

Is a colourless liquid with faintly ammoniacal odour; has great affinity for water, in which it is soluble, as also in alcohol, ether, chloroform and benzene; fumes in air and destroys cork and caoutchouc; reduces Fehling's solution in the cold. Br water liberates N. It precipitates metallic oxides and gives the isonitrile reaction with KOH and $CHCl_3$. Forms two chlorides: (1) $C_2H_8N_2.2HCl$ white needles very soluble in water and alcohol; on heating to 110° yields (2) $C_2H_8N_2.HCl$ an amorphous horny deliquescent body. The sulphate crystallises from alcohol in fine plates, and is very soluble in water. By heating $C_2H_5HN.NH_2$ with $K_2S_2O_7$ to 80-100°, *potassium ethyl hydrazine sulphonate* $C_2H_5NH.NHSO_3K$ is obtained; this forms fine needles very soluble in water, much less soluble in alcohol and ether (Fischer).

2. *Diethyl hydrazine* $(C_2H_5)_2N.NH_2$; b.p. 96-99°, prepared by action of zinc-dust and acetic acid upon a solution of nitrosodiethylamine $(C_2H_5)_2(NO)N$; 30 grs. $(C_2H_5)_2(NO)N$ dissolved in 300 grs. water are mixed with 150 grs. Zn dust and 150 grs. $C_2H_4O_2$ (of 50 p.c.) kept at 20-30° and, towards the end, at 40-50°. Excess of Zn is then dissolved by HCl, and an excess of NaOH added and the mixture distilled; the distillate is neutralised with HCl and NH_4Cl separated by crystallisation. From the mother liquor $(C_2H_5)_2N_2H_2$ mixed with $(C_2H_5)_2HN$ is freed by solid KOH. By the action of HCNO diethyl hydrazine urea (semi-carbazide) $CONH_2.NH.N(C_2H_5)_2$ is formed. Four grams of this body when heated with 15 grs. of HCl in sealed tubes to 100°, then diluted and the NH_4Cl separated, yields by treatment with KOH pure $(C_2H_5)_2N_2H_2$ (Fischer, A. 199, 308).

Is a colourless liquid with a faintly ammoniacal smell, very hygroscopic and soluble in water, alcohol, ether, chloroform, and benzene. Reduces Fehling's solution only on warming, is monobasic, the salts are soluble in water and alcohol, and difficult to crystallise; $[(C_2H_5)_2N_2H_2.HCl]_2PtCl_4$, forms fine yellow needles soluble in water.

Triethyl-azonium iodide $(C_2H_5)_3NNH_2I$ is formed by action of diethylhydrazine upon 1½ times its weight of C_2H_5I (Fischer, A. 199, 316). It forms needles very soluble in water and in hot alcohol, insoluble in ether and strong alkalis. By action of Ag_2O gives the strongly alkaline free base, which on heating, yields $(C_2H_5)_2N.NH_2$ and C_2H_4. By the action of nascent H (Zn and H_2SO_4) the iodide yields HI, NH_3, and $(C_2H_5)_3N$.

Tetra-ethyl tetrazone $(C_2H_5)_2N.N{:}N.N(C_2H_5)_2$, by the action of yellow HgO upon a cold aqueous solution of $(C_2H_5)_2N.NH_2$ (Fischer A. 199, 319), is an oily liquid with a disagreeable smell, not volatile without decomposition, and which does not freeze at −20°. When decomposed by heat yields N, and $(C_2H_5)H_2N$. Forms an explosive oily compound with I. Is a strong base, though its salts are very unstable. It reduces silver solutions with formation of a mirror. The solution decomposes on heating, yielding N, $N(C_2H_5)_2H$, and aldehyde. The Pt double salt $[(C_2H_5)_4N_42HCl]_2PtCl_4$ forms yellow prisms soluble in water.

ETHYL ACETATE *v. Alkyl acetates*, art. Acetic acid.

ETHYL BUTYRATE *v.* Butyric acid.

ETHYL DIPHENYLAMINE *v.* Diphenylamine.

ETHYLENE C_2H_4, *Olefiant gas*, *Heavy carburetted hydrogen*, *Bicarburetted hydrogen*, *Elayl*, *Ethene*, *Etherin*, discovered by Deiman, Van Troostwyk, Bondt, and Lauwerenburgh (Crell's Ann. 1795 [2] 195, 310, 430). Obtained by action of H_2SO_4 upon alcohol; by the dry distillation of many organic bodies (hence occurs to the extent of 4 or 5 p.c. in coal gas). Also formed when CS_2 and H_2S (or PH_3) are led over heated copper (Berthelot, A. 108, 194). To prepare the gas, a mixture of 25 parts (by weight) of alcohol and 150 parts sulphuric acid is heated to 170°, and a mixture of 1 part of alcohol and 2 of H_2SO_4 is allowed to drop slowly into the vessel by means of a funnel. The gas is passed through H_2SO_4, NaOH solution, and then again through H_2SO_4. For the preparation of small quantities of pure gas, an alcoholic solution of $C_2H_4Br_2$ is warmed with granulated Zn (Sabanejeff, J. R. 9, 33).

Properties.—A colourless gas liquefied by a pressure of 42½ atmospheres at $-1{\cdot}1°$; b.p. $-105°$ (Cailletet, C. R. 94, 1224), $-102°$ to 103° (Wroblewsky, Olszewsky, M. 4, 338); critical temp. 13°, becomes liquid at 1° and 45 atmospheres; at 4° and 50 atmospheres; at 8° and 56 atmospheres; and at 10° and 60 atmospheres (C.); sp.gr. (air = 1) ·9784. 1 volume of water absorbs at $t°$ $\cdot25629 - \cdot009136t + \cdot0001881t^2$ volumes C_2H_4 (Bunsen). Alcohol (of sp.gr. ·792 at 20°) absorbs $3{\cdot}59498 - \cdot05772t + \cdot000681t^2$ volumes (Carius, A. 94, 133); H.C.p. = 341·4 cal.; H.F. (from amorphous C.) = −9·4 cal. (Berthelot, A. Ch. [5] 23, 180).

Ethylene forms an explosive mixture with oxygen, and explodes, even in the cold in contact with ozonised oxygen (Houzeau and Renard, J. 1873, 319). Led through a hot tube it splits up into C, H, CH_4, C_2H_6, and C_2H_2 (Berthelot, A. 139, 277). By the action of the electric spark it forms C_2H_2 and H and then C and H (Wilde, Z., 1866, 735). It combines with H to form C_2H_6, when the mixture is passed through a hot tube (B., A. Ch. [4] 9, 431; Bl. 39, 145), or when in contact with Pt black in the cold (Wilde, B. 7, 354). By heating a mixture of C_2H_4 and CO_2 to 400° aldehyde is formed (Schützenberger, Bl. 31, 482). CrO_3 converts it into aldehyde at 120° (B., A. 150, 378). Fuming sulphuric acid absorbs readily large quantities of C_2H_4 at ordinary temperatures, as does also common H_2SO_4 at 160°–170° (Butlerow, B. 6, 193), forming $C_2H_5HSO_4$ (Faraday). C_2H_4 combines at 100° with strong HI or HBr solution, but not with HCl (Berthelot, A. 104, 184; 115, 114). In presence of $AlBr_3$, HBr unites at 0° with C_2H_4 forming C_2H_5Br. With Cl_2O *chlorethyl chloracetate* $C_2H_2ClO_2C_2H_4Cl$ is formed, while ClO_2 yields $HC_2H_2ClO_2$. C_2H_4 combines with BF_3 in sunlight to form $C_2H_4BF_3$ (Landolph, B. 12, 1586) a liquid; b.p. 124°–125°; sp.gr. $\frac{23°}{}$ 1·0478. Ethylene acts as a divalent radicle and forms salts with most of the acids.

Ethylene acetates (Wurtz, C. R. 43, 199; Atkinson, P. M. [4] 16, 433).

1. *Ethylene monoacetate* $C_2H_4C_2H_3O_2OH$ *monoacetic glycol*, b.p. 182°, 190°–190·5° cor. (Perkin, C. J. 45, 505); sp.gr. $\frac{15°}{15°} = 1{\cdot}1108$ $\frac{25°}{25°} = 1{\cdot}1018$ (P.), produced by action of $KC_2H_3O_2$ upon $C_2H_4Br_2$ in presence of alcohol (Atkinson). A liquid not miscible with water; yields glycol $C_2H_4(OH)_2$ by heating with $C_2H_4Br_2$ and alcohol (Demole, A. 177, 45); decomposed by heating with C_2H_3OCl into acetochlorhydrin and ethylene diacetate (Lourenço, A. 114, 127).

2. *Ethylene diacetate* $C_2H_4(C_2H_3O_2)_2$,

$C_2H_3O_2CH_2.CH_2.C_2H_3O_2$,

b.p. 186°–187°; sp. gr. $\frac{0°}{} = 1{\cdot}128$; prepared from $C_2H_4Br_2$ or $C_2H_4I_2$ and $AgC_2H_3O_2$ (Wurtz, A. Ch. [3] 55, 488), or from $C_2H_4Br_2$ and anhydrous $K(C_2H_3O_2)$ at 150°–200° (Demole).

A liquid soluble in 7 parts of water, isomeric with *ethylidene diacetate* $CH_3.CH(C_2H_3O_2)_2$; (b.p. 168·8°; sp.gr. $\frac{12°}{}$ 1·061), prepared from aldehyde and $(C_2H_3O)_2O$. *Dichlorethylene diacetate* $C_2H_2Cl_2(C_2H_3O_2)_2$, b.p. 120° at 20 mm., is produced by action of acetyl oxychloride $C_2H_3O_2Cl$ upon C_2H_2 (Prudhomme, Z. 1870, 397).

Ethylene acetochlorhydrin

$ClCH_2.CH_2.O.C_2H_3O$,

b.p. 145°; sp.gr. $\frac{0°}{} = 1{\cdot}1783$; by heating a mixture of glycol and acetic acid to 100° with HCl (Simpson, A. 112, 147), from C_2H_4 and $C_2H_3O_2.Cl$ (Schützenberger and Lippman, A. 138, 325), insoluble in water, yields ethylene oxide by action of KOH.

Ethylene acetoiodohydrin $ICH_2.CH_2OC_2H_3O$, heavy oil, and

Ethylene acetobromohydrin

$BrCH_2CH_2OC_2H_3O$,

b.p. 161°–163°, are prepared from $C_2H_4(C_2H_3O_2)OH$ by action of HI and HBr respectively, the former in the cold in presence of $C_2H_4(OH)_2$ and $HC_2H_3O_2$ (Simpson, A. 113, 123), the latter at 100° (Demole, A. 178, 120).

Ethylene alcohols.

1. **Monoethylene alcohol**

$C_2H_4(OH)_2 = CH_2OH.CH_2OH$;

glycol, ethylene glycol; b.p. 197–197·5° at 764·5 mm. (Wurtz); 196–199° (cor.) (Perkin, C. J. 45, 504); 195° at 751·3 mm. (Pribram and Handl, M. 2, 673); sp.gr. $\frac{0°}{} = 1{\cdot}125$ (W.); $\frac{0°}{} = 1{\cdot}1279$ (P. and H.); $\frac{15}{15°} = 1{\cdot}1168$, $\frac{25°}{25°} = 1{\cdot}1121$ (Perkin).

Discovered by Wurtz (C. R. 43, 199; A. Ch. [3] 45, 400). Formed by action of ethylene diacetate upon KOH (W.); from C_2H_4ClI and moist silver oxide at 160–200° (Simpson, A. Suppl. 6, 253); by heating ethylene monacetate with $Ba(OH)_2$ or with water in sealed tubes (Debus, A. 110, 316); by heating a strong aqueous solution of neurine, when glycol and $N(CH_3)_3$ are evolved (Wurtz, A. Suppl. 6,200); by heating ethylene chloride or bromide with PbO and 15–20 times its volume of water to 140–170° (Eltekow, B. 6, 558); from ethylene bromide and water at 140–150° (Niederist, A. 186, 393); together with polyethylenic alcohol, by action of C_2H_4O (oxide of ethylene) upon water in sealed tubes (Wurtz, A. 113, 255).

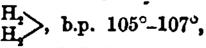
Preparation.—1. 600 grs. ethylene bromide, 700 grs. fused potassium acetate and 1500 grams alcohol (sp.gr. ·83) are heated in flask with reflux condenser until all action ceases, cooled, filtered from KBr and filtrate distilled, the portion distilled above 140° is decomposed by slight excess of $Ba(OH)_2$ and heated for 12 hours on water bath. The excess of baryta is removed by CO_2, the liquid evaporated to ⅓ its volume, the residue treated with a mixture of alcohol and ether, the liquid removed from the crystals and distilled, first on water bath, to separate alcohol and ether, and then over the flame; the portion distilling above 185° is then redistilled (Erlenmeyer, A. 192, 244).

2. A mixture of 188 grs. ethylene bromide, 138 grs. potassium carbonate and 1 litre of water [or 32 parts $C_2H_4Br_2$, 25 parts K_2CO_3, 350 parts H_2O (Groscheintz, Bl. 31, 293)] is heated with reflux condenser for 10 hours, is then evaporated to small volume on water-bath, the liquid portion poured off the crystals of KBr, the latter are washed with absolute alcohol. The filtrate and alcoholic washings are then distilled as in previous method; a loss owing to formation of C_2H_3Br is experienced by this process (Zeller and Hüffner, J. pr. [2] 11, 229).

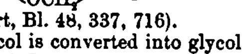
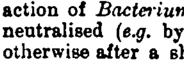
3. 1 part of ethylene bromide and 26 parts water are heated to 100° in a sealed vessel for 130 hours. This method gives a yield of over 60 p.c. of the theoretical amount (Niederist, A. 196, 354).

Glycol is a colourless, odourless, syrupy liquid with sweet taste, miscible with alcohol and water, but almost insoluble in ether. It dissolves NaCl, $ZnCl_2$, and many other chlorides; also K_2CO_3, KOH, and $Ca(OH)_2$.

By action of oxidising agents, *e.g.* platinum black, it forms glycollic acid. Nitric acid converts it into glycollic acid, glyoxylic acid, and oxalic acid (Debus, A. 110, 316). Heated with solid KOH to 250°, glycol yields potassium oxalate and hydrogen (Wurtz). Heated with large quantity of water at 200°–210° yields aldehyde (Nevole, Bl. 25, 289); $ZnCl_2$ at 250° decomposes glycol into aldehyde, crotonaldehyde and water. By electrolysis of an acid (H_2SO_4) solution of glycol, formic acid, glycollic acid, and polymers of formic aldehyde $(CH_2O)n$ are set free (Renard, A. Ch. [5] 17, 313). Chlorine forms a crystallisable halogen compound, m.p. 39°, b.p. 200°, and an oily body, $C_6H_{12}O_4$, b.p. 240° (Mitscherlich, J. 1863, 485). Heated with aldehydes, glycol yields ethylene oxide derivatives, *e.g.* glycol and œnanthaldehyde heated to 125°–130° for some days, yield ethylene œnanthylidene oxide



$$C_6H_{13}.CH\left<\begin{matrix}OCH_2\\OCH_2\end{matrix}\right>,$$

b.p. 180°; similarly valeraldehyde and propaldehyde yield  $C_4H_9CH\left<\begin{matrix}OCH_2\\OCH_2\end{matrix}\right>$, b.p. 142°, and  $C_2H_5CH\left<\begin{matrix}OCH_2\\OCH_2\end{matrix}\right>$, b.p. 105°–107°, respectively (Lochert, Bl. 48, 337, 716).

Glycol is converted into glycollic acid by the action of *Bacterium aceti*, provided the acid be neutralised (*e.g.* by $CaCO_3$) as fast as formed, otherwise after a short time the glycollic acid formed stops the further action (A. J. Brown, C. J. 51, 638). NH_4Cl and glycol at 300°–400° form *collidine*, $C_8H_{11}N.HCl$ (Hofmann, B. 17, 1905). Phosgene gas at ordinary temperatures converts glycol into *glycol carbonate* $CO(OCH_2)_2$ (with liberation of HCl) a stable componnd, sol. in water, alcohol, and ether, and crystallising in colourless needles (Nemirowsky, J. pr. [2] 28, 439). Heated with strong formic acid for some time (Henninger, B. 7, 263), or with oxalic acid (Lorin, Bl. 22, 104), gives *glycol diformin* $C_2H_4(CH_2O)_2$, b.p. 174°, in the latter case formic acid is also produced. With acids yields ethers in which one or both of the OH groups are replaced by acid radicles (Lourenço, A. 114, 122). By action of sodium on glycol we get *sodium ethylenate* $C_2H_4(OH)ONa$, a white crystalline deliquescent body which on heating to 190° with more sodium yields *disodium ethylenate*, a deliquescent mass. The former with C_2H_5Br in a sealed tube yields ethylene, glycol, NaBr, and probably $NaCHO_2$ (Wurtz).

2. **Diethylene alcohol**

$$C_4H_{10}O_3 = CH_2OH.CH_2.O.CH_2.CH_2.OH$$

diethylenic glycol; b.p. 250°; sp.gr. $\frac{0^\circ}{} = 1·132$, V. D. = 3·78 at 311°C. (calc. 3·67) (Lourenço, A. Ch. [3] 67, 275); from ethylene oxide and water. or better, ethylene oxide and glycol at 100° (Wurtz); from glycol and ethylene bromide or bromhydrin at 115°–120° (Lourenço); by action of glycol monoacetate upon sodium glycol at 130°–140° (Mohs, Z. 1866, 495).

An oily liquid, soluble in water, alcohol and ether; concentrated HI at 100° forms $C_2H_4I_2$; oxidised by HNO_3 to glycollic acid, oxalic acid, and diglycollic acid $C_4H_6O_5$. The *chlorhydrin* $C_4H_9O_2Cl$; b.p. 180°–185° (L.); 190°–200° (W.), is formed by leading HCl into ethylene oxide, or from ethylene oxide and ethylene chlorhydrin at 140° (Wurtz, A. Ch. [3] 69, 338). 1 mol. ethylene chlorhydrin and 2 mols. glycol are heated to 140°, saturated with HCl and again heated to 100° (Lourenço, A. Ch. [3] 67, 290): a liquid soluble in water.

The *bromhydrin*, b.p. 205°, is prepared from glycol and ethylene bromide at 160° (L.).

3. **Tri-ethylene alcohol**

$$C_6H_{14}O_4 = C_2H_4(OH).O.C_2H_4.O.C_2H_4OH,$$

b.p. 290°; sp.gr. = 1·138; a liquid miscible with alcohol and water, and oxidised by HNO_3 to *diglycol-ethylenic acid* $C_6H_{10}O_6$ (Lourenço; Wurtz).

The *chlorhydrin* $C_6H_{13}O_3.Cl$, b.p. 222–232°, is a liquid soluble in water (L.).

The *bromhydrin* $C_6H_{13}O_3.Br$, b.p. (with decomposition) 250° (L.).

4. **Tetra-ethylene alcohol** $C_8H_{18}O_5$, b.p. 230° at 25 mm. (L.; W.).

The *chlorhydrin* $C_8H_{17}O_4.Cl$, b.p. 262–272°, is soluble in water (L.).

5. **Penta-ethylene alcohol** $C_{10}H_{22}O_6$, b.p. 281° at 25 mm., a viscid liquid soluble in water, alcohol, and ether (L.).

6. **Hexa-ethylene alcohol** $C_{12}H_{26}O_7$, b.p. 325° at 25 mm.; a very viscid liquid (L.).

Ethylene bromide $C_2H_4Br_2 = CH_2Br.CH_2Br$, m.p. 9·53° (Regnault, A. Ch. [2] 59, 358); b.p. 131·6° (R.); 129·5° at 745 mm. (Anschütz, A. 221, 137); sp.gr. $\frac{20^\circ}{} = 2·1827$ (Haagen, Bl. 10, 355), $\frac{0^\circ}{} = 2·2132$, $\frac{4^\circ}{} = 2·1901$ (Thorpe, C. J. 37, 177), by action of C_2H_4 and Br (Balard, A. Ch. [2] 32, 375); formed together with ethylidene bromide CH_3CHBr_2 by heating C_2H_5Br with Br to 180° (Tawildarow, A. 176, 14).

Preparation.—Ethylene purified by passing through H_2SO_4 and NaOH solution is led into bromine covered with water, contained in a wide tube, until the colour of the Br disappears, the product is washed with NaOH and water, dried by $CaCl_2$ and distilled (Erlenmeyer and Bunte, A. 168, 64; Erlenmeyer, A. 192, 244).

Is a colourless mobile liquid with a pleasant smell and sweet taste. V.D. 6·485 (Regnault). When heated with water to 150°–160° it yields, first glycol, and on longer heating HBr and aldehyde (Carius, A. 131, 173). Zn acts upon an alcoholic solution of $C_2H_4Br_2$ with formation of C_2H_4 and $ZnBr_2$ (Gladstone, B. 7, 364); by heating with KI and water, ethane is produced. Alcoholic KOH yields C_2H_3Br, and in excess C_2H_2.

Aqueous KOH produces, after long contact, C_2H_3Br (Stempnevsky, A. 192, 240). By heating with strong NaOH or KOH solution, glycol and C_2H_3Br are produced. If $C_2H_4Br_2$ be heated with excess of H_2O and PbO to 220° aldehyde is formed (due to decomposition of $C_2H_4(OH)_2$ first formed into C_2H_4O and H_2O) (Eltekow, B. 6, 558, and Nevole, B. 9, 447). Heated with strong HI solution yields $C_2H_4I_2$ (Sororkin, Z. 1870, 519). Heated with Ag_2O and water, aldehyde is produced, and when heated with Ag_2CO_3 and water yields glycol (Beilstein and Wiegand, B. 15, 1368). Treated with Ag_2SO_4 and benzene yields dibromethyl sulphate $(C_2H_4Br)_2$ SO_4; with Ag_2SO_4 and water, bromethyl sulphuric acid $(C_2H_4Br)HSO_4$ (B. and W.).

BROMINATED COMPOUNDS OF ETHYLENE BROMIDE.

Bromethylene bromide $CH_2Br.CHBr_2$, b.p. 186·5° (Wurtz, A. 104, 243); 187°–188° at 721 mm. (Denzel, A. 195, 202); 191° (Tawildarow, A. 176, 22); 73° at 11·5 mm., 83° at 18 mm., 187°–188° at 751·5 mm. (Anschütz, A. 221, 138); sp.gr. $\frac{16^\circ}{}$ = 2·624 (T.), $\frac{23^\circ}{}$ = 2·620 (W.), $\frac{17\cdot5^\circ}{4^\circ}$ = 2·6189 $\frac{21\cdot5^\circ}{4^\circ}$ = 2·6107 (A.).

Prepared from monobromethylene and Br (Wurtz) from C_2H_3I and Br (Simpson, J. 1857, 461); from C_2H_3Br and Br at 170 (Hofmann, J. 1860, 364); or from $C_2H_4Br_2$ and Br at 200 (Tawildarow); decomposed by $KC_2H_3O_2$ at 150°, or by H_2O and PbO into dibromethylene and HBr. C_2H_5NaO yields dibromethylene $C_2H_2Br_2$ (b.p. 91°) and acetylene bromide $C_2H_2Br_2$, b.p. 157° (Tawildarow, A. 176, 22). Alcoholic KOH gives $C_2H_2Br_2$, C_2H_2, and bromacetylene C_2HBr. When heated with excess of absolute alcohol C_2H_3Br and probably C_2H_3BrO, bromaldehyde, are formed (Glöckner, A. Suppl. 7, 110).

The isomeric body CH_3CBr_3 is not known.

Dibromethylene dibromide $C_2H_2Br_4$. Two isomers are known.

1. *Unsymmetrical* (*acetylidine tetrabromide*) *a.* $CH_2Br.CBr_3$, boils with decomposition at 200°, b.p. 103·5° at 13·5 mm.; sp.gr. $\frac{17\cdot5^\circ}{4^\circ}$ = 2·9292 $\frac{21\cdot5^\circ}{4^\circ}$ = 2·9216 (Anschütz, A. 221, 140). Formed from *a*-dibromethylene $CH_2.CBr_2$ and bromine (Lennox, A. 122, 124; C. J. 13, 206; Reboul, A. 124, 270). From C_2H_3Br and Br at 180° a compound $C_2H_2Br_4$ is produced, which boils with decomposition at 208°–211° (Tawildarow). By heating a mixture of pyrotartaric acid and bromine with water to 150° (Bourgoin, A. Ch. [5] 12, 427).

2. *Symmetrical* (*acetylene tetrabromide*) *s.* $CHBr_2CHBr_2$, b.p. 137°–137·2°, at 36 mm.; 114° at 12 mm.; sp.gr. $\frac{17\cdot5^\circ}{4}$ = 2·9710, $\frac{21\cdot5^\circ}{4}$ = 2·9629 (Anschütz, B. 12, 2974, and A. 221, 139); decomposes at 190° into HBr, Br, and C_2HBr_3.

By leading C_2H_2 into bromine covered with water (Reboul, A. 124, 269; Berthelot, Bl. 5, 97); the crude $C_2H_2Br_4$ is then reduced by means of alcohol and Zn dust to $C_2H_2Br_2$, when the admixed $C_2H_3Br.Br_2$ is converted into C_2H_3Br; the $C_2H_2Br_2$ is then purified by distillation and treated with bromine (Anschütz, A. 221, 139); a liquid smelling of camphor and chloroform; decomposed by heating or by action of Na; by heating with alcoholic KOH, C_2H_2, and C_2HBr are produced. Cl produces $C_2Cl_4Br_2$ (Bourgoin, Bl. 23, 4); when heated with Br and water to 180° yields C_2Br_4 and C_2Br_6 (Anschütz); with C_6H_6 and $AlCl_3$ produces anthracene.

Pentabromethane $CHBr_2.CBr_3$, m.p. 56°–57° (Bourgoin), 54° (Denzel, B. 12, 2208), 48°–50° (Reboul); boils with decomposition at 210° (at 300 mm.) (Denzel). From C_2HBr_3 (Lennox, A. 122, 125) or C_2HBr (Reboul, A. 124, 268) and bromine. By slow oxidation (by exposure to air) of $C_2H.Br_3$ (Demole, Bl. 34, 204), from $C_2H_2Br_4$ and Br at 165° (Bourgoin, Bl. 23, 178). Forms prismatic needles soluble in alcohol and ether.

Perbromethane C_2Br_6 *v.* CARBON TRIBROMIDE.

Ethylene bromhydrin $C_2H_4Br.OH$, *Glycol bromhydrin*, b.p. 147° (Henry, J. 1872, 304), 155° (Lourenço, A. Ch. [3], 67, 287); sp.gr. $\frac{8^\circ}{}$ 1·66 (H.). From glycol and $C_2H_4Br_2$ at 115°–120° (Lourenço); from glycol and HBr at 100° Henry); also from 3 mols. glycol and 1 mol. PBr_3 (Demole, B. 9, 48).

Ethylene dichloride, *Elayl chloride*; *Dutch liquid* CH_2ClCH_2Cl; b.p. 84°·9 (Pierre, J. 1847–48, 63); 83°·5 cor. (Thorpe, C. J. 37, 182); 84·5–85° at 750·9 mm. (Brühl, A. 203, 10); 83°·3 at 749 mm. (R. Schiff, A. 220, 96); 84°·1 at 760 mm. (Städel, B. 15, 2563); sp.gr. $\frac{0^\circ}{4^\circ}$ 1·2808 (Thorpe); $\frac{0^\circ}{}$ 1·2803 (Pierre); $\frac{20^\circ}{}$ = 1·2562 (Haagen, Bl. 10, 355); $\frac{9\cdot8}{4^\circ}$ 1·2656, $\frac{83\cdot3}{4^\circ}$ 1·1576 (R. Schiff). Refractive index at t° $\mu_A = 1\cdot441466 - 0\cdot000446t$, mol. refract. = 34·06 (Kanonnikow); capill. constant at b.p. $a^2 = 4\cdot198$ (R. Schiff, A. 223, 72); by action of C_2H_4 upon Cl (Deiman, Troostwyk, Bondt, and Lauwerenburgh, Crell's Ann. (1795) 2, 200); by leading C_2H_4 into $SbCl_5$ or into molten $CuCl_2$ (Wöhler, P. 13, 297); also by action of glycol upon PCl_5 (Wurtz) or upon HCl at 100° (Schorlemmer, C. J. 1881, 1). Prepared best according to Limpricht's method (A. 94, 245). Ethylene is passed into a gently heated mixture of 2 parts manganese dioxide, 3 parts common salt, 4 parts water, and 5 parts sulphuric acid, and when the mass turns yellow it is distilled. It forms an oily liquid, insoluble in water. When heated with alcoholic KOH it yields KCl and C_2H_3Cl, and with K it forms H, KCl, and C_2H_3Cl (Liebig, A. 14, 37). With NH_3 it forms bases, $N_2H_4C_2H_4$, $N_2H_2(C_2H_4)_2$, &c. With ethylamine it yields *collidine* (*trimethylpyridine* $C_5H_2(CH_3)_3N$), C_2H_3Cl, and also NH_3 and $N(C_2H_5)_3$ (Hofmann, B. 17, 1907).

CHLORINE SUBSTITUTION PRODUCTS OF ETHYLENE.

Chlorethylene $C_2H_3Cl = CH_2:CHCl$, *Vinyl chloride*, at ordinary temp. a gas; b.p. −18° to −15°; by action of alcoholic KOH upon ethylene chloride (Regnault, A. 14, 28), or ethylidene chloride (Wurtz and Frapolli, A. 108, 224). To prepare it the $C_2H_4Cl_2$ and alcoholic potash are left in contact for 3 or 4 days in the cold, and the mixture is then warmed. Combines with Cl to form $C_2H_3Cl_3$. Polymerises in sunlight, and forms a solid insoluble mass of sp.gr. 1·406 (Baumann, A. 163, 317).

Chlorethylene chloride $C_2H_3Cl.Cl_2$ *v. Trichlorethane*, under *Ethyl chloride.*

Dichlorethylene $C_2H_2Cl_2$.

1. *u-Dichlorethylene* $CH_2{:}CCl_2$; b.p. 37° (Kramer, B. 3, 261); sp.gr. $\frac{15}{}$ 1·250, obtained by action of alcoholic KOH upon $CH_2ClCHCl_2$ (Regnault, J. pr. 18, 80). Polymerises easily into a solid amorphous insoluble body.

2. *s-Dichlorethylene* or *acetylene dichloride* $CHCl{:}CHCl$; b.p. 55°; by distillation of the compound of C_2H_2 with $SbCl_5$ (Berthelot and Jungfleisch, A. Suppl. 7, 253); also by action of Zn upon an alcoholic solution of CHClBr.CHClBr, or by leading C_2H_2 into aqueous solution of ClI (Sabanejeff, A. 216, 262).

Dichlorethylene dichloride *v. Tetrachlorethane*, under *Ethyl chloride.*

Trichlorethylene $C_2H.Cl_3 = CHCl{:}CCl_2$; b.p. 88°. From $CH_2Cl.CH_2Cl$ or $CH_3.CHCl_2$, and alcoholic KOH (Berthelot and Jungfleisch); also by action of nascent H (Zn and H_2SO_4) upon C_2Cl_6 (Fischer, J. 1864, 481); from anhydrous chloral and P_2S_5 at 160–170° (Paterno and Oglialoro, B. 7, 81); combines with Cl to form C_2HCl_5.

Trichlorethylene chloride *v. Pentachlorethane*, under *Ethyl chloride.*

Tetra-chlorethylene C_2Cl_4 *v. Carbon dichloride*, art. CARBON.

Hexachlorethane C_2Cl_6 *v. Carbon trichloride*, art. CARBON.

Ethylene chlorhydrine $C_2H_4.ClOH$. *Chlorethyl alcohol, Glycol chlorhydrine*; b.p. 128° (Wurtz, A. 110, 125); 130–131° (Henry, B. 7, 70); sp.gr. $\frac{8^\circ}{} = 1{\cdot}24$. From glycol and HCl (gas) at 100° (W.). If excess of HCl be used $C_2H_4Cl_2$ is produced (Schorlemmer, C. J. 39, 143); from glycol and Cl_2S_2 (Carius, 124, 257); from C_2H_4 and ClOH (Carius, A. 126, 197; Butlerow, A. 144, 40). Dry HCl is led into glycol kept at 148°; the $C_2H_4Cl.OH$ distils off (Ladenburg, B. 16, 1408). A liquid miscible with water; yields alcohol with Na amalgam and H_2O (Lourenço, A. 120, 92). Oxidised by CrO_3 to chloracetic acid (Kriwaxin, Z. 1871, 265); with KOH yields ethylene oxide.

Ethylene chlorobromide $CH_2Cl.CH_2Br$; b.p. 107–108° (Lescœur, Bl. 29, 484); sp.gr. $\frac{0^\circ}{}$ 1·79 (L.); $\frac{11^\circ}{} = 1{\cdot}705$ (Montgolfier and Giraud, Bl. 33, 12); $\frac{19^\circ}{} = 1{\cdot}689$. By action of Br upon $CH_2Cl.CH_2Cl$ (Henry, A. 156, 14); from $C_2H_4Br_2$ and $SbCl_5$ (Lössner, J. pr. [2] 13, 421) or $C_2H_4Br_2$ and $HgCl_2$ at 150–180° (M. and G.); by action of Br upon C_2H_4ClOH at 130° (Demole, B. 9, 556). To prepare it, first chlorine and then ethylene is passed into Br, kept under a mixture of equal vols. of strong HCl and water (James, J. pr. [2] 26, 380; also Simpson, Pr. 27, 118); decomposed by alcoholic KOH, with formation of C_2H_3Cl.

Ethylene chloriodide $CH_2Cl.CH_2I$; b.p. 140° (Sororkin, Z. 1870, 519); 140·1° cor. (Thorpe, C. J. 37, 189); 137–138° (Meyer and Wurster, B. 6, 964); sp.gr. $\frac{0^\circ}{} = 2{\cdot}151$ (S.); $\frac{0^\circ}{} = 2{\cdot}16439$; $\frac{15^\circ 3}{0^\circ} = 2{\cdot}13363$ (T.). From $CH_2Cl.CH_2Cl$ and ClI. C_2H_4 is led into an aqueous solution of ICl (Simpson, Pr. 12, 278). Decomposed by alcoholic KOH into HI and C_2H_3Cl; nascent H yields HCl, HI, and C_2H_4, moist Ag_2O at 160° produces glycol (Simpson). Finely divided silver at 160° yields C_2H_4 and $CH_2Cl.CH_2Cl$ (Friedel and Silva, Bl. 17, 242). Heated with HI solution yields C_2H_4 and $C_2H_4I_2$ (Sororkin).

Ethylene cyanhydrin $CH_2OH.CH_2CN$; b.p. 220–222° at 723·5 mm.; sp.gr. $\frac{0^\circ}{} = 1{\cdot}0588$. By long digestion of $C_2H_4.O$ (ethylene oxide) with anhydrous HCN at 50–60° (Erlenmeyer, A. 191, 273); miscible with alcohol and water; 100 parts ether dissolve 2·3 parts C_2H_4OHCN at 15°; insoluble in CS_2.

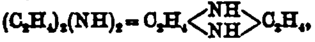
Ethylene cyanide $C_2H_4(CN)_2$. *Succinonitrile*; m.p. 54·5° (Nevole and Tscherniak, Bl. 30, 101); 51–52° (Henry, Bl. 48, 618); b.p. 158–160° at 20 mm. (Pinner, B. 16, 360); 265–267° (H.); sp.gr. $\frac{45^\circ}{}$ 1·023. By heating on a water-bath $CH_2Br.CH_2Br$. with KCN and alcohol (sp.gr. ·84) (Simpson, Pr. 10, 574); the liquid is filtered from the KBr, and distilled when the alcohol is first removed; then the distillation is conducted under diminished pressure; also is produced by electrolysis of K cyanacetate (Moore, B. 4, 520); is a white amorphous mass soluble in water, chloroform, and alcohol; slightly in carbon disulphide and ether; decomposed when distilled at ordinary pressure. Decomposed by heating with KOH or HCl into NH_3 and succinic acid; with $AgNO_3$ forms plates of $C_2H_4(CN)_2.4AgNO_3$, soluble in water and alcohol, which explode when heated (Simpson).

Ethylene diamine

$$C_2H_4(NH_2)_2 = NH_2.C_2H_4.NH_2;$$

m.p. 8·5° (Kraut, A. 212, 251); b.p. 116·5°; sp.gr. $\frac{15^\circ}{} = {\cdot}902$ (Kraut). By heating $C_2H_4Cl_2$ or $C_2H_4Br_2$ with alcoholic NH_3 to 100° (Cloëz, J. 1853, 468); by treatment of $C_2H_4(CN)_2$ with Sn and HCl (Fairley, A. Suppl. 3, 372); 42 grams of $CH_2Cl.CH_2Cl$ and 510 c.c. aqueous NH_3 are heated for 5 hours to 115–120° in a sealed tube; the product is then evaporated until it begins to crystallise, and is then precipitated with 3 times its volume of absolute alcohol; the precipitated $C_2H_4.2NH_2.2HCl$ is then washed with alcohol and the base set free by distillation with powdered NaOH (Kraut, *l.c.*; also Hofmann, B. 4, 666). The by-product from the manufacture of chloral, consisting of $CH_2Cl.CH_2Cl$, $CH_3.CHCl_2$, &c., can be used. A thick oily liquid, with faint ammoniacal smell, soluble in water, not miscible with ether or benzene; the aqueous liquid, which contains $C_2H_4(NH_2)_2.H_2O$ cannot be freed from water by BaO, but only by distillation over Na. Decomposed by HNO_3 into ethylene oxide and oxalic acid (Hofmann, J. 1859, 386); is a strong base and forms salts; combines with CS_2 to form crystals of $C_2H_4(NH_2)_2.CS_2$; soluble in water, insoluble in alcohol and ether. $C_2H_4(NH_2)_2.2HCl$, long silvery needles insoluble in alcohol. $C_2H_4(NH_2)2HCl.PtCl_4$, yellow leaflets, slightly soluble in water (Greiss and Martius, A. 120, 327); $C_2H_4(NH_2)_2(HCNS)_2$, large prisms, very soluble in water; m.p. 145° (Hofmann, B. 5, 245).

Diethylene diamine



$$(C_2H_4)_2(NH)_2 = C_2H_4\left<\begin{matrix}NH\\NH\end{matrix}\right>C_2H_4,$$

b.p. 170° (Hofmann, J. 1858, 343). From ethylene chloride and alcoholic NH_3 (Clöez; Hofmann; Natanson, A. 98, 291).

Diethylene diethyl diamine

$$(C_2H_4)_2(NH.C_2H_5)_2 + H_2O,$$

b.p. 185°, from $(C_2H_4)_2(NH_2)_2$ and C_2H_5I, or from $C_2H_4.Br_2$ and $NH_2.C_2H_5$ (Hofmann, J. 1859, 389).

Triethylene diamine $(C_2H_4)_3N_2$, b.p. 210° soluble in water (Hofmann, J. 1858, 343).

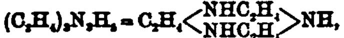
Diethylene triamine

$$(C_2H_4)_2N_3H_5 = NH_2.C_2H_4.NH.C_2H_4.NH_2$$

b.p. (with slight decomposition) 208°, formed with other products by action of NH_3 upon $C_2H_4.Br_2$; the double salt with $PtCl_4$ being less soluble than that of triethylene triamine it can be separated from that body (Hofmann, J. 1861, 514).

A strongly alkaline liquid miscible with water and alcohol. Its salts are soluble in water, less so in alcohol, $2[(C_2H_4)_2N_3H_5.3HCl.]3PtCl_4$ forms golden yellow needles.

Triethylene triamine



$$(C_2H_4)_3N_3H_3 = C_2H_4\left<\begin{matrix}NHC_2H_4\\NHC_2H_4\end{matrix}\right>NH,$$

b.p. 216° (Hofmann, J. 1861, 514), forms salts; $[(C_2H_4)_3N_3H_3 3HCl.]_2.PtCl_4$, long golden yellow needles moderately soluble in water; with hydrobromic acid gives $(C_2H_4)_3N_3H_3.3HBr$ from acid solutions, from weaker acid solution $(C_2H_4)_3N_3H_3 2HBr$.

Tetra-ethylene triamine $(C_2H_4)_4N_3H$, by action of alcoholic NH_3 upon $C_2H_4.Br_2$ (Hofmann, B. 3, 762); forms 3 series of salts with 1, 2, or 3 molecules of monobasic acid; the hydrobromates are amorphous bodies almost insoluble in water, alcohol, and ether.

Triethylene tetramine

$$C_6H_{18}N_4 = NH_2.C_2H_4.NH.C_2H_4.NH.C_2H_4.NH_2,$$

a strongly alkaline syrup from $C_2H_4.Cl_2$ and $C_2H_4(NH_2)_2$ or from $C_2H_4.Br_2$, and alcoholic NH_3 (Hofmann, J. 1861, 519); yields

$$C_6H_{18}N_4.4HCl.2PtCl_4,$$

a yellow amorphous powder almost insoluble in water.

Ethylene diformin $C_2H_4(CHO_2)_2$, b.p. 174°, by heating glycol with pure formic acid (Henninger, B. 7, 263); also by heating oxalic acid with glycol (Lorin, Bl. 22, 104). Decomposed when heated to 220° in sealed tube into CO_2, CO, H_2O and C_2H_4.

Ethylene ferrous chloride, $C_2H_4.FeCl_2 + 2H_2O$, by heating $FeCl_3$ and ether to 150° (Kachler, B. 2, 510); forms prisms fairly soluble in water. The corresponding compound $C_2H_4.FeBr_2 + 2H_2O$ is prepared by leading C_2H_4 into a strong aqueous solution of $FeBr_2$ in sunlight (Chojnacki, Z. 1870, 420); forms light-green deliquescent crystals.

Ethylene iodide $C_2H_4I_2 = CH_2ICH_2I$, m.p. 81–82° (Aronstein and Kramps, B. 13, 489), sp.gr. 2·07. From C_2H_4 and I in sunlight (Faraday, Gm. 4, 682), also in the shade especially if warmed (Regnault, A. 15, 67); a mixture of I and alcohol (absolute) is saturated with C_2H_4 with repeated agitation (Semenow, J. 1864, 483).

Crystalline plates or prisms decomposed by heating; when warmed with alcohol to 70° $IC_2H_4.OC_2H_5$ is produced; $HgCl_2$ gives in the cold C_2H_4ClI and on heating $C_2H_4Cl_2$ (Maumené, J. 1869, 345); alcoholic KOH converts it into C_2H_3I (Regnault, A. 15, 63).

Ethylene mercaptan $C_2H_4(SH)_2$ *v. Ethylene disulphydrate.*

Ethylene nitrate

$$C_2H_4(NO_3)_2 = CH_2NO_3.CH_2NO_3,$$

formed when glycol is treated with HNO_3 and H_2SO_4, is an oily liquid which is inflammable, explodes on percussion and is poisonous; KOH converts it into alcohol (Henry, B. 8, 529, also Champion, C. R. 73, 571).

Ethylene nitrite

$$C_2H_4(NO)_2 = CH_2NO_2.CH_2NO_2,$$

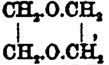
m.p. 37·5° sublimes with partial decomposition. Is prepared by passing C_2H_4 into ether into which liquid N_2O_3 or NO_2 is allowed to drop. It forms quadratic plates or prisms insoluble in water but soluble in alcohol and ether (Semenow, J. 1864, 480).

Ethylene oxide $C_2H_4.O$, b.p. 13°·5 at 746·5 mm.; sp.gr.$\frac{0^\circ}{}$ ·8966. From $C_2H_4.OH.Cl$ and KOH (Wurtz, A. 110, 125, A. Ch. [3] 69, 317), also from $C_2H(OH)Cl$ and $C_2H_4OH.ONa$ (Scheitz, Z. 1868, 379), also from $C_2H_4I_2$ and Ag_2O at 150°, from $C_2H_4Br_2$ and Ag_2O at 250° or from $C_2H_4Br_2$ and Na_2O at 180° (Greene, J. 1877, 522); also by treatment of $C_2H_4.Cl.(OC_2H_3O)$ with KOH (Demole, A. 173, 125).

A pleasant-smelling liquid miscible with water; when heated with water in a closed tube yields glycol. Has strong basic properties although not an alkaline reaction. It combines with acids and precipitates metallic hydrates from solutions of Mg, Al, Fe, and Cu. With Na amalgam forms C_2H_6O. Pt black oxidises it to glycollic acid; PCl_5 produces $CH_2Cl.CH_2Cl$ (Wurtz, A. Ch. [3] 69, 317 and 355).

Equal molecules of C_2H_4O and Br at 0° form $C_2H_4.OH.Br$, $C_2H_4Br_2$ and other bodies (Demole, B. 9, 47), but 2 molecules C_2H_4O and 1 molecule Br on standing yield large red or small yellow prisms of $(C_2H_4.O)_2Br_2$, m.p. 65°, b.p. with decomposition at 95°; they are insoluble in water, but soluble in alcohol. H_2S or contact with Hg separates the Br and leaves dioxyethylene (Wurtz, A. Ch. [3] 69, 321). By long contact with $ZnCl_2$ or KHO a polymeric body which melts at 56°, and is insoluble in ether is produced (Wurtz, Bl. 29, 530).

Dioxyethylene $(C_2H_4)_2O_2$, *Diethylene dioxide*



$$\begin{matrix}CH_2.O.CH_2\\ | \qquad\quad | \\ CH_2.O.CH_2\end{matrix}$$

, m.p. 9°, b.p. 102°, sp.gr. $\frac{0^\circ}{}$ 1·0482. From $(C_2H_4)_2O_2.Br_2$, and Hg by contact at ordinary temperature. The mixture is then distilled and distillate rectified over KOH (Wurtz, A. Ch. [3] 69, 323); has not marked basic properties, but combines slightly with acetic acid on heating to 120°. Lourenço (A. Ch. [3] 67, 288) obtained it by heating $C_2H_4(OH)_2$ and $C_2H_4.Br_2$ to 160°, but the product boiled at 95°.

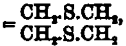
Chlorethylene oxide $C_2H_3Cl.O$, b.p. 70°-80°. By long contact of acetylene chloriodide CHCl:CHI with 40–50 vols. of water at 200°–220° (Sabanejeff, A. 216, 268); difficultly soluble in water.

Bromethylene oxide $C_2H_3Br.O$, b.p. 89–92°. From brominated glycol bromhydrin $CHBr_2.CH_2OH$ and KOH (Demole, B. 9, 51); soluble in water.

Ethylene phosphides *v.* PHOSPHORUS, ORGANIC COMPOUNDS OF.

Ethylene selenocyanate $C_2H_4(SeCN)_2$, m.p. 128°. From $CH_2Br.CH_2Br$ and alcoholic KCNSe (Proskauer, B. 7, 1281). Colourless needles insoluble in cold water and ether, difficultly soluble in hot water and cold alcohol; dissolves unchanged in strong HNO_3, but on heating gives ethylene selenious acid $C_2H_4(SeO_3H)_2$.

Ethylene sulphide C_2H_4S. When $C_2H_4Br_2$ is decomposed by K_2S a white amorphous precipitate is obtained which contains Br, and is insoluble in alcohol, ether, or CS_2 but on heating to 160° yields diethylene disulphide.

Diethylene disulphide 
$(C_2H_4)_2S_2=\begin{matrix}CH_2.S.CH_2,\\ CH_2.S.CH_2\end{matrix}$
m.p. 111°–112°, b.p. 199°–200°, V.D. = 4·28 (Husemann, A. 126, 280). From $C_2H_4Br_2$ and K_2S (Crafts, A. 124, 110; 128, 220). Also by heating $C_2H_4.CS_3$ or $C_2H_4.S_2.Hg$ with $C_2H_4Br_2$ to 150° (H.).

Crystallises from alcohol in needles or leaflets, from ether in thick prisms which are volatile at ordinary temperatures; combines with Br and certain salts, but not with NH_3; oxidised by HNO_3 to $(C_2H_4)_2S_2O_2$. The bromide $(C_2H_4)_2S_2Br_4$ is a lemon-yellow amorphous body, m.p. 96°, very unstable; the iodide $(C_2H_4)_2S_2I_4$, m.p. 132°–133°, forms iron-black monoclinic needles insoluble in water. The oxide $(C_2H_4)_2S_2O_2$ can also be obtained by decomposition of the chloride or bromide; with water forms crystals which decompose without fusion on heating, and are soluble in water, almost insoluble in alcohol. The peroxide $(C_2H_4)_2S_2O_4$ obtained by heating $(C_2H_4)_2S_2$ with fuming HNO_3 to 150° (Crafts, A. 125, 124) crystallises from strong HNO_3 in small crystals which are insoluble in water.

Ethylene hydroxysulphide $C_2H_4.OH.SH$ (*Thioethylene glycol*), from $CH_2OH.CH_2Cl$ and alcoholic KHS; the KCl is filtered off and the filtrate acidified with dilute HCl and evaporated at 30–40° (Carius, A. 124, 258). Is a heavy liquid almost insoluble in water, soluble in alcohol, the salts are fairly soluble in alcohol, the mercury compound $Hg(C_2H_5OS)_2$ crystallises from alcohol in needles.

Oxyethyl sulphide $(C_2H_4OH)S$ is formed when the above compound is heated, H_2S being evolved. It is a crystalline solid, m.p. under 60°, soluble in alcohol, insoluble in water, forms salts and double compounds with metallic salts.

Ethylene disulphydrate $C_2H_4(HS)_2$, *Ethylene mercaptan*; b.p. 146°; sp.gr. $\frac{23.5}{} = 1\cdot123$. From CH_2ClCH_2Cl (or bromide, Werner, J. 1862, 424) and alcoholic KHS (Löwig and Weidmann, A. 36, 322). A colourless liquid, soluble in alcohol and alkalis, forms insoluble mercaptides with heavy metals. $Pb(C_2H_4S_2)$ yellow; $Cu(C_2H_4S_2)$ chrome green. *Ethylene dimethyl sulphide* $C_2H_4(SCH_3)_2$; b.p. 183° from $C_2H_4Br_2$ and $CH_3S.Na$ (Ewerlöf, B. 4, 716). *Ethylene diethyl sulphide* $C_2H_4(SC_2H_5)_2$; b.p. 210–213° (E.) gives on oxidation first $(C_2H_5SO)_2C_2H_4$, m.p. 170°, and next $(C_2H_5SO_2)_2C_2H_4$, m.p. 136°·5 (Beckmann, J. pr. [2] 17, 469).

Ethylene thiocarbonates.

1. *Ethylene dithiocarbonate* $C_2H_4.COS_2$, *ethylene oxythiocarbonate*; m.p. 31°; by action of HNO_3 upon $C_2H_4CS_3$ in the cold (Husemann, A. 126, 269) forms long thin tables, insoluble in water, soluble in alcohol, ether, and chloroform.

2. *Ethylene trithiocarbonate* $C_2H_4.CS_3$; m.p. 39°·5; sp.gr. 1·4768. From $C_2H_4Br_2$ and Na_2CS_3 in presence of absolute alcohol (Husemann, A. 123, 83); forms golden yellow, rhombic prisms; slowly soluble in alcohol, easily soluble in ether, very soluble in CS_2, $CHCl_3$ and C_6H_6.

Ethylene thiochlorides (Guthrie, C. J. 13, 35; 14, 128).

1. *Ethylene thiodichloride* $C_2H_4SCl_2$, by passing C_2H_4 into SCl_2 kept cool. Is a liquid with a smell resembling mustard oil, and is decomposed on heating.

2. *Ethylene dithiodichloride* $(C_2H_4)_2S_2Cl_2$, by action of C_2H_4 upon S_2Cl_2 at 100°. A liquid with pungent odour.

Chlorethylene dithiodichloride $(C_2H_3Cl)_2S_2Cl_2$ by action of C_2H_4 upon boiling S_2Cl_2; a light-yellow liquid with pleasant smell.

Ethylene thiocyanate $C_4H_4N_2S_2 = C_2H_4(SCN)_2$, m.p. 90°. From $CH_2Cl.CH_2Cl$ and alcoholic KCNS (Sonnenschein, J. 1855, 609; Buff, A. 100, 229); CH_2BrCH_2Br may be used with advantage (Gentz, A, 153, 313); forms rhombic plates slightly soluble in cold water, more in hot, and in alcohol, decomposed by heat, volatile in steam; its vapour excites tears.

Ethylidene acetamide $CH_3CH(NHC_2H_3O)_2$, formed by acting on acetamide with aldehyde; forms large prisms decomposed by acids (Tawildarow, B. 5, 477).

Ethylidene acetate $CH_3.CH(C_2H_3O_2)_2$; b.p. 169°; sp.gr. $\frac{12^\circ}{}$ 1·061. From aldehyde and $(C_2H_3O)_2O$ at 180° (Geuther, A. 106, 249); from alcoholic $KC_2H_3O_2$ and $CH_3CH.Cl.C_2H_3O_2$ (Schiff, B. 9, 304); has a smell like that of onions and is decomposed by water into aldehyde and acetic acid.

Ethylidene biuret 
$NH\langle\begin{matrix}CONH\\ CONH\end{matrix}\rangle CH.CH_3$,
Trigenic acid; by leading HCNO into well cooled aldehyde (Liebig and Wöhler, A. 59, 296), crystallises in small prisms slightly soluble in water, nearly insoluble in alcohol, has a slightly acid taste. When heated liberates CO_2, NH_3 and a little collidine $C_8H_{11}N$ (Herzig, M. 2, 398). Is hardly decomposed by NaBrO. HNO_3 decomposes it and liberates cyanuric acid. The silver compound $AgC_4H_6N_3O_2$ forms a powdery precipitate soluble in boiling water.

Ethylidene bromacetin $CH_3CHBr(C_2H_3O_2)$; b.p. 135–145° (with decomposition). From aldehyde and PBr_5 (Wurtz and Frapolli); also from aldehyde and C_2H_3OBr (Tawildarow, A. 176, 12).

Ethylidene bromide $CH_3.CHBr_2$; b.p. 114–115° (Tawildarow, A. 176, 12); 109–110° at 751 mm. (Denzel, A. 195, 202); 110°·5 at 760 mm. (Anschütz, A. 221, 137); 108–110° (cor.) (Perkin, C. J. 45, 523); sp.gr. $\frac{10^\circ}{}$ 2·129 (T.), $\frac{21^\circ5}{4^\circ} = 2\cdot0822$ (A.), $\frac{15^\circ}{} = 2\cdot1029$, $\frac{25^\circ}{} = 2\cdot0854$ (P.). From C_2H_3Br and Br at 170° (Hofmann, Pr. 10, 619; Caventou, C. R. 52, 1330). Is produced by action of PCl_3Br_2 but not of PBr_5 upon aldehyde (Paterno a. Pisati, B. 5, 289), also by heating $CH_2.CHBr$ with HBr to 100° (Reboul, C. R. 70, 398). A heavy liquid: alcoholic KHS has no action upon it. On heating with water and PbO to 130° aldehyde and HBr are produced (T.). With $SbCl_5$ gives CH_3CHCl_2 (Henry, Bl. 42, 262).

Ethylidene bromiodide CH_3CBrI; m.p. below −20°; b.p. 142–143°; sp.gr. $\frac{1^\circ}{}$ 2·50, $\frac{16^\circ}{}$ = 2·452, from C_2H_3Br and HI in the cold (Pfaundler, J. 1865, 483; Reboul, A. 155, 212) by shaking CH_3CHI_2 with IBr solution (Simpson, Bl. 31, 412), decomposed by alcoholic KOH or Ag_2O into HI and C_2H_3Br; Br yields CH_3CHBr_2.

Ethylidene chloracetin $CH_3CH.Cl.C_2H_3O_2$; b.p. 120–124°. From aldehyde and Cl together with C_2H_3OCl (Wurtz, A. Ch. [3] 49, 58); from aldehyde and C_2H_3OCl (Maxwell Simpson, P. M. [4] 17, 195). A liquid with pleasant smell, lighter than water and slowly decomposed by that liquid into aldehyde, acetic acid, and HCl.

Ethylidene chlorobromide $CH_3CHClBr$.; b.p. 84–84·5° at 750 mm.; 82·7° at 760 mm. (Städel, B. 15, 2563); sp.gr. $\frac{16^\circ}{}$ 1·667. From C_2H_3Br and concentrated HCl at 100° (Reboul, A. 155, 215); from C_2H_3Cl and Br in sunlight (Denzel, A. 195, 193). By action of Cl upon C_2H_5Br (Lescœur, Bl. 29, 483). Is decomposed at ordinary temperature by alcoholic KOH on long standing; with Ag_2O gives aldehyde; and with $AgC_2H_3O_2$ forms $CH_3CH(C_2H_3O_2)_2$ (L.).

Ethylidene chloriodide CH_3CHClI; b.p. 117–119°; sp.gr. $\frac{19^\circ}{}$ 2·054. By agitating a mixture of CH_3CHI_2 and ICl; formed also from CH_3CHCl_2 and Al_2I_6 (Simpson, Bl. 31, 411).

Ethylidene or Ethidene chloride CH_3CHCl_2; b.p. 59°·9 (cor.); sp.gr. $\frac{0^\circ}{}$ 1·2044; $\frac{12·24^\circ}{4^\circ}$ 1·1863 (Thorpe, C. J. 37, 183); b.p. 57°·4–57°·6 at 750·9 mm.; sp.gr. $\frac{20^\circ}{4^\circ}$ = 1·1743 (Brühl, A. 203, 11); $\frac{0^\circ}{}$ = 1·2124; $\frac{22^\circ}{0}$ = 1·1805; refractive index μ_A (at 24°·7) = 1·405724. R_a = 34·1 (Kanonnikow); b.p. 57–57°·7 at 738·7 mm.; sp.gr. $\frac{0^\circ}{}$ 1·2013 (Pribram and Handl, M. 2·650); b.p. 56°·7–56°·9 at 749·1 mm. sp.gr. $\frac{9·3^\circ}{4^\circ}$ = 1·1895; $\frac{56·7}{4}$ = 1·11425 (R. Schiff, A. 220, 96); crit. temp. 254°·5 (Pawlewsky, B. 16, 2633); H.C.p. = 267·1 cal. (Berthelot and Ogier, Bl. 36, 68). From C_2H_3Cl and Cl (Regnault, A. 33, 312); from C_2H_4O and PCl_5 (Beilstein). By action of HCl upon copper acetylene (Sabanejeff, A. 178, 111). Is prepared by passing a mixture of chlorine and C_2H_5Cl over animal charcoal heated to 250–400° (Damoiseau, Bl. 27, 113). Is obtained as a by-product in the manufacture of chloral. Is decomposed by alcoholic KOH into HCl and C_2H_3Cl. Sodium produces at 180–200° hydrogen, acetylene, ethylene, and ethane, and C_2H_3Cl (Tollens, A. 137, 311). By action of Cl first CH_3CCl_3 and then CH_2ClCCl_3 are produced.

Ethylidene diethyl ether
$C_6H_{14}O_2 = CH_3.CH(OC_2H_5)_2$, *v.* ACETAL.

Ethylidene methyl ethyl ether
$CH_3CH(OCH_3).O.C_2H_5$;
according to Rübencamp (A. 225, 267) does not exist; the body (b.p. 85°) obtained by Wurtz (J. 1867, 597) by distillation of a mixture of ethyl and methyl alcohols with MnO_2 and dilute H_2SO_4 splits up by fractional distillation into *ethylidene dimethyl ether* and acetal.

Ethylidene dimethyl ether $CH_3CH(OCH_3)_2$, *Dimethyl acetal*; b.p. 64°·4 (Dancer, A. 132, 240); 62·7–63·3° at 757·6 mm. (R. Schiff, A. 220, 104); sp.gr. $\frac{0^\circ}{}$ ·8787, $\frac{14^\circ}{}$ ·8590, $\frac{25^\circ}{}$ = ·8476 (D.), $\frac{62·7}{4^\circ}$ ·8013 (S.); capillarity constant at b.p. a^2 = 4·092 (Schiff, A. 223, 74) occurs in crude wood spirit (D.), 2 volumes of wood spirit, 1 volume aldehyde, and ½ volume of glacial acetic acid are heated to 100° (Alsberg, J. 1864, 485); also by oxidation of CH_3OH and C_2H_5OH by MnO_2 and H_2SO_4 (Wurtz).

Ethylidene hydramine $CH_3.CH.OH.NH_2$ *v. Aldehyde-ammonia*, art. ALDEHYDE.

Ethylidene iodide CH_3CHI_2; b.p. 177–179°, sp.gr. $\frac{0^\circ}{}$ 2·84; by combination of C_2H_2 and HI (Berthelot, A. 132, 122; Semenow, Z. 1865, 725) from CH_3CHCl_2 and Al_2I_6 (Gustavson, J. R. 6, 164) from C_2H_3Br and HI (Friedel, B. 7, 823). Decomposed by alcoholic KOH into HI and C_2H_3I.

Ethylidene malonic acid $CH_3.CH:C(COOH)_2$, only known in combination, the *ethyl compound* $C_9H_{14}O_4 = CH_3CH:C(COOC_2H_5)_2$; b.p. 220°, 115–118° at 17 mm.; sp.gr. $\frac{15^\circ}{}$ 1·0435; from $C_3H_2O_4(C_2H_5)_2$ (1 mol.) aldehyde (2 mols.) and $(C_2H_3O)_2O$ (1½ mols.) at 100° (Komnenos, A. 218, 157). An ethereal oil smelling of camphor; by long contact with $Ba(OH)_2$ in the cold yields oxy-ethyl malonic acid $C_5H_8O_5$, malonic acid $C_3H_4O_4$, and aldehyde.

Ethylidene oxide $CH_3.CHO$, *v.* ALDEHYDE.

Ethylidene ethylene oxide

$$C_4H_8O_2 = CH_3CH\left<\begin{matrix}O.CH_2\\O.CH_2\end{matrix}\right.;$$

b.p. 82°·5 at 765·8 mm.; sp.gr. $\frac{0^\circ}{}$ 1·002. From aldehyde and excess of glycol at 100° (Wurtz, C. R. 53, 378; A. 120, 328); a liquid with irritating smell soluble in 1⅓ vols. water from which $CaCl_2$ separates it; with acetic acid gives glycol diacetate.

Ethylidene sulphonic acids:

1. *Ethylidene hydroxysulphonic acid*
$CH_3CHOH(HSO_3)$.
Salts of this acid are formed by action of aldehyde upon alkaline hydrogen sulphites; they are crystalline bodies, soluble in water and decomposed on heating into water, aldehyde, and sulphites.

2. *Ethylidene chlorsulphonic acid*
$CH_3.CH.Cl(SO_3H)$
obtained by action of CH_3CHCl_2 upon neutral alkaline sulphites at 140°; the salts are crystalline and the acid is fairly stable.

3. *Ethylidene disulphonic acid*
$CH_3CH(SO_3H)_2$.
By oxidation of trithioaldehyde $(C_2H_4S)_3$ or thialdin by $KMnO_4$ solution (Guareschi, G. 9, 75; A. 222, 302). 10 gr. thialdin are treated with 30–35 gr. $ZnMn_2O_8$ and 300 gr. water; after filtering BaH_2O_2 is added and excess of Ba precipitated by CO_2, the Ba salt is then precipitated by alcohol. It forms a strongly acid oily liquid very soluble in water and alcohol and is very stable; forms stable salts $Na_2C_2H_4S_2O_6 + H_2O$, small silky crystals soluble in 6071 parts of alcohol (90 p.c.) at 24°·5; $K_2C_2H_4S_2O_6 + 2H_2O$ forms large transparent crystals soluble in 1·56 parts of water at 17°.

ETHYLENINE *v.* Ptomaïnes.

ETNA POWDER *v.* Explosives.

EUCAIRITE or **EUKAIRITE** *v.* Selenium.

EUCALYPTOL. The volatile oil of the leaves of *Eucalyptus globulus*, consists mainly of a body $C_{10}H_{18}O$, b.p. 176–177°, sp.gr. 0·923 at 16°. It is optically inactive, has a camphor-like smell, and is probably identical with cineol and cajeputol (*v.* Oils, essential).

EUCALYPTUS OIL *v.* Oils, essential.

EUCLASE *v.* Beryllium.

EUGENOL (*Eugenic acid*) $C_{10}H_{12}O_2$ occurs in oil of cloves (from the leaves of *Caryophyllus aromaticus*), in the oil of cinnamon leaves and of the bay tree, *Laurus nobilis*, in the oil from the fruit of *Myrtus Pimenta*, and in several other ethereal oils.

Oil of cloves, which contains eugenol and a terpene, is treated with potash, potassium eugenol separates, and is pressed out, washed with alcohol, and the eugenol set free by the addition of a mineral acid. It is obtained by a similar process from oil of cinnamon leaves (Stenhouse, A. 95, 103), or from that of *Myrtus pimenta* (Oeser, A. 131, 277; Bl. 1865, 1, 434).

Pure eugenol is a colourless oil, of specific gravity 1·076 (Stenhouse), 1·0684 at 4° (Williams, Chem. Gaz. 1858, 170); 1·066 (Church, C. J. 1875, 118); 1·0788 at 0° and 1·0630 at 18·5° (Wassermann, A. 179, 366); 1·066 at 20° (Gladstone, C. J. [2] 2, 6). It boils at 242° (Stenhouse); 251° (Williams); at 244° (uncor.), 251°·8 (cor.), (Church); 246° (Wassermann); 252° (Gladstone); 251° (Oeser). It reddens litmus, smells strongly of cloves, and has a burning taste. It does not reduce alkaline cupric solutions, even on boiling, but reduces ammoniacal silver solutions on standing. Refractive index at 18° for the line D, 1·5402, and for the line F 1·5539 (Gladstone). Exposed to the air it darkens in colour and becomes resinised. Distilled with baryta it is converted into a neutral isomeric oil (Calvi, A. 99, 242). According to Church the small portion of the eugenol which is not carbonised in this process forms a hydrocarbon, b.p. 262°·5 (cor.), isomeric with methyl-eugenol, b.p. 237°–239°. With chromic acid, carbon dioxide, acetic acid, and water are produced (Wassermann), and with nitric acid a resin and oxalic acid.

With hydriodic acid it yields methyl iodide, and a resin having nearly the composition $C_9A_{10}O_2$ (Erlenmeyer, F. [2] 2, 430). Fused with potash protocatechuic and acetic acids are produced (Hlasiwetz and Grabowski, A. 139, 95). Phosphoric anhydride converts it into a resin intermediate in composition between $C_{10}H_{12}O_2$ and $C_{10}H_{12}O_3$, which gives a liquid analogous to creosote on distillation (Hlasiwetz and Barth, *ibid.* 83). Heated gently with phosphorus trichloride, on distilling off the excess of trichloride after the evolution of hydrochloric acid gas has ceased, a porous straw-yellow mass solidifying at 130° is obtained, from which ether extracts eugenic anhydride $(C_{10}H_{11}O)_2O$ and leaves the product eugenyl-phosphorous acid, $C_{10}H_{13}PO_4$ (Oeser, A. 131, 277). Eugenol absorbs the vapour of cyanic acid and forms

$$C_{10}H_{12}O_2,2HCNO$$

eugenallophanic acid (Baeyer).

Mononitroeugenol is prepared by acting on eugenol in ethereal solution with nitric acid. It melts at 43°–44° and forms large triclinic crystals. With tin and hydrochloric acid it produces amidochlorhydroeugenol hydrochloride.

Amidochlorhydroeugenol melts at 97°. Nitroeugenol heated with acetic anhydride and sodium acetate forms nitro-aceto-eugenol, m.p. 61°, which oxidised by potassium permanganate at 70° (Tieman's method, B. 9, 418) gives nitrovanillic acid $C_6H_2(COOH)(OMe)(OH)NO_2$, m.p. 202° (about) (Weselsky and R. R. Benedikt, M. 3, 386). By heating eugenol with phenyl cyanate in sealed tubes, eugenol phenyl-carbonate is produced $C_3H_5.C_6H_3(OCH_3).O.CO.NH.C_6H_5$ (Snape, C. J. 1885, 770).

Bromine in excess forms with eugenol dibromeugenol di-bromide, m.p. 118°–119°, which treated with zinc-dust in alcoholic solution yields dibromeugenol $HO.C_6H.Br_2(OMe)C_3H_5.Br_2$, M.P. 59° (Chasanowitz and Hell, B. 18, 823).

Eugenol glucoside is produced by the action of acetochlorhydrose on potassium eugenol. It melts at 132° (Michael, Am. 6, 336). Oxidised with potassium permanganate, eugenol forms homovanillin, vanillin, and vanillic acid. Acetyl eugenol in the same way, yields vanillin (De Laire, B. 15, 95). The constitution of eugenol, from the experiments of Tiemann and Kraaz (B. 15, 2059) is best represented by the formula $C_6H_3(CH_2.CH:CH_2)(OMe)(OH)$ proposed by Erlenmeyer (B. 10, 630). The formula

$$C_6H_3(CH:CH.CH_3)(OMe)(OH)$$

[1 : 3 : 4] originally assigned to eugenol is that of an isomer, isoeugenol. Eugenol forms a well defined series of substitution derivatives with both the acid and alcohol radicles, and with the metals. It behaves in its general properties as a phenol, and may be detected by its odour and the blue colour imparted to its alcoholic solution by ferric chloride.

EUPHORBIC ACID *v. Euphorbium*, art. Gum resins.

EUPHORBIUM *v.* Gum resins.

EUPHORBON *v.* Gum resins.

EUPITTONIC ACID, *Eupittone*, *Pittacal*, $C_{25}H_{26}O_9$. Pittacal is a blue colouring matter obtained by Reichenbach in 1835 (S. 68, 1) from the high-boiling portions of beech-wood tar. Grätzel also from the same products obtained a brown substance which gave the same blue colour reaction with baryta as the pittacal of Reichenbach. The colouring matter, which only exists in small quantity in this brown substance, was extracted and examined by Liebermann (B. 11, 334). It is an orange-red crystalline powder soluble in alcohol and acetic acid, forming brown solutions. It forms with alkalis purple, and with ammonia blue solutions, from which carbon dioxide precipitates blue salts, soluble in pure water. Calcium, magnesium, barium, and tin salts, also give blue precipitates with the alkaline solutions. The calcium and magnesium salts are soluble in pure water. Hydrochloric and sulphuric acids form red solutions, and the latter turns pure blue on warming. In acid solutions, it dyes animal fibres orange, in ammoniacal solution especially with tin mordant, blue-violet. Liebermann called this colouring matter *eupittone*, and regarded it at least closely allied to pittacal. Hofmann (B. 11, 1145; 12, 1371, 2126) by the action of hexachlorethane, C_2Cl_6 on dimethyl pyrogallate mixed with alcoholic potash or soda, obtained a substance identical in composition with the eupittone of Liebermann, and strongly resembling it in properties. It is an orange-yellow substance soluble in acetic acid and precipitated therefrom by alcohol. It melts at 200° and decomposes partly into a blue sublimate. It forms the same alkali salts and gives the same sulphuric acid reaction as eupittone. This body is hexamethoxyl-rosolic-acid $C_{19}H_8(OCH_3)_6O_3$. Heated with alcoholic ammonia, it yields hexamethoxyl-rosaniline. Pyrogallol is produced in attempting to replace the methoxyl groups by hydrogen. Its formation is analogous to that of rosolic acid $3C_8H_{10}O_3 + CO_2 = C_{25}H_{26}O_9 + 2H_2O$. Hofmann terms this body *eupittonic acid* and uses the name as synonymous with pittacal and eupittone. Eupittonic acid cannot be obtained by heating the sodium derivatives of dimethyl pyrogallate or of dimethyl methyl-pyrogallate separately, in air, a mixture of the two, however, with excess of soda gives sometimes as much as 10 p.c. of their own weight of the acid. The action is comparable to that in which rosaniline is produced from aniline and toluidine,

$$2C_8H_{10}O_3 + C_9H_{12}O_3 = C_{25}H_{26}O_9 + 3H_2.$$

The oxygen necessary to remove the hydrogen is obtained from the atmosphere, as in a closed vessel no such change as the above takes place. Eupittonic acid appears to be dibasic. Paper steeped in a solution of the acid, and dried, is a most sensitive test for free alkalis on account of the blue colour of the alkaline salts of eupittonic acid. Hydrochloric acid, however, produces the same blue colour. With acetic anhydride, a diacetyl derivative is produced which, curiously, is insoluble in alkalis, although its molecule ought to contain four hydroxyl groups.

EURHODINES *v.* AZINES.

EURHODOLS *v.* AZINES.

EUSCHYNITE *v.* VANADIUM.

EUXANTHON, *Purrenone*, *Purrone* $C_{13}H_8O_4$, was first obtained by Stenhouse (A. 51, 425), and soon afterwards by Erdmann, A. 52, 365, 60, 289) from euxanthin (euxanthic acid) a body occurring in purrée or piuri (*jaune indien*), a yellow dye-stuff from India and China (*v.* INDIAN YELLOW).

By heating euxanthin or its barium or lead salts, or by treating dry euxanthin with strong sulphuric acid, or its alcoholic solution with hydrochloric acid gas, euxanthon is obtained. Baeyer (A. 155, 257) showed that euxanthin, which occurs combined with magnesium in piuri, on heating with hydrochloric acid, besides yielding euxanthon, also gives rise to an acid. This acid was examined by Spiegel (B. 15, 1964) and found to be glycuronic acid; its anhydride being identical with the glycuronic anhydride of Schmedeberg and Mayer (J. 1879, 986). Graebe's equation representing the action of hydrochloric acid on euxanthin is

$$C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7.$$

The euxanthon may be separated from the glycuronic acid by crystallising out the anhydride, and treating the mixed euxanthon and unaltered euxanthin with ether or benzene, in which the former is readily soluble (Külz, H. 23, 475).

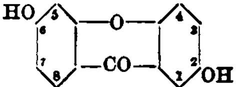
Euxanthon crystallises in pale-yellow shining needles or laminæ which sublime with little decomposition on careful heating. It melts at 240° (Graebe, A. 254, 298), V.D. = 7·96 (Graebe and Ebrard, B. 15, 1675). It is a neutral substance which dissolves in strong aqueous ammonia, and in potash, but not in dilute acids. An alcoholic solution is not precipitated by neutral lead acetate, lime or baryta, but with basic lead acetate it forms a precipitate.

Fused with potash, euxanthon is converted first of all into enxanthonic acid, $C_{13}H_{10}O_5$, the constitutional formula of which is

$$C_6H_3(OH)_2.CO.C_6H_3(OH)_2$$

(Graebe and Feer, B. 19, 2607) and eventually into quinol. Distilled with zinc-dust, methylene diphenyl oxide is produced (Graebe and Ebrard) (Wichelhaus and Salzmann, B. 10, 1397). In the animal organism euxanthon is converted into euxanthin, which is excreted in the urine (Külz) (Kostanecki, B. 19, 2918). The di-methyl and di-benzoyl derivatives of euxanthone have been prepared by Graebe and Ebrard.

The constitutional formula assigned by Graebe to euxanthon is



EUXENITE *v.* CERIUM METALS.

EVAPORATION. The term evaporation is used in connection with technical or manufacturing operations when a liquid is converted into vapour, but in chemical manufactures it is generally limited to those processes where the object is to separate a liquid from a solid which is dissolved in it, or to separate a more volatile from a less volatile liquid. In cases where the liquid to be evaporated is one of the products of the process, and is collected by condensation, the process is known as DISTILLATION (*q. v.*). Where a solid substance contains water, not as water of crystallisation, and without presenting visible moisture or wetness, the process of removing this moisture under suitable circumstances is known as *Desiccation* or *Drying*. The operation of evaporation, however, is conducted on the greatest scale in the generation of steam for steam engines, and in the production of steam generally for manufacturing purposes. Although more water is evaporated in connection with the steam engine than for any manufacturing processes, yet great quantities of steam are used as a convenient means of applying and distributing heat, especially when regulated and moderate temperatures are required. In such cases the heat is applied to the vessel to be heated by jacket spaces or through coils of pipes immersed in the liquid to be raised in temperature. Such applications are made in sugar and confectionery manufacture, and in distilleries, breweries, and dyeing, &c.

Water and many other liquids evaporate without the application of heat. A vessel of water freely exposed at the ordinary temperature of the atmosphere soon evaporates and disappears. This is due to the fact that water vapour has a sensible pressure at ordinary temperature, and as gases and vapours freely diffuse throughout each other, any water placed with a free surface in a confined space continues to evolve and diffuse its vapour until the pressure of water vapour present in the whole space is at the maximum pressure which corresponds to the temperature. Although evaporation occurs in this way without any application of increased temperature, yet heat is absorbed by the vapour formed from the liquid, and if the evaporation be rapid and be conducted under such circumstances that heat from surrounding objects is prevented from reaching the liquid, then its temperature will be greatly reduced. This fact is illustrated by the well-known lecture experiment of placing a shallow copper cup filled with ether upon a block of wood, and under it a drop of water. When air is blown upon the ether it rapidly evaporates and carries off so much heat from the copper that the water drop under it is frozen and the copper adheres to the wood. A liquid is said to be volatile when its vapour has a considerable pressure at ordinary atmospheric temperatures. At 20°C. for example the pressure of water vapour (or tension as it is somewhat incorrectly called) is 17·39 mm. mercury, whilst the pressure of ether vapour at the same temperature is 433·3 mm. and that of alcohol 44·5 mm. If the liquids be placed in atmospheres whose pressures could be kept at these points by artificial means, then these liquids would boil. As the evaporation under these circumstances is very rapid, relatively to the flow of heat to the liquid from surrounding bodies, if only atmospheric temperature be available, the heat is abstracted so quickly that many liquids freeze.

Advantage is taken of these properties for many purposes in the use of air currents passed over the surfaces of liquids to evaporate them without the application of other than natural heat. Reduced pressures are also applied to evaporate without heating or to reduce the temperature necessary in order to avoid chemical decomposition and also to produce cold mechanically.

Evaporation in steam boilers. The evaporative efficiency of the steam boiler has been more closely studied than that of any other type of evaporating apparatus, and as the principles of the economical application of heat for evaporating are more completely known in this connection it is advisable to consider it first.

The leading types of steam boilers now in use for the purposes of motive power are as follows: Lancashire, Cornish, Locomotive multitubular, Marine multitubular, and Water-tube or tubulous types.

The Lancashire boiler consists of a horizontal cylindrical steel or iron shell closed at the ends by flat plates suitably stayed, and having two cylindrical steel or iron flues parallel to each other passing from end to end. These flues serve to receive two furnaces at the front end in which the fuel is burned, and the products of combustion pass through the flues and are conducted round the lower part of the shell through flues arranged in the brickwork setting before they pass to the stack or chimney. Many modifications are made, the principal being in the use of Galloway's conical cross tubes in the flues, and in running both tubes into a common combustion chamber.

These boilers are extensively adopted for large stationary engines used for driving spinning mills and factories. The standard size is 30 feet by 7 feet diameter, with internal flues each 2 feet 9 inches diameter. The firegrates are generally 6 feet long. As the temperature at which the hot gases enter the stack is higher than is desirable, a heat-absorbing apparatus known as an *Economiser* is generally added. It consists of a series of vertical cast-iron pipes, suitably connected together, through which the cold feed water is pumped in the opposite direction to the flow of the burned gases around the exterior, so that the water is gradually heated as it passes along the pipes, and the gases as they cool come in contact with cooler water. By this arrangement a considerable addition is made to the heat absorbed by the water.

The following test of the evaporation efficiency of a pair of ordinary Lancashire boilers, with and without economisers, was made by Mr. Longridge, on October 10, 1888.

The two boilers were each 30 feet long by 7 feet in diameter, with internal flues of 2 feet 9 inches diameter, having five Galloway's cross tubes in each. The firegrates were 6 feet long, and boilers were housed and the tops covered with brick. The economiser had eighty tubes in sixteen rows. The heating surface of the boilers was 1,870 square feet. Heating surface of economiser 800 square feet. Total surface 2,670 square feet. The grate surface was 66 square feet, and the average steam pressure by steam gauges 83 lbs. per square inch above atmosphere.

Mr. Longridge found as the result of a 7½ hours' trial that 1 lb. of fuel under the actual conditions evaporated 9·66 lbs. of water, but allowing for moisture in the coal, 9·82 lbs. of water were evaporated by each lb. of dry fuel.

The calorific value of 1 lb. of dry fuel used was 13,363 British thermal units. The coal was Arley Mine, from Abram Colliery, Wigan, costing 6*s*. 7*d*. per ton. The total weight of gas, air, and water vapour per pound of dry fuel, passing through the furnaces, was 15·8 lbs.

These figures give the combined efficiency of boilers and economisers as 78·4 p.c., that is, out of 100 heat units placed upon the fire grate 78·4 were utilised for the intended purpose, that of raising steam, and 21·6 were employed in other ways, producing draught, drying fuel, losses by radiation, and unburned or partly burned fuel. Of this 78·4 p.c. utilised in evaporation, 71·6 was due to the boiler alone, and the remaining 6·8 p.c. was due to the economiser.

The following shows the disposal of 100 heat units placed upon the fire bars in the form of fuel, in the boilers only:—

Heat used in evaporating water .	71·57
Heat contained in products of combustion and excess air and vapour accompanying them . . .	17·81
Heat lost in evaporating moisture in coal	0·13
Heat lost by imperfect combustion .	0·00
Heat lost by unburned combustible falling through fire grate with ashes	4·28
Heat lost in drawing ash and clinker	0·36
Difference, radiation, and losses unaccounted for	5·85
	100·00

One hundred heat units given to the economiser were disposed of as follows:—

Heat used in evaporating water .	38·12
Heat contained in chimney gases .	58·12
Loss by radiation, &c.	3·76
	100·00

One hundred heat units put upon the firegrate in the form of fuel were disposed of by the combined apparatus as follows:—

Heat used in evaporating water .	78·38
Heat lost in chimney gases . . .	10·35
Heat lost in evaporating moisture in coal and lost carbon	4·75
Difference, radiation, &c. . . .	6·52
	100·00

In these trials the total fuel burned per hour was 1,090 lbs., or deducting moisture 1,072·72, and the water evaporated per square foot of total heating surface per hour was 3·94 lbs., or per square foot of boiler heating surface 5·63 lbs. per hour.

The total feed water to the boiler per hour was 10,533 lbs. The water level surface in the boiler was 390 square feet, and the total evaporated per square foot of that surface was 27lbs. water per hour.

As an average of many tests, the evaporative efficiency of an ordinary Lancashire boiler of good construction with a Green's economiser may be taken as 80 p.c. in ordinary work with careful firing.

The Cornish boiler is a cylindrical shell with flat ends like the Lancashire, but as it has only one internal flue its evaporative efficiency is inferior to the Lancashire.

The locomotive multitubular type of boiler consists essentially of a rectangular firebox containing the furnace surrounded by water, having its flat surfaces suitably stayed and riveted to a cylindrical shell through which pass a great number of metal tubes. The water surrounds these tubes, and the products of combustion pass through their interior and are discharged into the smokebox and thence pass away by the chimney. In a locomotive the draught is created by the exhaust steam blast discharged up the chimney. The advantage of these boilers is their enormous power of producing steam, in small bulk and weight, but they are not so economical of fuel as the stationary type. A common efficiency is 71 p.c., but with care and well designed feed-water heater arrangements, even in small boilers of this type an efficiency may be got as high as that obtained by Lancashire boilers with economisers. In the Society of Arts trial published in their journal in 1889, a boiler of this kind with a feed-water heater in the smokebox gave an evaporative efficiency of 82 p.c., that is 82 p.c. of all the heat placed upon the fire in the form of fuel was applied to its intended work of producing steam. These tests were most carefully conducted, and analysis made of fuel and escaping products to trace the disposal of all the heat. Only 10·5 p.c. of the total heat was lost in the heat of the furnace gases, and 9·0 was estimated as loss by radiation. This figure cannot be taken, however, as the value given in ordinary work, as the trial was most carefully made and the whole conduct of the machinery was under the direct supervision of the highest skill to be found in the works of the makers.

The standard *marine multitubular type* of boiler consists of a cylindrical shell of relatively great diameter, with cylindrical flues containing the furnace, and the products of combustion return through numerous tubes before discharge up the funnel.

The evaporative efficiency of such boilers is not so high as either the Lancashire or the locomotive type. Recent careful trials have been made by a research committee of the Institute of Mechanical Engineers, consisting of many leading engineers, on board the ss. 'Meteor.' The trial lasted fourteen hours, the consumption of fuel was 4,005 lbs. per hour, and the total evaporation 29,860 lbs. per hour, the heat accounted for in the steam evaporated amounting to 62 p.c. In boilers of this class it is unusual to have feed-water heaters or economisers. Mr. Ebenezer Kemp, of Glasgow, has fitted several steamers with compound boilers, or boilers to which large feed-water heaters or economisers were applied, with good results.

The following gives the main details of the set fitted on board the s.s. 'Caloric.' The high temperature boiler was single ended, 12 feet diameter and 11 feet 6 inches long, having two furnaces 3 feet 9 inches diameter, and a total heating surface of 1,613 square feet. There were four multitubular feed-water heaters or low-temperature boilers, as Mr. Kemp calls them, 4 feet 6 inches in diameter by 8 feet 4 inches long, with a total heating surface of 3,505 square feet. That is, the feed-water heater had rather more than double the heating surface of the boiler proper. The arrangement gives a saving of 15 p.c. as compared with ordinary marine boilers.

The *water tube or tubulous* type of boiler differs from the tubular in containing the water in the interior of the tubes, and allowing the furnace gases to play upon the exterior. Its supposed advantages are, safety, the steam and water vessels being of small diameter; and rapid water circulation, which is supposed to prevent deposit. The parts also are light and easily transported. This type, although largely used in America and on the Continent, has not found favour here on account of its large consumption of fuel, and difficulty in keeping in working order, using hard water. Longridge's recent experiments gave an efficiency of 54·4 p.c. in several tests of the best of the type.

Evaporation in open vessels. In many chemical manufactures it is necessary to evaporate off water in which the substance, the object of the process, is dissolved, and in such cases, when heat is to be applied, it is desirable to economise fuel to the greatest possible extent. The heat of waste gases is therefore used as much as possible. The method of applying heat varies considerably with the chemical nature of the substance dealt with, and choice of economical apparatus is often limited by the corrosive nature of the liquid to be evaporated. In the process of concentrating oil of vitriol from the dilute acid, a series of shallow open lead pans receive the diluted acid and heat is applied below. The hot furnace gases are allowed to impinge upon the bottom of the vessel containing the weakest acid and therefore requiring the greatest quantity of heat for evaporation, and as the gases cool they impinge upon the succeeding vessels of stronger and stronger acid, requiring less quantity of heat until the acid has become as concentrated as it is safe to trust to leaden vessels. It is then run into the platinum pan for its final concentration. Instead of this plan, in some cases the furnace gases are passed over the surface of the acid in order to heat it from above, and the volume of gases in motion removes the vapour as fast as it is formed. The advantage of surface evaporation arises not from the fact of its being economical, because liquids are heated with difficulty from above. The hot liquid in contact with the gases expands and has no tendency to cause convection currents, but rather remains stationary above the colder portions, and accordingly it is always advisable to heat from below when possible. In many processes, however, during evaporation a deposit comes down, and this, coating the bottom of the vessel, prevents the free contact of the metal with the liquid. The resistance to the passage of heat from the metal to the liquid is thereby much increased, and the bottom suffers rapid destruction from over-heating. In boilers using very hard water this is a fruitful source of trouble and danger.

When surface evaporation is resorted to, large surfaces are exposed in shallow tanks over which the flame and hot gases from a furnace are allowed to pass. The pans are covered in so that the radiant heat from the brickwork assists the action of the flame and hot gases. Arrangements of this kind are used in evaporating weak alum liquors, and the tanks are built up of bricks bound together with a cement composed of lime and alum shale. Sometimes an open pan is placed above the gases to contain the feed liquid and heat it in its progress to the evaporating pans.

In the system of sewage treatment in use at Rochdale an evaporating apparatus which is a refinement of the system of surface evaporation is in regular work. It consists of a cylindrical vessel in which is placed the matter to be dried, and it is rotated slowly on a horizontal axis. Through one hollow trunnion pass hot waste gases from the steam boiler flues, and leave the rotating vessel by a second trunnion and thence to the chimney. By the continued motion of the semi-solid mass, fresh surfaces are continually exposed and the matter is rapidly and thoroughly dried. The apparatus is constructed by Messrs. Manlove, Alliot & Co., Nottingham.

Evaporation of brine. Brine is sometimes evaporated by allowing the liquor from the springs to flow over masses of twigs in such a manner as to expose very extensive surfaces to the action of air currents; by pumping over a succession of these surfaces it is gradually concentrated. When artificial heat is applied to the evaporation of brine, large shallow saltpans are used. They consist of flat quadrangular vessels of plate iron supported upon suitable brick walls, forming flues which distribute the heat from furnaces placed in the centre part under the vessel. The flames strike directly upon the bottom of the vessel and the hot products of combustion are conducted outwards by flues leading to the stack or chimney. In this way they traverse the whole bottom surface of the evaporating pans. The pans are of great area, often 60 feet long by 30 feet wide. The water vapour is collected by a large conical hood and carried off by a separate chimney. The sides of the lower part of the cone are so constructed that they can be opened to admit air from the direction in which the wind is blowing. This assists the evaporation by carrying off the water vapour generated and exposing the surface to a continual air current.

If heat enough to cause a liquid to boil be applied, an air current will not increase the evaporation, but will tend to diminish it by cooling the vessel containing the liquid; but when the liquid does not reach the boiling-point, the continuous removal of the atmosphere in contact with the liquid is necessary. If this be not done, then so soon as the atmosphere has become saturated with the vapour, that is, so soon as the water vapour is present in quantity sufficient to produce the pressure which corresponds to the temperature of the liquid, the evaporation ceases.

It is a necessary condition of evaporation at temperatures less than the boiling-point that the atmosphere into which the evaporation takes place should be continuously renewed, and it is advisable that the air into which the water evaporates should not be of lower temperature than the liquid. When the temperature of the air is lower than that of the liquid, the volume of vapour carried off is much reduced, as the air must be heated by the vapour before it is capable of carrying off the volume equivalent to the vapour pressure. Producer gas is used for evaporating the brine at Ischl salt works, and the operation is conducted in deep rectangular plate iron vessels grouped together, and fed continuously by a system of distributing pipes.

Steam is much used to supply the heat required for evaporation, especially when the substances to be dealt with are of an easily decomposable nature if overheated. The heat is often applied to the vessel by means of a steam jacket, that is, the vessel is made double walled and the interspace is utilised to receive the hot steam. When the temperature requires to be higher than 100°C. the jacket space is constructed to withstand pressure, and steam under boiler pressure is supplied, but steam is most commonly used at atmospheric pressure and applied to the liquid by passing through rows or coils of pipes immersed in it. The arrangement of these pipes varies, and in some cases they are so connected as to be capable of hingeing out of the vessels for ready access and cleaning purposes.

Evaporation under reduced pressures. In the older processes of sugar manufacture the sugar liquors were concentrated by the direct application of heat from a fire upon the vessels containing them, but the greatest difficulty was experienced in preventing decomposition when the solution became concentrated. To avoid this difficulty the vacuum pan was introduced by Howard, and in various modified forms it is still used. The boiling-point of a liquid depends upon the pressure to which it is subjected, and by reducing the pressure the boiling-point is greatly reduced. The vacuum pan consists essentially of a globular copper vessel containing the sugar liquor, and having the lower portion steam jacketed, while steam also passes through a coil of pipe immersed in the liquid. The upper part of the vacuum pan carries a circular steam dome or cylinder from which a pipe passes to a vessel intended to collect any liquor which may have primed over. From this vessel it is run back into the pan again. An air pump exhausts the apparatus and passes the steam to a condenser of usual construction. Fig. 1 shows a vacuum pan of modern construction made by Messrs. Manlove, Alliot & Co. The vacuum pan A is formed in two portions and bolted together. It is fed with liquor from the vessel B by suitable cocks, the pipe connections *a*, *b* being arranged to equalise the pressure within the vessel, so that the flow may be towards A. The live steam is admitted at the valve C and passes through coil D into the jacket E, from whence it discharges and drains by the pipe F. The cylindrical dome or cylinder G prevents any great priming, but any liquid which may find its way by the pipe H is caught in the cylinder I and returned to A by the pipe K. The pipe L leads to the air pump and condenser. A thermometer placed in the upper part of the pan indicates the temperature of the operation, while a vacuum gauge or barometer column is used to show the pressure within. The boiling-point of the liquid at atmospheric pressure is about 250°F., and this is reduced to 150°F. by using the vacuum pan.

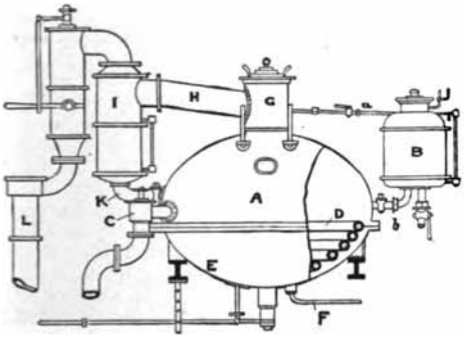


FIG. 1.

Evaporation under reduced pressure by triple and multiple effect. It is evident that as a liquor becomes more concentrated the boiling-point rises, and in evaporating liquids liable to chemical change by overheating, the pressures under which boiling is effected must be arranged to keep the temperature within safe limits. In the case of sugar liquor this safe limit is 227°F. Steam at 5 lbs. per square inch above atmosphere has this temperature, and if it be applied to a pan containing a weak sugar liquor at atmospheric pressure, the liquor will boil.

Neglecting losses by radiation and like causes, the steam coming from it has the same amount of heat as was imparted to the liquor by the steam under slight pressure, and if it be conducted to the coil and jacket of a second pan in which a slight vacuum is maintained, it will generate almost its own weight of steam at lower pressure and temperature, and so evaporate the water from the second pan. If the steam so generated be taken to the coil and jacket of a third pan, its heat can again be utilised to evaporate the liquor there, provided the vacuum is sufficient to allow it to boil. This process may be continued until the original heat of the steam supplied to the first pan is dissipated by conduction and radiation. This is the principle of the 'triple effect' apparatus, by which a great economy is effected in the amount of fuel needed to evaporate a given weight of liquor. The steam from one pan at higher pressure proceeds to the coil and jacket of the next, and the steam from the second proceeds to the coil and jacket of the third, the pressures within the pans proceeding in descending order as well as the temperatures.

Fig. 2 is an illustration of a triple effect apparatus constructed by Messrs. Manlove, Alliot & Co., Nottingham. The first pan A receives its charge of liquor from the vessel D, and is directly heated by steam from the reservoir E, supplied by exhaust or boiler steam. The vapour from A passes to A′ and thence to B, while the vapour from B passes by B′ to C, and from C by C′ to the exhausting pumps. The connecting pipes to the pumps are so arranged that the reduction in pressure in A is slight, and more considerable in B, while greatest of all in C, and the boiling-points are consequently lower in each succeeding vessel. Suitable pipes and valves F, G, H, communicate to allow the liquor to be transfused as it becomes more concentrated.

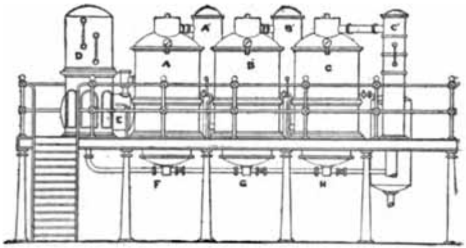


FIG. 2.

Evaporation under reduced pressures with multiple effect is also utilised in distilling sea-water in order to obtain fresh water in Normandy's, Kircaldy's, and other distilling apparatus for use on board ship.

The Yaryan evaporator. This ingenious evaporator is the invention of Mr. H. T. Yaryan, of Ohio, U.S.A., and it is now largely used in this country, the Continent, and America. It utilises evaporation under reduced pressures as with the triple effect and also multiple effect. It differs from other inventions of the same class in the method of applying heat to the liquid to be evaporated, whereby the liquid is heated in small quantities at a time, and is brought into very effective contact with the heating surfaces. Instead of using coils immersed in a liquid which is also heated by jacketed surfaces, the heat is applied by steam to the exterior surfaces of tubes, and the liquid to be evaporated is pumped within these tubes. The tubes are arranged in straight cylindrical drums, and pass from end to end, terminating in chambers with partitions so placed that when the liquid is pumped in at one end of a series it must pass through the whole series before escaping into

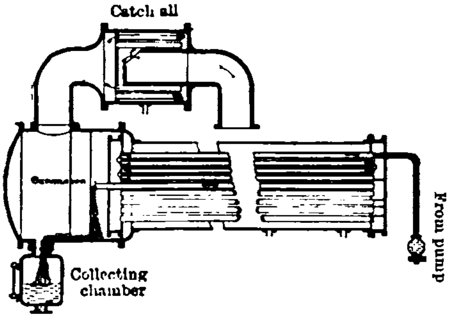


Fig. 3.

the separating chamber. Fig. 3 is a section of one drum of the evaporator, showing that the liquid is pumped in at one end, travels along in the direction of the arrows, and finally escapes with the steam which is generated into the separator. The tubes are divided into sections termed coils, and each section consists of five tubes coupled at the ends so as to form a continuous passage. The liquid and vapour pass from section to section in series, and so come into effective contact with the whole surface. As the liquid is pumped in it evaporates, and the steam produced carries it forward through the tubes, so that a mass of liquid and steam is brought in contact with every part of the whole heating surface, moving at a high velocity because of the steam generated, which has only the one direction of escape, that is, through the whole system of tubes in each towards the separator. On issuing from the last tube, the steam fills the separator and escapes by a pipe shown in the direction of the arrow, while the liquid falls to the bottom as shown, and drains off to the collecting chamber. The steam is further separated from any liquid which may form or prime over, in a vessel termed a *catchall*. This consists of a cylinder having a perforated plate carrying a number of tubes through which the steam passes and impinges upon the end of the vessel and so deposits any liquid it may carry, which drains off by a pipe to the collecting vessel while the steam discharges into another pipe as shown by the arrows. This steam heats the second vessel, and the steam from the second heats the third, and so on. The advantages claimed for this apparatus are, greatly increased efficiency of heating surface and a rapid and compulsory circulation. Only a small quantity of liquid is in the apparatus at one time, and so it is exposed to heat for a much shorter period than in the ordinary vacuum pan, which is an important point. The apparatus avoids entirely the inversion of sugar which always occurs to some extent in the older vacuum pans because of the long period of time taken to evaporate the large quantity of liquid they contain, amounting in some cases to thousands of gallons. The Yaryan evaporator can be started very rapidly, as it contains but a small mass to be heated. At the same time the details are arranged to permit of ready access to the tubes and ready cleaning. This is greatly assisted by the fact that the tubes are straight. Fig. 4 is a general external view of a triple effect apparatus upon this principle, showing the feed and exhausting pumps as well as the various pipe connections and intermediate receivers.

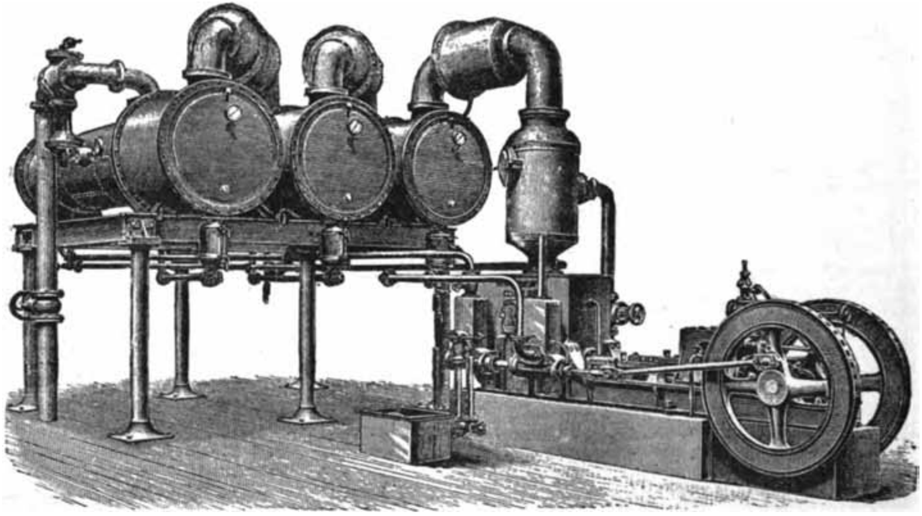


Fig. 4.

According to the patentees of the Yaryan apparatus their double effect will evaporate 16 lbs. of water for every pound of coal consumed under the boiler, 23½ lbs. in a triple effect, 30½ lbs. in a quadruple effect, assuming that the boiler is so constructed as to evaporate 8½ lbs. of water per pound of coal. The ordinary performance of a single vacuum pan is only 8½ lbs. of water evaporation per lb. of coal.

Evaporation in mechanical refrigerators. A separate class of mechanical refrigerators exist in which the cooling or refrigerating effect is produced by evaporation. The liquids used are ether, anhydrous ammonia, and anhydrous sulphur dioxide. In all of these the process of the machine is identical. The volatile liquid is introduced into a chamber at a pressure at which it is liquid, and the vapour is rapidly withdrawn from the vessel by a pump. The rapid evaporation absorbs heat so quickly that the temperature falls and a brine or other liquid is cooled within a coil of pipes immersed in the liquid. By circulating this brine the low temperature may be utilised for reducing the temperature of a cold store room or for producing ice.

The vapour drawn off by the pump is compressed and cooled by passing through tubes surrounded by water, and so becomes liquid again. It is then injected into the evaporating chamber again, so that the process is practically continuous, and but slight renewal of the volatile liquid is necessary to make up for small leakages.

The same principle is applied in Carre's Freezing Machine for freezing water. In this case the vapour is removed from the surface of the water by a pump and condensed by strong sulphuric acid. Ammonia is also utilised in another apparatus in solution in water for the same purpose. By alternate expulsion from the water and absorption, cold is obtained. D. C.

EVERNIIN *v.* Gums.

EXPLOSION OF GASEOUS MIXTURES. Within recent years the gas-engine has come extensively into use for all powers up to about twenty-horse actual, and it is rapidly superseding steam-engines for those moderate powers. The motive power is produced by the explosion of a mixture of coal gas and air in certain proportions, and the pressure produced by the explosion is utilised to propel the piston of an engine, as is done by the steam pressure in a steam-engine.

Although the explosive mixture used in engines is almost invariably coal gas and air, it is desirable first to consider simple gaseous explosions.

Explosion of mixtures of hydrogen and oxygen and hydrogen and air.—When a true explosive mixture of hydrogen and oxygen (2 vols. H and 1 vol. O) is confined within a closed vessel at atmospheric pressure and temperature, and it is fired by the electric spark or other means of ignition, the pressure rises rapidly to a maximum of about 10 atmospheres; that is, the pressure rises from 1 to 10 atmospheres, an increase of 9 atmospheres.

This increase of pressure at constant volume is entirely due to the intense heat of the chemical combination of the two gases, and notwithstanding the contraction of volume caused by the formation of steam gas, the temperature of the steam formed is so great that high pressure is produced. The fact of the contraction of three volumes mixture to two volumes of steam gas causes a difficulty in estimating the temperature corresponding to the pressure of explosion.

If the explosion vessel be considered an air thermometer, and the change of pressure as an indication of increase of temperature of a constant volume of permanent gas, then the temperature is very easily arrived at; thus, taking the temperature of the gases before explosion as 5°C. (Bunsen's experiments), an increase to 10 atmospheres means that the absolute temperature rises from $273 + 5 = 278^{\circ}$ to $278 \times 10 = 2780^{\circ}$ or 2507°C.; but it is impossible to assume no contraction, for in that case there would be no combination. If complete combination at the moment of maximum pressure be assumed, then the effect upon the measurement of temperature is the same as if in an air thermometer one-third of the whole volume had been abstracted during heating, that is the pressure of steam gas, reduced to 5°C. and assuming no condensation, would be only $\frac{2}{3}$ atmosphere. In which case 10 atmospheres pressure means $\frac{10}{\frac{2}{3}} = 15$ times the original temperature, or $278 \times 15 = 4170^{\circ}$, corresponding to 3897°C.

Calculating from the known amount of heat evolved by the combination, and assuming the specific heat of steam at constant volume to be 0·37 for high as well as low temperatures, then the maximum temperature of the explosion should be about 9000°C., assuming complete combination previous to maximum pressure and no loss of heat while attaining it. As Bunsen proved that maximum pressure was attained in his experiments in $\frac{1}{4000}$ of a second, and that the high temperature succeeding lasted at least $\frac{1}{85}$ of a second, any loss of heat while rising may for the present be disregarded.

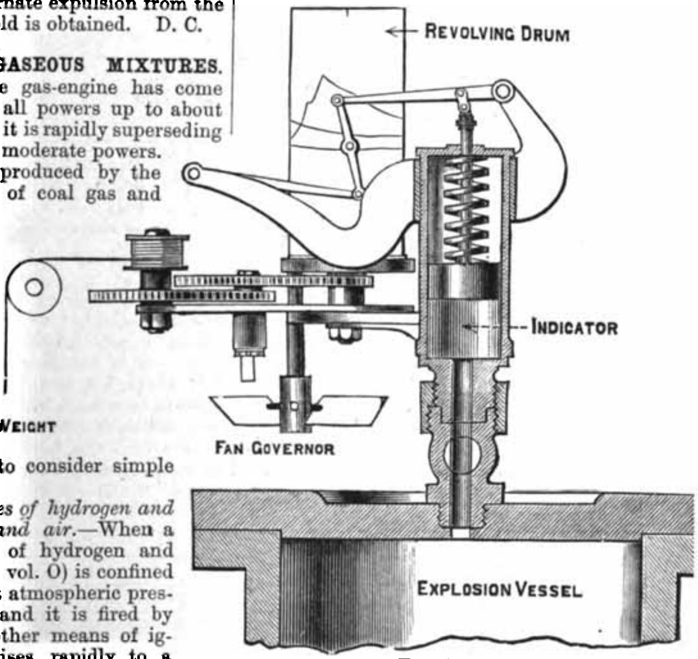


FIG. 1.

Without knowing the amount of combination it is impossible to accurately estimate the temperature from experiment, but it may be stated with confidence that it is higher than 2500°C. and lower than 3900°C., and it is certain that maximum temperature attained does not nearly account for the amount of heat evolved. Either, then, combination is incomplete, or, if complete, some change in the capacity for heat of the gases present has occurred.

With a mixture of 2 vols. H, 1 vol. O, and 3·75 vols. N, at an initial temperature of 10°C., Bunsen obtained an explosion pressure of 7·5 atmospheres. On assumption of no contraction, this corresponds to 1849°C.; assuming complete contraction it is 2220°C. Here the range of error is less, as the diluting nitrogen does not contract, and the maximum contraction possible is only $\frac{1}{6\cdot75}$ of the whole volume.

Bunsen's explosion vessel was of glass, and contained a column of gas 1·7 centimetres diameter and 8·15 centimetres long; the electric spark traversed the entire length of the tube so as to secure immediate inflammation of the whole mass of gas.

Clerk has made experiments in a large cast-iron vessel comparable in dimensions to the cylinder of a six-horse-power gas-engine. It is a cast-iron cylinder truly bored out and the end covers turned, internal dimensions 7 inches diameter and 8½ inches long, capacity 317 cubic inches. Upon the upper cover is placed a Richards indicator, in which the reciprocating drum has been replaced by a revolving one; the rate of revolution is adjusted by a small fan, a weight and gear giving the power. The cylinder is filled with the explosive mixture to be tested, the drum set in motion, the pencil of the indicator pressed gently against it, and the electric spark passed within the cylinder. The drum is enamelled, and the pencil is a blacklead one. The pressure of the explosion acts upon the indicator piston, and a line is traced upon the drum which shows the rise and fall of pressure. The rising line traces the progress of the explosion, the falling line the progress of loss of pressure by cooling. Fig. 1 shows the arrangement of the apparatus. Experiments with hydrogen and air mixtures gave the following results:

Mixtures of hydrogen and air (*Clerk*).

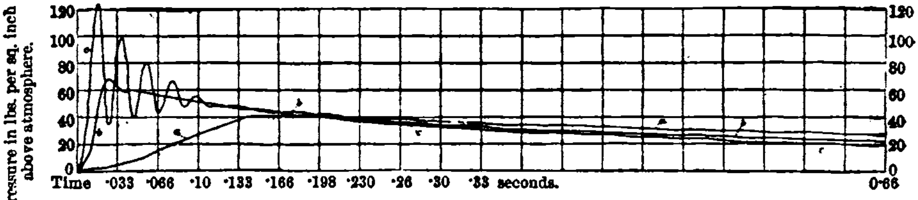
Experiment	Temp. before explosion 16°C. Pressure 14·7 lbs. (atmospheric)				
	Mixture		Max. pressure above atmosphere in lbs. per sq. in.	Time of explosion	Max. temp. of explosion
	H	Air			
a	1 vol.	6 vols.	41	0·15 secs.	826° to 909°C.
b	1 vol.	4 vols.	68	0·026 secs.	1358° to 1539°C.
c	2 vols.	5 vols.	80	0·01 secs.	1615° to 1929°C.

The curves of explosion from which these figures are deduced are given at fig. 2.

The rate of cooling is comparatively slow; for instance, in all these experiments, at the end of 0·66 second from the beginning of explosion there still remains above 20 lbs. per sq. in. above atmospheric pressure. The explosion is followed by a very slow fall of pressure.

Several terms have been used somewhat vaguely by engineers dealing with gaseous explosions. It is well to define them accurately.

The rapidity of increase of pressure is the measure of explosiveness, and therefore the time occupied from the commencement of increasing pressure to the moment of maximum pressure is called the *time of explosion*. The explosion is complete when maximum pressure is attained, but it does not follow that the combustion is complete. *Combustion* means burning, not mere ignition, and *complete combustion* means that the burning of carbon to carbonic acid and hydrogen to water has been completed.



Vessel used 7 ins. diam. and 8½ ins. long. Scale of indicator spring 1 lb. = $\frac{1}{40}$ inch.
Mixtures used pure hydrogen and air—Experiment *a*, 1 vol. hydrogen to 6 vols. air; *b*, 1 to 4; *c*, 1 to 5.
Temperature of gases before ignition 16°C.; pressure (atmospheric) 14·7 lbs.

FIG. 2.

So long as any portion of combustible remains uncombined with oxygen, the combustion is incomplete.

Complete inflammation is the complete filling of the explosion vessel with flame—that is, the complete ignition of every portion of the explosive mixture, and the gases not entering into the chemical action are ignited as well as those acting. It does not follow that complete inflammation coincides with maximum pressure; it may precede it.

In *Experiment a* (fig. 2) the mixture is diluted and the flame spreads slowly, the time of explosion being 0·15 second, and when maximum pressure is attained (see fig. 2) it remains constant for a time, showing that although explosion is complete yet combustion is still proceeding at a rate sufficient to compensate for loss of heat to the cold walls.

Experiment b, the time of explosion is 0·026 second, and fall of pressure commences almost immediately that maximum is attained.

In *Experiment c* the explosion is so rapid that the indicator piston cannot register fast enough, and consequently oscillates; the time of explosion is less than 0·01 second.

The maximum temperatures are calculated on the two extreme assumptions of complete contraction and no contraction. It will be observed that the range of error becomes less as dilution increases.

Calculating from these curves the total heat accounted for by maximum pressure, and allowing for loss of heat to the walls during time of explosion, as estimated from the falling curves, a great deficiency becomes evident.

	Experiment *a*	*b*	*c*
Heat of combustion of hydrogen present	100	100	100
Heat accounted for by maximum temperature and loss previous to its attainment	55	70	54

Even with hydrogen and air mixtures the deficiency ranges from 30 to 46 p.c. It is remarkable that the deficiency at the temperature of about 900°C. is identical with that at about 1800° within the limits of error.

Limits of inflammability.—A mixture of 1 vol. H and 7 vols. air cannot be exploded by the electric spark or by flame at atmospheric pressure and temperature (Clerk).

According to Harold Dixon, 2 vols. H and 1 vol. O, if diluted with 8 vols. of oxygen, ceases to be ignitible, and the same mixture with 7 vols. of nitrogen becomes uninflammable. In small tubes a mixture which readily ignites in a large vessel cannot be fired.

If the pressure of a true explosive mixture, such as electrolytic gas, is reduced sufficiently, it ceases to be ignitible. Electrolytic gas, if reduced to $\frac{1}{18}$ atmosphere will not fire, but if heated considerably at constant pressure it will fire again. Experimenters differ considerably in statements of limits of inflammability: differences in strength of spark, dimensions of vessel, and temperature cause variation, but all agree that reduction of pressure, dilution with excess of any gas, and use of small vessels destroys inflammability, while increase of pressure, preliminary heating, and large vessels increase inflammability.

Three vols. of marsh gas added to 2 vols. H and 1 vol. O prevent ignition, while 1½ vols. of ethylene added to the same mixture prevent firing. This fact has an important bearing in practice; a mixture will bear considerable dilution with air but very little excess of coal gas before losing explosiveness.

Rate of explosion in hydrogen mixtures.—Bunsen first determined the velocity of flame propagation in explosive mixtures. His method is as follows:

The explosive mixture is allowed to burn from a fine orifice of known diameter in a metal plate, and the current of issuing gas regulated by diminishing the flow until the flame passes back and ignites the mixture. This occurs when the velocity of issue is inappreciably less than the velocity of propagation of flame from layer to layer, from ignited to unignited portion of the mixture. At atmospheric pressure and temperature Bunsen determined the velocity in mixture 2 vols. H and 1 vol. O as 34 metres per second. Objections exist against the method. The mixture issuing as flame drags air into it and so cools. The metal plate also exercises a cooling effect, and if the hole were small enough the flame could not pass back at all, as the heat would be conducted away rapidly enough to extinguish the flame, as with the safety lamp. Mallard and Le Chatelier made experiments designed to obviate these objections. The mixture is contained in a long tube of considerable diameter, closed at one end and freely open to the air at the other. At each end a short rubber tube terminates in a cylindrical space closed by a flexible diaphragm. A light style is fixed upon each of the diaphragms. A cylinder revolves close to each style, both cylinders upon the same shaft. A tuning fork, marking the cylinder, determines the rate of revolution. The mixture is first ignited at the open end, and the flame, in passing the lateral opening leading to the first diaphragm, ignites the mixture there, and so moves the style and marks the cylinder; the arrival of the flame at the other end is signalled in the same way.

Determined in this way, Mallard and Le Chatelier estimate the velocity in hydrogen mixture (2 vols. O and 1 vol. H) as 20 metres per second, and in diluted mixtures:

Velocity of explosion in diluted mixtures (Mallard and Le Chatelier):

Mixtures	Metres per second
2 vols. H, 1 vol. O + 1 vol. O	= 17·3
2 „ H, 1 „ O + 3 vols. O	= 10·0
2 „ H, 1 „ O + 1½ „ H	= 18·0
2 „ H, 1 „ O + 3 „ H	= 11·9
2 „ H, 1 „ O + 6 „ H	= 8·1

A large excess of hydrogen causes little diminution in velocity compared with oxygen. With hydrogen and air mixtures the following numbers were obtained:

Velocity of explosion in hydrogen and air mixtures (Mallard and Le Chatelier):

Mixtures	
2 vols. H and 8 vols. air	= 2 metres per second.
2 „ H „ 6 „	= 2·8 „
2 „ H „ 4$\frac{2}{3}$ „	= 3·4 „
2 „ H „ 3$\frac{5}{7}$ „	= 4·1 „
2 „ H „ 3 „	= 4·4 „
2 „ H „ 2 „	= 3·8 „
2 „ H „ $\frac{2}{3}$ „	= 2·3 „

Strangely enough, the velocity is greatest when there is considerable excess of hydrogen. A mixture containing 2 vols. H and 5 vols. O has just enough oxygen for complete combustion, but the velocity is greatest when 2 vols. H have only 3 vols. of air.

These numbers are stated to be correct within 10 p.c.; they are all the rates of transmission of flame backwards from the open end of a tube to the closed end, and they are practically the rates of movement at constant pressure, without projection of ignited gases into unignited. When firing from the closed end of the tube very high and variable velocities were obtained: here, not only does the mixture ignite from particle to particle at a rate depending on inflammability alone, but the expansion of the ignited portion causes it to be projected into the unignited and so increases the rate of ignition. In a closed vessel the portion first fired expands and compresses the unignited gases into smaller space, and ignition goes on at a continually accelerated rate till complete.

With the same tube fired at the closed end a velocity of 1,000 metres per second was obtained with mixture 2 vols. H and 1 vol. O, instead of 20 metres per second as fired from the open end.

The velocity of ignition in Clerk's experiments, in a closed vessel, for a mixture of 1 vol. H, 4 vols. air, is equal to about 8 metres per second, 2 vols. H and 5 vols. air, about 20 metres per second.

The explosive wave.—With long tubes, of relatively small diameter, velocities of previously unsuspected magnitude are obtained. Berthelot and Vieille used a straight horizontal leaden tube, 42·45 metres long and 5 millimetres internal diameter, filled it with electrolytic mixture of H and O at atmospheric pressure and temperature, and arranged two metal strips passing across the tube at the ends; a current passed through these strips, and the explosion destroyed them on arriving; the times of interruption of the circuit were recorded by a chronograph, and so the rate of explosion known. For this mixture a mean result, from many experiments, of 2,810 metres per second was found. The velocity was the same in tubes varying from 5 to 35 millimetres in diameter, but with a tube of 1·5 millimetres the velocity fell to 2,341 metres. The maximum velocity is not attained till the explosion has travelled some distance from the point of origin, as shown by the following table:

Duration preceding establishment of explosive wave (Berthelot).

Distance of registering points from point of ignition	Mean velocity	
	From origin	in each interval
metres	metres per sec.	metres per sec.
0·02	72·7	72·7
0·05	146·2	448·0
0·50	924·4	2261·0

Distance of registering points from point of ignition	Mean velocity	
	From origin	in each interval
metres	metres per sec.	metres per sec.
5·25	2491	3031
20·19	2649	2710
40·43	2679	2706

The velocity rapidly increases up to half a metre; beyond this it is practically constant within experimental error.

The inflaming spark must be a powerful one; if weak, much greater distance is required to establish the explosive wave.

Harold Dixon confirms Berthelot's figures, and as a mean of ten experiments, finds a velocity of 2,819 metres per second. Berthelot considers that change of pressure does not affect the explosive rate; but Dixon finds that with electrolytic mixture at 300 mm. mercury, 2,670 metres per second is the velocity, and at 1,500 mm. mercury 2,917 metres per second.

The velocity does not increase indefinitely with increase of pressure, but at 1,100 mm. mercury practically attains a maximum.

The rate of the explosive wave diminishes with dilution with an excess of any gas; mixture 2 vols. H, 1 vol. O + 8 vols. O, rate of explosion 1,075 metres per second (Harold Dixon); 2 vols. H, 1 vol. O + 5 vols. O = 1,650 metres per second; 2 vols. H, 1 vol. O + 5 vols. N = 1,782 metres per second—all for atmospheric pressure and temperature. It appears that although ignition is arrested by less excess of nitrogen than oxygen, yet nitrogen retards the rate of explosion less than oxygen.

Explosion of mixtures of carbonic oxide and oxygen.—The maximum pressure produced by explosion of 2 vols. CO and 1 vol. O at atmospheric pressure and temperature 4·5°C. is 10·8 atmospheres (Bunsen), corresponding to a temperature of 2,612°C., assuming no contraction, and 4,140° assuming complete contraction due to combination. The maximum temperature calculated from heat of combustion at constant volume is 12,820°C., so that here also a great difference exists between heat evolved and heat accounted for. Dilution with excess of any gas reduces the pressure attained and lengthens the time of explosion, as with hydrogen.

Berthelot found time of explosion in a closed vessel 300 c.c. capacity, of this mixture (2 vols. CO + 1 vol. O) to be 0·0128 second; and in a vessel of 4,000 c.c. capacity, 0·0155 second.

By Bunsen's method the velocity of inflammation at constant pressure is 1 metre per second nearly, and by Mallard and Le Chatelier's method, also at constant pressure, it is 2·2 metres per second.

The velocity of the 'explosive wave' (Berthelot) is 1,090 metres per second, excited under similar circumstances to the hydrogen experiments. Harold Dixon has observed the remarkable fact that a mixture of carbonic oxide and oxygen, if thoroughly dried over phosphoric anhydride, could not be fired by the electric spark, but that, a trace of moisture added, the spark at once takes effect. He has made determinations of the rate of the explosive wave on mixtures 2 vols. CO and 1 vol. O, in which different quantities of water vapour are present, and finds that a well dried but not absolutely dry mixture gave a velocity of 1,264 metres per second, while, when saturated with steam at 35°C., the rate rose to 1,738 metres per second. The explosion travelled 10 feet before arriving at the first registering point, so that velocity might be a maximum before commencing measurement. This seems to indicate that water vapour enters into the reaction of the oxidation of CO, even when the explosive wave is propagated.

Explosion of mixtures of coal gas and air.—Experiments have been made by Clerk with mixtures of coal gas and air in the explosion apparatus already described, with the following results:—

Glasgow coal gas and air mixtures (Clerk).

Temperature of gases before ignition, 18°C. Pressure of atmosphere (14·7 lbs.)

Experiment	Proportion of gas by volume	Maximum pressure in lbs. per square inch above atmosphere	Maximum temperature centigrade	Time of explosion
a	$\frac{1}{14}$	52	1047°	0·28 second
b	$\frac{1}{12}$	63	1265°	0·18 „
c	$\frac{1}{10}$	69	1384°	0·13 „
d	$\frac{1}{8}$	89	1780°	0·07 „
e	$\frac{1}{6}$	96	1918°	0·05 „

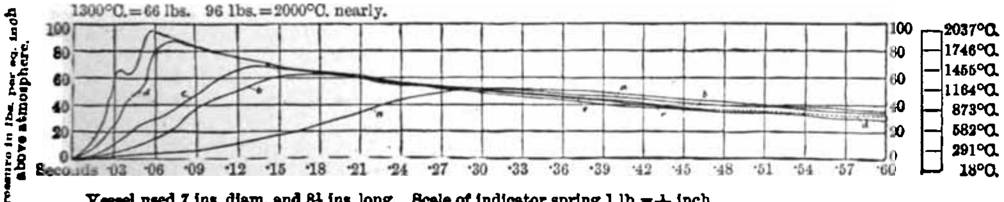
From these experiments it will be observed that the greatest possible pressure exerted by a mixture of Glasgow coal gas and air at atmospheric pressure and temperature is 96 lbs. per square inch above atmosphere, the maximum pressure falls as dilution with air increases, while the time of explosion also increases. The shortest time of explosion is $\frac{1}{20}$ second, and the longest over $\frac{1}{4}$ second, at the end of 0·60 second from 30 to 35lbs. per square inch pressure above atmosphere still remains in the vessel. It is very noticeable that, volume for volume, coal gas produces higher pressure than hydrogen.

Experiments with Oldham gas and air give the following:—

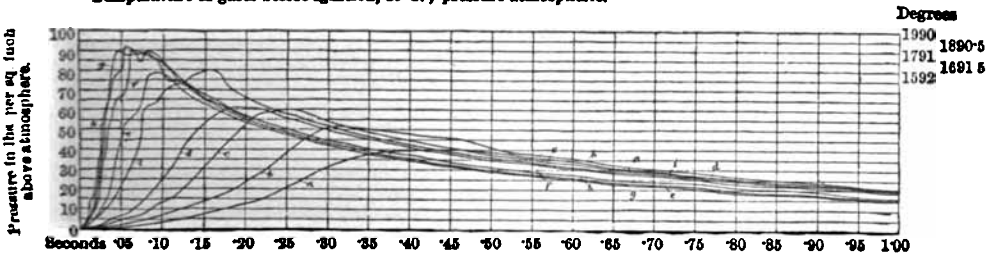
Oldham coal gas and air mixtures (Clerk).

Temperature of gases before ignition, 17°C. Pressure of atmosphere (14·7 lbs.)

Experiment	Proportion of gas by volume	Maximum pressure in lbs. per square inch above atmosphere	Maximum temperature centigrade	Time of explosion
a	$\frac{1}{15}$	40·0	806°	0·45 second
b	$\frac{1}{14}$	51·5	1033°	0·31 „
c	$\frac{1}{13}$	60·0	1202°	0·24 „
d	$\frac{1}{12}$	61·0	1220°	0·17 „
e	$\frac{1}{10}$	78·0	1557°	0·08 „
f	$\frac{1}{8}$	87·0	1733°	0·06 „
g	$\frac{1}{7}$	90·0	1792°	0·04 „
h	$\frac{1}{6}$	91·0	1812°	0·055 „
i	$\frac{1}{5}$	80·0	1595°	0·16 „



Vessel used 7 ins. diam. and 8½ ins. long. Scale of indicator spring 1 lb.=$\frac{1}{25}$ inch.
Mixtures used Glasgow coal-gas and air. Experiment *a*, 1 vol. gas to 13 vols. air; *b*, 1 to 11; *c*, 1 to 9; *d*, 1 to 7; *e*, 1 to 5.
Temperature of gases before ignition, 18°C.; pressure atmospheric.



Vessel used 7 ins. diam. and 8½ ins. long. Scale of indicator spring 1 lb.=$\frac{1}{25}$ inch.
Mixtures used Oldham coal-gas and air. Experiment *a*, 1 vol. gas to 14 vols. air, temp. (of explosion and measuring vessels) 18°C.; *b*, 1 to 13, 16·2°; *c*, 1 to 12, 16°; *d*, 1 to 11, 16·1°; *e*, 1 to 9, 16·7°; *f*, 1 to 7, 16·7°; *g*, 1 to 6, 16°; *h*, 1 to 5, 16°; *i*, 1 to 4, 19°.
Centigrade temperatures, assuming no loss of volume, owing to combination of mixtures. Atmospheric pressure, 14·7 lbs., and mean temperature before ignition, 17°C.

FIG. 3.

The greatest pressure produced by a mixture of this gas and air is 91 lbs. per square in. above atmosphere. Comparing these numbers with the Glasgow gas experiments, it appears that with $\frac{1}{14}$th vol. of Oldham gas present, the pressure attained is 0·5 lb. per square inch less, and the time of explosion is 0·31 second against 0·28 second with the same proportion of Glasgow gas. With $\frac{1}{8}$th of the two gases Oldham is 5 lbs. less maximum pressure and ·055 second against ·05 second Glasgow. At fig. 3 are shown reduced copies of the lines of explosion and cooling from which these values have been deduced.

In all these experiments the suppression of heat at the maximum temperature is very considerable, ranging from 50 to 60 p.c., and here there is greater certainty of calculation, as the percentage of possible contraction is not nearly so great as with hydrogen and carbonic oxide mixtures.

100 volumes, for instance, of Manchester gas requires 123 vols. of oxygen; total volume of mixture 223 vols., and the maximum possible contraction reduces it to 199 vols., or about 10 p.c. But this is with pure oxygen. One volume of this gas requires 6·14 vols. of air for complete combustion, and 100 vols. of the mixture will contract to 96·6 volumes on complete combustion and reduction to original temperature, assuming steam gaseous. The maximum error is only 3·4 p.c., and with more dilute mixtures it is less. These temperatures, although not quite true, are very nearly so, whatever be the theory adopted to explain the deficit. It does not follow, however, that they are the highest temperatures existing at the moment of explosion; they are merely averages.

The existence of such an intensely heated mass in a cold cylinder causes intense internal convection currents, so that the portion in close contact with the cold walls will be colder than that existing in the centre. It may be taken, then, that cold gas mixtures with air give, upon explosion, temperatures ranging from 800°C. to nearly 2,000°C., depending on the dilution of the mixtures.

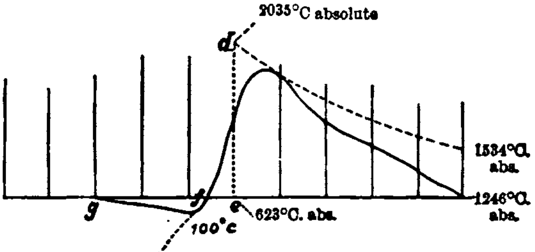
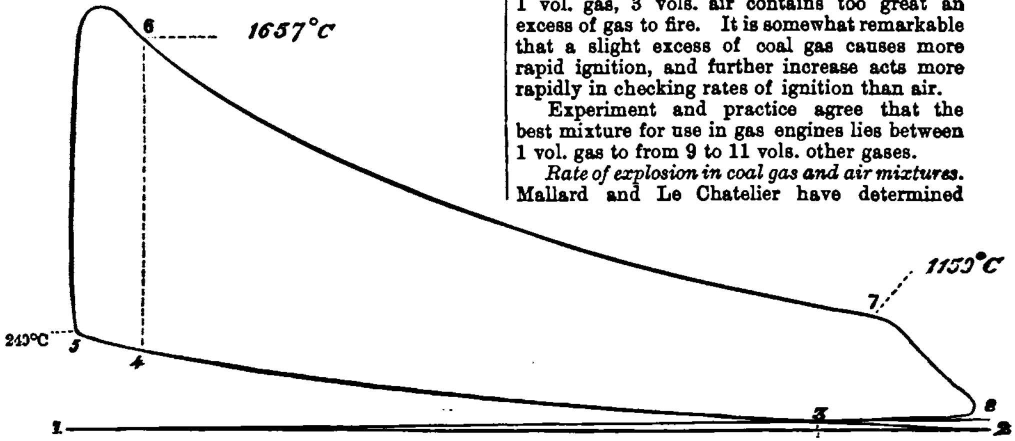


Fig. 4.

Experiments have been made by Clerk in the same vessel with mixtures previously compressed, and it is found that the pressures produced with any given mixture are proportional to the pressure before ignition—that is, with a mixture of constant composition, double the pressure before explosion; keeping the temperature constant doubles the pressure of explosion. A mixture of 1 vol. coal gas and 15 vols. air cannot be fired by the electric spark (Clerk), and 1 vol. gas, 3 vols. air contains too great an excess of gas to fire. It is somewhat remarkable that a slight excess of coal gas causes more rapid ignition, and further increase acts more rapidly in checking rates of ignition than air.

Experiment and practice agree that the best mixture for use in gas engines lies between 1 vol. gas to from 9 to 11 vols. other gases.

Rate of explosion in coal gas and air mixtures. Mallard and Le Chatelier have determined the rate of explosion at constant pressure in their apparatus of mixtures of coal gas and air.



8½ ins. dia. cylinder. 14 ins. stroke. 160 revs. per min.

Fig. 5.

Velocity of explosion in coal gas and air mixtures (Mallard and Le Chatelier):

Mixture	Velocity
1 vol. gas, 7 vols. air	. 0·83 metres per second.
„ 5·6 „	. 1·00 „
„ 4·7 „	. 1·16 „
„ 4·0 „	. 0·9 „

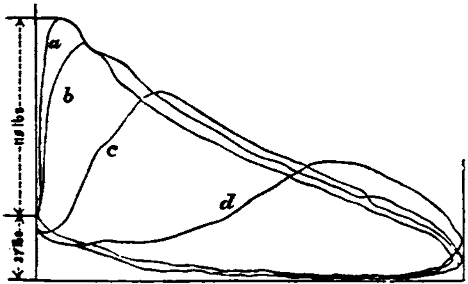
The maximum velocity is here also attained with a slight excess of coal gas. The 'explosive wave' can also be generated in coal gas and air mixtures, but little attention has been paid as yet to its rate of propagation. Clerk's experiments in a closed vessel give the maximum velocity of inflammation of gas and air mixtures as about 5 metres per second, with $\frac{1}{7}$ vol. of coal gas present Oldham experiments).

Explosion in gas engine cylinders.—In some gas engines the explosive mixture is not compressed previous to ignition, but is taken into the cylinder, mixing as it enters, and is ignited at atmospheric pressure.

Fig. 4 is an indicated diagram from an engine of this kind. The time of explosion is about $\frac{1}{25}$ second, the maximum temperature is about 1,750°C., and the temperature at the end of the expansion is about 1,000°C. The heat evolved at maximum temperature is 50 p.c., and the expansion line is below the adiabatic.

In other gas engines the mixture is compressed before ignition, and in these engines the time of explosion varies from $\frac{1}{20}$ to $\frac{1}{30}$ second, and the maximum temperature commonly attained is about 1,700°C., while the temperature of the hot gas at the moment of opening the exhaust valve is above 1,100°C. Fig. 5 is a diagram of this type. The line 1, 2, is that traced by the indicator pencil when the pressure upon the piston is zero; it is called the atmospheric line. The line 2, 5 is due to the compression of the gases previous to ignition; the line rising from 5 is due to the explosion; the maximum temperature is attained at the point 6, and is here 1,657°C.; the line 6, 7 is expansion doing work, temperature at point 7, 1,159°C.; and 7, 8 is the fall to atmospheric pressure on opening the exhaust valve; 8, 1 is the return of the piston, expelling the exhaust gases.

The result of using too dilute a mixture is seen at fig. 6; the line *d* is caused by the slow firing of the mixture and the piston overrunning the rate of spreading of the flame on the cylinder. This causes great loss of power, as is seen in the reduced area of diagram.



COMPRESSION GAS-ENGINE. DIAGRAM.

FIG. 6.

In the normal diagram, fig. 5, the expansion line is considerably above the adiabatic, proving that heat must be added to the gases during expansion to make up for the flow of heat through the cylinder walls; this shows that the heat is not lost previous to complete explosion, but is suppressed in some way, to be evolved as temperature falls. In all gas engines, compression and non-compression, the same amount of heat is suppressed at moment of complete explosion, just as in a closed vessel; but if the cooling on expansion is too great the line may fall below the adiabatic, although heat is being rapidly added to the gases. In others the heat lost is less, and the heat added is sufficient to keep the expanding line above the adiabatic.

D. C.

EXPLOSIVES. Explosives are solid, liquid, or gaseous mixtures or chemical compounds, which by chemical action (set up in them by flame, by a blow, or by other means) generate suddenly large volumes of heated gas.

The energetic action of an explosive largely depends on its rate of chemical change; in chemical compounds (like nitro-glycerin and gun-cotton) the reacting atoms are in much greater proximity than are those of a mechanical mixture of solids (such as gunpowder), and in the former class the rapidity of the chemical action will be greater than in those of the latter class, composed of constituents by themselves non-explosive. The latter class are more suited for the work of propulsion, the former for that of disintegration.

The explosives in actual use are instances of oxidation, oxygen being supplied by a nitrate, by nitric acid, by a NO_2 group, or by a chlorate. In this article, explosives are considered under the headings of Gunpowder, Gun-cotton, Nitroglycerin, Fulminate of Mercury, and other explosives.

Gunpowder.

Ordinary black gunpowder consists of an intimate mixture of potassium nitrate, sulphur, and charcoal. The composition of the black powder used for military purposes in different countries is given on p. 52; the statements being taken from Désortiaux's translation of Upmann and Von Meyer's work.

English black gunpowders contain about 1 to 1·3 p.c. moisture.

Manufacture.—A short account only of the process of manufacture will be given, mainly that used at Waltham Abbey; and for this, Major-General Wardell's Handbook of Gunpowder and Gun-cotton and Désortiaux's translation of Upmann and Von Meyer's work have been freely used.

The Ingredients.

The *nitre* employed at Waltham Abbey is wholly Indian nitre. As imported, it has been partially purified, but contains potassium and sodium chlorides, potassium, sodium, and calcium sulphates, sand, and organic matter; the total impurities averaging about 4½ p.c. It is submitted to a simple refining process, being first dissolved by heat in the water used for washing the purified nitre of a previous operation. The liquid is heated to boiling in large refining-coppers, the scum on the surface being carefully skimmed off; the temperature of the liquid is allowed to fall to 104°, and it is then filtered through bags of coarse cloth into the crystallising vessels. The temperature of the solution on entering the crystallising vessels is about 88° to 82°, the liquid is kept in constant agitation with wooden hoes, whereby as the liquid cools fine crystals are formed. The solution is not stirred when its temperature is lower than 32°. If the solution were left to crystallise undisturbed, large crystals would form, and would inclose mother-liquor. The crystals are drawn to the side of the crystalliser, and transferred to draining frames. The drained nitre flour then receives three washings with distilled water in quantities insufficient to dissolve the nitre, each washing is succeeded by draining; after the last washing the nitre is drained all night, and is removed (except the bottom part, which is very moist) to the store bins. After about three days in store it is ready for the powder manufacture, and contains from 8 to 5 p.c. of moisture, according to the season; the water is estimated and allowed for in weighing the charges.

The waters used for washing the crystals are employed for the solution of the crude nitre; the nitre is recovered from the crystallisation mother-liquors by evaporation, and is treated as crude nitre.

Composition of Black Powder used for Military Purposes.

—		Per 100 dry gunpowder		
		Potassium nitrate	Sulphur	Charcoal
England, Russia, Sweden, Italy, Turkey, United States[1]		75	10	15
Russia.—A more recent rifle powder. Lightly-baked charcoal		77	8	15
France	Cannon powder	75	12·5	12·5
	Large grain powder (old composition)	75	10	15
	Rifle powder B (old composition)	74	10·5	15·5
	Rifle powder F_1	77	8	15
Belgium, Spain, Persia		75	12·5	12·5
Prussia, Saxony		74	10	16
Austria		75·5	10	14·5
Portugal		75·7	10·7	13·6
Switzerland		76	10	14
Holland		70	14	16
China		61·5	15·5	23

[1] C. E. Munroe thus corrects the statements of the composition of the United States regulation gunpowder (C. N. 52, 81).

From Désortiaux it appears that the agitation of the solution of nitre during crystallisation in order to obtain fine crystals is in general use on the Continent; at least, he mentions it as in use at Lille, Wetteren, and Spandau. At the refineries at Lille, Wetteren, and Spandau, he states that glue is added to the boiling solution of the crude nitre (the weight of glue being about $\frac{1}{3000}$th that of the crude nitre); the glue coagulating and carrying down organic colouring matters. The process of purification was the invention of Beaumé and Lavoisier, and existing processes follow theirs with slight modifications.

The *sulphur* employed at Waltham Abbey is native Sicilian sulphur, of the best quality. In Sicily, the sulphur mineral is subjected to a liquation process, to separate the sulphur from the gangue. It still contains 3 to 4 p.c. gangue, from which it is freed by distillation. It is distilled from a large iron retort, provided with two tubes placed at right angles to each other; one tube (15 inches wide) communicates with a large dome-shaped subliming chamber, the other tube (5 inches wide) enters an iron pot which receives the distilled sulphur; this tube is jacketed for cooling with water. The tubes can be connected with the distilling vessel or cut off from it by means of valves. The distilling vessel receives its charge of sulphur, which is heated to boiling; during the earlier stages of the distillation the vapours are sent into the subliming chamber, where the sulphur condenses as flowers of sulphur; later on the sulphur vapour is sent through the condenser, from which it runs into the receiver in the liquid form. It is allowed to cool somewhat, but not to its solidifying-point, and is ladled into moist wooden moulds. The flowers of sulphur are not used in the manufacture of the gunpowder, but are redistilled.

The sulphur igniting in air at a low temperature—about 250°—renders the gunpowder inflammable.

The *charcoal.* For making the charcoal for gunpowder, soft and light woods are chosen, of an average growth of from two to ten years. The wood should be cut in the spring when it is in full vegetation, as then its bark can readily be removed; in the spring the tree is in fullest sap, but the sap is very watery, and contains but little salts in solution.

At Waltham Abbey, the woods used are:—The alder buckthorn (*Rhamnus frangula*), improperly called dogwood; it is cut about an inch in diameter and made into bundles six feet long. It is used for small-arm powders. Alder and willow charcoals (the latter from *Salix alba*) are used for cannon powders; the woods are grown in England, and are cut about four inches in diameter.

Désortiaux states that in France the so-called dogwood (*Rhamnus frangula*) is exclusively employed for making the charcoal for military and sporting powders; he states, however, that it is becoming increasingly difficult to procure, and that they are trying to replace it by willow, or by the wood of the spindle tree. In Germany, 'dogwood' (*R. frangula*), willow, and alder are used; in Russia, alder.

The amount of moisture in green wood varies, in general, from 20 to 50 p.c.; it is at its minimum in winter, and at its maximum during vegetation, when the moisture may reach 60 p.c. On free exposure of the wood to the air, a condition of equilibrium is gradually reached as regards its moisture: at the end of a year and a half to two years, the wood has lost all the moisture that the air is capable of taking from it, it then contains 12 to 15 p.c. water, which can be driven off by heating to 125°-150°. Removal of the bark greatly shortens the time of drying (Désortiaux's Upmann and Von Meyer).

'At Waltham Abbey, wood is usually kept for about three years, dogwood in thatched stacks, and willow and alder piled by cords in the open. By the method of carbonisation there followed, 25 p.c. of black charcoal should be obtained from the wood, rather more from dogwood. The wood is cut into three-feet lengths, which are split if differing much in thickness, and is packed into iron cylindrical cases called slips, 3 feet 6 inches long, and 2 feet 4 inches in diameter. The lid is fastened on, two openings (each about 4 inches in diameter) being left in the bottom of the slip. The slips are then placed in horizontal cylinders, the end of the slip with the openings going to the further end of the cylinder, in which end there are openings corresponding with those in the slips.

'The cylinders are closed by tightly fitting iron doors, and are built into the wall, with furnaces underneath, so arranged as to admit of the accurate regulation of the heat throughout the operation of charring; this occupies with dogwood about 4 hours for R.F.G., and 8 hours for R.F.G^2 gunpowders. With alder and willow, the time of burning varies from 3 to 5 hours, according to the nature of the powder for which it is required; the time, moreover, would in each case be increased if the wood were beyond the average size. The flames surround the cylinder, the heat acting as nearly as possible on its whole surface. The gases and volatilised tar from the wood pass out through the openings in the slip and the corresponding holes in the retort, into pipes communicating with the furnace in which they are burnt; this saves a considerable amount of fuel. When the wood has been sufficiently charred, which is known by the violet colour of the flame from the burning gas, indicating the formation of carbonic oxide, the slip is withdrawn by means of tackling, placed in a large iron case or cooler, covered with a closely fitting lid, and allowed to remain until all the fire is extinguished, which takes about 4 hours; the charcoal is then emptied into smaller coolers, and sent to store. The charcoal is carefully picked over by hand, to ascertain that it all is properly and evenly burnt, and that no rivets from the slips have broken off. It is then kept from ten days to a fortnight in store before being ground, to obviate the danger from spontaneous combustion (caused by absorption of oxygen from the air) to which charcoal is liable when ground directly after burning.' (General Wardell's Notes on Gunpowder and Gun-cotton.)

Kahl, at the Dresden powder works, has shown that very considerable differences exist in the percentage of carbon in charcoal forming part of the same charge, and taken from different parts of the cylinder. The difference in composition is due to want of homogeneity of the charge, and to differences of temperature existing in different parts of the cylinder. Thus the charcoal from the front and top of the cylinder, where the temperature was low, contained 78 to 85 p.c. C; from the middle of the cylinder, 90-91 p.c. C; from the back and bottom of the cylinder, where the temperature was highest, the charcoal contained 90-92 p.c. C.

The thorough mixing which the contents of a cylinder receives lessens the seriousness of this want of homogeneity.

The smaller the cylinders used, the more uniform is the composition of the charcoal produced, since so high a temperature is not needed to carry the heat to the centre of the charge; in the English powder mills, the tendency has been to use small cylinders, some of which hold only 77 lbs. of wood. The use of small cylinders, however, raises the cost of production (Désortiaux).

Violette states that, for the same temperature, a slow carbonisation gives a much higher yield of charcoal than a quick carbonisation; the percentage of carbon being also a little higher in the former case.

Instead of fixed carbonising cylinders, at Sévran-Livry movable cylinders have been employed since 1869; and since 1871, a similar arrangement has been introduced at Spandau. The cylinders at Sévran are 4½ feet long and 2 feet 4 inches in diameter, and will hold about 198 lbs. of dogwood or 286 lbs. of white wood. No 'slip' is used, but two cylinders are provided for each furnace, one being charged while a carbonisation is proceeding in the other. The charged cylinders are run into the furnace on rails, which support them over the fire. An elaborate arrangement for the regular distribution of the gases and products of distillation of the wood is used, by means of which they can at will be directed into any one of the furnaces or allowed partially to escape by the chimney; the combustion of the gases in each furnace is effected by means of a horizontal tube with two or three longitudinal grooves, the tube being placed parallel to the axis of the cylinder.

The principal advantages claimed for this system are homogeneity of the charcoal, and the ready regulation of the combustion of the gases by means of the distribution apparatus, so that slack-baked charcoal (*charbon roux*) can be as readily produced as black charcoal.

Böckmann mentions that some years since the use of rotating cylinders was introduced in Sweden; the cylinders being turned every half-hour during the carbonisation 90° about their horizontal axis. It is stated that a more uniform carbonisation is obtained, and fuel saved.

Violette, in 1848, introduced the carbonisation of wood by means of superheated steam. The steam was used at a pressure of ½ to 1 atmosphere, and was raised to the required temperature by being passed through a worm of wrought-iron heated by a fire. For the production (from dogwood) of *charbon roux* containing 70 p.c. carbon, the temperature of the steam had to be about 280°; by using steam heated to about 350°, charcoal containing 77 p.c. carbon was produced, and by heating both cylinder and steam to a temperature not exceeding 450°, charcoal of 89 p.c. carbon was obtained. The charcoal produced by means of superheated steam is remarkably uniform in composition. The method, however, was abandoned, because it gave a larger yield of *charbon roux*, but not of black charcoal, than the ordinary method of carbonisation in cylinders; and the lightly-burnt charcoal was then only required for sporting powder. Also, the cost of production of the charcoal by the superheated steam apparatus was greater. H. Güttler has recently patented (D. R. P. No. 42,470 of May 12, 1887) a process for carbonising wood, straw, peat, &c. in heated CO$_2$. Carbon dioxide is stated to be preferable to superheated steam, on account of the moist state of the charcoal when cooled in the steam. He introduces CO$_2$, containing as little oxygen as possible, and heated by passing through a spiral heater placed at the fire-bridge of the furnace, into the carbonising cylinder during the carbonising of the wood &c., and maintains the flow of CO$_2$ during the cooling, which in consequence of the presence of the gas may be very rapid (D. P. J. 268, 516, 517).

Composition &c. of the charcoal.—Carbonising the wood raises the percentage of carbon, diminishing the percentages of hydrogen and oxygen.

Désortiaux states that woods recently cut have almost the same percentage composition; the mean composition of the dried wood being 49·37 p.c. C, 6·14 p.c. H, 43·42 p.c. O and N, 1·07 p.c. ash.

Heintz gives the composition of alder wood (–ash) as 48·63 p.c. C, 5·94 p.c. H, 44·75 p.c. O, 0·68 p.c. N. Peterson and Schödler give alder wood (–ash) as 49·20 p.c. C, 6·22 p.c. H, 44·58 p.c. O and N.

On heating, water, carbon monoxide, carbon dioxide, hydrogen, acetic acid, methylic alcohol, and tar are produced.

Violette found that dogwood was converted into slack-baked charcoal (*charbon roux*) at a temperature of 280°–300°; at 300° the yield (on the small scale) was about 34 p.c., and the composition of the charcoal was 73·24 p.c. C, 4·25 p.c. H, 21·94 p.c. O and N, 0·57 p.c. ash. Between 350° and 400° black charcoals are produced, the yield being from 31 p.c. to 28 p.c., the composition ranging from about 77 p.c. to 81 p.c. C. Between 1000° and 1250°, the charcoal obtained was very black and hard, the yield was about 18 p.c., and the composition of the charcoal 82·0 p.c. C, 2·30 p.c. H, 14·10 p.c. O and N, 1·60 p.c. ash, at the lower temperature, and 88·14 p.c. C, 1·42 p.c. H, 9·24 p.c. O and N, 1·20 p.c. ash, at the higher temperature.

Experiments by Violette show a rapidly rising specific gravity of the charcoal for rising temperature of carbonisation, but his method of estimating the specific gravity does not seem satisfactory.

Experiments made at the Chemical Department of the War Department showed no great difference in the specific gravity of charcoals prepared from willow and alder at 394°–558°; their specific gravity at 15°·6 was 1·41 to 1·44. Willow charred at the maximum temperature of 394° for 9¼ hours had the composition 79·22 p.c. C, 4·02 p.c. H, 15·32 p.c. O and N, 1·44 p.c. ash, and specific gravity (at 15°·6) 1·414.

The higher the temperature of carbonisation, the less is the inflammability of the charcoal in air. Violette states that the charcoals prepared from any kind of wood at 300° take fire when heated in the air to 360°–380°; the charcoals from light and porous woods burning more easily than those from hard and close woods. For the same wood he makes the following statement as to the relation between temperature of charring and that of inflammation in air:—

Temperature of charring	Temperature of inflammation
260°–280°	340°–360°
290°–350°	360°–370°
432°	about 400°
1000°–1500°	600°–800°

The lightly-burnt charcoals are much more absorbent of water than those charred at a high temperature.

The charcoals used for the various kinds of Service black gunpowder range in composition from about 75 p.c. C to 86 p.c. C, according to the nature of the powder. All other conditions being the same (viz. proportion of KNO$_3$, S, and charcoal, size of powder, density, and moisture) the charcoal burnt at lower temperatures (having lower percentage of carbon) gives higher muzzle-velocities and pressures than charcoal burnt at higher temperatures and having higher percentage of carbon; that is, for gunpowder of the composition 75 p.c. nitre, 10 p.c. sulphur, and 15 p.c. charcoal. The greater inflammability of the lighter-burnt charcoal makes the gunpowder, of which it forms part, quicker-burning.

The wood is charred to expel moisture, which would lower the temperature of the explosion products of gunpowder, and to obtain a charcoal of suitable inflammability.

Appended is a table of the percentage composition of some charcoals from gunpowders of Waltham Abbey make, and of a sporting powder, which will serve as types of the charcoal used in the different kinds of black gunpowder:—

—	W. A. Pebble	W. A. Rifle Large Grain	W. A. Rifle Fine Grain	W. A. Fine Grain	Curtis & Harvey Sporting
C	85·26	80·32	75·72	77.88	77·36
H	2·98	3·08	3·70	3·37	3·77
O (and N) . . .	10·16	14·75	18·84	17·60	16·62
Ash	1·60	1·85	1·74	1·15	2·25

(Noble and Abel, Tr. part i. 1880, 218.)

Pulverising, mixing, and incorporating the ingredients.—At Waltham Abbey, the refined nitre is used for gunpowder without being previously dried or ground, but the moisture is estimated and allowed for. The charcoal is ground in a mill; the grinding is done by a cone working in a cylinder, both being suitably toothed. The ground charcoal is made to pass through a spout into a revolving reel of 32-mesh copper-wire gauze, 8½ feet long and 3 feet in diameter, inclined at an angle of about 4° to the horizontal, and making 38 revolutions per minute. The charcoal which passes through the gauze is fit for use, and is collected in a closed reel case; the charcoal too coarse to pass through the gauze falls through the further end of the reel into a vessel, and is re-ground. The sulphur is ground under a pair of iron edge-runners, a smaller-sized incorporating mill, and is sifted through a reel similar to that used for the charcoal.

The ground ingredients are carefully weighed out in their proper proportions; the largest charges worked in the incorporating mill are 50 lbs. for small-arm powders and 60 lbs. for cannon powders. The charge receives a preliminary mixing in the mixing machine, a cylindrical drum of gun-metal or copper, about 2 feet 9 inches in diameter and 1 foot 6 inches wide. An axle bearing eight rows of fork-shaped arms passes through the centre of the drum; the drum and arms are made to revolve in opposite directions, the former making about 40 revolutions per minute, the latter 80. The mixing occupies five minutes, the mixture being then hand-sifted to remove foreign substances; the 'green charge' is then tied up in a bag ready for the incorporating mill.

The incorporating mill consists of a circular iron or stone bed (fig. 1) about 7 feet in diameter, very firmly fixed in the floor of the building, on which two iron or stone cylindrical edge-runners revolve, stone running on stone and iron on iron; the old pattern beds and runners are of stone, the new of iron. Runners and bed are shown in elevation in A, and in plan in B (fig. 1).[1] The iron runners are 6½ feet in diameter, 15 inches wide, and weigh about four tons. They have a common axle resting in a solid cross-head attached to a vertical shaft, which passes through a bearing in the centre of the bed, and is in gear with the machinery M, which is above the bed in the old water mills and beneath it in the new steam mills.

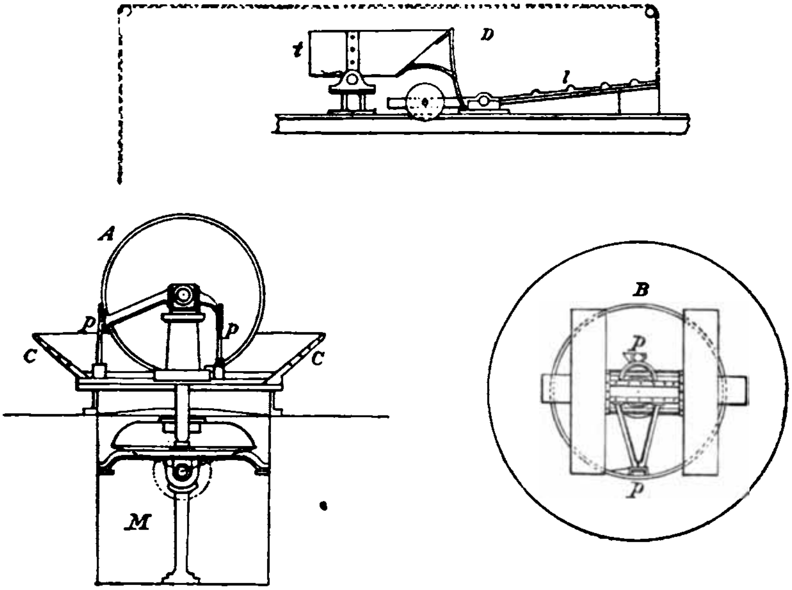


FIG. 1.

The bed has a sloping outside rim C. The runners are at an unequal distance from the axis, the eccentricity being equal to half the thickness of a runner; they thus work the charge in the inner and the outer part of the bed, their paths overlapping. The runners are followed by two 'ploughs' of wood P, covered with leather, attached to the cross-head by arms; one plough works near the vertical shaft, the other near the rim of the bed, throwing the composition under the runners.

The green charge is spread evenly on the bed of the mill by means of a wooden rake; it is damp with the moisture of the nitre, but an additional quantity of distilled water (2 to 7 pints) is added from time to time, according to the state of the atmosphere; the moisture assists the incorporation, and the charge is kept not too dry or it would be scattered as dust, not too wet or it would slip away from the runners or cling to them.

The iron runners make 8 revolutions per minute, the green charge is worked under them for 4 hours for R.F.G. powder, for 7 to 8 hours for R.F.G^2 powder, and for 3 hours for R.L.G^2 and R.L.G^4. Dust and re-worked charges are worked for 40 minutes.

A drenching apparatus D is placed over the bed of each mill, by means of which in case of an explosion a tank of water is overturned and the charge drowned. This is done by the action of the explosion gases on a flat wooden lever

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[1] I am indebted to Major-Gen. Wardell for figs. 1 and 2, which are taken from his 'Handbook.'

arrangement *l*, pivoted, and attached to the tank *t*. By means of a horizontal shaft connecting all the levers of a group of mills, an explosion in one mill drowns all the others. (Wardell, *l.c.*) A similar arrangement is in use at Sévran.

The short radius of the circular path traversed by the runners causes them to take a twisting as well as a rolling motion, and gives them a combined crushing and grinding action very favourable to the thorough trituration and incorporation of the ingredients.

The incorporating mills used in France are very similar to those of Waltham Abbey; the iron runners and beds are said to be of grey cast-iron, not brittle, and as hard and resisting as possible. The runners each weigh about 5 to 5½ tons; they are cylinders with rounded edges, about 5 feet in diameter and 18 inches wide; the sides are hollowed out to a depth of 1·58 to 1·66 inch. The two ploughs are of bronze, and there are also two bronze scrapers to each runner. The runners work at about 10 revolutions per minute.

Désortiaux states that most of the German mills are on the French model.

In France, for powders for military use, previously to the incorporation the sulphur and charcoal are triturated separately in barrels formed of a wooden framework lined internally with leather. 66 lbs. of sulphur are triturated in such a barrel by rotation with twice the weight of balls of hard bronze about 0·3 inch in diameter; half the weight of charcoal is taken. The barrel makes 20 to 22 revolutions per minute, and the trituration takes two hours. Or the nitre may be triturated with some charcoal, and sulphur and charcoal triturated together; larger bronze balls are then used, and the operation takes more time. The powdered materials are hand- or mechanically sifted. Désortiaux states that in Germany the charcoal is triturated separately, the sulphur and nitre together, the apparatus used being generally similar to the French.

The triturated materials appear to be worked under the incorporating mills for a shorter time in the French and German powder works than at Waltham Abbey.

The mill-cake, as the worked charge is called, should have a uniform appearance, and should contain 1 p.c. to 3 p.c. moisture for small-arm powders, 3 p.c. to 6 p.c. for the larger-grained powders. In France the amount of moisture in the mill-cake is 2 p.c. to 3 p.c., and 3 p.c. to 3·5 p.c. respectively.

Breaking down the mill-cake and pressing. The mill-cake is next reduced to meal, for convenience in charging the press-box, and in order that the powder may be uniformly pressed. The mill-cake is broken down by means of two pairs of gun-metal rollers, the upper pair being grooved and placed directly above the other pair, which are smooth. The rollers revolve towards each other, dangerous friction from the accidental presence of any hard substance being prevented by one roller of each pair working in sliding bearings connected with a weighted lever causing a pressure of about 56 lbs., so that the rollers would open at any greater pressure. The rollers are fed with mill-cake from a hopper (placed at one end of the machine, below the level of the upper pair of rollers), by means of an endless band of canvas 2½ feet wide, with cross strips of leather sewn on at intervals of about 4 inches. The band passes over a roller at the bottom of the hopper, and over another placed above the upper pair of rollers; on being set in motion it carries the cake from the hopper to a point from which it falls on to the first pair of rollers; the crushed cake then falls on to the second pair, by which it is reduced to meal. It falls into wooden boxes, and is transferred to a magazine ready for pressing.

The meal is pressed into cake by an hydraulic press. The press-box used at Waltham Abbey is a very strong oak box with gun-metal frame, 2 feet 6 inches square, and 2 feet 9 inches deep, so constructed that three of the sides can turn back on hinges or be screwed firmly together into a rigid box. In charging the box it is laid on its side, the top temporarily closed by a board, with only the upper side open, and a number of copper or gun-metal plates 2 feet 5½ inches square are placed vertically in the box, spaces (depending on the kind of powder required) being maintained between them by means of two grooved gun-metal racks, removed when the box is filled. About 800 lbs. of meal is put into the box, and rammed down uniformly between the plates by means of wooden laths; the racks are withdrawn, the upper open side of the box screwed down, the box turned up so that the plates are in a horizontal position, and placed on the table of the press under the fixed press-block. The pumps, which work the press in a separate house, are set in action, and the box is raised against the block until the powder has been compressed to an extent corresponding to the density required. The block is allowed to enter the box a certain measured distance, and this means of judging of the pressure is preferred to the indications of the pressure gauge on account of the varying elasticity of the meal, varying with the amount of moisture in the meal, and with the state of the atmosphere. After the charge has been compressed to the required extent (made known to the men in the pump-room by the edge of the box being made to ring a bell), the pressure is maintained for a few minutes; the box is then released from pressure, removed, and unloaded. The press-cake is taken out in layers of about half an inch thick for R.L.G^2 and small-arm powders, and is broken into pieces; for pebble and cubical powders the press-cake is ⅝ and 1½ inch respectively, and is not broken (Wardell, *l.c.*).

In France the pressing is effected by vertical hydraulic presses; but the press-box has been done away with on account of dangerous friction said to be caused by the considerable pressure on its sides. A cotton or hemp cloth is placed between the powder-meal and the copper plate on which it rests, and a cloth is also placed on the top of the powder, the press-cake having been found to stick to the plates. The press is charged as follows:—A copper plate 0·06 to 0·08 inch thick is covered with a cloth; a wooden frame of about 20 inches by 28 inches, about 1·2 inches broad, and of varying height, according to the thickness of press-cake required, is placed on the cloth, powder meal is filled in, stroked level, the frame removed, and so on until a charge of 330 lbs. to 880 lbs. is made up. This is transferred to the table of the press, and a pressure of 355 lbs. to 426 lbs. per square inch of cake slowly and repeatedly applied, the operation lasting 30 to 40 minutes. A pressure of 355 lbs. per square inch of cake exerted on meal containing 3 p.c. moisture, and which has had two hours' working in the incorporating mill, gives a press-cake of 1·7 to 1·8 density. The centre of the cake has, however, a greater density than the edges; the edges of the cake are on that account cut away to the extent of about an inch. The amount cut away need not exceed 10 p.c.

Another kind of press—a roller-press—has been used in Germany, and been introduced into France, in which the press-cake is made by passing the meal between rollers, one of wood, the other—the compresser cylinder—of bronze. The latter is heavy, and pressure is applied to it by means of weighted levers.

Granulating.—The press-cake is converted into grain by means of a machine consisting of three or four horizontal pairs of rollers (CC, fig. 2) in a gun-metal frame. The pairs of rollers are placed one above the other, on an axial line inclined at about 35° to the horizontal, the vertical distance between the pairs of rollers being about 2½ feet. For fine-grain powders the highest pair of rollers has teeth ½ inch apart, the next pair has ¼ inch teeth, and the two bottom pairs have no teeth. Like those of the breaking-down machine, the rollers work in sliding counter-weighted bearings; they make about 25 revolutions per minute. The machine is fed with press-cake from a hopper A by means of a moving endless band B. Short screens D covered with copper-wire gauze (10-mesh for small-arm powders) are placed under each pair of rollers except the bottom pair, so that the powder too large to pass through the gauze passes on from one pair of rollers to the next. Beneath the short screens are placed two long screens EE in an inclined position, the upper one of 10-mesh, and the lower one of 20-mesh copper gauze fixed in a frame. A rapid, longitudinal, vibratory motion is imparted to all the screens while the machine is working, to assist the sifting and the flow of the powder. The grain that passes through the short screens will fall through the 10-mesh long screen. That which is retained on the 20-mesh screen is R.F.G. or R.F.G^2 powder; it falls into boxes G made to move forward as they are filled. The grains too large to pass through the short screens fall into separate boxes H, and are transferred to the hopper to be passed again through the rollers; while the fine powder which passes through the 20-mesh sieve falls on to the wooden bottom K of the frame and is collected separately, to be sent back to the incorporating mill for a short re-working.

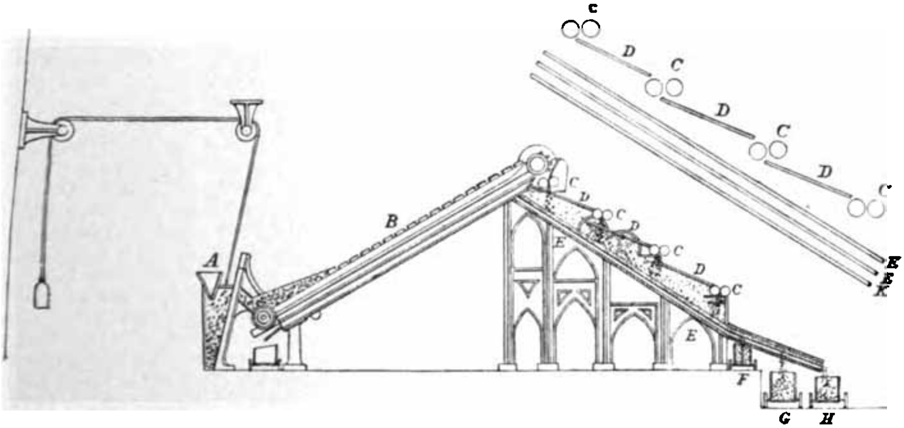

Fig. 2.

For granulating R.L.G^2 and R.L.G^4 powders, three pairs of rollers are usually employed, the two upper pairs with larger teeth, the bottom pair smooth (Wardell, *l.c.*).

Dusting and glazing.—R.F.G. and R.F.G^2 powders are freed from dust after granulation by being passed through a dusting-reel. This is a cylindrical frame about 8 feet long and 1½ feet in diameter, covered with 20-mesh copper-wire gauze, and set at a very small angle with the horizontal. The reel is inclosed in a case to catch the dust, but is open at both ends; it is fed continuously at the upper end with powder from a hopper, while the reel makes about 40 revolutions per minute. The powder falls from the lower end of the reel into barrels.

The polish given to the powder-grains by glazing is of advantage in diminishing the tendency of the powder to absorb moisture, and in enabling it to bear transport without going to dust. The small-arm powders, R.F.G. and R.F.G^2, are glazed in large drums—cylinders 2 feet wide and 6 feet in diameter (a pair of drums on one axle) making about 12 revolutions per minute. The drums each take about 900 lbs. of powder; they are run 5½ hours for R.F.G., and 10 hours for R.F.G^2. No graphite is used for these powders; the friction and heat caused by the motion suffice to produce a brilliant glaze. The glazed powder receives another dusting in a reel covered with 20-mesh wire-gauze, and is then sifted through an 11-mesh sieve into barrels. R.L.G^2 powder is run for 1½ hour in drums as above, with about one ounce of graphite per 100 lbs. powder. R.L.G^4 is glazed for 3 hours in the old pattern glazing barrels, the same proportion of graphite as for R.L.G^2 being added after the barrels have run for 2 hours. Each barrel takes about 400 lbs. of powder; they are 5 feet long by 2½ feet diameter of ends, and make 34 revolutions per minute.

Drying, finishing, blending.—The next operation is drying, which is carried out in a drying-room heated by steam pipes. The gunpowder is placed in copper trays, or in wooden frames about 3 feet × 1½ feet × 2½ inches with canvas bottoms, each holding about 12 lbs. of powder, and placed on open framework shelves with which the room is fitted, seven or eight tiers of shelves rising one above another, the steam-pipes running under them. The moist air of the room is constantly changed by means of ventilators. At Waltham Abbey about 50 cwt. of gunpowder is dried at one time. The time and temperature of drying varies with the kind of powder and the amount of moisture in it, the length of time and the temperature increasing with the size of the grain. Thus, R.F.G. requires one hour, and R.F.G^2 two hours at 38°, R.L.G^2 two hours at 43°, and R.L.G^4 six hours at 46°.

The dried powder is *finished* by being rotated in a horizontal reel—a long cylindrical wooden frame covered with canvas, making 45 revolutions per minute—the fine-grain being reeled longer than the large-grain powders. Finishing frees the powder grains from the small amount of dust produced in the process of drying, and gives them (and especially to small-arm powders) a final glaze.

Before drying, and again after finishing, a uniform blend or mixture is made of a large number of barrels of gunpowder. This is done by means of a wooden hopper divided into four equal compartments, each able to hold a barrel of gunpowder; the compartments can be emptied simultaneously into a central shoot by means of openings with sliding shutters in the bottom of each (Wardell, *l.c.*).

From 'granulating' to 'blending,' the processes described above refer exclusively to the Waltham Abbey manufacture.

Pebble and prismatic powder. The use of pebble powder in this country dates from about the year 1865. General Rodman, of the United States Artillery, had previously shown that in the gun the pressure diminished as the size of the grains of gunpowder increased, and that the velocity of the projectile could at the same time be maintained by an increased weight of charge.

Pebble powder (P, cubes of ⅝-inch; and P^2, 1½-inch cubes) are used for larger guns than are the rifle large-grain powders. Up to the formation of the press-cake, the processes of manufacture are, with some variations, the same as for the finer-grained powders.

The P powder is cut from the press-cake, which is pressed into slabs of about 15 inches by 30 inches, and of the required thickness. The cutting machine consists of two pairs of phosphor-bronze rollers, having longitudinal knife-edges with spaces between them corresponding to the required size of the powder. The rollers are fixed in a strong wooden frame, the axes of the first pair are in a horizontal plane and at right angles to the second pair of rollers, which are set in a vertical plane. The press-cake is fed by hand into the horizontal rollers and is cut by them into strips which fall upon a board placed beneath and close to the rollers. A series of laths, forming part (like the steps of a ladder) of an endless skeleton band, move sideways along upon the surface of the board; each strip of press-cake falls into the space between two laths and is carried sideways on to the end of the board, from which it drops on to an endless canvas band passing just below and at right angles to the skeleton band of laths, and by which the strips are carried end-on to the vertical pair of rollers, and cut by them into cubes. The board is made to move forward at the same rate and in the same direction as the laths, so that the strips of press-cake are placed clear of one another on the canvas band feeding the second pair of rollers. (The illustrations of this machine in Wardell's Handbook, or that in Désortiaux's book, should be consulted.) The cubes of powder fall into a dusting reel, with copper-wire meshes but little smaller than the cubes.

P^2 powder is cut by hand from the press-cake by means of lever-knives of gun-metal: knives hinged at one end, with a handle at the other. The press-cake is first cut into strips and then across into cubes.

Both P and P^2 powders are run in the glazing barrels, by which treatment the edges and corners of the cubes are rubbed down, and a harder surface produced. The powders are then dried at 54°, which requires a very much longer time than for the smaller-grained powders; a finishing process follows, the powders being run in wooden barrels with ribs wide enough apart to combine sifting with the finishing glazing. A small quantity of graphite is introduced into the barrels towards the end of the finishing process. A thorough blending of a large number of barrels of powder follows; this is done systematically by means of a 4-way hopper, as with the smaller-grained powders (Wardell, *l.c.*).

Prismatic powder. This may be regarded as a modification of the perforated cake powder devised by General Rodman in 1860. The latter powder consisted of cakes of powder compressed by the hydraulic press, of the diameter of the bore of the gun, and pierced longitudinally with holes of about ¼ inch diameter, the cakes being packed in the cartridge so that the holes should correspond. General Rodman was led to introduce this form of powder by the consideration that, with solid grains of gunpowder, the surface undergoing combustion in the gun diminishes as the combustion proceeds, and that consequently the strain on the gun is greatest in the earlier stages of the combustion. In the case of the perforated cake gunpowder, as the combustion progressed in the longitudinal holes, the surface undergoing combustion increased. Rodman's theoretical views were confirmed by experiment, but the liability of the perforated cake powder to break up by carriage or when handled, led to its replacement by much smaller hexagonal prisms with one central cylindrical hole; the prisms used in this country are about 1 inch high, the distance between opposite sides of the hexagon about 1·37 inch, the central hole about 0·4 inch in diameter. They are used for heavy breech-loading guns, and can be packed so as to form rigid cartridges.

The prisms are pressed from a moderately large-grained powder, granulated from press-cake and freed from dust in the ordinary way, but not glazed. At Waltham Abbey an hydraulic pressing machine is used, which presses 64 prisms at one operation. The exact quantity of grain-powder is introduced into each mould by means of small hoppers (a hopper to each mould), there being 64 hexagonal moulds in one firmly fixed metal plate. Two hydraulic rams, each working a plunger-block with hexagonal plungers to each mould, simultaneously compress the powder-grain from above and from below the mould plate; the holes in the prisms are made by rods passing through the lower plungers and fitting into holes in the upper set. Moulds, plungers, and rods are made of phosphor-bronze. The pressure is applied for from ten to twenty seconds.

In Germany, the compression is effected by means of small cam-machines, pressing about six prisms at one time, and working automatically and very rapidly. The cam machine is capable of giving a very hard smooth surface to the prisms, and of almost obliterating the traces of granular structure.

The prisms are subseqnently dried and blended (Wardell, *l.c.*).

Mining powder. This is a low-priced black powder used in mining, for rock-blasting, &c. Désortiaux gives the following as the composition of the mining powder in use some years since in the countries mentioned:—

	England	France	Italy
Potassium nitrate	65	62	70
Sulphur	20	20	18
Charcoal	15	18	12

These, and those attributed to other countries, have in common a smaller proportion of nitre and a higher proportion of sulphur than the respective military powders; but while some of the mining powder made in this country has the composition given above, other descriptions have approximately the composition (75 p.c. KNO_3, 10 p.c. S, 15 p.c. charcoal) of our black military powders, and others, again, are intermediate in composition.

It is a large-grained powder, sometimes coated with graphite. As will be mentioned farther on, while the mining powder with low nitre and high sulphur gives on explosion a larger volume of permanent gases, it gives a much smaller quantity of heat than black gunpowder.

Brown or cocoa gunpowder. The introduction of this powder by the Rottweil-Hamburg Powder Company and by the Westphalian Powder Company was a great innovation in powder making. It is composed of 79 p.c. nitre, 3 p.c. sulphur, and 18 p.c. charcoal per 100 of dry powder, and contains ordinarily about 2 p.c. moisture. The 'charcoal' also was a very lightly baked material, the percentage of carbon contained in it being but little higher than that in the (dry) wood or straw from which it is made. Heidemann, in 1884, patented the use of carbonised straw, the straw being baked to a chocolate-coloured material, which was to be pulverised and mixed with nitre and sulphur in the above-mentioned proportion.

This powder is used for heavy breech-loading guns in the form of hexagonal prisms, having the same dimensions as the black prismatic powder. The rate of combustion of the brown prismatic powder is slower than that of the black, and it was claimed for brown powder that for equal muzzle velocities of the projectile it produced less pressure in the powder-chamber of the gun than black powder, and that it gave a thinner smoke than the latter—claims which have been justified by subsequent experience.

As is subsequently mentioned, the brown or cocoa powder gives on explosion a greater quantity of heat and a smaller volume of permanent gases than does an equal weight of black gunpowder; but the larger amount of water vapour in the products of explosion of brown powder must have an important influence in lowering temperature.

Properties, and products of explosion.—The 'density' (as determined by Bianchi's densimeter) of the different kinds of gunpowder mentioned ranges from about 1·67 in the case of R.L.G^2 to about 1·87 in the case of brown prismatic powder. Increase of density of a gunpowder causes its slower combustion, and (under comparable circumstances) diminishes the muzzle velocity of the projectile and the pressure in the gun.

Increase of the amount of moisture in a gunpowder causes diminished temperature of the products of explosion, and lessens the muzzle velocity of the projectile and the pressure in the gun.

Black gunpowder explodes at about 300°. The exploding temperature was taken by heating small grains of the gunpowder buried in the sand of a small deep sand-bath, in which the bulb of a Geissler pressure mercurial thermometer was immersed. Black prismatic gunpowder inflamed at about 290°, brown prismatic at 304°.

The rate of combustion of gunpowder diminishes with diminished atmospheric pressure. In an atmosphere maintained at a pressure of about 0·5 inch mercury, gunpowder is not exploded by contact with a platinum wire heated to redness by an electric current; the grains in contact with the wire fuse, and, if the passage of the current be maintained, burn slowly without causing the explosion of the remainder. Under the high pressures produced in a gun when fired, the velocity of combustion of gunpowder very rapidly increases.

The products of the combustion of gunpowder have been examined by several chemists, of whom Gay-Lussac in 1823, and Chevreul in 1825, Bunsen and Schischkoff (1857), Karolyi (1863), Federow (1868), Noble and Abel (1875–80), may be more particularly mentioned.

The investigation of the subject by Capt. A. Noble and Sir Fredk. Abel is much more complete than the others, and some of their results will be briefly mentioned.

The quantity of heat evolved by the explosion of gunpowder was determined by firing 10 to 26 grams of gunpowder in strong steel explosion vessels of 32 and 119 c.c. capacity respectively, the explosion vessels being surrounded by water in a calorimeter of the usual kind.

The volume of permanent gases produced was determined by exploding in closed steel vessels, having an internal capacity of about one litre, quantities of gunpowder varying in weight from about 100 to 800 grammes. The vessels retained the whole of the products of explosion, and were provided with an arrangement by which the gases could be allowed to escape, and could be collected or measured. The pressure in the vessels was measured by means of the usual crusher-gauge (piston acting on, and compressing, a small copper cylinder) contained in a plug screwed into the vessel.

The pressures in the explosion vessels varied with the density of charge $\left(\frac{\text{volume of powder}}{\text{capacity of vessel}}\right)$. With a density of charge of 0·3, the pressure observed was about 5 tons per one square inch; with 0·7 density, the pressure was about 20 tons; with density 1, the pressure was about 42 tons; and with density 1·2, the pressure was about 56 tons.

The powders experimented with had the following percentage composition; the first three were of Waltham Abbey make:—

Nature of powder	Potassium nitrate	Potassium sulphate	Potassium chloride	Sulphur	Carbon	Hydrogen	Oxygen	Ash	Water
Pebble powder .	74·67	0·09	—	10·07	12·12	0·42	1·45	0·23	0·95
Rifled large grain R.L.G.	74·43	0·13	—	10·09	12·40	0·40	1·27	0·22	1·06
Fine grain . .	73·55	0·36	—	10·02	11·36	0·49	2·57	0·17	1·48
Sporting powder .	74·40	0·29	Trace	10·37	10·66	0·52	2·29	0·31	1·17
Mining powder .	61·66	0·12	0·14	15·06	17·93	0·66	2·23	0·59	1·61
Spanish spherical powder	75·30	0·27	0·02	12·42	8·65	0·38	1·68	0·63	0·65
Cocoa powder .	78·83	—	—	2·04	Charcoal 17·80				1·33

The composition of the solid and gaseous products of the explosion of these gunpowders is given in the following table; the numbers given for the first three powders are the means of 9 experiments with density of charge from 0·1 to 0·9, the sporting and mining powders had density of charge 0·3, the Spanish spherical, 0·7.

Percentage composition by volume of the dry permanent gases.

—	Pebble	R.L.G.	Fine grain	Sporting	Mining	Spanish spherical	Cocoa
Carbonic anhydride .	48·95	49·29	50·62	50·32	32·15	53·34	51·30
Carbonic oxide .	13·63	12·47	10·47	7·52	33·75	4·62	3·42
Nitrogen . . .	32·16	32·91	33·20	34·46	19·08	37·80	41·71
Hydrogen sulphide .	2·60	2·65	2·48	2·08	7·10	2·74	—
Marsh gas . .	0·31	0·43	0·19	2·46	2·73	—	0·31
Hydrogen . .	2·35	2·19	2·96	3·26	5·24	1·29	3·26
Oxygen . . .	—	0·06	0·08	—	—	0·21	—

Percentage composition by weight of the dry solid residue.

—	Pebble	R.L.G.	Fine grain	Sporting	Mining	Spanish spherical	Cocoa
Potassium carbonate .	59·26	61·05	51·88	59·10	41·36	35·66	$KHCO_3$ 13·55 K_2CO_3 64·12
„ sulphate .	12·93	15·10	22·71	21·65	0·59	48·55	22·33
„ monosulphide	18·98	14·46	18·16	12·42	37·10	7·72	none
Sulphur[1] . . .	8·08	8·74	6·90	6·45	14·11	7·04	—
Potassium sulphocyanate	0·25	0·22	0·13	—	2·95	0·04	—
„ nitrate . .	0·24	0·27	0·17	0·29	0·09	0·95	trace
Ammonium sesqui-carbonate	0·10	0·08	0·05	0·09	1·78	0·04	trace
Charcoal . . .	0·16	0·08	—	—	2·02	—	—

[1] Present in the residue as higher sulphide of potassium.

The cocoa powder gives a completely oxidised saline residue, and the proportion of incompletely oxidised gases is smaller with this powder than with the others.

The quantity of heat (in gram-degree units), and the volume (at 0° and 760 mm.) of the permanent gases, per 1 gram of dry powder, were found by Messrs. Noble and Abel to be:—

——	Units of heat	Cubic centimetres Permanent gases
Cocoa	837	198·0
Spanish spherical	767·3	234·2
Sporting	764·4	241·0
Fine grain	738·3	263·1
R.L.G.	725·7	274·2
Pebble	721·4	278·3
Mining	516·8	360·3

It will be seen that the order of decrease of units of heat is that of increase of volume of permanent gases; and Messrs. Noble and Abel observe that the products of heat-units by gas-volume do not differ greatly from a constant value, that this points to the conclusion that the pressures at any given density of charge, and the power of doing work of the various powders, are not very materially different: a conclusion verified by experiment for the three Waltham Abbey powders, and in a less degree also for the other powders. The total potential energy of gunpowder they estimate at about 340,000 kilogrammetres per 1 kgm. of powder, or a little under 500 foot-tons per 1 lb. This calculation supposes the infinite expansion of the products of combustion, but they estimate the actual energy of gunpowder realised by modern guns as varying from about one-tenth to one-fifth of the total theoretical effect.

The *temperature* produced by the explosion of gunpowder they estimate at about 2100° in the case of the pebble or R.L.G. powder, at about 2200° in that of the Spanish pellet powder (Noble and Abel, Tr. 1875, 1880; Noble, Heat-action of Explosives: a Lecture to Inst. Civil Eng. 1884).

GUNPOWDER CONTAINING OTHER NITRATES.

Barium nitrate. Captain Wynants, in Belgium, introduced a gunpowder in which $\frac{4}{5}$ of the nitre was replaced by barium nitrate. It was tried at Brussels, was found to be unsuitable for small arms on account of its slow combustion; was tried, with some success, in cannon, but was given up on account of the fouling it caused.

Sodium nitrate. This nitrate has been used, in partial substitution of the potassium nitrate, in several mining powders. Other mining powders have been used in which sodium nitrate was the only nitrate present, sulphur and charcoal or tan being the other constituents; such were De Tret's, Oxland's, Freiberg, and Wetzlar powders. A sodium nitrate mining powder has also been used on a large scale, and with economy, in the Suez Canal works.

The replacement of the potassium nitrate of black gunpowder by an equivalent quantity of sodium nitrate would give, according to Berthelot's calculation, if the chemical reactions were exactly the same in the two cases, a slightly greater quantity of heat and a larger volume of gases.

The hygroscopicity of sodium nitrate has been a hindrance to its use.

Ammonium nitrate (*amide powder*). Dr. H. Sprengel, in 1873, showed that a mixture of ammonium nitrate and lampblack or charcoal, mixed with ordinary sporting powder, when fired in a rifle, caused a considerable increase in the initial velocity of the bullet, as compared with the velocity imparted by the same weight of sporting powder (C. J. 1873, 805). Ammonium nitrate, although containing 60 p.c. oxygen, having a combustible base, has only 20 p.c. oxygen available for the oxidation of other substances: $NH_4NO_3 = N_2 + 2H_2O + O$; while potassium nitrate has 39·6 p.c. available oxygen, supposing K_2O to be formed.

An explosive powder for use in guns and for blasting purposes, recently patented by F. Gaens (Eng. pat. 1885, No. 14,412), and termed *amide powder*, is a mixture of ammonium and potassium nitrates with charcoal. The patentee in his complete specification, claims the use of the constituents in such proportions as to give on ignition potassamide KH_2N, in accordance with the equation

$$KNO_3 + NH_4NO_3 + 3C$$
$$= KH_2N + H_2O + CO + 2CO_2 + 2N,$$

according to which the powder should be composed of 101 parts by weight potassium nitrate, 80 parts ammonium nitrate, and 40 parts charcoal. The potassamide he states to be volatile at high temperatures, increasing the useful effect of the explosive and burning without residue. It is claimed further for the *amide powder* that when burned it leaves very little residue, and gives much less smoke than ordinary gunpowder.

The volatility at high temperatures of a potassium amide or nitride as such, is, however, a property not previously recorded; and the production of a larger volume of gas is probably the cause of the higher velocity mentioned above.

Analysis of gunpowder.—The only points that need special mention are (1) *the estimation of sulphur*, for which 1 gram of powder is heated in a beaker with strong nitric acid; charcoal and sulphur are thereby oxidised, and a dark-brown liquid produced. This is cooled a little, some potassium chlorate added, and the liquid re-heated, when oxidation is completed, and the liquid becomes pale yellow. It is evaporated to dryness in the beaker, and the saline residue converted into chloride by evaporation with strong hydrochloric acid. The residue is dissolved in water, *gritty inorganic matter* and *graphite* will be seen here, the latter very distinctly on the filter. The solution is filtered, and precipitated boiling with barium chloride; the barium sulphate is purified by boiling with small successive quantities of water until free from salts, the liquids being decanted on to the filter.

(2) *The analysis of the charcoal.*—The nitre is removed from the gunpowder by treatment with water, the charcoal and sulphur filtered off, dried, powdered, and treated with carbon bisulphide to remove sulphur. The dried charcoal still retains a small quantity of sulphur, which is estimated by the method given above, after the charcoal has been dried in hydrogen in the same manner as for a combustion. The weight of sulphur is, of course, deducted from the weight of charcoal used for the combustion. About 0·5 gram of charcoal is taken for combustion; it is dried (in the boat in which it is to be burnt) by heating for 15 minutes to 170°, in

the case of a black charcoal, in a current of hydrogen. The charcoal is allowed to cool in the current of hydrogen, and is transferred to an air-pump receiver, which is then exhausted. The boat with the charcoal is weighed in a closed tube. The combustion is made in oxygen, a length of granulated oxide of copper, maintained at a red heat, being in front of the boat; and in front of the oxide of copper is a shorter length of chromate of lead, heated to very low redness to absorb SO_2 or SO_3 (as proposed by Carius); in other respects the combustion is made as usual.

By the ***density***, or ***real density***, of a powder is understood the specific gravity of the grains or prisms, including the air contained in their pores. It is determined, probably universally, by the Mallet-Bianchi densimeter, the liquid employed being mercury. Fig. 3, from a photograph of the apparatus, will be almost self-explanatory, the apparatus being a modified specific gravity bottle. The cylinder will take four one-inch high prisms, weighing 180 grams, but the usual weight of powder employed is 100 grams. The lower stopcock is closed, the cylinder exhausted, the stopcock opened and mercury then allowed to rise to the height which the atmosphere will support, the lower stopcock closed again, and the upper part of the apparatus opened to the air by means of the air-pump gauge stopcock; the operations are repeated, and the cylinder closed, unscrewed, and weighed. The mercury surrounding the powder grains is thus subjected to 2 atmospheres' pressure.

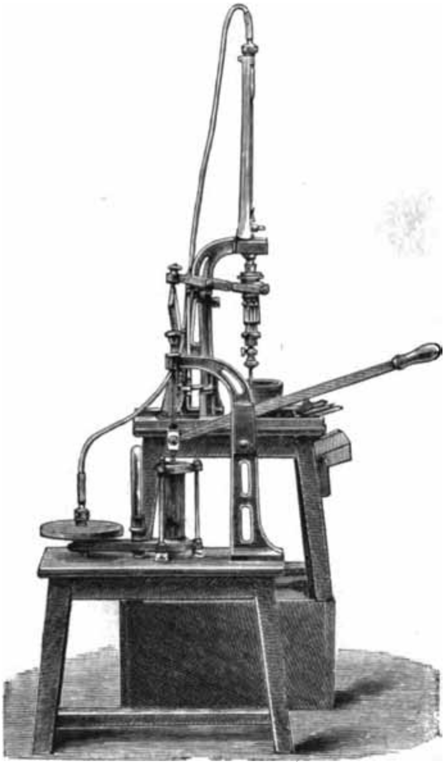

FIG. 3.

For the measurement of *velocity of projectile* and *pressure* in the bore of a gun, the reader is referred to Désortiaux's Upmann and von Meyer, where a good historical account of methods up to the date of that work will be found; to the Text Book of Service Ordnance (1886); or to the official Italian regulations for the proof of gunpowder—Regolamento per la Prova delle Polveri da Fuoco (1886).

Désignolle's, Brugère's, Abel's, Powders v. Picric acid.

E. C. Powder, Schultze's, and Johnson-Borland Powders v. Gun-cotton.[1]

Gun-cotton.

History and manufacture.—Braconnot, in 1832, observed that starch, woody fibre, and other similar substances, are converted by the action of strong nitric acid into a combustible product, which he called *xyloïdine*. Pelouze, in 1838, found that starch treated with strong nitric acid increased in weight; and that paper, cotton, and linen immersed in nitric acid of 1·5 sp.gr. become easily combustible. Schönbein, towards the end of 1845, announced the discovery of a new explosive substance, which he subsequently stated to have been obtained by treating cotton with a mixture of nitric and sulphuric acids. Böttger, in August 1846, found out the method of making gun-cotton, which Schönbein was keeping secret. The two chemists jointly submitted their discovery to the Germanic Confederation, but reserved the publication of their method of preparing gun-cotton. Several chemists having in 1847 independently discovered the method of preparing gun-cotton by means of a mixture of nitric and sulphuric acids, Schönbein and Böttger then stated this to be their process. The manufacture of gun-cotton was undertaken in England, France, and Russia; but the earlier attempts at manufacture were not satisfactory, the importance of purifying the cotton from fatty matter, and of washing the gun-cotton thoroughly free from acid, not having at first been sufficiently felt to be essential to obtaining a safe and stable gun-cotton.

Von Lenk, in Austria, between 1849 and 1852 made great improvements in the manufacture of gun-cotton; and in 1853 a factory was erected under his direction at Hirtenberg, near Vienna, in which (and at Reny in Vienna) the manufacture was continued until 1865, when the manufacture and use of gun-cotton were officially put a stop to in consequence of the explosion of two magazines. Von Lenk used the cotton in the form of yarn; his principal improvements were the purification of the cotton from oily and other matters by boiling with caustic alkali, the nitration of the cotton in separate small charges, the dividing the operation of nitration into two stages: a short immersion (of some minutes) of the cotton in the mixed acids, the removal of the cotton with a sufficiency of absorbed acids and allowing a long time (24 to 48 hours) for the completion of the nitration, also the careful washing of the gun-cotton to remove free acid.

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[1] See also a paper by the writer of the present article, read at Royal United Service Institution, April 5, 1889.

To remove acid, the gun-cotton after its nitration was whirled in a centrifugal machine, washed in copper drums with a large quantity of water, then placed in boxes in running water for three to six weeks, after which it was treated with a hot weak solution of potash, and again water-washed.

Von Lenk's gun-cotton was used in the form of yarn.

Sir Frederick Abel, adopting Von Lenk's method of nitrating the cotton, made very important improvements in the processes of manufacture, and by his researches has made large contributions to our knowledge of gun-cotton and of explosives in general. In the manufacturing process he introduced the use of cleaned cotton-waste, and by converting the gun-cotton into pulp so facilitated the washing that it can be effected in two or three days instead of in six or more weeks as in Von Lenk's process. Further, by compressing the finished pulp by hydraulic pressure, he rendered it possible to detonate it in an unconfined state. The pulping and compressing of the gun-cotton were introduced in 1865. These and other improvements have been embodied in the method of manufacture employed in the Government Gun-cotton Factory at Waltham Abbey, of which the following is a shortened account of that given in General Wardell's Handbook of Gunpowder and Guncotton.

The cotton employed is the best white cotton-waste, which has been freed from fatty oil by boiling with caustic alkali. The cotton is first picked over by hand to remove foreign substances, then passed through a teasing-machine which separates the fibre of the cotton and opens out knots and lumps, then cut by a machine into 2-inch lengths, and dried at about 80°. The dried cotton is weighed into charges of 1¼ lb., which are put into tin-plate boxes with tightly-fitting lids, and left until the next day.

To nitrate the cotton a mixture is previously made of 1 part by weight of nitric acid (of 1·5 sp.gr. at 15·6°) and of 3 parts by weight of sulphuric acid (of 1·85 sp.gr.); the employment of the strongest acids being of the greatest importance for the production of the most highly nitrated cotton. The acids are mixed in an iron vessel provided with an agitator, and are then run into iron store-tanks and left to cool. When required for use the mixed acids are drawn off from the store-tanks into a tank in connection with the dipping pans. These latter are of cast-iron; each holds about 220 lbs. of mixed acids, and is provided with a grating. The charge of cotton is then, by small portions, quickly immersed in the mixed acids. After an immersion of five or six minutes the cotton is removed to the grating, and squeezed by means of a lever with a plate at one end. The charge, which with the acid now weighs about 15 lbs., is placed in a closely-covered earthen pot, in which it is allowed to remain for at least twenty-four hours, during which time the pots are placed in constantly-flowing cold water. By this prolonged action the nitration of the cotton is completed; the cooling is needed to prevent complete decomposition of the product by oxidation, and the maintenance of a low temperature is said to be favourable to the production of gun-cotton with a low percentage of soluble nitro-cotton.

Much of the acids is then removed from the gun-cotton by means of the centrifugal machine, made entirely of iron, the contents of six pots being whirled for ten minutes at the rate of about 1,200 revolutions per minute. The gun-cotton is then, in small quantities, plunged by means of an iron fork beneath a cascade of water, which carries it into a large cistern, where it is kept stirred by a paddle-wheel, and is washed by fresh water continually admitted, until the gun-cotton has no perceptible acid taste, when it is whirled in a centrifugal machine, after which it receives two boilings by means of steam; the water being separated by the centrifugal machine after each boiling.

The next operation to which the gun-cotton is subjected is that of pulping, which is done by means of a slight modification of the machine like that known as 'the beater,' which is used in paper-making for pulping rags. The pulping takes five hours, and has to be so conducted that the pulp is not too coarse nor too fine.

From the pulping-machine the pulp is carried by pipes into large oval tanks called 'poachers,' each holding 1,500 gallons of water, in which a paddle-wheel rotates and keeps the pulp in agitation. About 18 cwt. of gun-cotton is washed in each poacher; after a six hours' washing, a sample of the pulp is tested by the 'heat test.' The treatment in the poacher serves not only to complete the washing, but also to thoroughly mix the products of a large number of nitrating operations, thus securing uniformity of product. If the pulp passes the heat-test after this treatment, it receives an addition of alkali sufficient to leave in the finished gun-cotton from 1 p.c. to 2 p.c. alkaline matter calculated as $CaCO_3$. By means of vacuum-pressure the pulp is then drawn up into the 'stuff-chest,' a cylindrical iron tank, large enough to hold the contents of one poacher, and in which revolving arms keep the pulp uniformly mixed with the water, so that it can be drawn off as required to be moulded into the cylinders and slabs required for service use. The requisite quantity of suspended pulp is found by means of small measuring-tanks, and is run into moulds of the required size and shape. The moulds have bottoms of fine wire gauze, through which a large part of the water is sucked from the pulp by evacuation. Hydraulic pressure of about 34 lbs. per sq. inch is then applied, which squeezes out some of the water, and gives sufficient consistency to the gun-cotton to allow of careful handling. The mass is then removed to the press-house, and there subjected to powerful hydraulic pressure of about 5 to 6 tons per sq. inch.

Those slabs and cylinders which are to serve as primers (*i.e.* which are dried and receive the fulminate charge, and by their own detonation cause that of the moist gun-cotton) have holes bored in them while moist, to receive the tube of the detonator; and the slabs of wet gun-cotton may be sawn, or turned on a lathe to any required shape. Primers are dried at a low temperature.

The 'heat-test,' referred to above, consists in heating in a test-tube placed in a water-bath maintained at 150°F. (65°·6C.) 20 grains of pulp, squeezed and dried at 120°F. (48°·8C.), or of washed and dried finished gun-cotton, and observing the time required to cause slight colouration of a small piece of moistened potassium iodide and starch paper. Fixed conditions have to be adhered to in carrying out the test, and the gun-cotton should cause no colouration of the test-paper in ten minutes.

Composition.—Gun-cotton, when the process of manufacture has been well conducted, and when the strongest acids have been used, has the composition of trinitrocellulose, $C_6H_7(NO_2)_3O_5$.

This composition was deduced by Sir Frederick Abel from the results of a large number of analyses (in which C, H, and N were determined) of gun-cotton of Waltham Abbey make. The mean numbers given by these analyses of the dry gun-cotton, ash deducted, are given below, and are compared with the percentages calculated for trinitrocellulose:—

	Mean of analyses.	$C_6H_7(NO_2)_3O_5$.
Carbon . . .	24·57	24·24
Hydrogen . .	2·46	2·36
Nitrogen . .	13·83	14·14
Oxygen . . .	59·14	59·26

The percentage of carbon is slightly raised, and that of nitrogen slightly depressed, by the presence in the gun-cotton of a few percents of less highly nitrated cellulose than the trinitro- derivative, and soluble in ether-alcohol (Abel, Tr. 1866, 156, 269–308).

The formation of trinitrocellulose from cellulose is represented by the equation:

$$C_6H_{10}O_5 + 3HNO_3 = C_6H_7(NO_2)_3O_5 + 3H_2O,$$

from which 100 parts by weight of cotton should give 183·3 parts by weight of trinitrocotton.

Sir Frederick Abel (in the above-mentioned paper) gives the results of a large number of synthetical experiments, in which a mixture of 1 part by weight of the strongest nitric acid (1·52 sp.gr.) and 3 of sulphuric acid, as in the Waltham Abbey manufacture, was employed. 3·7 grammes of purified and finely-carded cotton-wool, subjected at 15° to six successive treatments with 60 to 70 parts of mixed acids, increased in weight 79·4 p.c. by one hour's treatment, reached a maximum increase of 82·1 p.c. in about forty hours' treatment; longer treatment caused a slight falling off from the maximum. With 50 parts by weight acid to 1 of cotton, an increase of 82·0 p.c. and 82·6 p.c. resulted in two experiments from twenty-four hours' treatment, and of 81·9 p.c. from forty-eight hours' treatment of another portion of cotton. (The increase in weight refers of course to well-washed and dried product.) The products in these experiments contained very small quantities only of matter soluble in ether-alcohol. With 10 to 15 parts by weight of mixed acids to 1 of cotton (*i.e.* about the proportion of acids employed in the actual manufacture) the maximum increase was 80 p.c., the result of twenty-four hours' action; the products of three experiments contained notable proportions of matter soluble in ether-alcohol.

Purified cotton-yarn (such as then used for the manufacture of gun-cotton) treated with 60 parts mixed acids to 1 of cotton, increased in weight 81 p.c. by twenty-four hours' immersion, and about 78 p.c. by forty-eight hours' treatment.

The maximum increase found, 82·6 p.c., is a close approach to the theoretical 83·3 p.c., and confirms Hadow's previously observed increase of 81·3 p.c.

On the manufacturing scale, about 176 parts gun-cotton are obtained per 100 of cotton.

Berthelot, following Vieille, regards gun-cotton as $C_{24}H_{29}(NO_2)_{11}O_{20}$ (mol. wt. 1143).

He finds the heat evolved by the nitration of cotton in accordance with the equation

$$C_{24}H_{40}O_{20} + 11HNO_3 = C_{24}H_{29}(NO_2)_{11}O_{20} + 11H_2O,$$

to be 11 × 11·4 = 125·4 kilogramme degrees per 1·143 kilogramme of gun-cotton formed. The heat of formation of hendecanitrocellulose from its elements (diamond carbon, gaseous hydrogen, oxygen, and nitrogen) Berthelot finds to be + 624 kilogramme-degrees per 1·143 kilogramme; or, + 546 kilogramme-degrees per 1 kilogramme.

Properties.—Gun-cotton is a solid, having an absolute (*i.e.* when freed from air) specific gravity of 1·66 at 15·°6. The apparent specific gravity (*i.e.* with the included air) of dry compressed Waltham Abbey gun-cotton at 15·°6 is about 1 or a little higher than 1.

Gun-cotton is insoluble in water. Trinitrocellulose is insoluble in a mixture of ether and alcohol, but gun-cotton contains some percents of less highly nitrated cellulose soluble in ether-alcohol. Gun-cotton, when free from unnitrated cotton, is soluble in ethyl acetate; and in nitrobenzene, with which it forms a jelly.

Gun-cotton is reconverted into cotton by the action on it of alcoholic potassium sulphydrate. This reaction, due to Hadow, was found by Abel (*l.c.*) to give 53·6 p.c. to 55·4 p.c. cotton; trinitrocellulose should give 54·54 p.c. cotton. This reaction is of great importance, as it shows that gun-cotton (like nitroglycerin) is a nitric ether, yielding on reduction the hydroxylic body from which it was formed, and not an amido- derivative. It can therefore be represented as

$$C_6H_7O_2.(ONO_2)_3.$$

Air-dried (air under ordinary conditions) gun-cotton retains 2 p.c. of moisture. In this condition, on application of flame, a cylinder of compressed gun-cotton burns in the open air very rapidly with a long and fierce flame without smoke; the flame coloured yellow by the sodium salts. The rate of combustion of the gun-cotton varies with its condition; thus, gun-cotton plait in the form of a flat tube burns very much more quickly than gun-cotton yarn. The gun-cotton, as it leaves the hydraulic press, contains about 15 p.c. water, and is then not combustible; when held in a flame, it only smoulders as it partially dries.

Briskly heated in small quantity in the form of loosely-twisted yarn, gun-cotton was found to explode at 150° (Abel).

Gun-cotton can be exploded by percussion; but when struck by an iron hammer on an iron anvil, the portions directly struck by the hammer detonate, but the rest of the gun-cotton remains unexploded. Thus, cylinders of dry compressed gun-cotton 1 inch in diameter and 1 inch thick placed between two smooth brass plates and on a flat anvil, received the blow of a 50 lb. weight falling from various heights. Only partial detonation of the gun-cotton was obtained, even at the greatest available height of 39 feet; a small portion detonating, the rest being dispersed unburnt. Similar results were given by small slabs of dry gun-cotton 1 inch square and 0·1 inch thick. Cylinders of dry compressed gun-cotton (of the same density and diameter, but differing in thickness and therefore in weight) were suspended by strings round their circumference and fired at from a Martini-Henry rifle, using the service ammunition (the bullet being of lead hardened with tin), and at a distance of 100 yards. 4-ounce and 8-ounce cylinders were repeatedly perforated by the bullet without being ignited. 12-ounce cylinders were inflamed, but not exploded; 16-ounce cylinders were exploded, portions in some instances being dispersed burning. Wooden boxes containing dry compressed gun-cotton, both closely and loosely packed, have been repeatedly fired at from rifles, the result being that the contents of the box were generally inflamed, but never exploded; while similar packages containing dynamite or other nitroglycerin preparations were always violently exploded by being fired at (Abel, Tr. 1874, 359–362). The use of moist gun-cotton has rendered any danger from shock still more remote.

The experience of years has shown that well-washed gun-cotton is a safe and stable explosive, and there can be little doubt that many of the earlier explosions of gun-cotton must have had as their cause insufficient washing from acids.

Combustion, products and heat of.—Gun-cotton does not contain sufficient oxygen for complete combustion into CO_2, H_2O, and N; the equation

$$2C_6H_7O_2(NO_3)_3 + 9O = 12CO_2 + 7H_2O + 6N$$

shows that cellulose trinitrate requires 24·8 p.c. more oxygen for complete combustion. Carbonic oxide and hydrogen are, therefore, naturally to be expected in quantity in the gases of combustion.

In the flaming combustion of gun-cotton, when the gases were allowed to escape freely at nearly atmospheric pressure, Sarrau and Vieille found a large quantity of nitric oxide, NO, in the gases; about $\frac{1}{4}$ of the volume of the dry gases.

When the gun-cotton is inflamed in a closed vessel, in which the gases of combustion cause a moderate pressure, no oxide of nitrogen is formed. Von Karolyi exploded gun-cotton, in quantities of 10 grams, in small cast-iron cylinders of such strength as just to yield to the pressure of the gases produced by the combustion. These cylinders containing the gun-cotton were made air-tight, provided with the means of inflaming the gun-cotton by an electrically-ignited platinum wire, and inclosed in a spherical shell of about 5 litres capacity, which was exhausted before the explosion, and in which the permanent explosion-gases of the gun-cotton produced an excess of pressure of about half an atmosphere, which enabled portions of the gases to be removed, by means of a stopcock, for analysis. Von Karolyi found the permanent gases to consist of CO_2 28·5, CO 39·8, CH_4 9·9, H 4·4, N 17·4 volumes per 100 (P., April, 1863). Abel repeated Von Karolyi's experiments, and found acetylene always present in considerable quantity in the gases; an analysis of the permanent gases obtained from 10 grams of gun-cotton in two different experiments is given:—

Experiment 1: CO_2 19·69, CO 39·87, C_2H_2 7·85, CH_4 3·45, H 15·82, N 13·32 vols. per 100.

Experiment 2: CO_2 18·97, CO 41·80, C_2H_2 6·36, CH_4 3·87, H 17·02, N 11·98 vols. per 100.

Sarrau and Vieille (C. R. 90, 1058) have ascertained the volume (at 0° and 760 mm.) and the composition of the permanent gases produced by the explosion of gun-cotton in a closed vessel, and find that both vary with the density of the charge $\left(\frac{\text{volume of gun-cotton}}{\text{capacity of vessel}}\right)$, *i.e.* with the pressure ensuing on the explosion. The following are some of the results obtained:

	Density of charge	Volume of gases (at 0° and 760 mm.) given by 1 gram gun-cotton
(1) . .	0·01	658·5 cc.
(2) . .	0·023	670·8 cc.
(3) . .	0·2	682·4 cc.
(4) . .	0·3	—

Composition of the gases per 100 *volumes.*

	(1)	(2)	(3)	(4)
CO_2 . .	21·7	24·6	27·7	30·6
CO . .	49·3	43·3	37·6	34·8
H . .	12·7	17·2 [1]	18·4	17·4
N . .	16·3	15·9	15·7	15·6
CH_4 . .	none	trace	0·6	1·6

With these higher pressures, equivalent to higher temperatures, the composition of the gases is simpler; they contain neither acetylene nor oxide of nitrogen, and with increase of pressure there is increase of CO_2 and H, and decrease of CO; oxidation of CO by H_2O evidently occurring, and the composition of the gases being the result of a balance between the oxidising action of H_2O on CO, and of the reducing action of H on CO_2.

Sarrau and Vieille, using Berthelot's formula for gun-cotton, equate its decomposition by explosion thus: $C_{24}H_{29}(NO_2)_{11}O_{20}$

(*a*) When density of charge is 0·023

$$= 15CO + 9CO_2 + 11H + 9H_2O + 11N;$$

(*b*) When density of charge is 0·3

$$= 13CO + 11CO_2 + 15H + 7H_2O + 11N;$$

the reaction with high density of charge (which would be the condition in actual use) tends to approach the result:

(*c*) $12CO + 12CO_2 + 17H + 6H_2O + 11N$. The agreement of the equations with the results of analysis is, however, only moderately approximate.

For equation (*a*) the calculated quantity of heat evolved for constant pressure (for constant volume the quantities of heat are about $\frac{1}{100}$ higher), and the volume of the gases reduced to 0° and 760 mm. (per 1 kilogram of dry and ash-free gun-cotton), are as follow, compared with Sarrau and Vieille's experimental values:—

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[1] These gases add up to 101·0. Perhaps 17·2 H should be 16·2. The percentage composition of the gases is not given in Sarrau and Vieille's paper, but in Berthelot's book.

	Quantity heat. Calories.		Volume gas. Litres.	
	Calculated.	Found.	Calculated.	Found.
Water liquid	1076	1071	684	687·5[1]
Water gaseous	997·7	—	859	—
For equation (*c*):				
Water liquid	1074	—	743	—
Water gaseous	1022	—	859	—

Gun-cotton, therefore, on explosion gives (for equal weights) more gas and a greater quantity of heat than gunpowder or mining-powder, more gas but a smaller quantity of heat than nitroglycerin.

The heat evolved by the complete combustion of gun-cotton in oxygen gas, and under constant pressure, was found by Sarrau and Vieille to be per 1 kilogram of gun-cotton 2,302 kgm.-degrees when the water formed was liquid, 2,177 when gaseous.

Capt. A. Noble (Lecture to Inst. Civil Engin. April 3, 1884) obtained more permanent gases from detonated pellet gun-cotton than did Sarrau and Vieille with low densities of charge. Thus he states that 1 kilogram of gun-cotton (containing 2·36 p.c. moisture and 0·36 p.c. ash) produces, at 0° and 760 mm. pressure, about 730 litres of permanent gases (water liquid); or, per 1 kilogram of dry and ash-free gun-cotton, about 750 litres of permanent gases. The gases were produced in the steel explosion vessel under very high pressure. The volume of gases agrees fairly well with that calculated for Sarrau and Vieille's equation (*c*) for high density of charge.

Capt. Noble states that the *temperature* of explosion of gun-cotton is at least double that of gunpowder; the latter temperature he estimates for ordinary English gunpowder at about 2200°.

The composition of the gases produced by the detonation of dry and of moist gun-cotton is given on p. 69.

Detonation.—Nobel, in 1864, had discovered that nitroglycerin could be *detonated* by means of fulminate of mercury; and in 1868, Abel found that air-dry compressed gun-cotton (like nitroglycerin) could be *detonated* by the explosion in close contact with it of 5 grains (0·32 grm.) of fulminate of mercury, contained in a thin metal case (Tr. 1869, 159, 498). He subsequently (Tr. 1874, 337-395) found that by increasing the strength of the envelope, viz. by making the case for the fulminate of stout sheet-iron, and inserting it in a closely-fitting hole in the gun-cotton, the latter could be detonated with certainty with only 2 grains (0·13 grm.) of the fulminate. In practice, however, much larger quantities of fulminate are used, in order to have a good initial detonation, and to provide for the possibility of the detonator-tube fitting too easily into the hole in the gun-cotton.

The explosion of the gun-cotton thus caused by that of the fulminate has been called *detonation* on account of the loud sound by which it is followed; it differs from the flaming combustion of gun-cotton by the immensely greater speed at which chemical action (oxidation of one part of the compound, the C and H, by another part, the NO_2) progresses in the gun-cotton, and by the consequent powerful mechanical effects produced by the gases formed. Sir F. Abel found the velocity of detonation of air-dry compressed gun-cotton to be about 18,000 feet per second; consequently the large volumes of heated gases produced at this great rate work destructively on nearer objects, and give rise to a condensed wave in the air, propagated with great velocity. Moreover, the air offers resistance to the motion of the gases produced at so great a rate, consequently the gases exert pressure on the gun-cotton and on the ground or other support on which it rests, producing powerful reaction effects.

For the detonation of unconfined gun-cotton by fulminate of mercury, it is essential that the former shall be in a condition to offer resistance to the shock of the fulminate, so that the energy of the shock shall heat the gun-cotton, not disperse it. Compressed gun-cotton meets this requirement, while in the form of wool or loose yarn it is scattered or inflamed, but not detonated.

R. Threlfall (P. M. 1886, 172) thus gives Berthelot's views on the theory of detonation: 'The kinetic energy of the shock of the explosion (by the detonator) is transformed into heat at the point (of the explosive) struck; the temperature of this point is thus raised to the temperature of explosion, a new shock is produced which raises the temperature of the neighbouring portions to the same degree; they then explode, and the action is thus propagated with an ever-increasing velocity.' The 'ever-increasing velocity' must refer to the commencing stage of the detonation, as Abel's measurements of the rate of detonation of gun-cotton and dynamite do not bear it out.

The detonation of gun-cotton is transmissible across an intervening air-space which varies with the weight of the charge; thus, the detonation of a ½ lb. cylinder of compressed gun-cotton, 3 inches in diameter, will cause the detonation of another similar cylinder placed on the ground at a distance of 1 inch, but not at a distance of 2 inches.

Fulminate of silver is in no way superior to fulminate of mercury in causing the detonation of gun-cotton. Nitroglycerin, chloride and iodide of nitrogen show a remarkable want of reciprocity in their behaviour to gun-cotton as regards detonation. Thus, while the detonation of ¼ oz. of gun-cotton caused the simultaneous detonation of a charge of nitroglycerin in a tin-plate vessel at the distance of 1 inch, and ½ oz. produced the same result across an air-space of 3 inches, 1 oz. of nitroglycerin detonated in close contact with a disc of compressed gun-cotton did not detonate it but only dispersed it. 100 grains of dry iodide of nitrogen was unable to cause the detonation of a pellet of dry compressed gun-cotton on which it rested; and 50 grains of chloride of nitrogen (covered with a film of water and contained in a thin watch-glass resting on the gun-cotton) was about the minimum quantity required to effect the detonation of the latter (Abel, Tr. 1869, 489).

With increase in the amount of water in the compressed gun-cotton, more fulminate of mercury is needed to effect detonation; the fulminate as usual being contained in a tin-plate tube

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[1] 671 litres from gun-cotton containing 2·4 p.c. ash.

and fitting closely in a central hole in the gun-cotton. With a total of 5 p.c. of water (*i.e.* 3 p.c. above the 2 p.c. of normal air-dry gun-cotton), detonation by 15 grains of fulminate of mercury is doubtful. Moist gun-cotton containing 12 p.c. water was detonated only once in seven experiments by a detonator containing 100 grains of fulminate; when the gun-cotton contained 17 p.c. water it required 200 grains of fulminate to detonate it with certainty.

Gun-cotton as it leaves the press, containing about 15 p.c. water, although quite uninflammable, can be readily detonated by the detonation in contact with it of about half an ounce of air-dry compressed gun-cotton. For the certain detonation of gun-cotton containing 20 p.c. water, a primer of about 1 ounce of dry gun-cotton is required; and when the gun-cotton has absorbed the maximum amount of water it is capable of doing (30–35 p.c.), for its certain detonation 4 ounces air-dry gun-cotton applied in close contact are necessary (Abel, Tr. 1874, 337). This discovery (which is due to the late Mr. E. O. Brown) has been of the greatest practical importance, as it has rendered the use of gun-cotton for military purposes very safe; permitting the great bulk of the gun-cotton to be kept in a moist and uninflammable state, while a relatively small quantity only of dry gun-cotton is needed for 'primers,' the dry primers being detonated by a suitable fulminate of mercury detonator.

The velocity of detonation of moist gun-cotton is greater than that of the dry, and the work done by the same weight of gun-cotton appears to be equal, whether it be employed in the dry or moist state.

As in the case of dry gun-cotton, detonation is propagated in masses of moist compressed gun-cotton in contact, provided the piece first detonated does not contain less water than the others; but for transmission of detonation in the open air through any considerable number of cylinders or slabs of moist gun-cotton, it is essential that they should be in contact, much shorter air-spaces than in the case of dry gun-cotton stopping the detonation.

The rate of detonation of moist gun-cotton is a little quicker than that of dry gun-cotton; and that of gun-cotton saturated with water (containing about 30 p.c. of it) is considerably quicker than that of the dry. Sir Frederick Abel (Rl. Soc. 1874) measured (by means of Capt. A. Noble's chronoscope) the rate of detonation of gun-cotton under different conditions, of dynamite, and of nitroglycerin.

Cylinders of compressed gun-cotton 3 inches in diameter were employed; they were placed on their bases, and when in a continuous train with their circumferences touching, and the measurements of velocity of detonation were made at intervals of 6 feet, or sometimes of 4 feet, in the train of gun-cotton. The following are some of the results obtained:—

—	Rate of progression of the detonation; feet per second		
	First 6 feet	Last 6 feet	Mean (of all the measurements)
Dry gun-cotton, 170 cylinders, touching . . .	17,466	17,738	17,122
	4 feet	4 feet	
" " ½-inch air-spaces, 28 feet . . .	15,676	16,218	16,776
	4 feet	4 feet	
Moist gun-cotton (15 p.c. water), 28 feet, touching .	18,416	18,040	18,375
Wet gun-cotton (30 p.c. water), 36 feet, touching .	22,574	19,240	19,948
Dry gun-cotton, containing 38 p.c. KNO_3, touching .	—	—	15,981

The above results show that there is a decided increase in the rate of detonation of gun-cotton, when the air in the latter is replaced by the very slightly compressible water—a behaviour recalling the greater velocity of propagation of sound in water than in air.

The velocity of propagation of sound, too, comes nearest to the detonation-velocities just given; thus, the experimental values for sound (of low intensity) in water at 8° is 4,708 feet per second, and in ice is 9,512 feet.

Wet gun-cotton, when frozen, is detonated with certainty by the fulminate detonators ordinarily used for dry gun-cotton (Abel, *v. supra*).

The gases resulting from the detonation of dry and of wet compressed gun-cotton have been examined by Capt. A. Noble and Sir Frederick Abel in continuation of their researches on explosives, and from their unpublished results the two following analyses are by their kind permission taken. The detonation was effected in a very strong steel explosion-vessel, in which the gases were formed under very great pressure. A correction should be made in the dry gun-cotton gases for the permanent gases (2CO + 2N) of the fulminate of mercury detonator, and for the same and those from the small quantity of dry gun-cotton priming in the case of the wet gun-cotton gases; but as the CO would be oxidised by the gaseous water to an unknown extent, the direct results are given.

Composition of the permanent gases, vols. per 100.

	Dry gun-cotton. 1,620 grains pellet. 130 grains fulminate mercury detonator	Wet gun-cotton
CO_2	24·24	32·14
CO	40·50	27·12
H	20·20	26·74
N	14·86	14·00
CH_4	0·20	none
	100	100

It is noticeable that Sarrau and Vieille's results for the composition of the gases of explosion of gun-cotton for the lower density of charge (*v. supra*) approach the composition of these detonation-gases of dry gun-cotton. The influence of the additional water on the gases of detonated wet gun-cotton, in oxidising CO to CO_2 with formation of H, is very marked.

For the condition of gaseous water, a greater quantity of heat will be evolved by the detonation of dry gun-cotton than by that of moist gun-cotton containing the same weight of the dry material; the volume of the gases will, however, be greater from the moist than from the dry gun-cotton. The volume of the permanent gases also will be greater with moist gun-cotton, owing to the H formed from the water.

Von Förster, in Germany, for special military use, coats pieces of moist compressed gun-cotton with a skin of dry gun-cotton by immersing them for about a quarter of a minute in acetic ether.

It has also been proposed to use paraffined gun-cotton instead of moist gun-cotton; and one of the German gun-cotton factories, that of Kruppamühle in Silesia, prepares it by immersing dry compressed gun-cotton in melted paraffin. The paraffin has the advantage over water that it does not evaporate; it is said to make dry gun-cotton less sensitive to shock, but it lowers the percentage of oxygen, and is stated to be inflammable.

Intensity of action.—General Abbot, in his Report, gives the intensity of action of compressed gun-cotton, detonated under water, as 87, Kieselguhr dynamite No. 1 being 100. The gun-cotton was of Stowmarket make, imported in 1871. He found the same value also for San Francisco gun-cotton; but the latter was uncompressed, being in the form of a bulky powder. In comparative experiments made in this country, under different conditions to General Abbot's, gun-cotton has shown a slightly greater intensity than dynamite; as, for instance, in the displacement of earth by the detonation of buried charges, and in the work of excavation done by their detonation in the borehole of lead cylinders. Experiments of Sir Frederick Abel's, by the latter method, with Waltham Abbey dry compressed gun-cotton and Nobel's Ardeer Kieselguhr dynamite No. 1, both of recent make, give the intensity of action of gun-cotton as 101, the dynamite being 100; experiments in which the same weight of fulminate was used being compared.

Uses.—Gun-cotton is almost exclusively employed for military purposes: for use in offensive torpedoes and in submarine mines, and for demolitions on land. The fact that the great bulk of the gun-cotton required for the former purposes can be stored and used in a moist and uninflammable condition, combined with its high efficiency, has made it the principal high explosive for both services in this country. This is the case also in Germany; and it is employed for naval use in most of the countries of Europe.

Soluble gun-cotton.—The part of Waltham Abbey gun-cotton soluble in a mixture of alcohol and ether is a less highly nitrated compound than trinitrocellulose; it approaches in composition dinitrocellulose. The following are results of some analyses:—

—	C	H	N	O
	p.c.	p.c.		
Specimen 1. Portion soluble in ether-alcohol .	30·51	2·91	—	—
„ 2. „ „ .	29·23	—	11·85	—
Mean results furnished by the gun-cotton after digestion with ether-alcohol	24·15	2·46	13·83	59·56
Dinitrocellulose (calculated)	28·57	3·17	11·11	57·15
Trinitrocellulose (calculated)	24·24	2·36	14·14	59·26

(Abel, Roy. Soc. 1866.)

A number of experiments on the manufacturing scale, and carbon estimations of the products, were made in 1868 by Sir Frederick Abel; they show the influence on the nitration of the cotton of an addition of water to the acids. The following mixtures were used for nitration:

—	Nitric acid. Sp.gr. 1·42	Water	Sulphuric acid. Sp.gr. 1·835	Specific gravity of mixture
Mixture 1 . .	60 lbs.	—	65½ lbs.	1·645
„ 2 . .	60 „	3 lbs.	65½ „	1·629
„ 3 . .	60 „	6 „	66½ „	1·618
„ 4 . .	60 „	9 „	65½ „	1·600

The nitrocottons made with these mixtures were prepared for analysis by dissolving them in alcohol-ether, filtering and precipitating them with boiling water. Suitably dried, they gave the following percentages of carbon:

Mixture 1. Preparation *a* . 28·56 p.c. C.
„ 1. „ *b* . 28·13 p.c. C.
„ 2. . . . . . 29·07 p.c. C.
readily soluble in alcohol-ether.

Mixture 3. Mean of 3 analyses . 30·08 p.c. C.
„ 4. . . . . . 26·88 p.c. C.
No. 4 difficultly soluble in alcohol-ether; solution very thick.

The nitrocottons made with the mixtures of acids 1 and 2 come near to dinitrocellulose in percentage of carbon; mixture 3 gave a product less nitrated than dinitrocellulose. The low percentage of carbon in the nitrocotton from mixture 4 is in all probability due to the formation of an oxidised product.

Nitrated gun-cotton. It has already been mentioned that 100 lbs. trinitrocellulose require 24·3 lbs. additional oxygen for complete combustion into CO_2 and H_2O; and gun-cotton, on account of the dinitrocellulose present, would require more oxygen. At an early period in the history of gun-cotton, this oxygen was supplied in the form of potassium or other nitrate. Two such preparations, bearing the names *tonite* and *potentite*, may be mentioned. The latter consists of a mixture of gun-cotton and potassium nitrate.

Tonite is a mixture of about equal weights of gun-cotton and barium nitrate; the gun-cotton is pulped, the mixture compressed into cartridges having a central cavity to receive the fulminate detonator. 100 lbs. trinitrocellulose would require 79·3 lbs. barium nitrate for its complete combustion; or, trinitrocellulose 55·9 p.c., barium nitrate 44·1 p.c. Good gun-cotton would require some more of the nitrate, and material with considerable quantities of soluble nitrocotton would of course require still more.

Tonite has been made for many years at Faversham in Kent, and is used for rock-blasting.

Sir F. Abel found its intensity of action, by the lead cylinder method, to be 84; Kieselguhr dynamite No. 1 being = 100.

General Abbot (Addendum I. to his Report) examined tonite of San Francisco make, consisting of 52·5 p.c. gun-cotton, and 47·5 p.c. barium nitrate. Detonated under water it gave intensity = 81, dynamite being 100.

While the intensity is lower than that of gun-cotton, these values show that the gun-cotton is remarkably economised in tonite.

Two preparations, intended for use as sporting and rifle powders, may be briefly mentioned here:—

E. C. powder, a granulated mixture of nitrocotton (containing much nitrocotton soluble in ether-alcohol) and nitrates.

Johnson's powder is a granulated mixture of dinitrocellulose (or lower nitrocellulose) with barium and potassium nitrates, or with barium nitrate, according to circumstances. The dried explosive is steeped for a few minutes in a solution of camphor in a volatile solvent, such as petroleum ether, which is distilled off at a low temperature in a suitable pan provided with a still-head and stirring arrangement, and the camphorated explosive heated for a short time at a temperature not exceeding 100°. At this temperature it is claimed that the camphor exerts a remarkable gelatinising action on the nitrocellulose, the grains of which become tough and hardened throughout their mass. The camphor is sublimed off and recovered. It is claimed for this powder that, while it burns readily, its hardness and density cause it to burn with suitable slowness.

English Pat. No. 8,951, July 25, 1885; Austrian Pat. No. 2,387, Nov. 25, 1887.

Nitrolignin is wood which has been more or less nitrated by immersion in mixed nitric and sulphuric acids. The most noteworthy preparation having nitrolignin as a constituent is *Schultze's powder*, which was introduced in Germany more than twenty years ago by Captain E. Schulze. Wood grains are purified by boiling with dilute sodium carbonate, by washing with water, and treatment with solution of chloride of lime. They are then washed, dried, and immersed in the mixture of strong nitric and sulphuric acids for two or three hours, with frequent stirring, the acids being kept cool. The nitrated wood is freed from most of the acid in a centrifugal machine, washed with water, boiled with dilute sodium carbonate, and dried. The nitrolignin appears to contain a large quantity of matters soluble in ether-alcohol, and, besides insoluble nitrolignin, some unconverted wood. It is steeped in a solution of potassium and barium nitrates, and dried at a low temperature. Its principal use has been as a sporting powder. There is also a Schulze's blasting powder, containing charcoal as an additional constituent.

NITROGLYCERIN.

Nitroglycerin was discovered in 1847 by Sobrero. In a letter to M. Pelouze (C. R. 24, 247), he states that when glycerin is poured, with stirring, into a mixture of 2 vols. of sulphuric acid of 66° Baumé, and 1 vol. of nitric acid of 43°, cooled by a freezing mixture, the glycerin dissolves therein without perceptible reaction, and that on pouring the mixture into water an oily substance, heavier than water, is precipitated.

Sobrero described some of the properties of nitroglycerin, but did not analyse it.

No practical application of importance of the properties of nitroglycerin was made until 1863, when its preparation on a large scale was commenced by Mr. A. Nobel, who started two nitroglycerin factories near Stockholm and near Lauenburg. Between 1863 and 1865 increasingly large quantities of nitroglycerin were made and exported; but serious accidents occurred about the year 1866 in different parts of the world whither the nitroglycerin had been exported, and were followed by legislation on the part of several governments prohibitive of its use. This restrictive legislation was met by Nobel by the introduction of dynamite in 1866–67, the carriage and use of this preparation of nitroglycerin being comparatively safe.

The chemical basis of the processes by which by far the greater part of the total output of nitroglycerin is made is, essentially, that of Sobrero's method of preparation. In the earlier forms of apparatus the glycerin was allowed to flow in a thin stream into the mixed acids, the weights of the charges varying from about ¾ ton to about two tons of mixed acids (2 parts by weight of sulphuric acid to 1 of nitric acid) and glycerin equal to from about one half to one third of the weight of the nitric acid, all three substances being practically anhydrous. The nitrating vessel was a leaden or lead-lined, or cast-iron vat, and during the reaction the contents of the vat were mixed by a mechanical agitator, while cooling was effected by an external water-jacket, and internally, by water flowing through lead coils, the temperature not being allowed to exceed 27°.

Mowbray, in his earlier method of manufacture of nitroglycerin in the United States, introduced important improvements, by the use of pure glycerin and of nitric acid freed from nitrous acid by the passage through it of a current of air, and by the use of compressed air for mixing the reacting glycerin and mixed acids in the nitrating vessel. Mowbray carried out the nitration in earthenware pots, using a large number of them and small charges, each pot containing about 17 lbs. of mixed acids, into which 2 lbs. of glycerin was allowed to drop by means of a siphon; the operation of nitration taking place simultaneously in all the vessels.

The method of manufacture was improved, some years since, by introducing the glycerin in a spray into the mixed acids, compressed air and a simple injection apparatus being used to produce the spray. This is the method in use in the nitroglycerin factory of Nobel's Explosives Company, at Ardeer, Scotland. It was described by the manager, Mr. G. McRoberts, in a paper to the Glasgow Philosophical Society, April 25, 1883, and the following account of the method of manufacture at Ardeer is condensed from that paper, and is mainly in his own words. The sulphuric and nitric acids are first mixed together and cooled by means of cold water and by agitation with compressed air. The mixture is then run into a large leaden apparatus, which is kept cool by being surrounded with cold water, and by running cold water through leaden worms, which coil round the interior of the apparatus. When the acids have fallen to a low enough temperature, glycerin is injected into the mixture by means of compressed air, driven through a peculiar kind of injection apparatus. The glycerin enters the acids in a fine spray, and is immediately nitrated. Considerable heat is developed during the process, and is indicated by a delicate thermometer dipping into the mixture of acids and nitroglycerin, which is carefully watched during the operation. The temperature is thoroughly under control, and is never allowed to exceed a certain fixed limit; it is not allowed to exceed this limit, not only on account of the danger, but also because other bodies would be formed, with corresponding loss of nitroglycerin. The end of the nitration is made known at once to the attendant by the fall of the thermometer; and when the temperature has descended to a certain degree, the contents of the nitrating apparatus, amounting to about 4 tons of acids and nitroglycerin, are run off into another leaden tank in a separate building, in which the mixture is allowed to stand for some time. The nitroglycerin being of less specific gravity than the mixed acids, and being insoluble in them, immediately commences to separate; and in a short time, generally in about an hour, the separation is complete. It is then drawn off and washed in water, and the mixed acids are transferred to a settling tank, where any globules of nitroglycerin remaining in the acid come to the surface, and are subsequently removed. The acids are preserved for further treatment, and are again utilised in the manufacture. The nitroglycerin, after copious washing with water, is finally washed in an alkaline solution until every trace of free acid has disappeared. It is then carefully filtered into another tank, in which it is stored until required for conversion into dynamite. The operations in every part of the process are under careful superintendence, to guard against abnormal increase of temperature or deviation from the routine method of working, which might result in an accident. The arrangements and discipline are so good that there has been no fatal accident in the nitroglycerin department at Ardeer.

The sulphuric acid used at Ardeer is the purest and most highly concentrated procurable. The nitric acid is made there; it has a specific gravity of 1·50, and is of a pale straw colour. The glycerin is practically anhydrous, of 1·26 sp.gr., and is free from lime, iron, alumina, chlorides, and fatty acids. The presence of iron and alumina, or of chlorine, in the glycerin or in the acids, seriously interferes with the separation of the nitroglycerin. If the acids are not of the highest gravity, there is an immediate falling off in the yield of nitroglycerin; but when acids of uniformly high gravity and good glycerin of 1·26 sp.gr. are regularly used, Mr. McRoberts's experience is that the yield is remarkably regular.

From the equation representing the formation of nitroglycerin :—

$$C_3H_5(OH)_3 + 3HNO_3 = C_3H_5(ONO_2)_3 + 3H_2O,$$

1 part by weight of glycerin should yield 2·47 parts of nitroglycerin. But Mr. McRoberts states that in practice only 2 parts are as a rule obtained from 1 of glycerin, and says that on the working scale it may be broadly stated that 1·2 ton of nitric acid of 1·5 sp.gr., and 2 tons of sulphuric acid of 1·84 sp.gr., and 7½ cwts. of glycerin of 1·26 sp.gr., yield 15 cwts. of nitroglycerin.

A short account of the method of manufacturing nitroglycerin employed by the American Forcite Company is given by Eissler (Modern High Explosives, 88–90, 1886). He states that for every operation 600 lbs. of nitric acid and 1,100 lbs. of sulphuric acid are employed. The acids are mixed in a leaden vat, and allowed to stand twelve hours to cool; when cooled the mixed acids are charged into the nitroglycerin apparatus, in which water circulates through six lead worms, and around it is a water-jacket. 240 lbs. of glycerin is required for a charge; the glycerin is introduced in a spray into the acids by means of a special injector, which works by compressed air. The operation takes an hour and a half; during the operation the thermometer is constantly watched. When all the glycerin has been injected into the acids in the nitrating-vat, the contents of the latter are discharged into a separator made of lead, in which the nitroglycerin after a few minutes collects on the surface of the acids. It is skimmed off by means of a dipper as it rises to the surface, and is poured into washing vessels, in which it is washed with cold water. It is then run into another tank, and washed with solution of carbonate of soda until it shows alkaline reaction with litmus paper, and is then passed through a cotton filter into a tank in which it remains until required for use. During the operation of nitration, if the temperature rises above 28°, the contents of the nitrating vat are discharged into a large tank nearly full of water, and the same is done in case of a rise of temperature in the separator.

The building in which the nitroglycerin is made is a two-storied one; the nitrating vat is in the top story, and the separators and washing-vessels are placed each at a lower level than the one in which the preceding operation has been conducted, the different vessels being provided with taps near their bottoms.

The method of making nitro-glycerin introduced in 1872 at Vonges by MM. Boutmy and Faucher is essentially different from the foregoing methods of preparation. An account of their method is given in the Comptes Rendus of 1876, having been sent in in 1872. Their object was to render the process of manufacture safe by avoiding any considerable rise of temperature; and this they tried to do (1) by making the reaction slower by forming with the glycerin beforehand a compound, which would be decomposed only by degrees by the formation of nitroglycerin; and (2) by endeavouring to eliminate from the final reaction by which the nitroglycerin is formed, the heat disengaged by the combination of the water of hydration of the glycerin, and of the nitric acid, with the sulphuric acid.

To do this, they prepared beforehand sulphoglyceric acid, by treating glycerin of 30° Baumé with about three times its weight of sulphuric acid of 66° Baumé; also a mixture of equal weights of sulphuric acid of 66° Baumé and of nitric acid of 48° Baumé, which they called sulphonitric acid. Much heat is evolved in making these two mixtures. The two preparations were then to be mixed, keeping to the proportions: glycerin 100, nitric acid 280, sulphuric acid 600, or close to them. They state that the rise of temperature is then limited to from 10° to 15°, and that the reaction could be considered as terminated only at the end of twenty-four hours. The nitroglycerin forms a fairly distinct layer above the acids, from which it can be separated by decantation.

The decomposition of the sulphoglyceric acid by the nitric acid stops only when the water formed in the reaction becomes sufficient in quantity to create a new state of equilibrium; but secondary reactions must occur, as the weight of nitroglycerin actually obtained is always less than the theoretical amount (247 per 100 of glycerin), varying from 160 p.c. to 195 p.c., according to the temperature and hygrometric state of the air.

Désortiaux (Traité sur la Poudre, &c. 684-686) describes the Boutmy-Faucher process as having been in use at Vonges since 1872. The sulphoglyceric acid mixture was made in a cast-iron vessel provided with a suitable stirrer, and with a jacket through which water constantly flowed. The conversion into nitroglycerin was effected in cylindrical stoneware vessels, into which the sulphoglyceric mixture was poured, then the sulphonitric mixture; the scale of operation being 10 kilograms (about 22 lbs.) of glycerin, the proportions as given above. During the first quarter of an hour there is a rise of temperature; the maximum rise varies from 27° in November to 48° in August, according to the season. (This is a greater rise of temperature than stated by Boutmy and Faucher.) The nitroglycerin appears as drops on the surface of the liquid, eventually forming a tolerably distinct upper layer. The reaction is allowed the night to complete itself in, after which the nitroglycerin is removed by siphoning, then suitably washed with tepid water, then with water containing bicarbonate of soda. The washed nitroglycerin is turbid with water, from which it is freed by filtration through sponge. Désortiaux states that the yield of nitroglycerin by this process varied from 185 to 190 per 100 of glycerin.

The Boutmy-Faucher method of preparing nitroglycerin has been used in this country for a short time, in the year 1882, at Pembrey Burrows in Caermarthenshire, but was discontinued after an accident which occurred in the converter in November 1882. The process was worked on a very large scale, as from Colonel Majendie's report on the explosion it appears that the license permitted the nitration of 1,500 lbs. of glycerin at one charge. The report points out grave defects in the converter used; and in Dr. Dupré's report to the Inspector of Explosives he shows that an impure glycerin had been employed, and comments unfavourably on the Boutmy-Faucher process on the ground that the relative safety of the process during the period of reaction is balanced, and perhaps more than balanced, by the slowness of production and separation of the considerable quantity of nitroglycerin finally obtained. Consequently, the latter remains for several hours in contact with a strong acid, a condition very favourable to its decomposition; the danger from this cause being greater, the greater the quantity of nitroglycerin.

So far as the writer knows, this process is not now in use in this country; and the whole quantity of nitroglycerin made by it can never have been a large fraction of the total output.

Properties.—Nitroglycerin is a heavy oily liquid; its specific gravity, at 15°·6, is 1·60.

It is often described as being of a pale-yellow colour; but Böckmann (Die Explosiven Stoffe, 1880, 294) speaks of it as colourless, or but very slightly yellow; McRoberts (Notes on Nitroglycerin, &c. 1883), as being as colourless as water when pure, but of a pale-brown colour as obtained on the commercial scale. M. Hay (B. 18, 269, 1885, abstract from Moniteur Scientifique, [3] 15, 424-438) describes it as being colourless when pure, while the nitroglycerin obtained from dynamite is slightly coloured on account of the action upon it of the small quantity of alkali added to the dynamite. When pure, nitroglycerin may be kept for an indefinitely long time without decomposition. Thus, Berthelot records the keeping of a specimen for ten years, McRoberts one for nine years, without any appearance of decomposition. But the presence of moisture, or of a trace of free acid, is able to start the decomposition of nitroglycerin; sunlight also causes it to decompose (Berthelot).

When cooled, nitroglycerin solidifies. The freezing temperature appears to depend much on the time of exposure, so that nitroglycerin may be said to freeze at from +8° to −11°, different nitroglycerins behaving differently in this respect, minute quantities of impurities preventing or delaying crystallisation. The frozen nitroglycerin melts at about 11° (Beckerhinn, Jahresbericht der chemischen Technologie, 22, 481-7, 1876). Nitroglycerin crystallises at about +4·4°, and requires exposure for a considerable time to a temperature of 10° before it melts (McRoberts).

Mowbray found that his nitroglycerin contracted about $\frac{1}{12}$ of its original volume on freezing.

Beckerhinn (*l.c.*) made a number of estimations of the specific gravity of Nobel's nitroglycerin, which was procured from different factories. The specific gravity of the solid nitroglycerin was taken at +10° (nearly at its melting-point); all the nitroglycerins gave very concordant values, having a specific gravity of 1·735. The specific gravity of the liquid nitroglycerin was found by numerous estimations to be 1·599; whence, in solidifying, nitroglycerin contracts about $\frac{10}{121}$ of its original volume. Consequently, Nobel's and Mowbray's nitroglycerin agree in this respect.

Beckerhinn found for the specific heat of liquid nitroglycerin (between 9·5° and 98°) the value 0·4248, and for the latent heat of fusion of solid nitroglycerin the value 33·54 heat-units.

It is inodorous, has a sweet, pungent, aromatic flavour, and even in very small quantity has toxic properties, first noticed by Sobrero. Schuchardt (D. P. J. 180, 406) tried the effect on himself of swallowing a drop of nitroglycerin. He soon experienced vertigo, headache, lassitude, and drowsiness; and an hour later, having incautiously taken more nitroglycerin, the symptoms mentioned increased in severity, and were followed by nausea and loss of consciousness. No ill effects were, however, felt next day. Nitroglycerin has lately been used medicinally, for treatment of *angina pectoris*.

The handling of nitroglycerin is followed by similar unpleasant symptoms; but continued handling of the nitroglycerin for a day or two gives immunity from the headache. Mr. McRoberts states that at Ardeer the workmen who work with nitroglycerin every day never have headache, and are remarkably free from diseases of any kind.

Nitroglycerin is generally described as being almost insoluble in water, but Berthelot describes it as being slightly soluble in water, and M. Hay (*l.c.*) has recently stated that 1 gram of nitroglycerin dissolves in about 800 c.c. of water. McRoberts states that it is soluble in all proportions in ether, chloroform, glacial acetic acid, benzene, nitro-benzene, and nitric acid; soluble in 1·75 parts methylic alcohol, and in 2·8 parts absolute alcohol, sparingly soluble in sulphuric acid, and practically insoluble in water and carbon disulphide. M. Hay states that 1 gram of nitroglycerin dissolves readily in 4 c.c. absolute alcohol (*i.e.* 1 part by weight in 3·2 parts of alcohol).

Composition.—Nitroglycerin is glyceric trinitrate $C_3H_5(ONO_2)_3$. The recorded analyses of nitroglycerin are not numerous. Railton (C. J. [7] 222–224), in 1853, made two somewhat rough estimations of the ratio C:N in nitroglycerin. Beckerhinn made two analyses of a sample of nitroglycerin (quoted by Désortiaux) and found:

	Carbon p.c.	Hydrogen p.c.	Nitrogen p.c.	Oxygen p.c.
(*a*) . .	15·42	2·27	—	—
(*b*) . .	15·62	2·40	17·90	—
$C_3H_5(NO_3)_3$ requiring	15·86	2·20	18·50	63·44

Sauer and Ador (B. [10] 1982–1984), in 1877, made estimations of nitrogen by Dumas's method in three different nitroglycerins obtained from three different samples of dynamite. They found:

I. *a*.	18·35 p.c. N	II.	18·45 p.c. N
I. *b*.	18·50 p.c. N	III.	18·52 p.c. N

numbers agreeing well with 18·50 p.c. N, the calculated percentage for the trinitrate.

Hay and Masson (Moniteur Scientifique [3] 15, 507–510, short abstract in B. [18] Referate 376), have recently made estimations of carbon, hydrogen, and nitrogen in nitroglycerin; the numbers obtained confirm the composition, $C_3H_5(NO_3)_3$.

The following analyses of nitroglycerin, not hitherto published, were made in 1877 at Woolwich, at the Chemical Department of the War Department. Nitroglycerin I. was extracted from Nobel's dynamite (Ardeer make), by displacement by water; nitroglycerin II. was similarly extracted from a bad sample of dynamite of Ardeer make; nitroglycerin III. was made at Woolwich. The C and H determinations were made in the way usual for bodies containing nitrogen, the N determinations by Dumas's method.

	I.		
C .	16·07 p.c.	16·03 p·c.	—
H .	2·40 p.c.	2·36 p·c.	—
N .	—	—	(*a*) 18·44 p.c. (*b*) 18·54 p.c.

	II.	III.	
C .	16·19	16·44	16·11
H .	2·25	2·32	2·33
N .	18·49	—	—

		Calculated for $C_3H_5(NO_3)_3$
Mean of six carbon determinations . . .	16·17	15·86
Mean of six hydrogen determinations . . .	2·33	2·20
Mean of three nitrogen determinations . . .	18·49	18·50

The yield of 2 parts by weight of nitroglycerin (instead of the calculated 2·47 parts) per 1 part of glycerin, as obtained on the large manufacturing scale at Ardeer, would seem to be a result adverse to the acceptance of $C_3H_5(NO_3)_3$ as representing the composition of commercial nitroglycerin, but secondary reactions are said to occur, and the slight solubility in water attributed to nitroglycerin might slightly lessen the yield, if water were very freely used for washing. Kurtz's method and apparatus for making nitroglycerin (a glycerin injection apparatus worked by compressed air) is stated to have given 2·20 parts nitroglycerin, and Mowbray by his process to have obtained 2·24 parts nitroglycerin per 1 of glycerin (Böckmann, Die explosiven Stoffe, 1880).

Hay, on the small laboratory scale, obtained 2·34 parts nitroglycerin as a maximum.

Berthelot (Sur la Force des Matières explosives d'après la Thermochimie, 1883) gives for the heat of formation of liquid nitroglycerin from liquid glycerin and nitric acid, +14·7 kilogram-degrees per molecule (227 grams) of nitroglycerin; and for the heat of formation of nitroglycerin from its elements (diamond carbon, gaseous hydrogen, nitrogen, and oxygen), +98 kgm.-degrees per 227 grams; or, +432 gram-degrees per 1 gram nitroglycerin.

Reactions.—Of the reactions of nitroglycerin two may be mentioned. The decomposition of nitroglycerin by caustic potash was stated by Railton (C. J. [7] 222–224, 1853), to be

$$C_3H_5(NO_3)_3 + 3KHO = C_3H_8O_3 + 3KNO_3,$$

but this was not at all justified by the results of his experiments, as only a small fraction of the nitroglycerin seems to have been decomposed, and the formation of some potassium nitrate and glycerin to have been only qualitatively determined.

Hay (*l.c.*) has recently stated that, by the action of alkalis on nitroglycerin, glycerin is not regenerated, but is oxidised at the moment of formation at the expense of the nitric acid, potassium nitrite being formed. He sums the reactions into one equation thus,

$$C_3H_5(ONO_2)_3 + 5KHO$$
$$= KNO_3 + 2KNO_2 + CHKO_2 + C_2H_3KO_2 + 3H_2O,$$

stating that while the oxidation-products of glycerin may vary as regards their nature and proportions, the above equation expresses with approximate accuracy the course of the reaction. Nitroglycerin is acted on by potassic hydrate in aqueous and in alcoholic solution; but, naturally, much more slowly by aqueous potash.

The reaction of nitroglycerin with alkaline sulphides, by which glycerin is formed with reduction of the NO_2 group, and not an amido-derivative, is one of great theoretical interest, but has not been examined quantitatively as in the case of gun-cotton.

Some experiments were made in 1883 by Professor C. L. Bloxam (C. N. 47, 169), on the decomposition of nitroglycerin by alkaline sulphides, but more with the view of finding a safe means of disposing of nitroglycerin. He found that alcoholic solution of KHS, strong aqueous solution of K_2S, aqueous yellow sulphide of ammonium, the orange-coloured solution of calcium sulphide formed by boiling flowers of sulphur and slaked lime with water, are all able (the last solution more slowly than the others) to effect the conversion of nitroglycerin into glycerin.

Combustion and detonation.—On heating, nitroglycerin shows itself to be decidedly volatile, especially towards 100°; if kept long enough at that temperature, it can even be entirely volatilised. But heated rapidly to 200°, nitroglycerin inflames, and at a little higher temperature detonates with great violence (Berthelot, Sur la Force des Matières explosives).

The temperature of explosion of nitroglycerin is variously stated. Nobel states that when heated to 180° it explodes. Hagen gives 180° to 190° as the temperature of explosion of nitroglycerin, Leygue and Champion give a higher temperature. F. Hess observes that explosive substances when slowly heated, detonate at a lower temperature than when suddenly heated. The temperature of explosion of nitroglycerin (and of explosives in general) is evidently very dependent on the conditions of the experiment. MacRoberts (*l.c.*) says that the explosion of nitroglycerin can be brought about by heating it to a temperature at which decomposition takes place; the decomposition itself then speedily raises the temperature to the point of explosion.

Nitroglycerin is not readily inflamed at atmospheric temperatures by contact with flame or with a red-hot body. Thus, Nobel in 1865 showed that nitroglycerin was not inflamed when its surface was touched with a red-hot iron rod; the flame of a burning wood-shaving set on fire nitroglycerin, which burnt without explosion with a flame that went out when the source of heat was removed; and he states that burning nitroglycerin explodes only when its temperature is raised by the combustion to at least 180°.

The combustion of nitroglycerin, brought about by contact with an ignited body, gives rise to nitrous vapour and a complicated reaction; it burns with a yellow flame, but without explosion properly so called, at least in the case of small quantities. But if the quantity of nitroglycerin is too large, the combustion ends in detonation. The gases produced by burning nitroglycerin (or rather, ordinary dynamite: nitroglycerin and silicious matter) have been analysed by Sarrau and Vieille. The gases were allowed to escape freely, under approximately atmospheric pressure; they had the following composition per 100 volumes of gas:

NO . . .	48·2	H . . .	1·6
CO . . .	35·9	N . . .	1·3
CO_2 . . .	12·7	CH_4 . . .	0·3

The combustion, therefore, under these circumstances appears to be very incomplete.

In the early days of the use of nitroglycerin, Nobel effected its complete explosion in a bore-hole by means of the explosion of gunpowder. A zinc cartridge-case was filled with gunpowder, and nitroglycerin was poured in to fill the interstices between the grains (40 parts nitroglycerin being required per 100 gunpowder); the case was then closed by a cork, or otherwise. A small space was left between the cartridge-case and the side of the bore-hole, gunpowder was poured in to fill this space and to cover the top of the cartridge, the bore-hole was then tamped and the gunpowder fired by means of a fuse. Subsequently (in 1864) Nobel exploded the nitroglycerin by means of the detonation of fulminate of mercury contained in a strong copper cap.

The shock of two hard bodies capable of vibrating readily is able to cause the detonation of nitroglycerin coating the struck surfaces. Nobel noticed that a film of nitroglycerin on an anvil, struck lightly by a hammer, detonated only where struck by the hammer; but if struck heavily, the whole film of nitroglycerin detonated (McRoberts, *l.c.*). If the film be covered only with a sheet of paper, and struck, the detonation is propagated through the whole of the nitroglycerin (Désortiaux, Traité sur la Poudre, &c.). Reasoning that the blow of the hammer caused strong compression of the nitroglycerin, and raised its temperature to the exploding point, Mr. Nobel was led to try the effect of the blow caused by the detonation in the nitroglycerin of strongly-confined detonating mixtures, in the hope that the blow thus given would raise the temperature of the nitroglycerin locally, as was done by the blow of the hammer, and would thereby cause its explosion. He eventually (in 1864) found that the detonation of nitroglycerin could be rendered certain by the use of fulminate of mercury contained in a strong copper cap (McRoberts, *l.c.*). This discovery was of the highest importance, as it made the use of nitroglycerin as a blasting agent practicable.

It has been mentioned that the detonation of nitroglycerin is readily caused when it is subjected to the shock of two hard sonorous bodies, as that of iron on iron. The shock of copper on copper is believed to be less dangerous, and that of wood on wood still less so; but explosions of nitroglycerin have been caused by such shocks (Berthelot, Sur la Force des Matières explosives, &c.). The results of an experiment made by the members of a conference on dynamite &c. in 1879, are given by L. Roux. Fourteen vessels of different materials, each containing 100 to 300 grammes (0·22 to 0·66 lb. avd.), were thrown on the sea-coast from a height of 160 feet on to the rocks on the shore. Four only of this number exploded. The nitroglycerin in two out of four glass bottles exploded; that in one stoneware bottle out of four, that in one zinc can out of three exploded, while there was no explosion in the case of three tin-plate cans. All the vessels were securely closed against leakage; where no explosion occurred the vessels were found knocked out of shape or broken, lying in the spilt nitroglycerin. Roux attributes the explosions of nitroglycerin which occurred during transport in the early years of its use, to leakage from the vessels which contained it, nitroglycerin in thin layer being dangerously sensitive to shock (Chalon, Les Explosifs modernes).

Frozen nitroglycerin is less readily detonated by a blow, or by the detonation of fulminate of mercury, than when in the liquid state. This was to be expected, as detonation results in both cases from the transformation into heat of the kinetic energy imparted to the particles of nitroglycerin—heat sufficient at the part struck to raise the temperature of the nitroglycerin to the temperature of explosion; and to raise frozen nitroglycerin to that temperature, more heat would be required than in the case of the liquid, on account of the heat absorbed in melting the solid nitroglycerin. Thus, Beckerhinn states (Sitz. W. 72 and 73, in abstract in the Jahresbericht der chemischen Technologie, 1876, 22, 481-487) that quantities of fulminate of mercury which would have detonated liquid nitroglycerin with certainty, did not detonate crystallised nitroglycerin; also, that when a flat anvil of Bessemer steel was thinly coated with liquid and with solid nitroglycerin, and a wrought-iron weight allowed to fall on it, the mean height of fall required to effect detonation was for liquid nitroglycerin 0·78 metre (2·6 feet), for frozen nitroglycerin 2·13 metres (7 feet). McRoberts (*l.c.*) states that a detonator containing even so much as 1 gram of fulminate of mercury does not effect the detonation of thoroughly frozen nitroglycerin, while 0·1 gram of fulminate will detonate liquid nitroglycerin.

The products of the detonation of nitroglycerin are stated to be those of complete combustion, and the equation representing the change is given as $2C_3H_5(NO_3)_3 = 6CO_2 + 5H_2O + 6N + O$.

Sarrau and Vieille (C. R. 90, 1060) state that experiment shows that the decomposition of nitroglycerin in a closed vessel is represented by the above equation; but no analysis of the gases is given.

Calculated from the above equation, nitroglycerin contains an excess of 3·52 p.c. oxygen (per 100 nitroglycerin) above that required for complete combustion, and 100 grams of nitroglycerin would be converted into 58·15 grams CO_2, 19·83 grams H_2O, 3·52 grams O, and 18·50 grams N.

The quantity of heat evolved by the total combustion of nitroglycerin, as represented in the above equation, is given by Berthelot (Sur la Force des Matières explosives, &c.), for 227 grams nitroglycerin and in calories (kilogram-degree units), as follows:—

The water liquid, constant pressure, + 356·5 calories; constant volume, + 358·5 calories.

The water gaseous, constant pressure, + 331·1 calories; constant volume, + 335·6 calories.

Or, per 1 kilogram of nitroglycerin:

The water liquid, constant pressure, + 1,570 calories; constant volume, + 1,579.

Sarrau and Vieille obtained, by experiment, + 1,600 calories.

The volume (at 0° and 0·76 metre pressure) of the gases produced by the detonation of nitroglycerin, calculated from the equation given above, is 714 litres per 1 kilogram nitroglycerin, the water taken as gaseous; or 1,142 litres gas (under the given conditions) per 1 litre nitroglycerin. The calculated volume of the permanent gases (*i.e.* the water taken as liquid, tension of aqueous vapour at 0° disregarded) at 0° and 0·76 metre is 467·5 litres per 1 kilogram of nitroglycerin, or 748 litres per 1 litre of nitroglycerin. Berthelot mentions that Sarrau and Vieille found experimentally the volume of permanent gases to be 465 litres at 0° per 1 kilogram nitroglycerin. The gases at the moment of detonation are greatly expanded by the heat of the combustion; according to an early statement of Berthelot (in 1871), the gases are expanded to eight times their volume at 0°.

It will be convenient to re-quote the numbers obtained by Noble and Abel (Fired Gunpowder, No. 2, T. 1880) with Waltham Abbey fine grain gunpowder and ordinary English mining powder.

One kilogram perfectly dry powder gave on explosion:

	W. A. fine grain	Mining powder
Quantity of heat in calories (kilogram-degrees)	738·3	516·8
Permanent gases in litres at 0° and 0·76 metre	263·1	360·3

The statements as to the relative power of nitroglycerin and ordinary blasting powder as blasting agents vary; partly no doubt on account of differences in the rocks blasted, as nitroglycerin is most effective in a compact rock, offering equal resistance in all directions to the gases produced by the explosion. Thus, Trauzl (quoted by Berthelot) stated in 1870 that nitroglycerin used for blasting in quarries produced five to six times the effect of an equal weight of blasting-powder; and for equal volumes the difference would be much greater. The effects produced are those of dislocation, specially dependent on the initial pressures. Schwanert (quoted by Böckmann) states that the mean blasting power of nitroglycerin may be taken as being 3·5 to 4 times greater than that of ordinary blasting-powder: equal weights being in all probability intended.

The velocity of the propagation of detonation in liquid nitroglycerin has been determined by Sir F. Abel (T. 1874, 385, 386). The length of nitroglycerin used was 14 feet, the weight 3 oz. per foot of the train. The liquid was contained in a V-shaped trough of thin sheet-metal; at intervals of 2 feet, fine insulated copper wires crossed the trough (having been passed through, and cemented into, small holes in the sides of the trough) sufficiently near the bottom to be covered by the nitroglycerin. The velocities were measured by Capt. A. Noble's chronoscope; the mean rate of detonation was found to be 5,305 feet (1,612 metres) per second, or little more than one-fourth the rate of detonation of cylinders of compressed gun-cotton in a continuous row.

Use.—As has been already mentioned, the sale and transport of nitroglycerin, as such, is not permitted in this country. In Europe, too, liquid nitroglycerin is said to be no longer used; but in the United States the liquid has been largely used as an explosive, and is still so employed. Mowbray's (Eissler, Modern High Explosives) nitroglycerin was largely used in the making of the Hoosac Tunnel in Massachusetts in 1874, a tunnel about five miles long. The cut is 9 feet in height by 9 in width; and 12 holes, each about 9 or 10 feet deep, were fired simultaneously by electricity. The average consumption of nitroglycerin was 2 to 3 lbs. per cubic yard of rock in the headings, and from 6 to 12 oz. per cubic yard at the bench-work and at the roof—a consumption subsequently reduced. A very weak detonator was used—about 8 grains of a mixture of chlorate of potassium, powdered catechu, and sulphur, in a copper cap. Mr. Mowbray thinks that a weak cap would cause only an imperfect detonation of the nitroglycerin, and that the use of detonators containing a heavy charge of fulminate of mercury would have saved 20 p.c. of the explosive.

About 70 tons (Böckmann, Die explosiven Stoffe) of nitroglycerin were used in making the Hoosac Tunnel. It was supplied by Mowbray in the frozen state, in tin cans internally coated with paraffin, and holding 56 lbs. nitroglycerin, which had been frozen in the cans at the factory by means of ice or ice and salt. The cans were packed for carriage in open wooden boxes, the bottoms of which were lined with a 2-inch thick layer of sponge; india-rubber tubing was wound round the outside of the boxes to deaden shocks. In summer the boxes were surrounded with ice. Mowbray states that more than 90 tons of frozen nitroglycerin was carried over the roughest mountain-paths without accident.

NITROGLYCERIN PREPARATIONS.

It has been already mentioned that the serious accidents which, in 1864–66, attended the transport or manufacture of nitroglycerin were followed by a reaction against its use, and in this country by a prohibitive Act in 1869. To render its transport safe, Nobel introduced the use of a solution of nitroglycerin in wood-spirit (methylic alcohol): a solution which is not explosive, and from which the nitroglycerin was to be separated by precipitation by water at the place where it was to be used. This method of protection was soon abandoned, as the separation of the nitroglycerin was troublesome, and at low temperatures it crystallised out from the solution. Subsequently Nobel succeeded in making the use of nitroglycerin comparatively safe by employing porous substances to absorb the liquid; to these preparations he gave the name Dynamite. It will be convenient to divide the nitroglycerin preparations into (1) *those with non-explosive absorbents*, and (2) *those with explosive absorbents*.

1. *Preparations with non-explosive absorbents.*

Kieselguhr dynamite No. 1.—Dynamite is stated to have been first used in 1866. Mr. Nobel used first charcoal as an absorbent, and various other substances were subsequently tried, but he found so-called infusorial earth to be the best absorbent of nitroglycerin. The earth is found in several places; that first used was obtained from Oberlohe, in Hanover, where there is an extensive bed of it. It consists of the frustules of diatoms, and is mainly silica; Beckerhinn examined some kieselguhr, and found it to contain 95 p.c. SiO_2, and its specific heat to be 0·2089. The kieselguhr is moderately calcined to remove water and organic matter, then ground and sifted; that which passes through the sieve is mixed with three times its weight of nitroglycerin by hand-kneading. After thorough kneading, the mixture is squeezed by the hand through the meshes of a coarse sieve; it has then only to be made into cartridges.

The kieselguhr used at Ardeer is obtained from Aberdeenshire; it absorbs three or four times its weight of nitroglycerin, retaining it under considerable pressure. The calcined material contains about 98 p.c. SiO_2 (McRoberts, *l.c.*). The dynamite cartridges are small cylinders, in which form they are squeezed out from the cartridge-machine; the latter is a cylindrical metal tube in which a wooden piston works, pressure being applied to the piston by means of a lever. One end of the tube is terminated by a funnel-shaped piece with orifice of the same diameter as that of the cartridges. The cartridges are sent out wrapped in parchment-paper.

Kieselguhr dynamite No. 1 is a plastic, pasty substance, usually of a reddish-brown colour, and should contain 75 p.c. nitroglycerin. The Home Office (1887) permits the addition of 1½ part by weight of ammonium carbonate to every 100 parts of dynamite, and the substitution of a maximum of 8 parts of the kieselguhr by other specified inert substances. Water separates the nitroglycerin from ordinary kieselguhr dynamite. The specific gravity of dynamite (of

Ardeer make) varies from about 1·59 to 1·65. When unfrozen dynamite is set fire to by application of flame, the nitroglycerin burns quickly with yellowish flame, giving off nitrous fumes. Large quantities can thus be burnt without explosion; but eventually the unburnt portion becomes heated to the temperature of explosion, and explodes. Dynamite usually freezes at about 4°. Frozen dynamite burns very slowly, thawing preceding combustion. When a comparatively small heap of frozen dynamite cartridges is set fire to, an explosion often ensues. Like nitroglycerin, frozen dynamite is less sensitive to shock than unfrozen, and the ordinary detonator does not explode thoroughly frozen dynamite, although one-tenth part of the detonator charge is sufficient to cause the detonation of unfrozen dynamite (McRoberts, *l.c.*). Dynamite is less sensitive to shock than nitroglycerin; the sensitiveness increases with the percentage of nitroglycerin in the dynamite, and (like explosives in general) with increase of temperature. It is detonated by the shock of iron on iron, or of iron on stone, but not by that of wood on wood. In the unfrozen state it is readily detonated by the shock of a rifle-bullet; Berthelot states that it detonates under the direct blow of the bullet when fired at 50 metres (164 feet) distance, and even more. Placed on an anvil and struck, it requires a smart blow of the hammer to cause an explosion, and then only the portions directly struck detonate, the rest being scattered without exploding. The silicious skeletons of the frustules of diatoms composing the kieselguhr form separate receptacles for the nitroglycerin, and have a cushioning effect towards a mechanical blow, the energy thereby imparted being divided between the absorbent and the nitroglycerin. Berthelot (Sur la Force des Matières explosives, &c.) remarks that dynamite is less crushing in its action than nitroglycerin, because the heat evolved on its detonation is shared between the products of the explosion and the inert substance, the latter by its presence lowering the temperature. Thus, the specific heat of kieselguhr (0·2) is almost the same as the mean specific heat of the gaseous products of explosion of nitroglycerin at constant volume; in the case of No. 1 dynamite with 25 p.c. kieselguhr, in a vessel completely filled by it, and too strong to be burst by its detonation, the kieselguhr would lower the temperature of the gases by one-fourth, and consequently diminish the initial pressure. In blasting, the condition of the gases of explosion would be intermediate between constant volume and constant pressure. In using dynamite, its detonation is effected by means of the explosion of fulminate of mercury contained in a cap of copper or steel, and fired by an electric current or by means of Bickford fuse, the cap being imbedded in the dynamite. The detonator supplied for the purpose by Nobel's Explosives Company contains about 0·5 gram of a mixture of 70 p.c. fulminate of mercury and 30 p.c. chlorate of potassium.

The velocity of propagation of the detonation of this dynamite was found by Sir Frederick Abel (T. 1874, 384, 385) to be 20,000 feet per second. The experiment was made with half-inch cartridges of dynamite in a continuous train of 42 feet, the rate being measured at intervals of 6 feet by means of Capt. A. Noble's chronoscope.

General Abbot (U.S. Engineers) obtained from his experiments (Report upon a System of Submarine Mines, &c., 1881, 111) the remarkable result that the intensity of action of ordinary kieselguhr dynamite containing 75 p.c. nitroglycerin, fired under water, is greater than that of nitroglycerin. Thus, in a series of experiments he found the intensity of action of nitroglycerin detonated under water to be 81, that of an equal weight of dynamite being 100. To confirm the results, nitroglycerin was mixed, under General Abbot's supervision, with prepared kieselguhr into dynamite of 75 p.c., and shots were immediately fired under water with this dynamite, and with the nitroglycerin from which it had been made. The mean of five shots gave the intensity of the liquid nitroglycerin as 85, that of the dynamite being 100 (equal weights compared). General Abbot remarks that in blasting hard rock, nitroglycerin is admitted to be by far stronger than dynamite; in explanation he supposes that in dynamite the particles of kieselguhr slightly retard chemical action, and that the resistance opposed by water being of a slightly yielding character, may exact more time than is required by pure nitroglycerin. According to Sir F. Abel's experiments, however, the rate of detonation of dynamite is very much quicker than that of liquid nitroglycerin; a result agreeing with those of General Abbot's experiments, but not with his explanation of them. It is true, as Sir F. Abel points out, that the determination of the rate of detonation of liquid nitroglycerin (which was contained in an open trough) was likely to be given too low, owing to the tendency of the liquid particles to escape from the blow of the detonation, and that experiments with *confined* nitroglycerin would be desirable.

The consumption of this dynamite has been very large. Mr. McRoberts states that the amount of dynamite sold from the factories with which Mr. Nobel is associated amounted in 1882 to 9,500 tons.

Instead of kieselguhr, in France a similar silicious earth called *Randanite* (from Randan in the Puy-de-Dôme) is used as the absorbent in the Vonges make of dynamite. Tripoli and the ashes of Boghead coal have also there been employed as substitutes for kieselguhr.

Magnesia alba has also been used as the absorbent of nitroglycerin. The combination was proposed in 1879 and named *Nitromagnite* or *Dynamagnite*.

Mica powder (Abbot, Report upon a System of Submarine Mines, &c., 93, 110) consists of finely-divided mica scales and nitroglycerin. It was made in the United States by Mr. Mowbray, and was largely used, with good results, in completing the Hoosac Tunnel. The nitroglycerin adheres to the scales, but is not absorbed by them. Mowbray claimed that, owing to the very large surface exposed, a more instantaneous reaction is secured than with liquid nitroglycerin. He estimates the interstitial spaces at one-fourth the volume of the powder when tolerably well rammed.

General Abbot experimented with a No. 1 mica powder containing 52 p.c. nitroglycerin, and with a No. 2 containing 40 p.c., the charges being detonated under water. He found the intensity of action of No. 1 to be 83, of No. 2 to be 62; that of liquid nitroglycerin, under the same circumstances, being 81, and that of kieselguhr dynamite No. 1, containing 75 p.c. nitroglycerin, being 100 (equal weights compared). The result is remarkable, as it gives the intensity of action of the nitroglycerin in mica powder as double that of an equal weight of liquid nitroglycerin.

Carbodynamite is a preparation quite recently introduced by Messrs. W. D. Borland and W. F. Reid. It consists of 10 p.c. cork-charcoal, which has absorbed 90 p.c. nitroglycerin. Sodium or ammonium carbonates and water may or may not be present.

It is claimed for carbodynamite that it can be kept under water for weeks without losing its nitroglycerin, which would be a great advantage over kieselguhr dynamite.

As was to be expected from the high percentage of nitroglycerin, the intensity of action of carbo-dynamite is very high—much higher than that of kieselguhr dynamite. The inventors propose to make milder dynamites by adding water to their carbodynamite; and, by using a large quantity of water, hope to prepare a dynamite which can be safely used in fiery mines in place of the water-cartridge.

2. *Preparations with explosive absorbents.*

Blasting gelatin. This explosive, the invention of Mr. A. Nobel, consists of nitroglycerin gelatinised by a little nitrocotton, and although the latter cannot be said to act as an absorbent, the structure of the blasting gelatin being continuous—that of a solidified solution—it is included here for the sake of convenience. It has been mentioned that nitroglycerin contains an excess of 3·52 p.c. of oxygen above that required for the complete combustion of the carbon and hydrogen of the nitroglycerin; this oxygen is utilised in effecting the complete combustion of the nitrocotton, itself deficient in oxygen. The nitrocotton used is less highly nitrated than guncotton; it is stated to be a mixture of mononitro- and dinitro-cellulose, and (if free from unnitrated cotton and from trinitro-cellulose) to dissolve readily in warm nitroglycerin.

Mr. McRoberts (*l.c.*) thus describes the preparation and properties of blasting gelatin. '93 parts by weight of nitroglycerin are taken, and 7 parts of nitrocotton. The nitroglycerin is heated in a copper vessel by means of water at 50°, and the nitrocotton in a fine state of division is added to it in small portions at a time, the whole being mechanically stirred. The temperature of the mixture during the whole operation is carefully watched by means of a thermometer, and is never allowed to exceed 85°, at which temperature the nitrocotton is perfectly soluble in nitroglycerin, and at which the operations can be safely conducted. As the stirring proceeds, the nitrocotton and nitroglycerin gelatinise, and in the course of an hour the material forms a homogeneous mass, somewhat resembling thin dough in consistency. As it cools, the blasting gelatin becomes stiffer, and assumes a semi-transparent aspect. . . . The manufacture is thus attended with considerable difficulty and danger; but, once made, blasting gelatin is the safest of explosives. It is a viscous, translucent semi-solid, of yellowish colour, and of sp.gr. 1·55 to 1·59. It does not deteriorate by submergence in water, water not separating the nitroglycerin—an advantage over kieselguhr dynamite No. 1. It freezes at low temperatures; but while some cartridges freeze readily at about 2° to 4°, others are sometimes found which are not frozen by twenty-four hours' exposure to the temperature of a mixture of ice and salt. In the frozen state, blasting gelatin is more sensitive to shock; a rifle bullet can be fired through any number of unfrozen cartridges without exploding them, but similarly fired through frozen cartridges never fails to cause their explosion. The transmission of detonation through unfrozen blasting gelatin is much slower than through either nitroglycerin or dynamite, but the frozen gelatin cartridges appear to detonate as quickly as those of dynamite. Blasting gelatin cannot be exploded in trains in the open like dynamite, but it explodes readily when confined in bore-holes, and its comparatively slow detonation makes it especially useful in blasting soft rock. From experiments made at Ardeer, it was found that while kieselguhr dynamite No. 1 could be unfailingly exploded by a detonator containing 0·05 gram of cap mixture (70 p.c. fulminate of mercury and 30 p.c. potassium chlorate), the least quantity required to detonate the best blasting gelatin is 0·2 gram; and if the latter is tough, with an extra proportion of nitrocotton (*e.g.* with 9 p.c. or 10 p.c.), it fails to detonate completely even with a 0·8 gram charge of cap composition. It is necessary, therefore, in order to get unfailing detonations with tough blasting gelatin, to use in actual mining a detonator with at least 1 gram of cap composition, or to use a dynamite primer.'

The addition of camphor (about 4 p.c.) to blasting gelatin deadens the sensitiveness of the latter to shock to a very remarkable extent. Berthelot attributes this effect to a certain amount of elasticity and solidity caused in the gelatin by the added camphor, on account of which the energy of the shock of the detonator, and the heat into which some of it is converted, are imparted to a much greater mass of substance than when no camphor is present; a condition unfavourable to a sudden and local rise of temperature.

Sir Frederick Abel finds (by the work done in expanding the bore of a lead cylinder) the intensity of action of Nobel's blasting gelatin of recent make to be about 160 when a sufficiently strong detonator is used, kieselguhr dynamite No. 1, exploded by the same detonator, being equal to 100. General Abbot finds the intensity of the same kind of blasting gelatin, detonated under water and referred to the same standard, to be 142. Hence it is not surprising that, although higher in price, blasting gelatin has to a large extent replaced kieselguhr dynamite.

Gelatin dynamite, made by Nobel's Explosives Company, consists of thin blasting gelatin mixed with wood-meal and potassium nitrate. Its composition is:—gelatinised nitroglycerin 65 p.c., potassium nitrate 26·25 p.c., 8·4 p.c. wood-meal, 0·35 p.c. soda. The gelatinised nitroglycerin consists of 97·5 p.c. nitroglycerin and

2·5 p.c. soluble nitrocellulose. As made at Ardeer, the finished explosive is of pale buff colour and is very elastic. Recent experiments of Sir Frederick Abel's, by the lead-cylinder method, gave its intensity of action when suitably detonated as 127 and 123 (mean 125 p.c.), ordinary kieselguhr dynamite being 100. It is said, like blasting gelatin, to be gradually replacing kieselguhr dynamite.

Gelignite is a modification of gelatin dynamite, its composition being stated to be :—nitroglycerin 56·5 p.c., nitrocotton 3·5 p.c., woodmeal 8 p.c., potassium nitrate 32 p.c. An estimation by Sir Frederick Abel of its intensity of action, suitably detonated in a lead cylinder, makes it 100, *i.e.* the same as the Ardeer kieselguhr dynamite No. 1.

Forcite is the name given to explosives manufactured in various grades by the American Forcite Company, New Jersey. The original patent (of 1881) describes forcite as consisting of nitroglycerin incorporated with unnitrated gelatinised cellulose and with nitre. Cotton or other form of cellulose was to be purified chemically as in paper-making, to be reduced to powder and to be subjected to the action of high-pressure steam, by which it was converted into a gelatinous mass. It was then allowed to cool, and was to be incorporated at 40° with nitroglycerin and with nitre. One of the best compositions was stated to be :—nitroglycerin 75 p.c., gelatinised cotton 7 p.c., nitre 18 p.c. Dextrin and ordinary cellulose in powder might partly replace the gelatinised cotton.

Forcite is described as a hard plastic substance having very much the appearance and toughness of india-rubber. Economy, non-exudation of nitroglycerin, and imperviousness to water, were claimed for it. There is considerable variation in the statements as to the composition of forcite; thus, in one kind the gelatinised nitroglycerin is said to be incorporated with a mixture composed of sodium nitrate, wood-tar, a little sulphur and wood-pulp. It is made in various grades containing different amounts of nitroglycerin. Eissler states that the type mostly in use (in the United States, and in 1886), and which possesses the best qualities, is the No. 1, containing from 65 p.c. to 85 p.c. nitroglycerin; also that the quantity of nitroglycerin in different grades varies from the large amount mentioned to only 20 p.c. to 25 p.c. He states that quadruple-force caps are employed to explode forcite.

General Abbot (U. S. Engineers) made estimations of the intensity of forcite exploded under water; the intensity varied with the grade, between 88 and 133, ordinary kieselguhr dynamite No. 1 being 100 (Addendum II. to Report on Submarine Mines).

Judson powder is an explosive which has been largely used in the United States in quarrying and railway work; it is a roughly-made sodium nitrate blasting-powder, the grains of which are coated with nitroglycerin. The grade R.R.P. is the one most commonly used, and is sold at the price of common saltpetre blasting-powder; it is composed of sodium nitrate 64 p.c., sulphur 16 p.c., cannel coal 15 p.c., nitroglycerin 5 p.c. The nitrate, sulphur, and coal are thoroughly mixed in fine powder, and the mixture heated on a pan by steam under pressure, and constantly stirred until the sulphur melts. The mass is then allowed to cool, when it is found agglomerated in grains, which are sorted by sieves and coated with nitroglycerin by stirring. The object of coating the powder-grains with the nitroglycerin was to promote the quickness of explosion. It is exploded by the detonation of a primer of Giant or Atlas powder. Abbot (*v. supra*) found the intensity of action of the R.R.P. grade, exploded under water, to be 38 to 39, kieselguhr dynamite No. 1 being 100.

Dynamite No. 2, Lithofracteur, and **Vulcan powder** can be conveniently mentioned together. Dynamite No. 2, as licensed for use in this country, consists of (not more than) 18 p.c. of nitroglycerin, uniformly mixed with 82 p.c. of a pulverised preparation, composed of 71 p.c. potassium nitrate, 10 p.c. charcoal, 1 p.c. paraffin. Scarcely used at all in this country.

Giant powder No. 2, supplied by the Atlantic Giant Powder Company, and composed of nitroglycerin 36 p.c., potassium or sodium nitrate 48 p.c., sulphur 8 p.c., resin, powdered coal or charcoal 8 p.c. Exploded under water its intensity of action was 83 p.c. of that of dynamite No. 1.

Vulcan powder was used in some of the earlier blasting work at Hellgate, New York Harbour. The usual trade explosive, of the composition nitroglycerin 30 p.c., sodium nitrate 52·5 p.c., charcoal 10·5 p.c., sulphur 7 p.c., fired under water gave intensity = 78 p.c.; and a No. 2 sample containing 35 p.c. nitroglycerin, gave intensity = 82 p.c. compared with the usual standard (Abbot).

Lithofracteur, invented by Engels, and made by Krebs & Co., of Cologne, is said to consist of 55 p.c. nitroglycerin, 21 p.c. kieselguhr, and 24 p.c. of charcoal (bran or sawdust), nitrate of baryta, bicarbonate of soda, peroxide of manganese, and sulphur; the latter ingredients in such proportion as to give the highest temperature and greatest quantity of gas. Stated to be nearly equal in intensity to kieselguhr dynamite No. 1 (Böckmann, Die explosiven Stoffe). Is but little used in this country. A modified form of lithofracteur has been made in the United States, and under the name of *Rendrock* has been experimented with by General Abbot. He found the intensity of action, when fired under water, of three qualities of rendrock containing 20 p.c., 40 p.c., 60 p.c. nitroglycerin to be respectively 78 p.c., 94 p.c., 95 p.c. that of the usual standard: kieselguhr dynamite No. 1. The manufacturer would not state the ingredients, but according to the terms of his patent, the second quality should contain nitroglycerin 40 p.c., sodium or potassium nitrate 40 p.c., cellulose 13 p.c., paraffin 7 p.c.

Ammonia dynamite was a nitroglycerin preparation proposed and patented several years since by Ohlson and Norrbin, which consisted of nitroglycerin 10 p.c. to 20 p.c., ammonium nitrate 80 p.c., charcoal 6 p.c. The material is deliquescent, and paraffin was added to the mixture to waterproof it. Berthelot states that practical tests have shown ordinary dynamite of 60 p.c. nitroglycerin, and the preparation consisting of 75 p.c. ammonium nitrate, 3 p.c. charcoal, 4 p.c. paraffin, and 18 p.c. nitroglycerin, to be approximately equal in intensity of action.

Lignin dynamites. In the United States large quantities of nitroglycerin preparations are used in rock-blasting, consisting of nitroglycerin absorbed by a mixture of wood-pulp (or of sawdust in some of the lower grades) and a nitrate, usually sodium nitrate. For the complete combustion of wood with formation of sodium carbonate, about 2·5 parts by weight of sodium nitrate are required to 1 of wood. General Abbot, in 1885, says: 'Development in the United States is at present most actively directed to the dynamites with explosive bases, economy being sought in making use of the least possible percentage of nitroglycerin.'

Atlas powder may be taken as a type of several American preparations. It consists essentially of sodium nitrate, wood-pulp (or sometimes of sawdust), magnesium carbonate, and nitroglycerin. A series of grades is made, containing 75 p.c. to 10 p.c. nitroglycerin, and 2 p.c. to 68 p.c. of sodium nitrate respectively.

General Abbot experimented with two grades, A and B, of Atlas powder; they were composed of:

	Grade A	Grade B
Sodium nitrate . .	2	34
Wood fibre . .	21	14
Magnesium carbonate .	2	2
Nitroglycerin . .	75	50

Fired under water, the intensity of grade A was just that of an equal weight of kieselguhr dynamite No. 1 (75 p.c. nitroglycerin); while the intensity of Atlas B was = 99 p.c. of the same standard (Abbot, Addendum II. to Report on Submarine Mines). Grade A shows no economy in nitroglycerin over kieselguhr dynamite of the same percentage, probably owing to the too low ratio of sodium nitrate to wood fibre. Grade B, in which the ratio of nitrate to wood is that of complete combustion, shows a great economy in nitroglycerin.

Sir F. Abel found (by the lead cylinder method) the intensity of an Atlas powder of American make to be 106, kieselguhr dynamite No. 1 being = 100.

Hercules powder has essentially the same composition as Atlas powder. Several grades of it are made in the United States, containing from 70 p.c. to 20 p.c. nitroglycerin. Some years since, two grades were tried by General Abbot, and fired under water; their composition and intensity of action were:

	No. 1	No. 2
Nitroglycerin . .	77	42
Sodium nitrate . .	1	43·5
Wood pulp . .	2	11
Magnesium carbonate .	20	3·5
Intensity . .	106 p.c.	83 p.c.

(Kieselguhr dynamite No. 1 being = 100.)

Giant powder, as made by the Californian and Atlantic factories, appears to be 'Hercules powder' or 'Atlas powder,' without the magnesium carbonate. Essentially similar, also, are a number of American explosives bearing the names of 'safety nitro-powder,' 'Hecla powder,' 'Etna powder,' 'Miner's friend,' and others.

FULMINATE OF MERCURY.

Fulminate of mercury, discovered by Howard in 1800, is produced by the reaction which ensues on mixing together alcohol and a solution of mercury in excess of nitric acid.

In Liebig's process, and Chevalier's modification of it as used in France, the solution of mercury in nitric acid is used cold, in Chandelon's process it is used warm.

Chevalier's process. 3 parts by weight of mercury (300 grams) are dissolved in the cold in 30 parts of nitric acid of 40° Baumé, and the solution is poured into a flask containing 19 parts of alcohol (of 90 p.c. strength). After some minutes an energetic reaction commences, with formation of crystals of fulminate of mercury. Towards the end of the operation, two successive additions of 2·38 and 1·58 parts of alcohol are made; the fulminate obtained is thoroughly washed and dried.

The addition of too large a quantity of cold alcohol towards the end of the operation is stated to yield an impure fulminate.

Chandelon's process. 1 part by weight of mercury is dissolved in 10 parts of nitric acid (sp.gr. 1·4) at a gentle heat; the solution, at a temperature of about 55°, is poured into a capacious flask (its capacity must be at least equal to six times the volume of the liquid) containing 8·3 parts of alcohol (of sp.gr. 0·83). The flask is connected by a cork and tube with a stoneware condenser, to recover spirit.

In about a quarter of an hour the reaction commences with a slight formation of gas-bubbles; very soon the liquid boils, and the flask becomes filled with voluminous white vapour. The violence of the action can be checked by adding as required a little alcohol; for this purpose the recovered spirit after redistillation with caustic soda can be utilised. If the reaction be too much restrained in this way, the fulminate is likely to contain metallic mercury.

The fulminate of mercury is precipitated from the liquid in small greyish-coloured needles. When the action is over, the fulminate is filtered off, and washed until free from acidity. The nitric acid liquid, after cooling, does not contain any appreciable quantity of mercury. The calculated yield of fulminate is 142 per 100 of mercury; by this process the mean yield is 125 p.c. fulminate of mercury.

A process very similar to the above is employed in this country, methylated spirit being used; the yield of fulminate is about 123 parts per 100 of mercury.

Properties.—Commercial fulminate of mercury is in the form of small crystals, of white or pale-brown colour.

In a state of purity it crystallises in white silky needles, almost insoluble in cold water, soluble in 130 times its weight of boiling water, soluble in ammonia. It has a sweetish metallic taste, and is very poisonous.

Its sp.gr. is 4·42 (Berthelot and Vieille). In the dry state it explodes violently by a moderate blow or by slight friction; its sensitiveness is lessened when it is moistened with water. Thus, Berthelot states that the presence of 30 p.c. of water prevents the decomposition of the fulminate in fine powder by friction or shock, that with 10 p.c. of water it decomposes without detonation, that with 5 p.c. water only the portion struck detonates. These results were, however, obtained with small quantities of fulminate, and should not be presumed on in manipulating the substance.

It is detonated by heat; the temperature of explosion is variously stated as 187°, 200°, and 149°.

The products of its detonation are carbonic oxide, nitrogen, and metallic mercury. Berthelot and Vieille examined them, the fulminate being detonated in an atmosphere of nitrogen, and obtained in five experiments per 1 gram fulminate 234·2 c.c. of gases, consisting of CO_2 0·15 vols., CO 65·70 vols., N 32·26 vols., H 1·89 vol. per 100 vols. gas. This agrees with

$$C_2HgN_2O_2 = 2CO + 2N + Hg,$$

requiring 235·6 c.c. From these results and from an estimation of the mercury, they obtain for the composition by weight of fulminate of mercury, C 8·35 p.c., Hg 71·30 p.c., N 9·60 p.c., O 11·05 p.c., H 0·04 p.c. Total 100·34, every constituent having been estimated. This confirms the accepted formula $C_2HgN_2O_2$, requiring C 8·45 p.c., Hg 70·42 p.c., N 9·86 p.c., O 11·27 p.c. The fulminate analysed contained a trace of metallic mercury.

The decomposition $C_2HgN_2O_2$ into

$$2CO + 2N + Hg$$

disengages +114·5 calories (kgm.-degrees) of heat, at constant pressure, per 284 grams fulminate, the mercury supposed liquid; for mercury gaseous, +99·1 cals. Or per 1 kilogramme fulminate, 403 cals. and 349 cals. respectively. Fulminate of mercury is an endothermic substance; in its formation from its elements, there is absorption of heat, −62·9 cals. per 284 grams, or −221·5 cals. per 1 kgm.

The pressure produced by the detonation of fulminate of mercury in a space entirely filled by it has been estimated by Berthelot and Vieille in the crusher-gauge apparatus of the former; they find it to be more than twice that of nitroglycerin, and about three times that of guncotton, detonated in spaces filled by them (but including the interstitial air of the gun-cotton). They attribute the power of fulminate of mercury in effecting detonation to the greatness of this pressure, coupled with its sudden development (Berthelot and Vieille, A. [21] 569, 1880).

A mixture of 22·3 p.c. potassium chlorate and 77·7 p.c. mercury fulminate, *i.e.* in the proportion required for the oxidation of the carbon to carbon dioxide, gives by its explosion 706 calories (mercury liquid) or 668 cals. (mercury gaseous) per 1 kgm. of mixture. The volume of gases (at 0° and 760 mm.) produced is 183 litres per 1 kgm.—less than with the fulminate alone; the theoretical pressure is very near that of pure fulminate. The chlorate renders the mixture very sensitive (Berthelot). Commercial fulminate of mercury generally contains about 70·5 p.c. Hg, but it contains a trace of metallic mercury and sometimes some oxalate of mercury. The estimation of the percentage of mercury does not give much information as to the presence of oxalate, as a mercuric oxalate C_2HgO_4 would contain 69·4 p.c. Hg, nearly the same percentage as the fulminate. A weighed quantity of dried fulminate should be dissolved in ammonia solution of 0·880 sp.gr., at a gentle heat if necessary: metallic mercury will be seen and can be filtered off and estimated. To the filtrate ammonium sulphide is added; the HgS can be filtered off and estimated as usual. To the filtrate from HgS some NH_4Cl and $CaCl_2$ are added, whereby the oxalate can be detected and estimated.

Fulminate of mercury is used for detonators for gun-cotton and for nitroglycerin preparations, also for cap- and detonating-compositions.

For the reactions of fulminate of mercury, and for the views held as to its constitution, *v.* Fulminic acid.

Other Explosives

can be mentioned only very briefly.[1]

Sprengel's explosives. Dr. H. Sprengel, in a well-known and suggestive paper 'On a new class of explosives which are non-explosive during their manufacture, storage, and transport' (C. J. 1873, 796), made known the fact that a variety of organic substances dissolved in nitric acid of about 1·5 sp.gr. explode by detonation. He effected the detonation by means of fulminate of mercury, 0·65 gram (10 grains) of which, contained in a narrow tube of metal (this placed in a thin glass tube sealed at one end for the nitric acid explosives), was placed in the middle of the nitric acid solution and exploded by safety-fuse. The nitric acid solution was contained in an open, wide-mouthed glass bottle. Solutions in nitric acid of nitrobenzene, and of picric acid, were tried; also a partially dissolved mixture of naphthalene with the acid. The nitro- derivatives were used to lessen, or wholly to avoid, chemical action. The mixtures were made in the proportion required for complete combustion to CO_2 and H_2O, no excess of nitric acid having been used. The following were tried:—

(1) Solution of nitrobenzene in nitric acid. This solution detonated with intense violence (by means of fulminate of mercury, as mentioned above), and showed itself to be a very powerful explosive. There is some evolution of heat on mixing the nitrobenzene and nitric acid, arising from chemical action. Dr. Sprengel mentions that dinitrobenzene would probably lower the temperature (of the acid), but he does not appear to have actually experimented with it.

(2) Solution of picric acid in nitric acid. The picric acid was observed to dissolve freely in the nitric acid with considerable absorption of heat, and the solution to explode with very great violence when fired by a detonator.

Dr. Sprengel also discovered that picric acid alone could be detonated, and that it was a powerful explosive.

(3) A semi-fluid mixture of naphthalene in nitric acid was also found to be susceptible of detonation.

Sprengel's potassium chlorate explosives. These consisted of porous lumps or cakes of potassium chlorate which had absorbed combustible liquids. The cakes were formed by compressing in moulds to the required extent

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[1] See also a paper by the writer, *Journal of the Society of Arts*, Dec. 14, 1888.

powdered chlorate of suitable fineness; the chlorate is slightly damped with water before pressing, then dried. By using liquids with the chlorate, friction is avoided.

Using a detonator containing 0·65 gram (10 grains) of fulminate, Dr. Sprengel found the cakes to be non-explosive unless the liquid absorbed contained a certain amount of sulphur or a nitro- compound. Potassium chlorate and carbon bisulphide, and the chlorate and nitrobenzene, detonated violently with the fulminate. Good detonations were also obtained when the liquid absorbed was a mixture of carbon bisulphide with benzene, phenol, or petroleum. Benzene and potassium chlorate was not detonated by the 0·65 gram of fulminate.

Sprengel found, however, that mixtures of potassium chlorate with benzene, petroleum, or phenol, but neither sulphur nor nitro- compound, could be satisfactorily detonated by surrounding the fulminate cap with an envelope of gun-cotton; and cakes of such mixtures, weighing 80 grams, detonated violently, unconfined, when a priming charge of 15, 8, and 7 grams of gun-cotton was used.

Hellhoffite is a Sprengel explosive, consisting of a solution of dinitrobenzene in nitric acid. The dinitrobenzene dissolves with fall of temperature; suitably detonated, the solution is a powerful explosive, more so than gun-cotton or ordinary dynamite. It was brought forward by Hellhoff, of Berlin, and was tried for a special military use.

Oxonite is a name given to a mixture of picric acid and nitric acid.

Panclastite. Mixtures of liquid nitrogen tetroxide with carbon bisulphide, ether, benzene or nitrobenzene, petroleum, and other hydrocarbons, were so called by their patentee, E. Turpin (Eng. Patent No. 4,544, 1881, and No. 1,461, 1882). The name was also given by M. Turpin to certain potassium chlorate mixtures.

The nitrogen tetroxide was prepared by strongly heating lead nitrate, and was condensed in enamelled cast-iron condensers, maintained at freezing-point. The liquid boils at 22°. Bisulphide of carbon is stated to readily mix with it with fall of temperature. A mixture of equal quantities of carbon bisulphide and nitrogen tetroxide is said to give the maximum effect on detonation. This is $3CS_2 + 5NO_2$, insufficient NO_2 for complete oxidation. The mixture is stated not to be exploded by shock, and to burn in the open air quietly and with a brilliant flame; it was to be detonated by means of fulminate of mercury or by a charge of fine powder.

Nitrogen tetroxide has the advantage over nitric acid as an oxidiser that it contains 69·6 p.c. oxygen available, instead of 63·5 p.c.; its heat of formation is also somewhat less, moreover the water of the nitric acid has to be volatilised or decomposed without contributing to the oxidation. Nitrogen tetroxide, however, would be inconvenient in actual use; and although some of the mixtures are powerful explosives, their use appears for the present to have been abandoned.

There are several explosives in which a nitrate, generally ammonium nitrate, has been substituted for the nitric acid of Sprengel's explosives; such are—

Bellite, an explosive patented by C. Lamm, Stockholm (Eng. Patent 13,690, November 10, 1885). The specification states that bellite is a mixture of a nitrate with dinitrobenzene, trinitronaphthalene, or nitrotoluene, the mixture being heated to a temperature of 50° to 100°, in order to coat the particles of the nitrate with fused nitro- compound. Mixtures proposed are, 1 part dinitrobenzene with at least 0·96 part potassium nitrate; or 1 part trinitronaphthalene with at least 1·41 part of potassium nitrate—proportions of nitrate insufficient for complete oxidation.

The actual composition of bellite is said to be dinitrobenzene 15 p.c., ammonium nitrate 85 p.c., and in that proportion the effect produced by the explosive is said to be at a maximum. This amount of ammonium nitrate is rather more than that required for complete oxidation to carbon dioxide and water.

Securite is very similar to the foregoing, and consists of a mixture of 218 parts of dinitronaphthalene with 720 parts of ammonium nitrate; or for use with less powerful detonators, a mixture of 2 parts dinitrobenzene with 5 parts ammonium nitrate. The former mixture is in the proportion for formation of carbonic oxide, the latter contains a little more nitrate. The mixtures are coated with nitrated resin. Patented by H. Schöneweg, Dudweiler, Germany (Eng. Pat. 6,664, May 18, 1886).

Carbonite is an explosive introduced by Hellhoff, of Berlin; stated to be composed of nitrobenzene, potassium nitrate, sulphur, and Kieselguhr; said to be plastic enough to fill a bore-hole, to be non-explosive by blows, when inflamed to burn away quietly without explosion, and when detonated to have the same explosive force as Kieselguhr dynamite. It has been used in coal mines in Germany (Margraf, Zeitschft. f. Berg-, Hütten-, und Salinenwesen, 1886; or Jahresbericht Chem. Technol. 1886, 323).

Favier's explosive was patented by P. A. Favier (French Patent, July 21, 1883, D. R. P. No. 31,411), and is stated to consist of nitrates mixed with paraffin, resin, or preferably with nitronaphthalene. The proportions recommended are, for 100 parts ammonium nitrate, 5·75 parts paraffin or 9·02 parts nitronaphthalene; or for 100 parts sodium nitrate, 9·26 parts paraffin or 18·93 parts nitronaphthalene. These appear to be calculated proportions. The materials were to be mixed and kneaded warm, and pressed while warm, and coated with a solution of lac or resin. For detonation, about 20 p.c. of dynamite, gun-cotton, or similar substance, said to be required as a primer, to be placed in a cavity in the pressed cartridge (D. P. J. 255, p. 239).

A recent make of the explosive by the Belgian Favier Company contained about 8 p.c. mononitronaphthalene and 92 p.c. ammonium nitrate, the cartridges being coated with paraffin; said to require 2 grams of fulminate of mercury to cause explosion (S. C. I. 11, 241). Elsewhere the explosive is stated to have given results equal to those obtained with dynamite when tried at the quarries of Soignies, Belgium, in April 1887.

In at least three of the four explosives just mentioned there is very great similarity of composition; and while they appear to be non-sensitive to shock, they seem to be inert and to require a considerable initial detonation in order to detonate them. The particles of combustible and oxidiser must be remote from each other compared with those of the nitric acid solutions, or of the constituent elements of an explosive chemical compound.

Some of them have been used in Germany in coal-mining, and claims of superior safety are made on behalf of some of them in respect to their not exploding air containing fire-damp and coal-dust.

Roburite. Patented by Dr. C. Roth (Eng. Pat. 1887, 2679), the invention consisting in the use of chloronitro- compounds with nitrates; the chloronitro- derivatives of benzene, phenol, cresol, and naphthalene are mentioned as being especially valuable. In his provisional specification (1886, 9,766), the advantage claimed for the introduction of chlorine into the nitro- compound is that the chlorine exerts a loosening effect on the NO_2 groups, and enables the compound to burn more readily than when nitro- groups only are present. Dr. Roth further states that numerous experiments have proved that the dynamic effect is considerably increased by the introduction of chlorine into a nitro- compound. He gives methods for preparing the chloronitro- compounds. One part of the latter is to be mixed (according to the C and H present) with from about 2 to 3·5 parts of a nitrate, and the detonation of the mixture is to be effected by means of fulminate of mercury.

The complete specification claims the use of an addition of sulphur to the explosive mixture, to facilitate the explosion and to produce a better 'heaving' action for blasting purposes; also nitro- compounds (such as nitrobenzene or dinitrobenzene) may be used in the mixture, together with the chloronitro- compounds.

The report for 1887 of H.M. Inspector of Explosives adds roburite to the list of authorised explosives, and gives its composition as a mixture of ammonium nitrate and thoroughly purified chlorinated dinitrobenzene, which is not to contain more than 4 parts by weight of chlorine per 100 of chlorinated dinitrobenzene. Roburite burns quietly, and is not sensitive to shock. It must be used dry. It has been employed in coal-mining, and is said to give the coal in large lumps with comparatively little dust.

Romite, probably so called from *ῥώμη strength*, is an explosive patented by R. Sjöberg, Stockholm (Eng. Pat. 1887, 448 and 11,658). According to the latter specification, it consists of ammonium nitrate mixed with a solid melted hydrocarbon (naphthalene, paraffin, and the like) gelatinised with a liquid hydrocarbon (such as paraffin oil), and contains pure or similarly gelatinised potassium chlorate. For the chlorate, a crude nitrolactin may be substituted.

The explosive is said to be very safe, and to need confinement and a strong fuse-cap for its explosion.

Rackarock. This is a Sprengel explosive, composed of potassium chlorate and nitrobenzene; it received the name of rackarock in the United States, where it was used in 1885 by General Newton for the important work of blowing up Flood Rock, Hellgate, which had always been a danger to vessels entering or quitting New York Harbour.

The best proportions of the two constituents, and other points in the preparation of the explosive, were investigated by General Abbot (U. S. Engineers), and are given in Addendum III. to his Report. The chlorate in moderately fine powder was mixed by hand with the nitrobenzene, and 3-lb. charges in water-tight tin cans fired in deep water in his ring apparatus bearing pistons and lead crushers. He found that the maximum intensity of action was given by a mixture containing 79 p.c. potassium chlorate and 21 p.c. nitrobenzene. The equation

$$6C_6H_5NO_2 + 25KClO_3$$
$$= 25KCl + 36CO_2 + 15H_2O + 6N$$

corresponds to 19·4 p.c. nitrobenzene. The mixture with 21 p.c. nitrobenzene was used. Further experiments showed the intensity of action of this mixture detonated under water to be 108 p.c. of that of dynamite No. 1, that a few percents of water caused a serious diminution of this intensity, that whether the rackarock were loosely or solidly compacted in the can, whether fired by two service detonators each containing 24 grains of fulminate of mercury, or by one detonator and a 3-oz. tonite primer, the resulting intensity did not differ.

In the use of rackarock for the removal of Flood Rock, there were the advantages of safety and economy, it being a cheap explosive. The blasting charge was composed of 107 tons of rackarock and 33 tons of dynamite; the rackarock was used in 6-lb. cartridges, into each of which a dynamite exploder was inserted; the dynamite exploder was a closed copper tube filled with No. 1 dynamite, in which was inserted a thin copper shell containing fulminate of mercury. The rackarock cartridges were not fired electrically, but by the shock transmitted from separate electrically-fired dynamite cartridges, placed at intervals in the galleries, to a priming cartridge of dynamite projecting from the mouth of each hole.

The rock was tunnelled, numerous galleries and cross-galleries (of a total length of 21,670 feet) being formed, the roof being supported by 467 enormous piers of rock. The roof and tops of the piers were drilled with 13,236 holes (3 inches in diameter and having an average depth of 9 feet), which were filled with cartridges of rackarock except at the open end of the drill-hole, in which a priming cartridge of dynamite was placed, with its end projecting about 6 inches beyond the face of the rock. The rock was most successfully blasted on October 10, 1885.

Rackarock has also been used in another important engineering work, in blasting the headings of the Vosburg Tunnel (3,902 feet long) in Pennsylvania.

Kinetite. Gun-cotton dissolves in nitrobenzene forming a jelly, and kinetite is a mixture of such a jelly with finely-powdered potassium (or other metallic) chlorate or nitrate, together with sulphur free or combined as sulphide. The powdered salts are first well mixed and kneaded with the jelly to a homogeneous mass. The sulphur or sulphide is then added and the whole well worked up. Patented by Petry, Fallenstein, and Lisch of Düren (Ger. Pat. 1884, 31,786; Eng. Pat. 1884, 10,986). The proportions recommended are:

Nitrobenzene (or similar nitro-compounds)	16 p.c. to 21 p.c.
Gun-cotton (or other form of nitro-cellulose)	¾ p.c. to 1 p.c.
Alkaline chlorates and nitrates	82¼ p.c. to 75 p.c.
Sulphur, as antimony pentasulphide (or other sulphide)	1 p.c. to 3 p.c.

Kinetite is stated to require a powerful initial detonation. A modified kinetite was made by omitting the antimony pentasulphide, and appears to be the explosive patented by H. Dulitz, Düren, Germany (Eng. Pat. 1886, 12,838), consisting of 20 parts of a 5 p.c. solution of gun-cotton in nitrobenzene and 80 parts of potassium chlorate, for which another oxidising agent may be substituted up to a maximum of 10 p.c.

The sulphide was omitted in order to make the explosive less sensitive to combined friction and percussion.

For an account of kinetite, see a paper by Watson Smith (S. C. I. 6, 2–12).

Picric acid, Picrates. Picrates and picric acid have received much attention in France, mixtures of the potassium and ammonium salts with nitre (Désignolles' and Brugère's powders, respectively) having been introduced there in 1869, and the *melinite* of recent times being in all probability mainly composed of picric acid.

Désignolles' powders.—Three kinds of potassium picrate powder were made in 1869 at Le Bouchet under Désignolles' direction; they had the following composition:—

—	Potassium picrate	Potassium nitrate	Charcoal
Powders for torpedoes and shells	55	45	—
" "	50	50	—
Cannon powders (ordinary) . . .	16·4	74·4	9·2
	9·6	79·7	10·7
" (for large calibres) . . .	9	80	11
Small arms powders	28·6	65	6·4
" "	22·9	69·4	7·7

The constituents were moistened with 6 p.c. to 14 p.c. water, and incorporated under edge-runners, a cake formed by means of the hydraulic press, granulation, &c., as usual. The dry powder, like the potassium picrate itself, is sensitive to shock and friction. The torpedo- and shell-powders were tried at Brest and Toulon with results which were considered good at the time. The small-arms and cannon powders were very regular in their action; 60 grams were said to give the same results as 350 grams of ordinary gunpowder, with but little smoke (Désortiaux, 738).

General Abbot found the intensity of action of Désignolles' powder, composed of equal weights of potassium picrate and nitrate (which is the proportion for complete oxidation), fired under water, to be 68; dynamite No. 1 being 100 (*v.* his Report, p. 100).

Brugère's powder is composed of 54 p.c. ammonium picrate and 46 p.c. potassium nitrate. (The proportion for complete oxidation of the picrate is 43·2 p.c. picrate and 56·8 p.c. nitrate.) Like the ammonium picrate itself, this powder is not sensitive to shock or friction. Fired in the Chassepot rifle, 2·6 grams produced the same effect as the service charge of 5·5 grams of ordinary black gunpowder. General Abbot fired under water charges of this powder, composed of equal weights of the two constituents, and found its intensity of action to be 81, dynamite No. 1 being 100.

Picric powder was introduced by Sir Frederick Abel almost simultaneously with the introduction of Brugère's powder. It is composed of 40 p.c. ammonium picrate and 60 p.c. potassium nitrate, and was proposed for use in shells.

Potassium picrate and chlorate form Fontaine's powder, proposed for use in shells and torpedoes, but not now in use. Its explosive force is said to be greater than that of the nitrate mixtures; but it is stated to be dangerous to manipulate owing to its great sensitiveness to shock, friction, and inflammation.

Mixtures of potassium picrate and chlorate have been patented by Désignolles and Castelhaz as general explosives; and mixtures of the same with lead chromate, also mixtures of lead picrate and chromate with potassium chlorate have been patented by them for use as priming materials (1867, No. 3,469).

Picric acid. Sprengel observes in his paper already noticed that picric acid alone contains a sufficient amount of available oxygen[1] to render it, without the help of foreign oxidisers, a powerful explosive when fired by a detonator, and that its explosion is almost unaccompanied by smoke (C. J. 1873, 803).

The use of picric acid, unmixed with any oxidising agent, was patented by E. Turpin (Eng. Pat. 1885, No. 15,089). He claims for it the properties of insensibility to shock, and, when suitably detonated, of very high explosive force. He proposes still further to lessen its sensitiveness to shock by compressing the picric acid, by agglomerating it by means of a solution of collodion in alcohol and ether, or by melting and casting the picric acid. The commercial acid melts at about 120°, and the cast acid has a sp.gr. of 1·6 to 1·7, which is advantageous to picric acid when comparison has to be made by volume, not by weight. The cast picric acid, when unconfined, is much more difficult of detonation by fulminate of mercury than the crystals or powder; it can be detonated, however, by a priming of picric acid in powder, this priming being detonated by fulminate of mercury.

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[1] For the formation of water and carbonic oxide, picric acid is 3·49 p.c. deficient in oxygen; for that of water and carbon dioxide it is 45·41 p.c. deficient.

It has been already stated that Melinite consists, in all probability, mainly of picric acid.

A very serious explosion which occurred at Messrs. Roberts, Dale & Co.'s chemical works at Cornbrook, near Manchester, in June, 1887, was caused by picric acid. Colonel Majendie, H.M. Chief Inspector of Explosives, reported that the explosion was in all probability caused by burning and melted picric acid flowing into litharge not far off, detonating with it, and thereby acting as a primer to cause the detonation of all the picric acid present.

Experiments made in connection with the inquiry into the cause of this explosion showed that while a pound of picric acid when heated took fire, and burnt quietly away with a red, smoky flame, the heating of a roughly-made mixture of picric acid with litharge, lead nitrate, strontium nitrate, or with lime, was followed by violent detonation.

On the same occasion it was observed that 5 grains (0·32 grams) fulminate of mercury caused the complete detonation of picric acid crystals, and that picric acid crystals containing 15 p.c. water could readily be detonated (*v.* Report on this explosion, No. LXXXI. August 15, 1887).

MEASUREMENT OF THE INTENSITY OF ACTION OF EXPLOSIVES.

The intensity of action of an explosive depends on the volume of gases produced, on their temperature, and on the velocity of explosion or detonation of the substance. The volume of permanent gases and the quantity of heat evolved have been determined for many of the more important explosives; but the gases collected and examined are those remaining after cooling down to atmospheric temperatures, not those existing at the period of maximum temperature. The uncertainty as to the specific heat of the products of explosion at the high temperatures produced, renders the calculation of quantity of heat into temperature hazardous. Some kind of direct experimental estimation of the pressure produced, or of the work done, by an explosive must be resorted to. A very slight reference can only, however, be made to some of the methods in use.

General Abbot, in his classical 'Report upon Experiments and Investigations to develop a System of Submarine Mines,' describes his ring apparatus, by means of which he compared the intensity of action of various explosives. The accompanying illustration (fig. 4) shows the apparatus. It is a ring of wrought iron (the one most frequently employed was 4 feet in diameter), into which six pressure gauges were screwed at intervals of 60°, two of them being placed horizontally. The explosive, in a suitable case, was held in the centre of the ring by lashings of iron wire, and was fired electrically; 1 lb. to 5 lbs. was the weight of charge used. The pressure gauges contained a piston, which transmitted the pressure to a small cylinder of lead, which, by the amount of its compression (by its shortening), afforded a register of the work done on it. This is, therefore, a lead crusher-gauge method.

A considerable range of scale was obtained by the use of five sizes of lead cylinders; the actual heights varied from about 1 inch to 0·6 inch, the diameters from 0·75 to 0·30 inch. A further extension of scale was obtained by the use of two different sizes of piston, having sectional areas of 0·1 and 0·785 square inch respectively. The ring was submerged in deep water (about 100 feet deep), and supported by a suitable wrought-iron buoy at about 35 feet from the surface.

The net kinetic energy to which the shortening of the lead was due was determined experimentally by means of a heavy hammer-head hung as a pendulum, and this value in foot-pounds was transformed into mean pressures expressed in pounds, by causing the hammer-pendulum to act on a Rodman indenting-tool, and to produce cuts in discs of copper which could be expressed in pounds pressure by the use of Rodman's tables. For the interesting details the report must be consulted. Abbot gives the values for intensity of action of the explosives he examined in terms of dynamite No. 1 of 75 p.c. nitroglycerin; they have been given in this article under the headings of the different explosives. It must be remembered that these values are for the explosives detonated under water, the intensity of action of nitroglycerin being given as 81 p.c. that of dynamite No. 1; while in rock-blasting, nitroglycerin is by far the stronger. Abbot suggests, as the explanation of this paradoxical result, that in dynamite the particles of silica slightly retard chemical action, and that the resistance opposed by water being of a slightly yielding character may exact more time than is afforded by nitroglycerin pure and simple. The value given for the intensity of

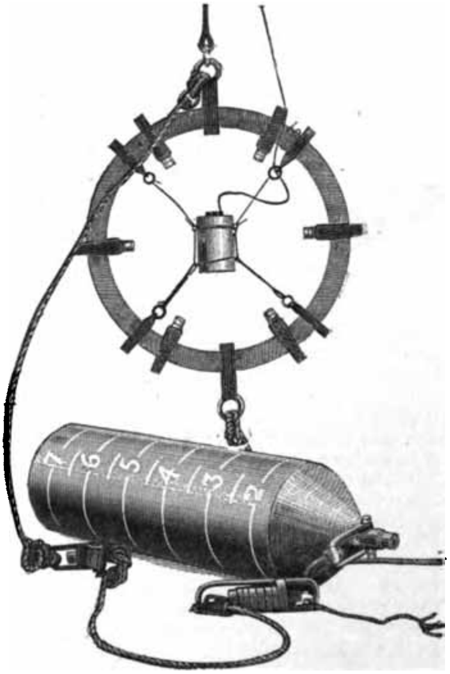

FIG. 4.

action of gun-cotton (of Stowmarket 1871 make), 87 p.c. that of dynamite No. 1, is very low and not in accordance with practical experience of the two explosives.

Abbot's ring apparatus needs for its use deep water and a boat's crew, and when these are not available a valuable result may be obtained by the employment of lead-cylinders as used by Sir Frederick Abel. These are cylinders of soft, pure lead, 12 inches high and 12 inches in diameter, with a central cylindrical hole 7 inches deep and 1·3 inch in diameter, in which 1 ounce of explosive is detonated. With cylinders of these dimensions no cracking through of the bottom is to be anticipated; the diameter of the bore-hole just takes a service 1 ounce dry gun-cotton primer, which is used as a standard of reference. The lead cylinder is placed on a stout iron plate, the weighed explosive (cast or compressed into a cake, or rammed to a known volume in the bore-hole, according to circumstances) with a fulminate of mercury detonator (or suitable priming such as will produce a maximum effect on detonation) inserted into it is placed at the bottom of the bore-hole, the latter filled with fine sand poured into it without pressure, and the detonator fired electrically or by safety-fuse. The volume of the cavity produced is ascertained by means of water and a graduated vessel, and the volume of the bore-hole being deducted gives the enlargement. With an unknown explosive, several experiments are necessary to ascertain the best conditions of detonation. Fig. 5 shows the section of a cylinder before and after a detonation. After they have been used, the cylinders are re-melted with a small addition of pure lead to make up weight, and recast. Out of a set of nine or a dozen cylinders cast from the same melting, one or two are used for the detonation in them of gun-cotton, or of dynamite No. 1 rammed to a known volume, as a standard of reference. Several of the values of intensity of action so determined have been given in the course of this article; some of them agree fairly with General Abbot's values, but the value for gun-cotton by the lead-cylinder method is higher than his.

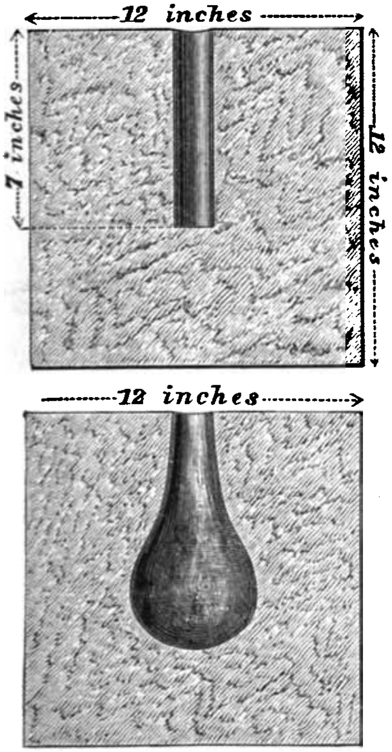

FIG. 5.

Berthelot and Vieille have used a piston and crusher apparatus, in which a copper cylinder is compressed. The deduction (from the compression of the crusher) of the maximum pressure produced by explosives, however, evidently requires circumspection (Berthelot, Sur la Force des Matières explosives [1] 47–53).

Mr. McRoberts describes a method of comparing explosives by the reaction-effect their detonation produces on a pendulum-hung mortar weighing about 600 lbs. The distance from the centre of suspension to centre of trunnions is exactly 10 feet; the mortar is set with its axis horizontal. 10 grams of explosive are placed in a small recess behind the chamber for the projectile; the latter weighs about 40 lbs. and fits the bore gas-tight. The explosive is fired by means of a fuse and detonator; the angle of recoil of the mortar is marked on a graduated index by a pencil which the former carries. The work done by the explosive is twice that done in raising the mortar through the versed sine of the angle of recoil; this is expressed in foot-pounds. Failing these appliances, information of value may be obtained by detonating a charge (a pound or so in weight) buried in earth, and observing the size of the crater; or by noting the reaction effects (the dimensions of the crater) produced on undisturbed earth, or the bulge or hole produced in wrought-iron plates, by the detonation on them of the explosive; comparison being made with an equal weight of gun-cotton or other known explosive, the charges having the same area and shape (most conveniently, cylindrical). W. H. D.

EXTRACTION APPARATUS. The object of extraction is to dissolve out some constituent or constituents from a substance by treating it with a solvent. When the substance is a solid the various ways of effecting this are the following. It may be allowed to soak in the solvent at ordinary temperatures (*maceration*) or at higher temperatures (*digestion*), the solution being after a time poured off, both methods being included under the term *infusion*. A third method is to boil the substance with the solvent (*decoction*), and a fourth is to allow the solvent to descend through a column of the substance placed in a suitable vessel (*percolation* or *displacement*).

The treatment when the substance is a liquid will be considered further on.

Processes of extraction are involved in many of the large industries; for instance, in brewing; in the 'diffusion' process of obtaining sugar from sugar beet or sugar cane; in the 'lixiviation' employed in the manufacture of various inorganic salts, &c. &c., and descriptions of them will be found elsewhere. Besides these, extraction apparatuses are employed in the laboratory of a small size for quantitative work, and on a larger scale for making various preparations; in the manufactory they are used for preparing medicinal extracts, alkaloids, and dyestuffs, and in removing oil from seeds and fat from bones.

An account of some of the numerous forms employed is given below.

When water is the solvent employed the operation may be conducted in a large copper pan fixed in an outer jacket of iron so that a space is left between the copper and the iron through which steam can be made to circulate and heat the contents of the pan. Such pans are either fixed and have a pipe and tap at the bottom to draw off the solution as shown in section fig. 1, or else they are movable about an axis, fig. 2, so that the pan can be tilted and the solution poured off; in these the axes on which the pan rotates are tubular to permit steam to enter and escape from the space between the pan and its iron jacket. When the infusion has been continued for a suitable time and the liquid has been drained off, the residue is placed in a canvas bag and subjected to strong pressure in a screw press, in order to squeeze out as far as possible the last portions of the solution. A common form of press consists of a base to which two uprights with a cross bar at top are fixed; in a thread cut through the centre of the cross bar works a powerful vertical screw. Between the uprights is a strong metal or wooden cylinder perforated with a number of holes; in this the bag of residue is placed and on top is placed a thick plate which transfers the pressure exerted by the screw to the bag and its contents. The iron cylinder rests in a tray of a somewhat wider diameter, and provided with a spout: this tray collects and conducts off the expressed liquid to a vessel placed beneath the spout. Instead of pressing the residue it may be infused several times more with water until it is completely exhausted of the desired constituents, but this method involves a large amount of subsequent evaporation. The solutions obtained by the above processes are next strained through conical bags of linen or flannel and then evaporated down in jacketed pans like those described before, the liquid being kept in motion by a mechanical stirrer.

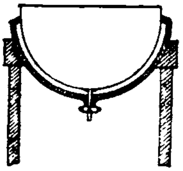

FIG. 1.

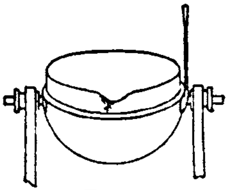

FIG. 2.

In many cases evaporation at temperatures near 100° has an injurious effect on the substances in solution, and some arrangement for evaporation in a partial vacuum is adopted; this enables the evaporation to be conducted at a lower temperature than when the liquid is subjected to the pressure of the atmosphere.

In the process of *percolation* or *displacement* the powdered substance is placed in a long cylindrical or conical vessel (fig. 3), and rests on a perforated disc placed near the bottom and which can be covered with a circle of linen or flannel. A conical vessel is preferable to a cylindrical one, as the mass adjusts itself more readily to the vessel when any change of volume occurs; in a cylinder, if the mass swells on absorbing the solvent it is apt to become so tightly packed that the liquid cannot pass, or if it contracts owing to the removal of soluble constituents it is more liable to form cracks and channels. A second perforated disc or circle of linen or of paper pierced with holes is laid on top of the substance to distribute the solvent uniformly. It is often advisable to damp the powder with about half its volume of the solvent before packing it into the percolator, otherwise some portions may be found to have escaped getting wet during the whole operation. Care must be taken in packing that the substance is throughout in as uniform state of compression as possible or else the solvent will pass more freely through the loosely packed portions. Different substances require to be packed with different degrees of tightness; and when alcohol or ether are the solvents employed the packing may be tighter than in the case of water as they do not cause such a swelling of the substance as water does. The conical vessel is supported in a circular hole cut in a table or wooden stand, a vessel is placed underneath to receive the solution, and the solvent is poured from time to time on the top. A row of such percolators can be arranged so that the solution from the first is poured on to the next and so on along the row, by which plan the liquid from the last will be a strong solution and the percolators that are more nearly exhausted will receive the weaker and therefore more active liquids.

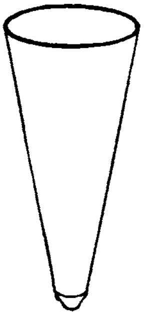

FIG. 3.

For some purposes more elaborate forms of aqueous extraction apparatus are preferable; of these the following is an example:—

Hänig and Reinhard's apparatus (fig. 4).—This is designed for extracting dyewoods &c. by the action of steam and water. A and B are two similar vessels (A is shown in section) which can be made to revolve about the axes x y x y by means of the gearing G G, so as to facilitate filling and emptying. The axes are tubular and serve for conducting steam and water. In communication with the axis x are two pipes having taps a' and a; one ascends and leads into the upper part of the vessel, and the other descends and passing through the bottom of the vessel leads to a perforated pipe g, which forms a ring underneath a perforated false bottom h. Communicating with the axis y is a pipe which descends and following the dotted lines joins on to the back of the threeway tap b. This tap b communicates with the space beneath the false bottom and also with the air. Another three-way tap *c* affords means of communication between the two axes *y y* and also with a pipe at the back indicated by the circle of dots. The covers of A and B can readily be taken off and fastened on again by the row of screws *s s s*. These covers form the condensing apparatus; inside they possess one or more flat horizontal coils *w w*, to which water enters through the tube *m*, and escapes through *n*, and then flows over the whole lid forming a layer on the top, and is thence conducted away. *e* and *f* are openings for air and safety valves, and *d d d*, are taps for ascertaining the level of the liquid inside the vessel.

To work the apparatus A and B are filled with the substance to be extracted, and the covers are fastened on. A suitable quantity of hot water is introduced into A through the tap *c*, placed in such a position that it passes down the pipe *t* and through the tap *b* into A. Steam is now passed in through the axis *x*, and through the valve corresponding to *a*, and escapes through the perforations of the pipe *g*; heating the water and the substance and ascending to the top where it is condensed and flows as liquid back to the bottom again. The action is further accelerated by opening the valve corresponding to *a'* and passing steam in at the top of the apparatus. The first few solutions which are strong are drawn off by the tap *b*, then the later and weaker ones are forced by the pressure of the steam into the vessel B, the taps *b* and *c* being placed so as to lead to that vessel. A is then emptied and refilled with fresh material, and B is now worked in the same way that A was. By proceeding in this way alternately with A and B, the later and weaker solutions from one vessel come into contact with fresh material in the other and become strong, and thus economy in evaporation is effected. (German Patent, 18,922, 1881 and D. P. J. 1882, 246, 22, a later form of that in German Patent 10,771, 1880, and D. P. J. 1880, 238, 332.)

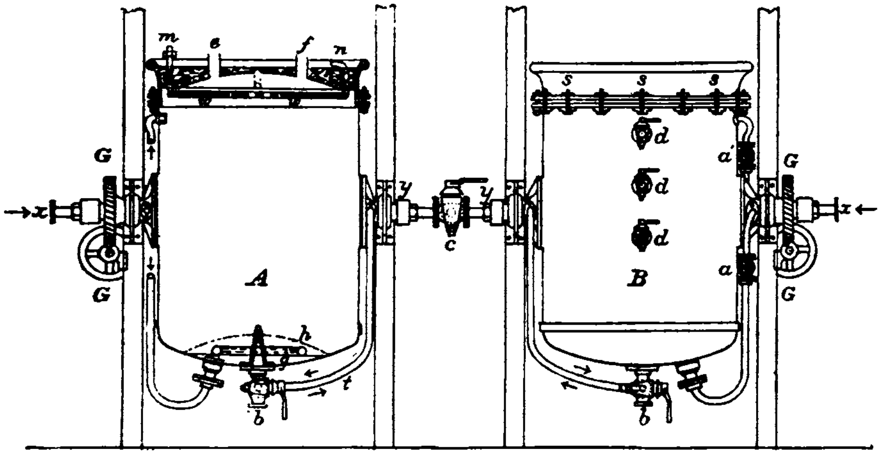

FIG. 4.

When solvents other than water are used it becomes desirable to avoid the loss that would be involved in pouring off the solvent and pressing the residue, and also to make a minimum of solvent do a maximum of dissolving; numerous forms of apparatus have been devised to attain these ends, the principle involved being to distil off the solvent from the solution and use it over and over again, and many of the forms are arranged so as to work continuously and to require but little attention. There are three main plans on which they are constructed. In one, continuous percolation is effected; in the second, continuous infusion, an overflow tube conducting the solution from the bottom of the column of substance and allowing it to escape at a level slightly above the top of the column; and in the third, intermittent infusion is the result attained. This last plan has the advantage of removing one lot of solution and bringing quite fresh solvent into contact with the substance from time to time; it has recently been brought to a high degree of perfection by exchanging the overflow tube of the second plan for a syphon, which makes the action an automatic one. Below are given descriptions of well-known or typical apparatuses, and also references to other forms that have been described. Apparatuses suitable for the laboratory are taken first, and are grouped on the classification given above, percolation forms coming first and the two infusion groups next. Then follow some examples of manufacturing plant.

Mohr's apparatus (fig. 5).—This, though old, is one often referred to. The substance to be extracted is placed in the cylinder E, and rests on a piece of fabric placed on a perforated curved plate *b*, which forms the bottom of the inner cylinder. The solvent is then poured on to it, and the top vessel C is put in its place; it fits into the top of the inner cylinder, making an air-tight joint at *a*. A funnel *f*, which forms the lower external part of the middle piece of the apparatus, fits into the centre neck of a Woulff's bottle R, and conducts the solution into the bottle. The solvent is evaporated off by placing the bottle in a vessel of hot water, and its vapour passes by the tube *t* back into the inner cylinder E, and is there condensed and brought into use again by causing cold water to circulate in the space between the inner cylinder and the outer wall of the apparatus; the water is run into this space through the tubulure *u*, and escapes by an overflow pipe not shown in the diagram. The top vessel C also forms part of the condensing apparatus; water is run into the top of it, and passes down the centre pipe *p*, then rises and fills the vessel C, and is conducted away by an overflow pipe. The two upper pieces of the apparatus E and C are constructed of metal.

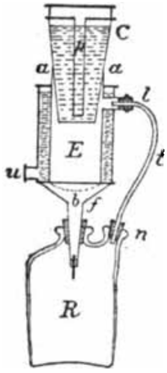

FIG. 5.

When the extraction is complete, which can be seen by the solvent dropping colourless from the funnel, the excess of solvent is recovered by removing the tube *t*, corking the neck *n* of the Woulff's bottle, and connecting the tubulure *l* with a Liebig's condenser. The vessel C is emptied, as also is the annular space of the middle cylinder, and the cold water in the latter is replaced by hot. This causes the solvent that the substance has absorbed to distil off, and it can then be collected at the end of the Liebig's condenser. The top vessels are next removed, and by connecting the Woulff's bottle with the Liebig's condenser the rest of the solvent can be obtained (Mohr's Lehrbuch der Pharm. Technik, 1847, p. 108).

Jacobi (D. P. J. 1862, 164, 343) has described some improvements in Mohr's apparatus.

Hoffmann's apparatus (fig. 6).—The substance to be extracted is mixed with fragments of glass and placed in the short wide tube E, which is closed at the bottom with a plug of cotton wool. The solvent is placed in the weighed flask R, and then converted into vapour by placing the flask on a water-bath; the vapours pass up past the substance and through the tube T into a second flask C, kept cool by being immersed in water or in a freezing mixture, and are there condensed. The air escapes by the short elbow tube A. When all the solvent has been boiled off from R the water-bath is removed, and as R cools the pressure of the atmosphere forces the solvent back through T and E into R, dissolving and washing out on its way the soluble constituents of the substance undergoing extraction. The solvent is again boiled off from R, leaving the soluble matter behind, and the operation is repeated several times until the substance ceases to yield anything to the solvent. The solvent is then evaporated off for the last time from R, which is at once disconnected, and heated in a water bath until it ceases to lose weight (Fr. 1867, 6,370).

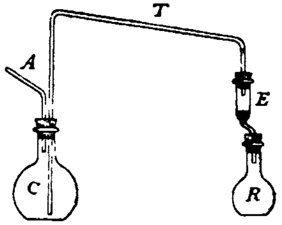

FIG. 6.

Von Bibra's apparatus (v. Gorup-Besanez's Anleitung zur zoo-chem. Analyse, 1850, p. 353) differs very slightly from that of Hoffmann.

Storch's apparatus (fig. 7).—In a wide and somewhat conical glass tube E (the neck of a retort will answer) there is placed a tube *t*, with its lower end projecting a little below the narrow end of E, where a plug of cotton wool, fairly tightly packed, serves both to keep the tube *t* in its place and also to form a support for the substance to be extracted. The substance is filled into E up to within half an inch of the top of *t*, which is temporarily plugged with cotton wool during the filling operation, in order to prevent any of the substance entering it. The extractor E is fixed by a cork into a flask R containing the solvent, and its top is closed by another cork, through which passes a tube *c* leading to a condenser. On warming R on a water-bath the vapours of the solvent ascend through *t*, escape by *c*, and, when condensed, flow back and percolate through the substance undergoing extraction. The cross section of *t*, without being too small, should be less in area than that of the space between it and the outer tube E at its lower end; otherwise, the downflow of the solution is impeded. This apparatus is designed for quantitative analyses, but it can also be constructed of metal and used for larger operations (Fr. 1868, 7, 68).

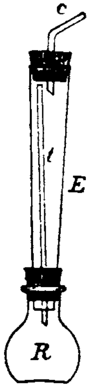

FIG. 7.

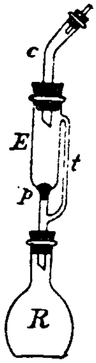

FIG. 8.

Vohl (D. P. J. 1871, 200, 236) has described an apparatus on a plan similar to Storch's, but it is more elaborate in its fittings.

Gantter's apparatus (D. P. J. 1880, 236, 221) is on a plan similar to that of Storch.

Zulkowski's apparatus (fig. 8).—This is a modification of that of Storch. The substance is placed in the extractor E, and is supported by a plug of cotton wool *p*. The vapours of the solvent, as they boil off from the flask R, pass upwards through the side tube *t*, which is fused on to E, and then pass through the adaptor *c* to a condenser. The condensed liquid flows back and percolates through the substance in E, and drops again into B (Fr. 1873, 12, 303).

Maly (A. 1875, 175, 80), Wolfbauer (Ber. der Versuchsstationen, Wien, 1878, 1), Weigelt (Repertorium der analytischen Chemie, 1881, 1, 7), and Flückiger (Fr. 1882, 21, 467) have described apparatuses which resemble or else are modifications of that of Zulkowski.

Drechsel's apparatus (fig. 9).—A folded filter, having double the usual number of folds, so that it may fit well to the sides of the vessel, is placed in the glass globe E, and on this paper the substance to be extracted is put. The solvent is placed in the flask B, which has a tube *t* fused into its side; on warming B the vapour ascending through *t* and through the tube *m*, which is held in contact with *t* by a cork and is fused on to the glass apparatus C, passes on to a reflux condenser connected with C by the tube *r*. The condensed liquid flows back into C and is led by the tube *n* into the globe E where it falls on the substance, and after having percolated through it returns to B again (J. pr. 1877, 123, 350).

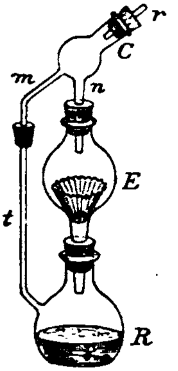

FIG. 9.

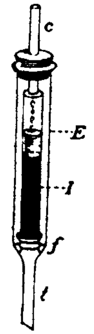

FIG. 10.

Payen's apparatus is somewhat similar to that of Drechsel. In the place of E there is a long conical vessel in which the substance rests on a cotton wool plug, and the tube *t* proceeds from a tubulure and cork in B, and bends over at the top and passes through the cork at the top of E. (A. Ch. 1845 [3] 13, 59).

Kopp's apparatus (Comptes Rendus des Travaux de Chimie par Laurent et Gerhardt, 1849, 5, 305) is an improved form of that of Payen.

Weyl's apparatus (Zeitschrift fur Instrumentenkunde, 1885, 5, 126) is an arrangement like Drechsel's, but by the employment of mercury joints an ordinary funnel can be used instead of the glass globe E.

Tollens' apparatus (fig. 10).—This is an improvement on an earlier form which was described by Tollens (Fr. 1875, 14, 82). The substance is placed in the inner tube I, which is slightly contracted at the bottom *f*, and then spread out into a rim over which a piece of filter paper is tied. This tube I is placed in a wider tube E and rests on a bit of bent glass rod at *f*, which prevents it from closing the aperture into the narrower part *t*. The neck *t* is fitted by means of a cork into a flask containing the solvent, the vapours of which ascend through the space between I and E, and then through *c* to the condenser. The condensed liquid drops into I and after percolating through the substance passes through the filter paper and back into the flask again (Fr. 1878, 17, 320).

Schulze and v. Rampach's apparatus (fig. 11).—This was an improvement on the earlier form of Tollens' apparatus. It resembles Tollens' later form with the exception that the inner tube I in which the substance is placed passes through and is held in its place by the cork at the top of the outer tube E. The inner tube I is connected with a condenser and is perforated just below the cork with one or more holes through which the ascending vapours pass and enter the condenser (Fr. 1878, 17, 171).

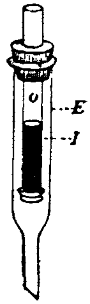

FIG. 11.

Scheibler's 1st apparatus (German Pat. 3,573, 1878, and 7,453, 1879; D. P. J. 1879, 234, 128), and also those of West-Knights (The Analyst, 1883, 8, 65) and of Besemann (Repertorium der analytischen Chemie, 1886, 6, 390) differ but little from Schulze and v. Rampach's.

Gawalowski (Fr. 1883, 20, 528) describes some improvements in percolating forms of extractors; one of these is to provide a stopcock to close at will the side tube up which the vapours ascend; if this is closed from time to time and the source of heat is removed the contraction in the flask sucks the liquid through the substance undergoing extraction. Another is to employ an arrangement like Drechsel's in addition to and underneath an improved form of Zulkowski's tube, whereby perfect filtration is attained.

One disadvantage in the percolation apparatus is that the drops from the condenser always fall on nearly the same spot of the surface of the substance, so that some portions do not get such a good chance of being extracted as others. To remedy this Barbier (J. Ph. 1878 [4] 27, 200) employed an apparatus in which a syphon in a vessel above the percolator pours a considerable volume of the solvent from time to time on the substance, so that the surface of the latter becomes covered with a layer of liquid. The apparatuses of Guérin (J. Ph. 1879 [4] 30, 511), Stockbridge (C. C. 1885 [3] 16, 280), and of Wollny are others that adopt this plan, and that of the last mentioned is given below as a type of the class.

Wollny's apparatus (fig. 12).—This consists of a receiving flask B to contain the solvent, and two other pieces shown in section in the figure. These bits are united together by the mercury joints *a*, *b*, *c*, *d*, which are provided with small tubes to permit of their being emptied without tilting the apparatus. The top joint *d* connects the apparatus with the condenser. The substance to be extracted, contained in a cartridge of paper which must be permeable by the vapours, is placed in the tube E. The vapours of the solvent ascend the tube *p*, and then pass downwards through E, heating the substance on their way, into the space F whence they escape up the tube *t* to the condenser. The condensed liquid collects in the vessel V, and is syphoned off from time to time by the tube *s*, thus ensuring the complete extraction of the substance. The solution returns through F and the long tube *q* to the flask again. In cases where boiling the solution injures the dissolved constituents, vapours of the solvent can be introduced through the side tube *r* from another vessel of solvent heated separately, and the flask R can be left cold (Fr. 1885, 24, 48).

References to other authors who have described forms of percolation apparatus are:—Robiquet (J. Ph. 1851 [3] 20, 168); Dragendorff (Fr. 1862, 1, 490); Berjot (Bulletin de la Société d'Encouragement, 1862, 61, 396), and Wagner (Fr. 1870, 9, 354) describe forms using only cold percolation and requiring the distillation to be done apart from the percolator. Schloesing (A. Ch. 1847 [3] 19, 239); Arnaudon (Il Nuovo Cimento, 1858, 8, 260); Gerber (B. 1876, 9, 656); Cazeneuve and Caillol (J. Ph. 1877 [4] 25, 265); Tschlapowitz (Fr. 1879, 18, 441); Biechele (Correspondenz-Blatt des Vereins analytischer Chemiker, 2, 70); Wolff (*ibid.* 91); Guichard and Damoiseau (Répertoire de Pharmacie, 1880, 8, 97); Medicus (Fr. 1880, 19, 163); Thorn (German Pat. 14,523, 1880, and D. P. J. 1882, 243, 248, and with later improvements German Pat. 18,850, 1881, and D. P. J. 1882, 246, 374); Dunstan and Short (Ph. 1883 [3] 13, 663); Kreusler (C. Z. 1884, 8, 1323); Thresh (Ph. 1884 [3] 15, 281); Will (*ibid.* 363); Waite (*ibid.* 376); Johnson (C. N. 1885, 52, 39, and 82); Foerster (Fr. 1888, 27, 30, and 173); Neubauer (D. P. J. 1888, 267, 513).

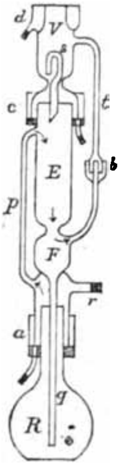

FIG. 12.

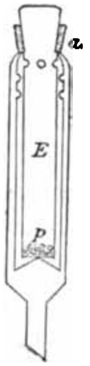

FIG. 13.

The following are continuous infusion apparatuses.

Scheibler's 2nd apparatus (fig. 13).—As the first apparatus could not be constructed wider to hold large quantities without danger of the solvent percolating in one channel through the substance and leaving part unextracted, Scheibler designed a modification involving continuous infusion with an overflow. The apparatus (shown in section in the figure) is made of metal, and the substance is placed in the innermost tube E, which is closed at the bottom with a piece of wire gauze with a layer of cotton wool *p* above it. The inner tube slightly widens at the top and is ground into the top of the outer vessel so as to be removable. The outer vessel is composed of two tubes which are permanently united at the neck *a*; the outside one ends below in a funnel which fits into the vessel of solvent; the inner one is closed below, the bottom being bent up as shown; it has two rows of perforations in it near the top. The innermost tube has one row of perforations just below the neck. The vapours pass up the outer space and through the perforations to a condenser fitted to the neck of the inner tube, the condensed liquid drops on to the substance, descends through it, then passes up the space between E and the next tube and overflows through the lower row of perforations and so back into the vessel of solvent again (German Pat. 9,481, 1879).

Rempel's apparatus (C. Z. 1887, 11, 936) is also an overflow apparatus, but is so arranged that the substance is placed in the outside vessel and the liquid rises and overflows, and the vapours ascend through tubes in the centre.

Scheibler's 3rd apparatus (fig. 14).—This was used in isolating vanillin from raw beetroot sugar. The substance to be extracted is placed in the vessel E (an elutriating vessel such as is used in the mechanical analysis of soils) and rests on a plug of cotton wool *b*. The solvent is poured on to it, until some escapes from the tube *t* into the flask R which is placed on a water-bath. The vapours of the solvent are conducted by the tube *p* back into E whence they pass through *c* to a reflux condenser. The condensed liquid flows back through *c* on to the substance in E, thus causing a constant overflow of liquid from the end of *t* carrying with it the soluble constituents of the substance which thus accumulate in R (B. 1880, 13, 338*a*).

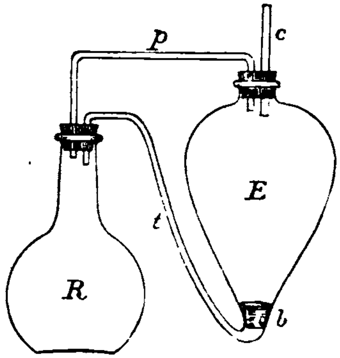

FIG. 14.

References to other continuous infusion apparatuses are:—Wynter Blythe (C. J. 1880, 37, 140); Johnstone (The Analyst, 1885, 10, 81); Stoddart (*ibid.* 108); Schmidt and Hänisch (German Pat. 42,753, 1887, and D. P. J. 1888, 268, 564); Koch (D. P. J. 1888, 267, 515).

Intermittent infusion apparatuses are—

Simon's apparatus (fig. 15).—Both the substance to be extracted and the solvent are placed in the flask E, and are there heated together. The vapours ascend the tube *c* and are condensed by causing a current of water to circulate in the surrounding vessel B; the water enters through the tube *i*, and escapes by the tubulure *e*. A filtering apparatus, F, which is shown in section both in the flask and in the enlarged figure at the side, is constructed by drawing a piece of flannel or fine linen over the end of the tube *t*, which passes for a little way into a perforated cork *k*; another piece of flannel is tied over the lower end of the cork, and the space left between the two flannel surfaces is filled with some pulled out wadding.

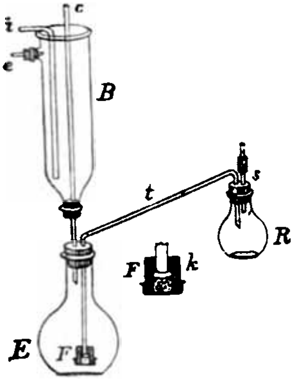

Fig. 15.

The other end of *t* passes through a cork into the flask R, and through the same cork a short glass tube passes, to which is fitted, by means of a small cork, a short closed piece of glass tubing. When E has been heated for a time, *s* is opened by removing the small cork, with its closed tube, and the upper end of *c* is closed; then by means of an india-rubber tube attached to *i* the water is syphoned out of the vessel B. The vapour of the solvent being no longer condensed and being unable to escape, forces the solution up through *t* into the flask R, and the arrangement F filters it on its way. When no more passes over, *c* is opened and *s* is closed; the current of water is re-started in B, the source of heat is removed from beneath E, and the solvent is distilled from R back into E, leaving the dissolved matter behind in R. These operations are repeated until the substance yields nothing more to the solvent (Fr. 1873, 12, 179).

Schwaerzler (J. Ph. 1853 [3] 24, 134) and Schiel (A. 1858, 105, 257) have also described apparatuses in which the pressure of heated vapour is used to force the solution from one vessel to another.

References to other apparatuses of the intermittent infusion group are: Daubrawa (Vierteljahrschrift für practische Pharmacie, 1859, 8, 36); Fleury (J. Ph. 1862 [3] 41, 282); v. Schroeder (Fr. 1886, 25, 132); Barlow (C. N. 1888, 57, 56).

Soxhlet and Szombathy's apparatus (fig. 16). This was the first apparatus to introduce the use of the syphon to effect automatic intermittent infusion. The substance to be extracted, contained in a cartridge of filter paper, is placed in the wide tube E, at the bottom of which a tube, *s*, bent so as to form a syphon, is fused on. Another tube, N, not quite so wide as E, is fused on to the bottom of the latter, without, however, opening into it. The down tube of the syphon *s* passes through the side of N, and is sealed in by fusion. A condenser is fitted to the top of E, and the tube N is fixed by a cork into a vessel of the solvent. On boiling the solvent the vapours ascend through N and through the side tube *t*, which is sealed into both N and E, and reach the condenser, whence the condensed liquid drops back into E and accumulates until it rises to the level of the top of the syphon *s*, when the syphon flows and empties the contents of E into the vessel beneath; E then fills again, and its contents are syphoned off every time the level reaches the top of the syphon-tube. The top of the cartridge should be below the level of the top of the syphon, so that it may be completely immersed in the solvent, and it should rest on a plug of glass wool or strip of metal bent into a ring so that the opening to the syphon may not be closed (D. P. J. 1879, 232, 461).

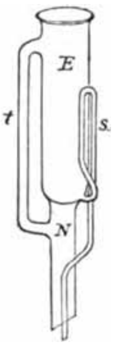

Fig. 16.

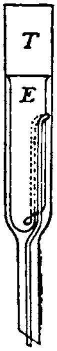

Fig. 17.

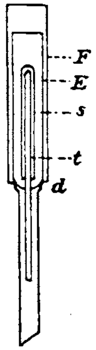

Fig. 18.

Wollny (Fr. 1885, 24, 51) describes an improved form of Soxhlet's and Szombathy's apparatus.

Clausnizer and Wollny's apparatus (fig. 17). This is a modification of Soxhlet and Szombathy's apparatus. The bottom of the inner tube E is drawn out, and to it a syphon-tube is sealed on, as shown in the figure. The tube E and its syphon fit loosely into an outer tube T, which is fitted into a vessel of the solvent below and leads to a condenser above. The substance to be extracted is placed in E, and the mode of working is similar to that of the previous apparatus. The vapours passing up in the space between E and T maintain the substance and the solvent at a temperature approaching the boiling-point of the latter (Fr. 1881, 20, 81).

King's apparatus (fig. 18).—This is another modification of Soxhlet and Szombathy's apparatus. Into the bottom of the wide tube E there is fused the long narrow tube *t*, which is ground off at an angle at its upper end. A tube, *s*, slightly wider than *t*, and closed at one end, is inverted over *t*, and rests on the upper end of the latter: it does not quite reach to the bottom of E. The tube E slips into a still wider one, F, which is dented in in several places at *d*, in order that the dents may support E and prevent it closing the narrower part of F. The substance to be extracted is placed in E, and rests on a plug of glass wool at the bottom. It is fitted up as in the two previous apparatuses, and when the liquid in E rises to the top of *s*, *s* and *t* form a syphon and draw off the liquid into the vessel below (C. N. 1888, 57, 235).

Masojídek (Zeitschrift für Zuckerindustrie in Böhmen, 1881, 6, 51) and Boessneck (C. Z. 1887, 11, 1600) had previously described apparatuses on the same plan as King's.

Roth's apparatus (figs. 19 and 20).—This is employed for extracting oil from seeds by means of carbon disulphide. The solvent is stored in a reservoir, which is kept immersed in water to check evaporation. A pipe from an elevated water reservoir enters at the top of the carbon disulphide reservoir, and another pipe communicating with the extractor passes through the top of the reservoir and descends nearly to the bottom, so that when the tap of the water-pipe is opened the carbon disulphide is forced into the extractor. The latter is a cylindrical vessel, shown in section in fig. 19; it is provided with a perforated false bottom, F, supported by struts GG. The false bottom F is covered with sackcloth, and on it the ground seed or oil cake is placed and filled in up to another perforated plate, J, also covered with sackcloth. The top of the extractor is fastened on with screw clamps so as to be readily removable. At the bottom is a T piece, communicating by the opening B with the carbon disulphide reservoir and, by the branch C, with a steam boiler. When filled and closed carbon disulphide is forced in through B, and when it has dissolved the oil fresh carbon disulphide is forced in at B, causing the first charge to overflow down the pipe L, the entrance to which is protected with a strainer, and to pass to the distilling apparatus. A gauge, Q, shows the level of the liquid, and also allows samples to be drawn. The material is treated some three times or so with the fresh solvent until a sample taken at Q is found to be free from oil; half of the last charge is then conducted through the tap E, and a pipe connected with it to another similar extractor, and the other half is returned to the carbon disulphide reservoir. In order to recover the last portions of solvent adhering to the material the valve N is opened and steam is sent in through C; the carbon disulphide is thus boiled off and passes through N to a condenser. When all carbon disulphide is driven off, the taps R and D are opened; the former allows the steam to escape and the latter allows the condensed water to run off. The cover is then removed and the extractor is emptied and refilled with fresh material.

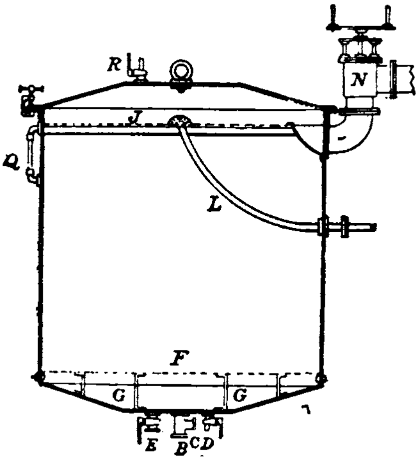

FIG. 19.

The distilling apparatus, shown in section in fig. 20, is a cylindrical vessel, into which the solution of oil is introduced through the tap E, and pipe attached which descends nearly to the bottom. The vessel is half filled with liquid, the level being ascertained by the gauges FF. At the bottom of the vessel are two steam coils; the lower one is perforated with a number of small holes and is fed by the tap H; the upper one is not perforated and is fed by the tap J, and the condensed water from it escapes through the tap L. At first steam is slowly passed through the upper coil and heats the carbon disulphide, the vapours of which pass by the wide tube C to a special form of condenser; when nearly all the carbon disulphide has escaped steam is passed through H, and escaping by the perforations through the oil removes the last traces of the solvent. The tap D allows the steam to escape at the end of the distillation. The oil is finally run off through the tap K to a reservoir, where it is allowed to stand until the condensed water has separated in a layer (Schaedler's Technologie der Fette und Oele, 1883, vol. i. p. 292).

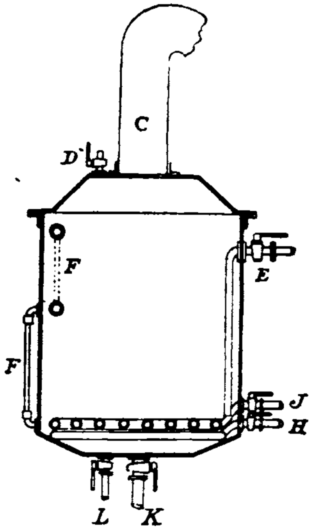

FIG. 20.

Leuner's apparatus (fig. 21).—This is employed for removing fat from bones. The bones are filled into the cylindrical vessel A (shown in section in the figure), and rest on the perforated false bottom *aa*; then all the taps are closed except *p* and steam is injected through the pipe *b*; when all the air is expelled, *p* is closed, and the bones are kept in contact with steam under pressure for a time. Steam is then shut off, and the taps *p*, and one attached to the tube *d* are opened, and the condensed water is drawn off. In the cylindrical vessel B there is placed equal volumes of water and petroleum naphtha, or other volatile solvent; taps *p* and *d* are closed, and taps *g* and *i* are opened, as also are the taps *q* and *r*, to allow the water and solvent to flow into A; *q* and *r* are then closed and an equal volume of water is introduced into B. Steam is now passed through the pipe *cc*, and this heats the water which forms the lower layer in A, and the heat is communicated to the upper layer of solvent. The vapours rise through the bones and pass through the pipe *ss* to the small vessel C, and thence to the reflux condenser contained in D. The condensed liquid collects in C until it reaches the opening into *s*, when it flows back into A and is spread over the bones by the arrangement shown at the top. Any vapours that are not condensed pass through the pipe *l* and are led under the surface of the water in B, which is provided with a small condenser E to prevent the escape of vapours of the solvent to the air. The bones are thus subjected at the same time to the action of steam and petroleum vapour and also of liquid petroleum. After this action has gone on for some time the tap *g* is closed and *h* is opened; the vapours evolved from A then pass to a second condenser, which is contained in D and communicates with C—it is indicated by dotted lines—and the tap *k* is opened; this allows the solvent to flow from C down the tube *nn* and collect in B. The heating is continued until all the solvent is driven off and water only enters C: this can be seen by glazed apertures in that vessel. When this occurs the operation is finished, and a mixture of fat and of aqueous liquid is drawn off by the pipe *d*, and the latter is used in preparing glue (German Pat. 17,181, 1881, and S. C. I. 1882, 1, 155).

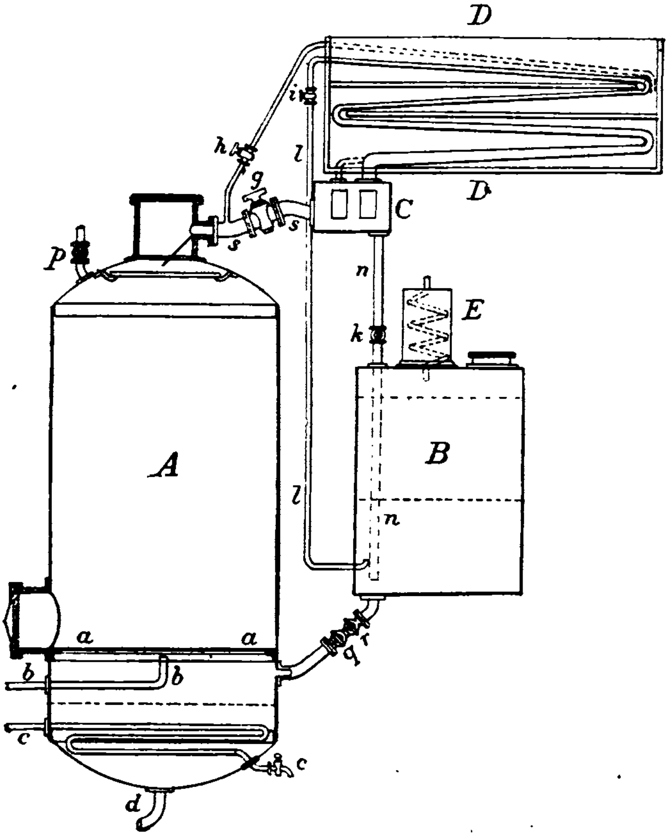

Fig. 21.

Merz's apparatus (fig. 22).—This apparatus is designed for the extraction of various substances with volatile solvents; it can also be used with animal charcoal for decolourising purposes. It consists of an inner vessel E, which is open at the top and is contained in a closed outer vessel R. The substance is filled into E through the manhole *a*, and at the end of the operation it is removed through the manhole *b*. The solvent is stored in a reservoir S, which forms the lower part of the condensing vessel T, and is divided from the upper part by the partition *d*. The extractor E is filled with solvent by opening the tap *t*. When the level of the liquid rises as high as the top of the syphon *s* the latter begins to act and runs off the liquid from E into the outer vessel B. The entrance to the syphon is protected by the sieve arrangement shown at the bottom of E. Steam is made to circulate through the coil *eee* at the bottom of R; this causes the solvent to boil, and its vapours circulate in the space between B and E, warming the latter and its contents, and then pass to the condensing tubes *ccc*, round which water is circulating. The condensed liquid falls back into E, and when the level again reaches that of the top of the syphon the syphoning-off is repeated and so on over and over again. The substance is thus submitted to intermittent infusion. Samples can be drawn off at *u*, and when the extraction is found to be complete the water that surrounds the tubes *ccc* is withdrawn. The solvent then boils off, and after condensation in the worm W returns to the reservoir S. The extract is drawn off by the tap *v*. By regulating the tap *u* the substance can be made to undergo continuous instead of intermittent infusion, if desired (German Pat. 20,742, 1882, and S. C. I. 1883, 2, 234).

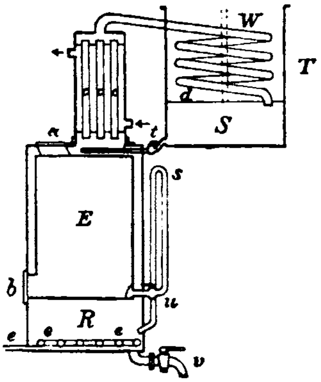

FIG. 22.

Other forms of extraction apparatus for manufacturing purposes will be found in the following references. The list includes those intended for use with water as well as with other solvents: Hänig and Reinhard (Germ. Pat. 6,737, 1878, and Horatius' Fabrication der Aether und Grundessenzen, 1881, p. 126); Knobel (Germ. Pat. 9,700, 1878, and D. P. J. 1880, 237, 452; Kohlrausch (Germ. Pat. 12,296, 1880, and D. P. J. 1881, 240, 72, and 1883, 249, 307); Rostock & Co. (Germ. Pat. 17,101, 1881, and D. P. J. 1882, 246, 22); Schorm (Austrian Pat. of Nov. 10, 1881, and D. P. J. 1882, 246, 23); Hart (Germ. Pat. 19,185, 1881, and S. C. I. 1882, 1, 439); Küsel (Germ. Pat. 20,734, 1882, and S. C. I. 1883, 2, 279); König (Germ. Pat. 21,188, 1882, and S. C. I. 1883, 2, 235); Brönner (Germ. Pat. 21,681, 1882, and D. P. J. 1883, 249, 274); Naudir (Moniteur Scientifique, 1883, 25, 174); Ax (Germ. Pat. 24,752, 1883, and D. P. J. 1884, 252, 71); Bense (Germ. Pat. 30,850, 1884, and D. P. J. 1885, 256, 275); Weber & Co. (Germ. Pat. 32,849, 1885, and D. P. J. 1887, 263, 285); Breithaupt (Germ. Pat. 36,885, 1886, and D. P. J. 1886, 262, 419); Grauer (*v. infra* under *Liquids*); Lewin (D. P. J. 1887, 264, 25). Several other forms will be found in Schaedler's Technologie der Fette und Oele.

Liquids. A substance held in solution by a liquid can often be removed by treating the liquid with a solvent that is not miscible with it. The ordinary procedure is to shake the liquid and the solvent vigorously up together in a separator, which is a pear-shaped glass vessel terminating in a stoppered tubulure at its broad end, and in a stopcock and short tube at its narrow end, all the parts being constructed of stout glass. After shaking, the vessel is allowed to stand, narrow end downwards, until the liquid and the solvent have separated into two layers. The stopper is then removed, and the lowermost layer tapped off by means of the stopcock and tube. This treatment is repeated with fresh solvent until the liquid has given up all the dissolved substance it contained.

Schwarz has invented an apparatus which works automatically and avoids the tedious operations of the old method.

Schwarz's apparatus (fig. 23).—The liquid from which the substance is to be extracted is placed in the flask E, and the solvent, which must be lighter than the liquid, is placed in the receiving-flask R, and is there boiled. The vapours ascend through the tube *t* to the upper vessel V, and thence through the tube *c* to a reflux condenser. The condensed solvent descends the tube *p*, then rises through the liquid in E, and collects as a layer above it until it reaches the opening into the side tube *q*, when it overflows and returns to the flask R. This circulation goes on automatically, and when on testing a drop of the overflowing liquid the extraction is found to be complete, water is poured down V until all the solvent overflows down *q* into R; the parts are then disconnected, E is emptied, and by reconnecting and heating R the solvent can be distilled off into E, leaving the desired substance in R. At *a* and *b* are mercury joints, which enable connection and disconnection to be readily made (Fr. 1884, 23, 368).

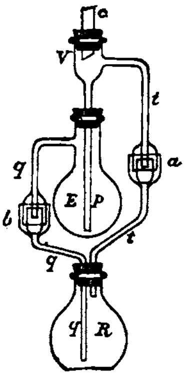

FIG. 23.

Other apparatuses for extracting liquids have been described by Wollny (Fr. 1885, 24, 52, and 202), and by Grauer (D. P. J. 1886, 262, 475). These two authors describe forms for using both when the solvent is specifically lighter, and also when it is heavier, than the liquid to be extracted; Grauer's apparatuses are on a manufacturing scale. Neumann (B. 1885, 18, 3061); Eiloart (C. N. 1886, 53, 281); and Schutze (C. Z. 1887, 11, 1159) have also described apparatuses for this purpose. Schutze's apparatus is not automatic. H. H. R.

F

FAHL-ORE, a name applied to a group of metallic minerals, consisting of isomorphous mixtures of various sulphides crystallising in the regular system. The common forms are tetrahedral, whence the typical species is often termed *Tetrahedrite*. The crystals have been exhaustively studied by Sadebeck, Klein, and Seligmann. The mineral presents an iron-black or steel-grey colour, with metallic lustre, and yields when scratched a black streak, inclining to red when much zinc is present: it is rather brittle, breaking with a conchoidal or uneven fracture. H. 3 to 4; sp.gr. 4·3 to 5·8.

The chemical composition of fahl-ore, which is extremely complex and variable, was studied first by Klaproth and afterwards by H. Rose. It usually conforms to the formula:

$$4(Cu_2,Ag_2,Fe,Zn,Hg)S + (Sb,As)_2S_3.$$

Copper is always present, and may form as much as 44 p.c. of the mineral: fahlerz is therefore often worked as an ore of copper, and is sometimes known as *grey copper-ore*—a name also applied to copper-glance. Silver may be present to the extent of 30 p.c. (*v.* FREIBERGITE). Cobalt is found in some varieties, but lead rarely occurs; bismuth has been detected in certain kinds of fahl-ore, that from Neubulach in the Black Forest having yielded, according to Senfter, upwards of 6 p.c. The blowpipe reactions necessarily vary with the composition of the mineral.

According to Rammelsberg, three distinct groups of fahl-ore may be recognised: 1. an *antimonial* series, including the dark-coloured varieties; (2) an *arsenical* series, generally of light colour; and (3) an *antimonio-arsenical* series, the As being subordinate to the Sb. The first group comprises those varieties which are used as ores of copper and silver; the second group includes *Tennantite*, an iron-bearing arsenical fahl-ore found near Redruth in Cornwall, and named after Smithson Tennant; the third group contains certain varieties which carry mercury, that of Kotterbach in Hungary yielding upwards of 17 p.c. Mercurial fahl-ore has been named *Schwatzite*, from Schwatz in Tyrol.

The following selected analyses illustrate the composition of fahl-ore:—

—	I	II	III	IV	V
S .	23·52	24·80	28·11	26·83	22·53
Sb .	26·63	26·56	—	12·46	19·34
As .	—	—	18·87	10·19	2·94
Bi .	—	—	—	—	0·81
Ag .	17·71	10·48	—	0·60	—
Cu .	25·23	30·47	41·07	40·60	35·34
Fe .	3·72	3·52	2·22	4·66	0·87
Zn .	3·10	3·39	8·89	3·69	0·69
Pb .	—	0·78	0·34	—	0·21
Hg .	—	—	—	—	17·27
	99·91	100·00	99·50	99·03	100·00

1. From near Wolfach, by H. Rose. 2. Near Neudorf, Hartz, by Rammelsberg. 3. Prophet Jonas Mine, near Freiberg (copper blende), by Plattner. 4. S. Marie aux Mines, Alsace, by H. Rose. 5. Kotterbach, near Iglo, by Vom Rath.

The localities yielding fahl-ore are very numerous. Fine tetrahedral crystals, often incrusted with copper-pyrites, occur near Liskeard in Cornwall. Other typical localities are Clausthal and Andreasberg in the Hartz; Dillenburg in Nassau; Freiberg in Saxony; Przibram in Bohemia; Kremnitz in Hungary; and Kapnik in Transylvania. Fahl-ore also occurs in Chile, Mexico, California, Nevada, Arizona, &c.

F. W. R.

FALSE MYRRH *v.* GUM RESINS.

FARINA, or **POTATO STARCH.** The starch of the potato, *Solanum tuberosum*. The tubers are placed in a cylinder furnished with teeth by means of which the starch cells are lacerated whilst the mass of potatoes is reduced to a stiff pulp. The starch granules are washed out and allowed to settle in vessels of water, when the water is drawn off. The moist starch after being separated from the cellulose is dried and broken up between iron rollers. It is then ready for its purpose, which is in the main the sizing of textiles.

As a material for the purpose of sizing, farina produces when boiled a thicker paste than any other starch; consequently a small amount of it will furnish a liquor of the same density as a much larger quantity of, for instance, wheaten flour. On the other hand, the starch cells of the potato being exceptionally large, a certain amount of coarseness is felt in cotton goods stiffened by it. For this reason it is seldom used with China clay alone, but is usually mixed with a greater or smaller proportion of flour. It is claimed for farina that, since the potato contains a small amount of nitrogenous matter, it is not so prone to induce mildew in cotton goods as are other forms of starch.

Farina has a glistening appearance and a crisp feeling when pressed between the fingers. It contains a larger proportion of moisture than any other starch, varying from 17 to 20 p.c. The granules are very characteristic, being for the most part large though irregular in size and resembling an oyster-shell in form, being moreover marked with similar eccentric rings.

The following is the average composition of ordinary commercial farina:

Water	16·72
Cellulose	0·36
Ash	0·22
Starch	82·70
	100·00

Farina is preferred to other starches for the manufacture of British gum, its great purity making it especially suitable for this purpose *v.* STARCH.

FAST BLUE B, FAST BLUE 2B, FAST BLUE R *v.* INDULINES; OXAZINES.

FAST BROWN N, ACID BROWN, NAPHTHYLAMINE BROWN *v.* Azo- colouring matters.

FAST BROWN 3B *v.* Azo- colouring matters.

FAST GREEN or **MALACHITE GREEN, VICTORIA GREEN, NEW GREEN, VERT DIAMANT, BENZOL-** and **BENZAL-GREEN** *v.* Triphenylmethane colouring matters.

FAST PONCEAU B and **2B, BIEBRICH SCARLET, PONCEAU 3R** or **3R B, AZO-BENZENE RED** *v.* Azo- colouring matters.

FAST RED, FAST RED A, or **ROCELLIN, RUBIDINE, ORSEILLINE** *v.* Azo- colouring matters.

FAST RED D (Badische Co.), **BORDEAUX S,** *v.* Azo- colouring matters.

FAST SCARLET *v.* Azo- colouring matters.

FAST YELLOW or **JAUNE SOLIDE** *v.* Azo- colouring matters.

FAT LUTE *v.* Lutes.

FATTY ACIDS. A numerous and important group of acids of the general formula $C_nH_{2n}O_2$ certain members of which are essential constituents of the animal and vegetable fats. The lowest term of the series is *Formic acid* CH.COOH; the highest term at present known is *Theobromic acid* $C_{63}H_{127}$.COOH. As the alcohol radicle C_nH_{2n+1} may exist in a great variety of modifications, it follows that the fatty acids are also capable of existing in numerous isomeric forms. The fatty acids may, like the monovalent alcohols, be distinguished as primary, secondary, and tertiary. The secondary acids are usually termed *iso acids*, whilst the acids containing the groups $CH_3CH_2CH_2$ . . . are called *normal acids*.

The naturally occurring fatty acids are found partly free and partly in the form of ethers. Formic acid is found in ants, caterpillars, and in the stinging-nettle; butyric acid in butter, in perspiration, and, combined with hexyl alcohol, in the fruit of *Heracleum giganteum*; cerotic acid in beeswax, stearic acid in animal fats &c. The higher members of the series in combination with glycerin, forming the so-called *glycerides*, constitute the greater part of the more important animal and vegetable fats and oils and the different varieties of the waxes.

The lower members of the series, formic, acetic, propionic, are mobile volatile liquids miscible with water, alcohol, and ether in all proportions. As the number of carbon atoms increases they become less soluble in water, more oily and viscid, and less volatile. Thus *Œnanthylic* (*heptoic*) *acid* $C_7H_{14}O_2$ is insoluble in water; *Capric* (*Decylic*) *acid* $C_{10}H_{20}O_2$ is solid at ordinary temperatures, whilst *Lauric acid* $C_{12}H_{24}O_2$ and the higher homologues cannot be distilled under ordinary pressure without decomposition.

(For the synthetical methods of formation of the fatty acids and their general modes of decomposition and particulars of their salts *v.* Watts' Dictionary of Chemistry.)

Formic acid H.COOH. Discovered by Rey in 1670 by distilling red ants with water. Formed in the acid secretions of certain caterpillars; in the common nettle; in the fruit of the soap-nut tree (*Sapindus saponaria*); in tamarinds &c. Occurs in sweat, urine, and muscular plasma. Formed by the dry distillation of starch, sugar, gum, tartaric and oxalic acids, &c. Best obtained by heating a mixture of glycerin (or other polyatomic alcohol of high boiling point) with crystallised oxalic acid. The anhydrous glycerin is heated with the oxalic acid to 75°–90° until the evolution of carbon dioxide ceases, when a fresh quantity of oxalic acid is added and the process repeated. The oxalic acid $C_2H_2O_4.2H_2O$ decomposes into water, carbon dioxide, and formic acid, which reacts upon the glycerin, forming *mono-formin*.

$$\underset{\text{Glycerin}}{C_3H_5(OH)_3} + \underset{\text{Formic acid}}{H.COOH} = \underset{\text{Monoformin}}{C_3H_5(OH)_2COOH} + H_2O.$$

On the addition of a further quantity of crystallised oxalic acid, the water of crystallisation decomposes the monoformin, producing glycerin and formic acid, which distils over; monoformin is thus being continually formed and destroyed, with the eventual production of formic acid of from 87 to 88 p.c. (Lorin, Bl. 5, 7; 20, 241; 24, 22, and 436).

Anhydrous formic acid may be obtained by gently heating lead formate with sulphuretted hydrogen, or by heating the dehydrated sodium salt with anhydrous oxalic acid. Is a colourless, slightly fuming liquid, with a penetrating smell, and is intensely corrosive. Boils at 99·9, sp.gr. 1·2211, solidifies at a low temperature, forming large brilliant plates, m.p. 8°·6. Traces of water lower the m.p. and raise the b.p. Is a powerful antiseptic and a strong reducing agent. Heated with concentrated sulphuric acid it evolves carbon monoxide. With ferric chloride, neutral solutions of formates give a red colour. Silver nitrate is reduced to metallic silver, which is precipitated, partly as a black powder and partly as a lustrous deposit on the tube. Mercuric chloride is reduced to calomel.

Potassium formate CHO_2K and *Sodium formate* CHO_2Na are readily soluble deliquescent salts which according to Bineau form acid salts on solution in hot concentrated formic acid. *Calcium formate* $(CHO_2)_2Ca$, and *Barium formate* $(CHO_2)_2Ba$ crystallise in rhombic prisms, readily soluble in water, insoluble in alcohol. *Lead formate* $(CH.O_2)_2Pb$ is also soluble in water but insoluble in alcohol; the solution forms a series of basic formates on being warmed with lead oxide, which have an alkaline reaction and crystallise in needles. *Copper formate* $(CHO_2)_2Cu.4H_2O$ crystallises in light blue monoclinic prisms: forms an acid salt $(CHO_2)_2Cu.2C.H_2O_2.3H_2O$. Silver and mercurous formates decompose even in the dark, and the latter deflagrates when heated and decomposes on percussion. *Methyl formate* boils at 30·4 (712 mm.), sp.gr. 0·9928: it is best made by acting on dry sodium formate with a mixture of methyl alcohol and aqueous hydrochloric acid, or by digesting methyl alcohol with concentrated formic acid.

Acetic acid CH_3COOH *v.* Acetic acid, vol. i.

Propionic acid CH_3CH_2COOH. Discovered by Gottlieb in 1844 by oxidising metacetone, and termed by him *metacetonic acid*; he also obtained it by heating gum, sugar, starch &c. with concentrated potash solution. Produced in the fermentation of calcium lactate, tartrate, and malate, and also in the fermentation of glycerin (Fitz, B. 12, 476). Found among the products of the distillation of wood. Usually prepared by heating the nitrile with dilute sulphuric acid (for details *v.* Beckurts and Otto, B. 10, 262). Colourless liquid smelling like acetic acid; b.p. 140°, sp.gr. 1·016 at 0°. Soluble in water, but on addition of calcium chloride to the solution it separates out as an oil.

Butyric acid C_3H_7COOH. Two modifications are known, *normal butyric acid* and *isobutyric acid.*

1. *n. Butyric acid* $CH_3(CH_2)_2COOH$. Discovered by Chevreul in 1818 in butter, in which it occurs to the extent of about 2 p.c. as glyceryl butyrate. Found in many other animal fats, *e.g.* cod-liver oil; in muscle-plasma; perspiration, &c. Present also in many vegetable oils, as in croton-oil; in tamarinds; soap-nut, &c. A frequent product of putrefaction and fermentation; found in putrid yeast; in cheese; in spent-tan liquor. Produced by the action of ferments on calcium lactate, glycerin, &c., and by the dry distillation of wood, amber, &c. Usually prepared by the fermentation of a mixture of sugar, tartaric acid, putrid cheese, and sour milk and chalk (for details *v.* Bensch, A. 61, 177; *v.* also Fitz, B. 11, 52). A colourless liquid, of strong unpleasant rancid smell, miscible with water; m.p. – 3°, b.p. 162°, sp.gr. 0·9594 $\frac{20}{4}$ (Brühl), 0·9588 $\frac{25}{25}$ (Perkin), C. J. 45.

Calcium butyrate $(C_4H_7O_2)_2Ca.H_2O$ crystallises in transparent scales which are more soluble in cold than in hot water: hence a saturated solution in cold water becomes turbid on heating. By repeatedly heating the solution the salt is transformed into *calcium isobutyrate*, which is more soluble in hot than in cold water.

Ethyl butyrate $C_4H_7O_2.C_2H_5$; b.p. 121°, sp.gr. 0·8892 $\frac{20}{4}$ (Brühl), 0·8762 $\frac{25}{25}$ (Perkin), is obtained by warming a mixture of 2 parts of spirits of wine, 2 parts of butyric acid, and 1 part sulphuric acid for some time to 80°, pouring the mixture into water and washing the ether which separates out with dilute solution of soda, drying over calcium chloride, and distilling. Has a pleasant fruity smell resembling that of the pine-apple, in which it is said to occur. A solution of the crude ether in 8 to 10 parts of alcohol is known as *essence of pine-apple* or *Ananas-oil* (*q. v.*) and is used for flavouring rum, confectionery, &c.

2. *Isobutyric acid* $(CH_3)_2CH.COOH$. Found in St. John's bread, the fruit of *Ceratonia siliqua*, in which it was first discovered by Redtenbacher; among the acids of croton oil; in the root of *Arnica montana*; as *isobutyl isobutylate* in Roman chamomile oil. Obtained synthetically by Erlenmeyer by the action of potash on isopropyl cyanide. Best prepared by the action of chromic acid upon isobutyl alcohol (Pierre and Puchot, A. Ch. [4] 28, 366). A liquid of unpleasant smell, boiling at 153°, sp.gr. 0·9490 $\frac{20}{4}$ (Brühl) 0·9457, $\frac{25}{25}$ (Perkin). Easily oxidised to acetic acid and carbon dioxide.

The isobutyrates resemble the salts of the normal acid, but are as a rule more soluble in water.

Valeric or **pentoic acid** $C_4H_9.COOH$. Exists in four isomeric modifications.

1. *n. Valeric acid* or *propylacetic acid* $CH_3(CH_2)_3.COOH$. is found in pyroligneous acid, and may be obtained by boiling *n.* butyl cyanide with potash (Lieben and Rossi, A. 159, 58); by oxidation of *a n.* oxycapric acid (Erlenmeyer, B. 9, 1840); by reduction of lævulinic acid (β-aceto-propionic acid) by phosphorus iodide or sodium amalgam (Kehrer and Tollens, A. 206, 233; Fittig and Wolff, A. 208, 109); by heating propylmelonic acid; or by the fermentation of calcium lactate (Fitz, B. 13, 1309). A colourless oil of disagreeable smell, b.p. 185·4°, sp.gr. 0·9391 $\frac{20}{4}$; 1 vol. of acid requires 27 vols. of water at 16° for solution.

2. *Isovaleric* or *isopropylacetic acid*

$$CH(CH_3)_2CH_2COOH.$$

Discovered in 1817 by Chevreul in dolphin oil from *Delphinus globiceps* and *D. phocæna*, and termed by him *phocenic acid.* Found in other fish oils and in perspiration. In the roots of *Valeriana officinalis*, *Angelica Archangelica*, and in the berries of *Viburnum opulus.* Formed in the putrefaction of albuminoids; by the oxidation of glue, oleic acid fats, and from optically inactive amyl alcohol. Obtained by the action of alcoholic potash on isopropyl cyanide. Colourless oily liquid, smelling like valerian root and putrid cheese; b.p. 173·7, sp.gr. 0·9309 $\frac{17\cdot4}{}$. Soluble in 30 parts of water. The valeric acid of pharmacy is prepared from valerian root or from amyl alcohol. The ammonium and zinc valerates are also used in medicine.

Amyl valerate $C_5H_{11}O(C_5H_9O)$; b.p. 194°; dissolved in spirits of wine is used in confectionery as *essence of apples.*

3. *Methyl ethyl acetic acid*

$$CH_3.C_2H_5CH.COOH$$

is found in the oil of *Angelica Archangelica*, and may be obtained by heating methyl crotonic acid (tiglic acid) with hydriodic acid (Schmidt and Berendes, A. 191, 117); by the action of sodium amalgam in a sulphuric acid solution of brommethyl ethyl acetic acid (Pagenstecher, A. 195, 109); and by heating methyl ethyl malonic acid (Conrad and Bischoff, A. 204, 151). On oxidising optically active amyl alcohol, a mixture of isovaleric and methyl ethyl acetic acids is obtained which can be separated by converting them into their silver salts, silver isovalerate being six times less soluble in water than silver methyl ethyl acetate. A colourless somewhat mobile liquid; b.p. 177°, sp.gr. 0·9405 $\frac{17°}{}$.

4. *Trimethyl acetic acid* $(CH_3)_3C.COOH$. Obtained by heating trimethyl acetonitrile with strong hydrochloric acid (Butlerow, A. 170, 151), or by the oxidation of pinacolin (Butlerow, A. 170, 151, 173, 355; Friedel and Silva, B. 6, 146 and 816). Crystallises in the regular system; m.p. 35·°4, b.p. 163·°8, sp.gr. 0·905 $\frac{50°}{}$.

Caproic or **Hexoic acids** $C_5H_{11}.COOH$. Six isomerides are known. 1. *n. caproic acid*

$$CH_3(CH_2)_4COOH$$

occurs in the fats; in cheese; and, possibly, mixed with certain of its isomerides, in cocoa-nut oil, in St. John's bread; in the fruit of *Heracleum sphondylium* and in the flowers of

Satyrium hircinum, and in the fusel-oil from the fermented molasses of mangel wurzel. Is best prepared by fractionating crude fermentation butyric acid; b.p. 204·°5, sp.gr. 0·9446 $\underline{0^{\circ}}$.

Amido-caproic acid or *Leucin*

$CH_3(CH)_2CH(NH_2).COOH.$

Occurs, accompanied by *tyrosin*, in many animal organs, as in the pancreas, spleen, salivary and lymphatic glands. Found also in the vegetable kingdom, particularly in the vetch, gourd, potato, and in *Chenopodium album.* Best prepared by boiling horn or glue with dilute sulphuric acid. White crystalline body; m.p. 170°; soluble in 49 parts water at 12°; in 1040 parts alcohol.

2. *Isobutyl acetic acid*

$(CH_3)_2CHCH_2CH_2COOH.$

Best obtained by the action of hydriodic acid upon caprolacton; b.p. 198·0; sp.gr. 0·925 $\underline{0^{\circ}}$. (Mielk, A. 180, 57; Rühlmann and Fittig, A. 226, 347).

3. *Diethylacetic acid* or *pseudocaproic acid*

$(C_2H_5)_2CH.COOH$

may be obtained by the action of sodium upon acetic ether and treatment of the product by ethyl iodide (Frankland and Duppa, A. 138, 221); by boiling diethyl carbinol cyanide with potash (Saytzeff, A. 193, 249); by reduction of dichlorethyl acetic ether by sodium amalgam (Markownikoff, B. 6, 1175); by heating sodium ethylate and sodium acetate in a stream of carbon monoxide (Geuther a. Fröhlich, A. 202, 308); by heating diethylmalonic acid to 170°–180° (Conrad, A. 204, 141); by heating α-diethyl-β-oxybutyric acid (Schnapp, A. 201, 70); b.p. 190° (756·5 mm.), sp.gr. 0·9355 $\underline{0^{\circ}}$

4. *Methyl propyl acetic acid*

$CH_3CH_2CH_2CH_3CH.COOH$

is obtained by the oxidation of its aldehyde, and by the reduction of methylacrylic acid (Lieben and Zeisel, B. 16, 786); by heating α-methyl valerolacton or isosaccharin with hydriodic acid and red phosphorus (Liebermann and Scheibler, B. 16, 1823; Kiliani, B. 18, 632); by heating α-methyl propyl-β-oxybutyric acid (Jones, A. 226, 292), and by the distillation of turpentine; b.p. 193–194, sp.gr. 0·9414 $\underline{0^{\circ}}$; 1 part water dissolves 0·5693 part at 17°.

5. *Methyl isopropyl acetic acid*

$(CH_3.)_2CHCH_3CH.COOH$

may be formed from methylisopropyl carbinol cyanide (Markownikoff, Z. 1860, 205), or by the oxidation of the corresponding hexyl alcohol from Roman chamomile oil (Köbig, A. 195, 102).

6. *Dimethyl ethyl acetic acid*

$(CH_3)_2C_2H_5OCOOH$

is formed by the action of hydrochloric acid upon dimethyl ethyl carbinol cyanide (Wyschnegratzky, A. 174, 56), and by the oxidation of the methyl ethylketone prepared from pinacolin. A colourless liquid; b.p. 187, m.p. −14°.

Heptoic acid. $C_7H_{14}O_2$.

1. *n. heptoic acid, œnanthic acid*

$CH_3(CH_2)_5COOH.$

Obtained by the oxidation of œnanthol (Bussy, A. 60, 248; Schorlemmer and Grimshaw, A. 170, 141), also formed by the oxidation of castor-oil, of oleic acid, and normal heptyl alcohol (Schorlemmer, A. 161, 279), and from the normal hexyl cyanide (Franchimont, A. 165, 237). An oily liquid; b.p. 223·°5, m.p. −10·5, sp.gr. 0·9313 $\underline{0^{\circ}}$.

2. *Isoheptoic acid; methylbutyl acetic acid*

$CH_3(CH_2)_3CHCH_3COOH.$

Obtained by boiling hexyl cyanide with alcoholic potash. An oily rancid smelling liquid; b.p. 211·5 (745·8 mm.), sp.gr. 0·9305 $\underline{0^{\circ}}$. Soluble in 278 parts water (Hecht, A. 209, 309).

3. *Isoœnanic acid*, found among the products obtained by heating a mixture of sodium acetate and sodium isovalerate; b.p. 217°, sp.gr. 0·9260 $\underline{15}$ (Portsch, A. 218, 66).

4. *Isoamyl acetic acid*

$(CH_3)_2CH.(CH_2)_3COOH.$

Obtained by the action of sodium and isoamyl iodide upon acetic ether.

5. *Methyl diethyl acetic acid*

$CH_3(C_2H_5)_2C.COOH.$

Obtained by prolonged heating of methyl diethyl carbinol cyanide with strong hydrochloric acid: b.p. 207–208°; almost insoluble in water.

6. *Methyl isopropyl propionic acid*

$CH_3C_3H_7CHCH_2COOH.$

Obtained by heating sodium isovalerate with sodium ethylate in a stream of carbon monoxide; b.p. 220°.

Octoic acids. $C_8H_{16}O_2$.

1. *n. Octoic acid* or *caprylic acid*

$CH_3.(CH_2)_6COOH.$

Exists as a glyceride in butter, and in human fat, and especially in cocoa-nut oil. It is also found in cheese, among the products of the distillation of fat by superheated steam, and in many fusel oils, partly free and partly in combination with different alcohol radicles. It melts at 16·5 and boils at 236–237°; sp.gr. 0·9139 $\underline{20}$. Sparingly soluble in cold water: 400 parts of water at 100° dissolve 1 part of the acid; readily soluble in alcohol and ether (Zincke, A. 152, 9).

2. *Dipropyl acetic acid* $(C_3H_7)_2CH.COOH$. is obtained by boiling ethyl dipropylacetoacetate with potash; b.p. 219·5; sp.gr. 0·9215 $^{0^{\circ}}_{4}$. Sparingly soluble in water (B. S. Burton, Am. 3, 385).

3. *Isooctoic acid* $(CH_3)_2C_4H_6(CH_3)COOH$ is obtained by the oxidation of iso-octyl alcohol; b.p. 218–220°, sp. gr. 0·926 $\underline{0^{\circ}}$.

4. *Octoic acid* from isodibutylene

$C(CH_3)_3CH_2CHCH_3COOH$

formed by the oxidation of the hydrocarbon; boils at about 215° with partial decomposition (Butlerow, A. 189, 72).

5. *Hexylacetic acid* $C_6H_{13}CH_2COOH$. Obtained from hexylmalonic acid; boils at 232–234°.

Nonoic acids $C_9H_{18}O_2$.

1. *Pelargonic acid* is probably the normal acid, and is contained as an ether in the oil from *Pelargonium roseum*, and may be obtained by the oxidation of oil of rue (from *Ruta graveolens*) and of oleic acid. Also formed by the oxidation of stearolic acid ($C_{18}H_{32}O_2$) and by boiling normal octyl cyanide with potash; m.p. 12·5°, b.p. 253–254°, sp.gr. 0·9068 $\frac{17}{17}$.

The characteristic odour of the quince is probably due to ethyl pelargonate. The ether (b.p. 227–228°; sp.gr. 0·8685 $\frac{17\cdot5}{}$) is prepared commercially for flavouring common wines, brandy, &c., from the oxidised products of oil of rue.

2. *Isononoic acid* or *methylhexyl acetic acid* $CH(CH_3)(C_6H_{13})COOH$, is formed by boiling methylhexyl carbinol cyanide with potash; b.p. 244–246° (cor.); sp.gr. 0·9032 $\frac{18}{}$. Almost insoluble in water; readily soluble in alcohol and ether.

3. *Isoheptyl acetic acid* $C_7H_{15}CH_2COOH$. Obtained by heating isoheptyl malonic acid; b.p. 232°. Insoluble in water; soluble in alcohol and ether (Venable, B. 13, 1652).

Decatoic acids $C_{10}H_{20}O_2$.

Capric acid $CH_3(CH_2)_8COOH$ is formed as a glyceride in the butter of the cow and goat, and in cocoa-nut oil, in association with caproic and caprylic acids. Many fusel-oils also contain it, and it is found as amyl caprate in certain Hungarian wines, and is formed by the oxidation or distillation of oleic acid. A white crystalline substance of m.p. 31·3, b.p. 268–269°, sp.gr. 0·930 $\frac{37^\circ}{}$, possessing a goat-like smell. Insoluble in cold water, but slightly soluble in boiling water.

Isocapric acid is obtained by the oxidation of isocapric alcohol formed by the action of sodium on valeraldehyde; b.p. 241·5°; does not solidify at −37°; sp.gr. 0·9096.

Hendecatoic acids $C_{11}H_{22}O_2$.

1. *Methyl dibutyl acetic acid*

$$C(CH_3).[C(CH_3)_3]_2.COOH$$

is obtained with other products by the oxidation of isotributylene. A white crystalline solid, insoluble in water, but soluble in alcohol and ether; m.p. 66–70°, b.p. 266°.

2. *Undecylic acid* is a crystalline solid having a faint smell of caproic acid; m.p. 28·5; b.p. 228° (160 mm.) (Krafft, B. 12, 1664).

3. *Umbellulic acid* $C_{11}H_{22}O_2$. The nuts of the Californian bay tree (*Umbellularia Californica*) contain about 60 p.c. of a fat easily soluble in ether. It is a white, hard, tallowy mass; m.p. 31°. By saponification with caustic potash and decomposition with hydrochloric acid, the acid is obtained as a white solid with a faint odour and very disagreeable and irritating taste; m.p. 31–34°; b.p. 275–280°. Its alkyl ethers are colourless mobile liquids of agreeable odour (Spillman and O'Neill, Am. Ch. J. 1882). Possibly identical with *cocinic acid* found by Saint-Evre in cocoa-nut oil, and with the *undecylic acid* of Krafft (*v. supra*).

Dodecatoic acids $C_{12}H_{24}O_2$.

1. *Lauric acid*, found by Marsson in laurel fat, a glyceride obtained from *Laurus nobilis*; also present in cocoa-nut oil, in pichurim beans, in Dika bread, and in the fruit of *Cyticodaphne sebifera*; m.p. 43·5; sp.gr. 0·883 $\frac{0^\circ}{}$ and 0·875 $\frac{43\cdot6^\circ}{}$; b.p. 225·5 (100 mm.).

2. *Hordeic acid* is found among the products of the distillation of dried barley with dilute sulphuric acid; forms crystalline plates; m.p. 60°.

Tridecatoic or **tridecylic acid** $C_{12}H_{25}COOH$, obtained by the oxidation of methyl-tridecatyl-ketone: crystallises in thin plates; m.p. 40·5°, and b.p. 236° (100 mm.) (Krafft, B. 12, 1668).

Myristic acid $C_{13}H_{27}COOH$, discovered by Playfair in nutmeg butter, from *Myristica moschata*; is found also in otoba fat, from *M. otoba*, in Dika bread, in cocoa-nut oil, and in butter, and may be obtained by melting stearolic acid with potash. Crystallises in needles; m.p. 53·8°; b.p. 195·6° (15 mm.) and 250·5° (100 mm.); sp.gr. 0·8622 $\frac{53\cdot8^\circ}{}$.

Myristin or *trimyristil glyceride*

$$C_3H_5(C_{14}H_{27}O_2)_3,$$

in which form myristic acid occurs in the various *myristica* fats: crystallises from ether in needles; m.p. 55°.

Pentadecatoic acid $C_{14}H_{29}COOH$ is obtained by the oxidation of methyl-pentadecatyl-ketone, and is probably identical with the acid obtained from the seeds of *Jatropha curcas*; m.p. 51°, b.p. 257° (100 mm.).

An acid of the same composition may be extracted from the fungus *Agaricus integer* by treatment with alcohol; m.p. 69·5–70°.

Palmitic acid $C_{15}H_{31}COOH$ is a constituent of the greater number of animal and vegetable fats, in which it occurs as the glyceride *tripalmitin* $C_3H_5(C_{16}H_{31}O_2)_3$. It is most easily obtained from palm-oil (whence its name) by saponification. It also occurs in Chinese wax (from *Stillingia sebifera*), in Japanese wax (from *Rhus succedanea*), in butter, spermaceti, human fat, &c. Crystallises from alcohol in needles; m.p. 62°, and distils, with slight decomposition, between 339 and 356°, b.p. 268·5° (100 mm.); sp.gr. 0·8527 $\frac{62^\circ}{}$.

Cetyl palmitate $C_{16}H_{31}O_2.C_{16}H_{33}$ is the chief constituent of spermaceti. Crystallises from ether in thin plates; m.p. 53·5°.

Ceryl palmitate $C_{16}H_{31}O_2.C_{27}H_{55}$ is the main constituent of opium wax. *Myricyl palmitate* $C_{16}H_{31}O_2.C_{30}H_{61}$ is found in beeswax.

By heating palmitic acid with glycerin, the mono-, di-, and tri-palmitins are prepared. *Tripalmitin* melts at 61°.

Margaric acid $C_{16}H_{33}COOH$ may be formed by boiling margonitrile with alcoholic potash; m.p. 59·9°, b.p. 277° (100 mm.).

Stearic or **Cetyl acetic acid** $C_{17}H_{35}COOH$ occurs as a glyceride in most hard fats (as beef- and mutton-suet), associated with similar ethers of palmitic and oleic acids. An abundant source of stearic acid is shea butter, a vegetable fat from West Africa. It may be readily obtained from suet or shea butter by saponification with soda, decomposition of the soap by hydrochloric acid, and repeated crystallisation from alcohol.

The commercial stearic acid used in the manufacture of candles consists of a mixture of stearic and palmitic acids, which may be separated by partial precipitation as the magnesium salts.

Stearic acid crystallises from alcohol in lustrous tables; m.p. 69·5°; b.p. 291° (100 mm.); sp.gr. 0·8454 $\frac{69\cdot5^\circ}{}$.

The stearates are of importance as the chief constituents of all ordinary soaps.

Potassium stearate $C_{18}H_{35}O_2K$ forms needles, soluble in water. On pouring the solution into a large volume of water it is decomposed, forming an *acid potassium-stearate* $C_{18}H_{35}O_2K.C_{18}H_{36}O_2$.

Sodium stearate $C_{18}H_{35}O_2Na$ is one of the main constituents of ordinary white soap. Its aqueous solution is decomposed by further dilution into an acid stearate and free alkali.

Magnesium, *calcium*, and *lead stearates* are insoluble in water.

Tristearin $C_3H_5(C_{18}H_{35}O_2)_3$ is a chief constituent of most animal fats, and may be obtained synthetically by heating glycerin and stearic acid together. Crystalline body; softens at 55°, and melts completely at 71·6°.

Neurostearic acid is formed by heating *phrenosin*, a glucoside found in the brain, with dilute sulphuric acid; m.p. 84°.

Isostearic acid or *dioctyl acetic acid* $CH(C_8H_{17})_2COOH$ is obtained by boiling dioctyl aceto-acetic ether with potash, or by heating dioctyl malonic acid. Crystallises from alcohol in plates; m.p. 38·5°; b.p. 270–275° (100 mm.) (Guthzeit, A. 204, 11; Conrad and Bischoff, A. 204, 165).

Nondecatoic acid $CH_3(CH_2)_{17}COOH$, obtained from decyl cyanide; m.p. 66·5°, b.p. 297–299° (100 mm.).

Arachidic acid $CH_3(CH_2)_{18}COOH$ is found, partly free and partly as a glyceride, in earth-nut oil (from *Arachis hypogæa*), in butter, and in the fruit of *Nephelium lappaceum*; m.p. 75·5°.

Medullic acid $C_{20}H_{41}COOH$ is found as a glyceride in beef-fat; m.p. 72·5°.

Behenic acid $C_{21}H_{43}COOH$ is contained as a glyceride in oil of ben, from the seeds of *Moringa oleïfera*; m.p. 73°.

Lignoceric acid $C_{23}H_{47}COOH$ is found in the solid paraffin from beechwood tar (m.p. 80·5°), and is probably isomeric with the *paraffinic acid* of Pouchet obtained by oxidising solid paraffin with nitric acid; m.p. 45–47°.

Carnaüba wax contains an acid of the same composition; m.p. 72·5°. *Gingkoic acid*, from the fruit of *Salisburia adantifolia*, is another acid of the formula $C_{24}H_{48}O_2$; m.p. 35°.

Hyænic acid $C_{24}H_{49}COOH$ was found by Carius in the anal glandular pouches of the striped hyæna; m.p. 77·5°.

Cerotic acid $C_{27}H_{54}O_2$, or $C_{26}H_{52}O_2$, is found free in beeswax, of which it is the chief constituent (Brodie), as a ceryl ether in Chinese wax, and in opium wax (Hesse), and has been obtained from paraffin by oxidation with chromic acid; m.p. 78°.

Melissic acid $C_{29}H_{59}COOH$ is obtained by heating myricyl alcohol with soda-lime to 250° so long as hydrogen is evolved; m.p. 90°. Probably identical with an acid found in beeswax (Nafzger, A. 224, 225).

Dicetylic acid $CH(C_{16}H_{33})_2COOH$, obtained by heating dicetyl malonic acid; m.p. 69–70°.

Theobromic acid $C_{63}H_{127}COOH$ is found in cocoa butter, and melts at 72·2°.

FAVIER'S EXPLOSIVE *v.* Explosives.

FAYENCE *v.* Pottery and Porcelain.

FEATHER ALUM. A form of naturally-occurring aluminium sulphate $Al_2O_3.3SO_3.18H_2O$ (*q.v.*). The term is also applied to iron-alum or *nelotrichite*.

FEATHER ORE. A capillary form of heteromorphite or lead sulphantimonite $2Pb_2S.Sb_2S_3$; *v.* Antimony.

FEHLING'S SOLUTION. When cupric tartrate is dissolved in ammonia, soda, or potash, a solution is produced which is readily reduced, with precipitation of cuprous oxide, when heated with glucose and various other bodies, and may be used for detecting and determining those substances.

Fehling's solution is prepared for this purpose as follows. 34·64 grams of pure crystallised copper sulphate, powdered and dried by pressure between filter paper, is dissolved in distilled water and diluted to 500 c.c.; and 70 grams sodium hydrate (of not less than 97 p.c.) and 180 grams of potassium sodium tartrate (Rochelle salt) are dissolved in 400 c.c. of distilled water and diluted to 500 c.c. Equal volumes of the two solutions are mixed to form the test, which should be kept in a carefully closed bottle to prevent absorption of carbonic acid gas, and should not be unduly exposed to light. As the solution is liable to decomposition, a small portion should always be heated to boiling before commencing the test, and the liquid should not be used if any precipitation occurs. It is, however, preferable to keep the two solutions separate until shortly before use.

The Rochelle salt used is best prepared by dissolving commercial cream of tartar in hot water, rendering the liquid slightly alkaline after boiling by addition of sodium carbonate, filtering off the precipitated calcium carbonate, and crystallising the Rochelle salt from the filtrate.

Fehling's solution is *not reduced* by cane sugar, dextrin, or cellulose, but is *reduced* by dextrose, lævulose, maltose, mannitose, milk-sugar, galactose, arabinose, gallisin, aldehyde, chloral, chloroform, valeraldehyde, resorcinol, and pyrogallic, gallotannic, and trichloracetic acids, and by arsenious acid.

The action of these bodies on the solution is doubtful. Among the products are formic, acetic, tartronic and other acids of doubtful composition and a gum-like substance. Its use is almost restricted to the detection and estimation of reducing sugars. For the *detection* of sugars, the clear, acid-free liquid is heated with two volumes of Fehling's solution. If one of the above reducing compounds be present, a yellow precipitate of the hydrated cuprous oxide, which rapidly becomes converted into the orange-red anhydrous oxide, is produced.

If the liquid to be tested is much coloured, it must be first clarified, as described under Saccharimetry. When the clarification has been performed with lead, an amount of the solution containing a known weight (2 to 5 grams) of glucose or other body, *estimated*, is placed in a 100 c.c. flask and is treated with sulphurous acid gas, or with a strong solution of that gas, until the whole of the lead is precipitated, and, after the addition of a little freshly-precipitated, washed alumina, is diluted to 100 c.c., agitated and filtered.

Cane sugar, when estimated, is first clarified, if necessary, and then 'inverted'—*i.e.* converted into a mixture of two glucoses, dextrose and lævulose. For this purpose a solution containing not more than 1 gram of sugar to 4 c.c. of solution is mixed with one-tenth its bulk of fuming hydrochloric acid and is heated to 70°C. for ten to fifteen minutes, and finally neutralised by addition of sodium carbonate.

Starch and starchy bodies may also be converted into invert sugar and estimated by Fehling's solution. Two or three strong flasks, each containing from one-half to one gram of the substance and 50 or 60 c.c. of decinormal sulphuric acid solution, are closed with caoutchouc corks carefully tied down, and are heated in a water-bath. After four hours, one flask is taken out and titrated with Fehling's solution as hereafter described, and after a further interval of two hours the second is similarly examined. If the amount of sugar found in the second flask does not exceed that in the first, the result may be taken as correct; but if the quantities differ markedly, the third flask is heated a further period of from two to four hours and then titrated. Each 100 parts of invert sugar found represents 90 parts of starch.

In titrating solutions of any of these substances 10 c.c. of Fehling's solution is carefully measured into a wide test-tube and diluted to about 40 c.c. and heated to boiling. The sugar solution, which should contain from one-half to one gram per 100 c.c., is then run in from a burette in portions of 2 c.c., the mixture being heated to boiling after each addition until the blue colour has nearly disappeared. The sugar is then added more cautiously until the supernatant liquid is colourless or slightly yellow. A few drops of the solution may be filtered and tested for copper by addition of sulphuretted hydrogen or of a mixture of potassium ferrocyanide and acetic acid.

Experience has shown that the time occupied during the analysis, the amount of excess of copper present at any moment in the solution, the concentration of the liquid, and other slight details, seriously affect the result. Soxhlet (P. J. [3] 11, 721) has examined this question, and recommends close adherence to the following process where extreme delicacy is required. Having approximately found the strength of the solution by running the sugar solution into 50 c.c. of Fehling's solution as above until the blue colour disappears, dilute it until containing about 1 gram per 100 c.c., and heat 50 c.c. Fehling's solution with as much of the diluted solution as should precipitate all the copper. When the sugar estimated is invert sugar, grape sugar, or lactose, the heating should occupy two minutes, while for maltose and lactose four and six minutes respectively should be allowed. The whole fluid is then filtered and tested for copper. A third titration is next performed with a larger amount of the fluid with 1 c.c. less of sugar (according to the presence or absence of copper), and the titrations are repeated with varying amounts of sugar solution, each time adding the whole of that solution at once, until 1 c.c. more or less would give a filtrate free from or containing a trace of copper, after which the variation in the amount of sugar solution is decreased. In this way the volume of sugar solution required may be determined to 0·1 c.c. The following may be taken as the weight of sugar capable of reducing 10 c.c. of Fehling's solution:

	Gram
Dextrose, lævulose, or invert sugar	0·0500
Cane sugar (inverted) . . .	0·0475
Milk sugar (lactose) . . .	0·0678
Malt sugar (maltose) . . .	0·0807

Soxhlet (P. J. [3] 11, 721), by operating by his method as described above, has obtained the following results. His method of 'inverting' cane sugar has been somewhat objected to.

Weight of Sugar Reducing 10 *c.c. of Fehling's Solution.*

—	Time of heating (minutes)	Undiluted	Diluted with			
			One volume of water	Two volumes of water	Three volumes of water	Four volumes of water
Dextrose . . .	2	0·0475	0·04825	0·0488	0·0492	0·0494
Invert sugar . .	2	0·0494	0·0503	0·0509	0·0514	0·0515
Lævulose . . .	2	0·0513	0·05235	0·0530	0·0536	0·0526
Milk sugar . .	6	0·0676	Unaffected by dilution			0·0676
Lacto-glucose . .	2	0·0511		„	„	0·0533
Maltose . . .	3 to 4	0·0778		„	„	0·0740

A modification of Fehling's process, devised by Pavy, is based on the fact that precipitation of the cuprous oxide is prevented by the presence of excess of ammonia, the solution losing its intense blue colour and becoming absolutely colourless after the whole of the copper has been reduced.

The solution used is prepared by mixing 120 c.c. of Fehling's solution with 300 c.c. of ammonia (0·880 sp.gr.) and 400 c.c. of 12 p.c. caustic soda solution, and diluting to 1 litre. 100 c.c. of this solution corresponds with 10 c.c. of Fehling's solution. The larger quantity of Fehling's solution (120 c.c. instead of 100 c.c.) used to prepare this test is required on account of the lower oxidising power of Pavy's solution, whose action on invert sugar is only five-sixths of that of Fehling's solution. Its action on maltose and lactose also differs from that of Fehling's solution.

To prevent re-oxidation of the decolourised solution, with reproduction of the blue colour, the operation should be performed without access of air, by connecting the burette supplying the sugar solution with a tube passing through a cork into the flask containing the Fehling's solution, the steam from which escapes through another tube dipping beneath the surface of mercury. A slow current of coal gas may be passed through the flask during the operation.

The sugar solution is run into the flask, in which 100 c.c. of the copper solution has been heated to ebullition, and the boiling is continued until the colour has disappeared. Hehner (An. 6, 218) has shown that alkaline tartrates, carbonates, and other salts affect the results.

The most accurate method of using Fehling's solution, especially when the sugar solution is unclarified, consists in separating and estimating the precipitated cuprous oxide. One of the many processes recommended is that of Pavy. The Fehling's solution is boiled, in slight excess, with the sugar solution, whose strength should be about 1 p.c., and the precipitated suboxide is rapidly separated by filtering the liquid through a funnel loosely packed at the neck with glass wool or asbestos. The precipitate, after washing, is dissolved in hydroxyl with addition of a drop of nitric acid, and the copper is estimated by electrodeposition. The weight of copper obtained is multiplied by 0·5395 to obtain its equivalent in inverted cane sugar, or by other factors, which may be calculated from the tables given above, to obtain the equivalent of any other sugar which may be estimated.

Brunner recommends solution of the cuprous oxide, filtered as above, in a solution of pure ferric chloride acidulated with sulphuric acid, and the estimation of the cuprous chloride so produced, by titration with a standard solution of potassium permanganate or bichromate.

The cuprous oxide might also be weighed directly, or after conversion into cupric oxide.

FELSPAR. A name applied to a group of silicates, of great importance as rock-forming minerals. The felspars may be classified according to their crystallographic symmetry, in two great series. One series crystallises in the monoclinic system, and since its members present two well-marked cleavage-planes, at right angles to each other, they are distinguished as *orthoclastic* or *orthotomous* felspars. The other series crystallises in the triclinic or anorthic system, and as these felspars have their principal directions of cleavage more or less inclined to each other they are termed *plagioclastic* or *clinotomous*. The first series is represented by *orthoclase*, or common potash-felspar; while the plagioclastic group includes *albite* or soda-felspar, and *anorthite* or lime-felspar, with several intermediate species, such as oligoclase and labradorite, which contain both soda and lime. As the proportion of Ca increases, that of Na diminishes, and the felspar becomes more basic.

According to Tschermak only two distinct species of plagioclase are to be recognised—viz. albite, containing $Na_2Al_2Si_6O_{16}$, and anorthite, with $Ca_2Al_4Si_4O_{16}$. The other felspars of this group may be regarded as isomorphous mixtures of these extreme types, as shown in the following scheme, where Ab represents the molecule of albite, and An that of anorthite:

Albite series	.	$Ab_1\ An_0$ to $Ab_8\ An_1$
Oligoclase „	.	$Ab_6\ An_1$ „ $Ab_2\ An_1$
Andesine „	.	$Ab_3\ An_2$ „ $Ab_4\ An_3$
Labradorite „	.	$Ab_1\ An_1$ „ $Ab_1\ An_3$
Bytownite „	.	$Ab_1\ An_3$ „ $Ab_1\ An_6$
Anorthite „	.	$Ab_1\ An_8$ „ $Ab_0\ An_1$

For Tschermak's views *v.* Sitz. B., 50, 1864, p. 566. These views were supported on crystallographic grounds by the late Vom Rath (Zeitsch. deutsch. Geol. Ges., 27, 1875, p. 295), while Max Schuster showed that the optical characters of the plagioclastic felspars exactly agreed with this theory (Min. Mitt. 3, 1881, p. 117). Where a felspar contains both K and Na, the isomorphous hypothesis seems inadmissible; but it may be supposed that orthoclase and plagioclase are mechanically associated, an association often seen in microscopic sections. Thus, orthoclase ($K_2Al_2Si_6O_{16}$) frequently contains Na, but microscopic examination usually reveals the presence of lamellæ of albite. A true potash-soda felspar is, however, now recognised under the name of anorthoclase.

As illustrations of the chemical composition of the chief felspars, the following analyses are selected:

—	I	II	III	IV	V	VI
SiO_2 .	65·72	68·46	62·90	58·11	52·55	45·97
Al_2O_3 .	18·57	19·30	22·00	28·16	28·32	33·28
Fe_2O_3 .	—	0·28	0·04	—	2·44	1·12
K_2O . .	14·02	—	0·94	0·44	0·64	—
Na_2O .	1·25	11·27	8·20	5·17	4·52	1·85
CaO . .	0·34	0·68	4·66	5·35	11·61	17·21
MgO . .	0·10	—	—	1·52	0·48	—
	100·00	100·00	98·74	98·75	100·56	99·43

I. Orthoclase, sp.gr. 2·55; from Baveno, by Abich. II. Albite, sp.gr. 2·61; from Arendal, by G. Rose. III. Oligoclase, sp.gr. 2·66; from Elba, by Damour. IV. Andesine, sp.gr. 2·64; from near Marmato, by Deville. V. Labradorite, sp.gr. 2·71; from Neurode, Silesia, by Vom Rath. VI. Anorthite, sp.gr. 2·75; from Hecla, by Damour.

The specific determination of the felspars is often a matter of difficulty, without recourse to analysis; but much aid is afforded by the sp.gr., which is tolerably constant in each species, and in the plagioclastic group is found to increase with the proportion of anorthite. The sp.gr. is most conveniently taken by suspending fragments of the mineral in heavy solutions of known density. The sp.gr. of the felspars has been carefully determined by Tschermak and later by Goldschmidt. The following are given by Rosenbusch as the typical average values: orthoclase and microcline, 2·57; albite, 2·62; oligoclase, 2·64; andesine, 2·65; labradorite, 2·69; bytownite, 2·71; and anorthite, 2·75.

Optical characters often enable the observer to ascertain the nature of a given felspar when the mineral is examined in microscopic sections, cut in known directions. To the chemist a more ready means of determination is afforded by Szabó's method, which consists in examining the flame-reactions produced on exposing a fragment of the mineral in a Bunsen flame, the colouration of the flame being compared with standard tables (Szabó: Ueber eine neue Methode die Feldspathe zu bestimmen, Budapest, 1876; F. Rutley, Rock-forming Minerals, 1888, p. 9).

Without introducing mineralogical details of the numerous felspars, which would require a long article, it may be convenient to refer briefly to the principal varieties. *Orthoclase* occurs usually in white, grey, or flesh-coloured crystals, often twinned; the finest examples being obtained from the granite of Elba, Baveno, and Carlsbad. The clear translucent variety, known as *adularia*, is found chiefly in the Swiss Alps and in Ceylon. The orthoclastic felspar of volcanic rocks is termed *sanidine*, and occurs in tabular glassy crystals, which are especially fine in the trachyte of the Drachenfels on the Rhine. The transparent orthoclase of Vesuvian lavas is sometimes known as *rhyacolite* and *ice-spar*.

Microcline is a felspar closely related to orthoclase, and formerly regarded as monoclinic, but shown by Descloiseaux to be triclinic. A green variety known as *amazon stone* occurs in fine crystals in the Ilmen mountains, in Siberia, and at Pike's Peak in Colorado. The colour is lost on heating the mineral, and is therefore not due, as formerly supposed, to the presence of copper. An organic salt of iron has been suggested by König as the probable colouring matter in the Pike's Peak mineral.

Anorthoclase is a name now given to certain potash-soda felspars, which though triclinic have two apparently rectangular cleavages. *Albite*, the ordinary soda-felspar, so called from its dead white colour, occurs chiefly in granites and diorites; fine crystals being found, with chlorite, in the rocks of Tyrol. *Pericline* and *cleavelandite* are names applied to varieties of albite. A mixture of albite and orthoclase or microcline, in red bands, occurs at Perth in Canada, and is hence known as *perthite*. *Oligoclase* is a soda-lime plagioclase, occurring in granite and gneiss, notably at Arendal, in Norway and at Miask in Siberia; while it is found also in volcanic rocks, as at Vesuvius. *Andesine* is a somewhat rare felspar, originally described by Abich from the rocks of the Andes. *Labradorite* is an important mineral, brought originally from the coast of Labrador, where it constitutes with hypersthene the rock known as hyperite. Exhibiting in many cases a beautiful change of colour when viewed in different directions, it is valued as an ornamental stone; but most of the labradorite which occurs in gabbro, dolerite, basalt, and other basic rocks does not present this appearance. The *Bytownite* of Thomson has been shown to be rather widely distributed as a constituent of certain eruptive rocks; while the *anorthite* of G. Rose is found in gabbro, porphyrite, andesite, and basalt; distinct crystals, though rare, occurring at Monzoni in Tyrol and at Monte Somma.

The chief use of felspar in the industrial arts is for the manufacture of porcelain. Orthoclase is employed partly as a constituent of the body in certain wares, but principally as a glaze, for which purpose large quantities are imported from Norway and elsewhere. The discovery of a vein of red felspar at Belleek, in co. Fermanagh, Ireland, led to the establishment of porcelain works at this locality. The red felspar becomes white on calcination, the iron passing into the condition of magnetite, the particles of which may be removed by means of a magnet.

Felspars rich in alkalis have been sometimes used as manures. Very pure felspar finds a limited application in the manufacture of artificial teeth. Several varieties of felspar are cut and polished as ornamental stones, the most important being labradorite, which is used for table tops, umbrella handles, and various trivial objects. The mineral was first brought to this country in the last century, by the Moravian missionaries, from St. Paul's Island off the coast of Labrador. The *schiller* and colour of labradorite are partly due to microlitic inclosures and lamellæ of diallage. *Moonstone* is a variety of adularia from Ceylon, exhibiting a faint bluish opalescence, which has led to its employment in jewellery. *Sunstone* is a form of oligoclase, occurring at Tvedestrand in Norway, remarkable for its reddish sheen, due to interposed lamellæ of specular iron-ore. Among other ornamental felspars may be mentioned the opalescent albite from Canada, known as *peristerite* (*περιστερά*, a pigeon) from the resemblance of its colours to those on the neck of a pigeon; and an opalescent variety of anorthoclase from the augite-syenite of Norway. F. W. R.

FENNEL OIL *v.* OILS, ESSENTIAL.

FERGUSONITE *v.* CERIUM METALS.

FERMENTATION. *Significance.*—This term is derived from *fervere*, to boil, and was formerly applied to all those cases in which a liquid or semi-liquid mass was seen to become puffed up and disengage gas without apparent cause, *i.e.* spontaneously; the earliest observed forms of this phenomenon being the fermentation of grape-juice and the raising of the dough in bread-making. Owing to the obscurity with which these well-known processes were surrounded, the term fermentation was gradually applied to all those chemical changes brought about through the agency of some body termed a *ferment*, the presence of which was as indispensable as its action was unintelligible.

At the present day the term fermentation is generally understood to include all those chemical reactions in which a substance, mineral or organic, undergoes change through the agency of an organic substance directly derived either from the vegetable or animal kingdom, and known as a ferment, which latter remains qualitatively the same both before and after the reaction. This modern acceptation of the term, therefore, is wholly irrespective of whether the change is accompanied by the evolution of gas or not, and includes a number of reactions to which the etymological sense of the word *fermentation* is wholly misapplied.

Certain properties are possessed by all ferments in common, thus:

1. All ferments are nitrogenous organic substances of either vegetable or animal origin.
2. All ferments are unstable bodies the activity of which is destroyed by powerful reagents, and generally by a temperature of even less than 100°C.
3. A small quantity of the ferment is capable of inducing the particular change in a relatively large quantity of the fermentable substance.

On the other hand, whilst some ferments have a definitely organised structure, and are capable of independent growth and multiplication, others are wholly devoid of such structure, are incapable of reproduction, and can pass into solution and be recovered therefrom after the fashion of ordinary chemical compounds. These differences have led to the natural division of ferments into two classes:—

1. Formed or Organised Ferments.
2. Unformed or Soluble „

As types of these two different kinds of fermentation may be mentioned, firstly, the conversion of glucose into alcohol by the organised ferment *yeast*, and, secondly, the transmutation of starch into maltose and dextrin by the soluble ferment *diastase*.

Whether the action of these two classes of ferments is intrinsically different or not is still an open question, but whilst the action of the soluble ferments is traceable to the chemical molecules of which they are composed and which are the carriers of the chemical forces coming into play in the reactions which they bring about, the changes occasioned by the formed ferments cannot at present be dissociated from the living cell upon the physiological functions of which these changes appear to be dependent.

The organised and unorganised ferments exhibit certain differences in their behaviour towards reagents. Thus compressed oxygen (Bert, C. R. 80, 1579) destroys the activity of the formed but does not affect that of the soluble ferments. Similarly the organised ferments are much more susceptible to the action of hydrocyanic acid (Fiechter, Inaug. Dissert., Basel, 1875), which only affects the unformed ferments when it is present in large quantities. Again, salicylic acid (Kolbe, J. pr. (N. Z.) 10, 107; Erlenmeyer, Münch. Akad. Sitzb. 1875, 82; Kühne, Verh. d. naturh. med. Ver. zu Heidelberg (N.Z.) 1, 3; 4, 9), which is particularly deleterious to most organised ferments, and enjoys such a high reputation as an antiseptic, has but little action on soluble ferments. Borax (Dumas, C. R. 75, 298; Schützenberger, Die Gährungserscheinungen, Leipzig, 1876), on the other hand, is far more potent in destroying the activity of the unformed than that of the formed ferments. In the case of diastase (Bouchardat, A. Ch. [3] 14, 61), it has been further shown that whilst hydrocyanic acid, alcohol, ether, chloroform, salts of mercury, and some ethereal oils, are all substances more or less inimical to the vitality of organised ferments, they exert but little effect on the activity of this body; on the other hand, citric and tartaric acids completely prevent the action of diastase, whilst they only slightly diminish the vigour of the vinous fermentation. Many reagents act on both kinds of ferments, destroying the vitality of the organised and chemically altering the soluble, thus chlorine, nitric and chromic acids, arsenic, many metallic salts, as well as phenols. Thymol (Levin, Centralbl. f. d. med. Wiss. 1875, No. 21), however, appears to have no influence on pepsin; and phenol, whilst it interferes with the action of pepsin, is without influence on the action of emulsin on amygdalin, of saliva and other diastatic ferments on starch, and of myrosin on myronic acid (Zapolsky, B. 1871, 810). Arsenic (Schäfer and Böhm, Verh. d. Phys. med. Ges. in Würzburg (N.Z.), 3, 238) again appears to be without effect either on diastase or pepsin. Carbon disulphide (Zöller, B. 1876, 707, 1080), again, is highly poisonous to organised ferments, but without effect on soluble ones. Peroxide of hydrogen again is said only to destroy the action of organised ferments, the soluble ones being unaffected (P. Bert and Regnard, C. R. 94, 1383).

Authorities frequently disagree as to the action of various substances on soluble ferments; thus, according to Kjeldahl (Meddelelser fra Carlsberg Labor. Bd. 1, Heft. 2, 3), phenol interferes with emulsin and ptyalin, but even ·2 to ·4 p.c. hardly affects diastase, whilst salicylic acid (·03 p.c.) greatly reduces, and with ·1 p.c. altogether stops diastatic action.

It must be pointed out, moreover, that nearly all of the experiments on organised ferments referred to above were made at a time when the methods of handling micro-organisms were extremely imperfect, and the results cannot, therefore, be regarded as final.

Organised ferments. As already pointed out, one class of fermentative changes appears inseparably connected with the vital phenomena of certain unicellular organisms known as organised ferments or micro-organisms. It is especially noticeable that many of the changes effected by these ferments are peculiar to the presence of these organisms and have hitherto not been produced by artificial means, thus the conversion of glucose into alcohol, butyric acid, and mannite, are all reactions of this kind; on the other hand, the oxidation of alcohol to acetic acid, of ammonia to nitrous and nitric acids, and the reduction of nitric acid to nitrous acid and ammonia, are changes which can be accomplished either with or without the assistance of micro-organisms. Of all the processes of fermentation the one which has received the most attention and with which the history of the whole subject is most intimately bound up, is that of the conversion of sugar into alcohol, known as the alcoholic or vinous fermentation.

It was in 1680 that Leuwenhoek first discovered by the aid of the microscope that the scum and deposit which is so largely produced in the alcoholic fermentation consists of minute spherical particles. By the further investigations of Cagniard Latour (A. Ch. [2] 68, 206); Schwann (P. 41, 184; A. Ch. 1837, 41, 184); Kützing (J. pr. 11, 385), Quevenne (J. Ph. 24, 1838, 36, 265), Turpin (C. R. 4, 369), Mitscherlich (P. 55, 225), and Ch. Schmidt (A. Ch. 61, 168), it was conclusively proved that brewers' yeast was composed of definite living cells capable of self-nutrition and multiplication. *Pari passu* with these researches the whole theory of alcoholic fermentation and of fermentation in general underwent a profound and fundamental change. Thus, before the vital nature of the yeast had been fully established, it had been attempted by Willis and Stahl, and afterwards by Liebig, to explain all the phenomena of fermentation from a chemical or mechanical point of view. According to Liebig (A. Ch. 29, 100; 30, 250, 363; 41, 357; Verh. d. Münch. Akademie d. Wiss. 1861 and 1869; Die Chemie in ihrer Anwendung auf Agric. und Physiol. Braunschweig, 1846, 374–584; Ueber Gährung, Quelle d. Muskelkraft und Ernährung, Leipzig and Heidelberg, 1870), yeast and ferments in general were to be regarded as extremely unstable bodies, which through their own decomposition were capable of communicating an intra-molecular instability to fermentable substances with which they were in contact. The dead and decomposing, and not the living yeast-cells, were thus credited with the power of splitting up the molecule of glucose into alcohol and carbonic anhydride. These views, which now possess only historical interest, were still adhered to and obstinately urged by Liebig long after the distinctly biological nature of the alcoholic and other fermentations had been demonstrated by the classical researches of Pasteur.

To Pasteur is due the credit of having shown by the most laborious and systematic investigations that the fermentative change is inseparably connected with the life and not with the death of the yeast-cell, although the precise relationship of the two is still a matter of uncertainty. By Béchamp (A. Ch. 153) the fermentable substance is simply regarded as the food of the ferment, and the products of fermentation as its excreta. More recently an endeavour has been made by Nägeli (Theorie d. Gährung, München, 1879), to show that the fermentative change does not necessarily take place within the cell, but that it may also go on in its immediate vicinity. There are several facts which appear to support this remarkable theory. Thus the large quantity of sugar decomposed in a given time renders it extremely improbable that the whole should have been united with the protoplasm of the cell, although it has been shown by Cochin (C. R. 96, 852) that a part of the sugar at least enters the yeast-cell and is there rapidly decomposed. Again, as will be seen below, the alcoholic fermentation is frequently accompanied by the formation of acetic ether, a substance which cannot be formed by the mere mixture of alcohol and acetic acid, but which requires that the molecules of the two substances shall be brought together in a nascent state. If, therefore, both alcohol and acetic acid were produced by the same cell, the formation of acetic ether would be readily intelligible, but, inasmuch as the alcohol is the product of a yeast-cell and the acetic acid of a bacterial cell (*Bacterium aceti*), the conclusion is forced upon one that these substances exist together in the nascent state externally to the respective cells. Nägeli further found that certain micro-organisms bleach litmus, which colouring-matter was unable to enter the living cell of the organisms in question. It has been, moreover, established by numerous observations that alcoholic fermentation may take place within the substance of fruits apparently through the agency of yeast-cells resting upon the outer surface of the perfectly uninjured skin. All these facts as well as others are explained by Nägeli on the assumption that the decompositions in question are brought about by the vibrations of the cell-protoplasm being communicated to external but immediately adjacent molecules of the fermentable substance.

The production of acetic ether, however, can be readily explained in another way, since it has been shown by Fitz that certain bacteria decompose glycerine, which, as will be seen, is an invariable product of the fermentation of sugar by yeast, with the formation of alcohol and acetic acid, the two substances being thus generated by one and the same organism. There is thus no difficulty in accounting for the appearance of acetic ether without having recourse to the theory of Nägeli, which, on the other hand, is in no way opposed to known facts.

Having thus seen that these processes of fermentation are undoubtedly the result of the vital functions of the organised ferments, we must, in the next place, glance at the nature of these micro-organisms themselves before considering more in detail the several important chemical changes to which they are capable of giving rise.

Classification and morphology of organised ferments.—All the organised ferments with which we are acquainted belong to that group of cryptogams or non-flowering plants known as the *fungi*. The classification of the various kinds of fungi is a matter on which great differences of opinion still exist, and it would be beyond the scope of this article to give an account of the various systems which have been proposed. For our purposes, however, it will be sufficient to divide these micro-organisms with which we are concerned in the study of fermentation into the following three groups:

1. *Moulds, or fungi proper.*
2. *Saccharomycetes, or Blastomycetes*
3. *Schisomycetes, or Bacteria.*

THE MOULDS, OR FUNGI PROPER.

These, which play a comparatively unimportant part in fermentation, are the most highly organised of the microbial ferments, and consist of microscopic cells in which a cell-wall and protoplasmic contents are distinguishable. The cell-wall is composed of a substance resembling cellulose; it gives no violet colouration with iodine; the protoplasm is generally free from nuclei, and contains neither starch granules nor chlorophyll. The growth takes place by elongation of the cells, which thus give rise to threads or *hyphæ*, the latter generally becoming subdivided by transverse diaphragms. The aggregation of hyphæ is known as the *thallus*, in which are further distinguished the *mycelium*, formed by the general network of hyphæ, and the *aerial hyphæ* bearing the fructifying organs, the varied forms of which serve for the purpose of further classification. The mode of reproduction is generally by means of spores.

The following is the chemical composition given by Sieber (J. pr. [2] 23, 412) of a mixture of moulds (*Penicillium*, *Aspergillus glaucus*, and *Mucor mucedo*) growing on gelatine and sugar respectively:—

	Moulds growing on sugar and gelatine	Moulds growing on solution of sugar and ammon. chloride
Matter soluble in ether	18·7	11·2
„ „ alcohol	6·9	3·4
Albuminoids . .	29·9	28·9
Cellulose . . .	39·6	55·8
Ash	4·9	·7
	100·0	100·0
Water . . .	85 p.c.	85·7 p.c.

From the above it appears the moulds are less rich in nitrogen than the two other groups of micro-organisms to be considered hereafter.

Stutzer gives for moulds, washed with water and dried over sulphuric acid:

$$\text{Total Nitrogen } 3{\cdot}776 \text{ p.c.} \begin{cases} \text{Proteïn N. } 3{\cdot}026 \text{ p.c.} \\ \text{Nucleïn N. } 1{\cdot}539 \text{ „} \end{cases}$$

The recent and extensive investigations of Nägeli (Untersuchungen über niedere Pilze, München, 1882) have established the following facts concerning the nutrition of the moulds. These organisms are unable to assimilate either free nitrogen or that combined as cyanogen; oxidised nitrogen in organic compounds, *e.g.* in picric and nitrobenzoic acids, proved very unsuitable. Compounds containing the amido- or imido-groups as well as ammonia-salts and nitrates were found suitable sources of nitrogen, whilst the soluble albuminoids and peptones proved the most available. The moulds are able to derive their carbon from a great variety of organic substances, but not from those in which the carbon is principally united with oxygen or nitrogen, *e.g.* carbonic, oxalic, and formic acids, oxamide, cyanogen and urea. Pasteur showed in 1858 (C. R. 46, 617) that a solution of ammonic tartrate was capable of maintaining moulds, and, moreover, that with ammonium racemate it was only the dextrorotatory tartaric acid which was assimilated, the lævorotatory being left unacted upon. Nägeli arranges a number of organic compounds capable of furnishing the necessary carbon to moulds in the following order of readiness with which they are assimilated: (1) sugars; (2) mannitol, glycerol, and leucin; (3) tartaric, citric, and succinic acids, and asparagine; (4) acetic acid, ethylic alcohol, and quinic acid; (5) benzoic and salicylic acids, and propylamine; (6) methylamine and phenol; whilst even pyrogallol and tannic acid proved to be fairly good sources of carbon. The moulds are thus able to decompose and assimilate many bodies of highly antiseptic properties. The mineral requirements are sulphuric and phosphoric acids, potassium, and calcium or magnesium. As Pasteur had already shown, the moulds are normally aërobic, or consumers of free oxygen, but the amount of free oxygen absolutely necessary for their growth is very small, thus, according to Brefeld, growth only ceases in an atmosphere of carbonic acid which contains less than $\frac{1}{800}$ of its volume of air. When moulds are immersed in liquids free from dissolved oxygen normal growth ceases, but some forms then give rise to cellular buds, resembling yeast-cells, which are capable of setting up fermentations in suitable media, but to this point we shall have to return later. It has, moreover, been recently shown that the spores of some forms of *mucor* and *aspergillus* are capable of branching out into a mycelium within the kidney and other animal organs, but in no case has fructification been observed in the absence of free oxygen.

The moulds are capable of growing in much more concentrated media than the bacteria and saccharomycetes, whilst they are, equally with the latter, capable of vitality in liquids containing the merest traces of food materials. Thus salt meat, containing only 50 p.c. of water, does not form a suitable nidus for schizomycetes, whilst its capacity for supporting mould-growths is not destroyed until the proportion of water falls below 10 or 12 p.c.; in the presence of much sugar, however, the limit is reached with 30 p.c. of water. Although some moulds are capable of growth in a distinctly alkaline medium, they are, on the whole, more favoured by a slightly acid reaction; thus tartaric acid up to 5 p.c., and phosphoric acid up to 1 p.c., do not prevent the appearance of mould-growths. In this the moulds differ very materially from the schizomycetes, which, as a rule, are very powerfully affected even by a small excess of acid.

The limits of temperature within which mould-growth may take place, as well as the most favourable temperature, vary considerably for the different forms of mould, thus:

	Limits of temperature	Most favourable temperature
Penicillium glaucum[1] .	2°·5–43°C.	20°C.
Aspergillus glaucus .	„	10°–12°C.
„ flavus .	„	28°C.
„ niger . .	„	34°–35°C.
„ fumigatus .	„	37°–40°C.
Oidium lactis . .	„	19°-33°C.

THE SACCHAROMYCETES, BLASTOMYCETES, OR YEASTS.

This group of micro-organisms, which is of the greatest importance in connection with fermentation, includes microscopic cells round or oval in form, and generally multiplying by the process of *gemmation* or budding. The buds formed become divided from the parent-cell by a diaphragm, but they frequently still remain adherent after giving rise to further buds themselves, so that chains of greater or less length are formed according to the number of generations remaining attached to each other. As has been pointed out, the true moulds, under exceptional conditions of growth, viz., when submerged in a liquid, multiply in a similar manner, but in no case are true hyphæ or mycelia known of the saccharomycetes. The cells are clothed with a thin membranous wall, and the granular protoplasmic contents exhibit one, two, or more vacuoles. Provided that the conditions of life remain suitable, the multiplication by gemmation goes on almost indefinitely, but if the yeast is washed free from the saccharine solution in which it has been growing, and is placed on the surface of a medium containing but little nourishment, *e.g.* on the surface of a slice of potato (Rees), or on a moist plate of plaster of Paris (Engel), a most remarkable alteration in the process of reproduction is observed. In the course of a few hours some of the cells will be seen to have increased in size, their contents to have become homogeneous, and in the course of a few more hours such cells are found to contain two to four bright shining spots, which, becoming spherical, surround themselves with a thick membrane. In course of time these new cells or *spores*, as they are called, become liberated by dissolution of the mother-cell. On introducing these spores, which are 4–5μ[2] in diameter, into a saccharine liquid they germinate and further multiply by gemmation as usual. Sometimes the growth of the saccharomycetes by the elongation of the adhering cells exhibits a misleading resemblance to a fungoid mycelium; this is especially the case when yeast is cultivated on the surface of solid media; they, however, never give rise to a true mycelium nor to typical fruit-bearing hyphæ.

The term *torula* has been employed both by Pasteur (Etudes sur la bière, 77) and Hansen (Hansen and Lindner, Centralbl. f. Bakteriologie, [3] 1888, 329, 330) to denote a number of or-

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[1] Wiesner, Sitzungsber. d. kais. Akad. d. Wiss. 1 Abth. 1873; Siebenmann, Die Fadenpilze, Wiesbaden, 1883.

[2] μ is the symbol used by microscopists to denote a *micromillimetre*, or the $\frac{1}{1000}$ of a millimetre.

ganisms closely resembling the saccharomycetes in their form and multiplication by gemmation, but differing from them in not giving rise to spores, even when they are cultivated in the most diverse solid media, and yielding little or no alcohol when growing in saccharine liquids. To this group apparently belong the saccharomyces rosaceus, niger, and albus which have frequently been discovered in the air (G. C. and P. F. Frankland, Tr. 1887).

The chemical composition of the saccharomycetes, more especially of brewers' yeast, has formed the subject of very numerous investigations by Marcet, Dumas (Essais de statique chimique, 1842), Schlossberger (A. 51, 193), Mulder and Wagner (Wagner, J. pr. 45, 241), Mitscherlich (Lehrbuch d. Chem. 1884, 1, 370), Payen (Mém. d. sav. Étrang. 1846, 9, 32), and Liebig (Meyer, Lehrbuch d. Gährungschemie, 1879, 110; Schützenberger, Gährungserscheinungen, 58), the average figures for washed yeast, as free as possible from ash, and dried, were:

Carbon	48 p.c.
Nitrogen	9–12 p.c.
Hydrogen	6–7 p.c.
Sulphur	·6 p.c.

More recent analyses by Nägeli and Loew (J. pr. 17, 403) of 'under-fermentation' yeast yielded the following results:

Cellulose and mucilage . . .	37
Albuminoids (mycoproteïn, &c.) .	36
„ (soluble in alcohol) .	9
Peptones (precipitable by sub-acetate of lead)	2
Fat	5
Extractive matters (leucin, glycerol, &c.)	4
Ash	7
	100

Fresh yeast, capable of germination, contains 40–80 p.c. of water.

The residue left, after treating the yeast with caustic potash, and subsequently with acetic acid and water, yielded, on analysis,

Carbon, 41·4 p.c. Hydrogen, 6·6 p.c.

and thus corresponds closely with pure cellulose; this residue is, moreover, convertible into sugar by boiling with sulphuric acid, but differs from ordinary cellulose in being insoluble in ammoniacal solution of copper oxide (Schweizer's reagent).

The mucilage dried at 110°C. contains $C_{18}H_{24}O_{17}$. It is easily soluble in boiling water, does not reduce Fehling's solution, but has a dextro-rotary power of 78°.

An albuminous substance, known as mycoproteïn, has been obtained by extracting with boiling dilute hydrochloric acid, and then precipitating with common salt, this appears to be the same body as that also obtained by Nencki from putrefactive bacteria (Nencki, Beiträge z. Biologie d. Spaltpilze, 1880, 48).

In yeast which had been extracted with cold alcohol, and then dried over sulphuric acid, Stutzer (Zeitsch. f. physiol. Chem. 6, 572), found:

$$\text{Total Nitrogen 8·648 p.c.}\begin{cases}\text{Proteïn N. 5·519 p.c.}\\ \text{Nucleïn N. 2·257 „}\end{cases}$$

From Nägeli's analysis given above it will be seen that the proportion of albuminoids to cellulose in yeast is much higher than in the fungi.

The following analyses of the ash of yeast are given by Mitscherlich:

	Upper fermentation. Yeast	Lower fermentation. Yeast
Potash . .	38·8 p.c.	28·3 p.c.
Lime . .	1·0 „	4·3 „
Magnesia . .	6·0 „	8·1 „
Phosphoric acid	53·9 „	59·4 „
Silica . .	Trace	—

The proportion of phosphoric acid is thus much higher than in the ash of moulds.

Although the saccharomycetes exhibit on the whole a close resemblance to the moulds, as regards the sources from which they can derive their necessary nutriment, yet they also present some striking points of contrast. Thus, like the moulds, they can derive their nitrogen both from organic and inorganic nitrogenous substances, but of the latter only the salts of ammonia and not those of nitric acid are available; moreover, yeast when continuously fed with ammoniacal nitrogen, gradually suffers degeneration, especially in the absence of free oxygen. The carbon, on the other hand, can be drawn from the same sources as in the case of the moulds; in the case of *Saccharomyces mycoderma* (*Mycoderma vini*), however, the presence of alcohol appears to be indispensable, or, at any rate, only replaceable by malates.

The necessary mineral materials are, as in the case of the moulds, phosphoric acid, potash, and lime.

Particularly important is the relationship of the saccharomycetes towards free oxygen. Thus, whilst the presence of the latter is highly advantageous to the growth and multiplication of these organisms, yet those forms which are capable of breaking up sugar into alcohol and carbonic anhydride have the property of being able to carry on an active existence in media free from oxygen provided these media contain sugar, and it is precisely under these circumstances—*i.e.* in the absence of free oxygen—that this fermentation of sugar takes place with most vigour. This point will, however, be more fully treated of in connection with the process of alcoholic fermentation itself.

As regards the degree of concentration of the media in which these organisms can grow, it has already been pointed out that they do not tolerate such a high degree of concentration as the moulds. Moreover, large quantities of the less available forms of food act more prejudicially than readily assimilable materials; thus ammonia-salts should not exceed 1 p.c., whilst sugar does not prevent the growth of yeast when present even to the amount of 35 p.c.

Although the yeasts resemble the moulds in being tolerant of acid media, yet the excess of acid which they are capable of enduring is less than in the case of the moulds, and on this account the presence of considerable proportions of acids (*e.g.* 5 p.c. of tartaric or 1 p.c. of phosphoric acid) favours the moulds when these are competing for supremacy with the yeasts in one and the same medium. On the other hand, both of these groups of micro-organisms are protected by acidity from the competition of the schizomycetes, which, with a few exceptions such as the acetic ferment, are extremely sensitive even to a weakly acid reaction.

Light and electricity appear to have no influence on the saccharomycetes, and even a pressure of 300–400 atmospheres continuing over a period of several days left the vitality of yeast-cells practically unimpaired (Certes and Cochin, Comp. Rend. Soc. Biol. 1884). Hansen (Meddelelser fra Carlsberg Lab., 1), has found that the multiplication of yeast is rather increased than diminished, by subjecting the medium to constant agitation.

The most favourable temperature for the growth of the yeast cell is from 25–30°C.; slow growth may, however, still take place only a few degrees above the freezing-point, whilst the upper limit is 53°C. Again the spore-formation, under the special conditions already described, may take place between ·5° and 37°·5C.

THE SCHIZOMYCETES, OR BACTERIA.

This group of micro-organisms includes a far larger number of known members than either of the two previous ones; their form is more varied, as are also the chemical changes which they bring about. They have received especial attention during recent years owing to the fact that a number of them are capable of existing as parasites on the higher animals, amongst which they are the cause of well-known and much dreaded diseases of a zymotic character.

All the members of this group are extremely minute unicellular organisms multiplying by division. In form they are either round, oval, cylindrical, spindle-shaped, filamentous, straight, curved, or even spiral.

To the round and oval forms the term *Micrococcus* is applied, amongst which further distinctions are made according to the manner in which the cells are grouped together. Thus when forming irregular conglomerates they are known as *Staphylococcus*, when arranged in pairs as *Diplococcus*, in chains as *Streptococcus* or *Torula*, and in packets of 4 or multiples of 4 as *Sarcina*. These different forms of micrococci range in size from ·2–2·0μ in diameter.

The cylindrical forms are now generally known as *Bacillus*, although formerly this term was reserved for those in which the long was greatly in excess of the short diameter, whilst those in which the two diameters are more equal were designated as *Bacterium*. This distinction, which serves no practical purpose, has now happily been abandoned, and the term 'Bacteria' has been applied both by Pasteur and De Bary to denote the entire group of schizomycetes, and will be used in that sense in the present article.

The spindle-shaped forms are sometimes known as *Clostridium*; it is, however, far simpler to describe these as spindle-shaped bacilli.

The bacilli frequently become greatly elongated into threads and are then known as *Leptothrix*, but often this elongation is only apparent and not real, being caused by the arrangement end to end of a series of bacilli. These leptothrix forms have frequently the ramified appearance of a mould-mycelium, but the branching is always only apparent and not real as in the case of the true mould. The bacilli and threads or filaments are sometimes slightly curved, when they receive the name *Vibrio*, whilst when very strongly curved so as to resemble a corkscrew they are designated *Spirillum* or *Spirochæta*, and when two such spirilla are interlaced they are described as *Spirulina*.

Many bacteria are known only in one of the above forms, whilst others in the course of their life-history assume several different shapes; indeed, it has been urged by Zopf that all the schizomycetes are capable of assuming these various modifications, but that the cycle of morphological changes has in the majority of cases not yet been ascertained. Although it is impossible, with our present imperfect knowledge, to disprove Zopf's theory, yet the latter is entirely unsupported by trustworthy observations, excepting in the case of quite exceptional forms of organisms. It is true that numerous transmutations of form, such as from bacilli to micrococci and *vice versâ*, have been recorded, but almost invariably by incompetent observers insufficiently acquainted either with the use of the microscope or with the precautions which have to be observed in the cultivation of micro-organisms. On the other hand, nothing is more striking than the constancy of form which is manifested by the great majority of micro-organisms when these are cultivated under conditions which do not admit of the accidental introduction of other varieties.

But, although it is generally not difficult to decide from its appearance under the microscope whether a particular micro-organism is to be described as a bacillus, a micrococcus, or a spirillum, still the differences in form between undoubtedly different organisms is often so slight that such differentiation by microscopic appearance alone is rarely to be relied upon; moreover the microscopic appearances of organisms are often complicated by what is known as '*involution-forms*,' which are frequently found in preparations made from old and weak cultivations. These involution-forms assume the most grotesque shapes and may often be mistaken for entirely different organisms; there can be no doubt that many of the observations which have been supposed to support Zopf's views are to be accounted for by the misinterpretation of such degenerated individuals.

In their minute structure the cells of the schizomycetes consist of wall and contents; the latter is generally free from colouring matter, but some forms have recently been found by Van Tieghem to produce chlorophyll, and some are coloured with a pigment known as *bacteriopurpurin*. The cells contain no nuclei, but some forms (*Beggiatoa*) exhibit shining granules of liquid sulphur. Iodine gives a blue colouration with some micro-organisms (*B. aceti*) indicating the presence of granulose. In many cases the cell-wall appears to be further clothed with a gelatinous zone often only indicated by the relative distances preserved between the individual cells.

Of the various forms of the schizomycetes some, like the micrococci, are invariably non-motile or rather only exhibit that oscillatory

'Brownian-motion' which is common to all finely suspended particles, organic and inorganic alike; the bacilli and spirilla, on the other hand, are frequently motile, executing rapid movements both of translation and rotation. In many of these motile forms one or more long vibratile cilia situated at one or both extremities of the organism have been observed, and it is probable that all the motile forms are provided with these organs of propulsion.

The multiplication of the schizomycetes is effected by division, the latter taking place in any direction in the case of the spherical, whilst it is invariably transverse in the cylindrical forms. This multiplication by division is, under favourable circumstances, accomplished with fabulous rapidity, and entirely surpasses anything observed in the case of the moulds and saccharomycetes. Thus, the transverse division in bacilli has been observed to take place in twenty minutes at 35°C., and it has been calculated (Cohn) that starting with a single organism and assuming one hour to be requisite for its conversion into two, at the end of twenty-four hours there would be 16,000,000, and at the end of two days they would be numbered by billions, viz., 2^{48}. In practice, however, multiplication does not take place with such extravagant rapidity, although the rate of increase is sufficiently striking.

Another mode of multiplication, viz. by means of *spores*, has been observed in the case of a number of bacilli, and perhaps in the case of some spirilla. These spores appear usually as oval highly refracting bodies, 1–2·5μ in length, in the interior of the bacillus, the spore being situated either in the middle, at one or both ends of the bacillus, or in a series of 2, 3, or 4 along its whole length. The bacilli before giving rise to spores frequently grow out into long apparently undivided threads; the individual bacilli composing these threads soon become distinctly indicated, and then the spores make their appearance at regular intervals. The threads subsequently degenerate, leaving the spores. In other cases the bacilli, instead of growing out into threads, become swollen and thickened before the spores are formed. The spores exhibiting the above morphological differences from the parent bacilli are known as *endospores*. Another and more doubtful form of sporulation consists in certain members of a chain or group of bacilli exhibiting greater vitality than the others surrounding it, and whilst the latter degenerate and die, the *arthrospores*, as these more refractory and persistent forms are called, become the parents of further generations of bacilli.

The process of sporulation is of great importance in maintaining the vitality of the schizomycetes against unfavourable conditions of food, temperature, and desiccation, for the spores are generally enormously more hardy than the parent bacilli, and are capable of enduring prolonged drying and extreme cold, and in some cases even a moist heat of 100°C. for a few minutes. When introduced into a suitable medium, the spores germinate and give rise to the original bacillar forms.

The chemical composition of the schizomycetes has been investigated by Nencki, Brieger, Vandevelde, Scheibler and Durin, Nägeli, and Loew. The following figures were obtained by Nencki from putrefactive bacteria growing in 2 p.c. gelatine:—

—	Pure zooglœa	Zooglœa with bacteria	Mature bacteria
Water . .	84·81 p.c.	84·26 p.c.	83·42 p.c.
On the dry substance.			
Albuminoids .	85·76	87·46	84·20
Fat . .	7·89	6·41	6·04
Ash . .	4·20	3·04	4·72
Undetermined	2·15	3·09	5·04
	100·00	100·00	100·00

The albuminoids were principally composed of a substance having the composition C = 52·32 p.c., H = 7·55 p.c., N = 14·75 p.c., and differing from other proteïds in not being precipitated by alcohol and in containing neither sulphur nor phosphorus; this substance Nencki has termed *mycoproteïn*. These analyses show that the proportion of albuminoids to carbohydrates is even greater than in the yeasts, and much greater than in the moulds. Nägeli and Loew, on the other hand, found that the gelatinous mass composing the 'mother of vinegar' contained in the dry substance only 1·82 p.c. N, and, similarly, Scheibler and Durin have shown that the membranous products of the organism (*Leuconostoc mesenterioïdes*) were principally composed of a carbohydrate closely resembling cellulose. Thus in some cases there can be no doubt that the principal products of the schizomycetes may be also non-nitrogenous substances.

Brieger (Zeitsch. f. physiol. Chemie, 9) found in the ash of the pneumonia-bacilli, calcium and magnesium phosphates, sulphate and chloride of sodium.

The best nitrogenous food for the schizomycetes is undoubtedly soluble albumen or peptone, but the nitrogen may also be derived from other organic substances, and from ammonia; according to Nägeli also from nitrates. There can be no doubt, however, that there are great differences amongst the schizomycetes in their power of assimilating nitrogen from various sources; thus many forms, especially amongst the pathogenic ones, require albuminoid nitrogen, and even amongst the ordinary bacteria present in air and water, the author of this article has shown that many forms do not affect the nitrogen combined as nitrate or nitrite (P. F. Frankland, C. J. 1888).

The most available sources of carbon appear in general to be sugars or other carbohydrates such as glycerin, numerous acids of the fatty series may likewise serve the same purpose—*e.g.* the alkaline salts of tartaric, citric, malic, mucic, lactic, acetic, and formic acids. Even substances which in comparatively small doses are decided antiseptics, *e.g.* alcohol, phenol, and salicylic acid, may furnish the necessary carbon, provided they are present in sufficiently minute quantities, but in the case of the *B. aceti* (the vinegar ferment) ethyl alcohol is even tolerated up to 10 p.c. Special investigations on the sources of carbon and nitrogen available in the case of the *Micrococcus ureæ*, and of the *B. lactis*, have been made by v. Jaksch (Zeitschr. f. Physiol. Chem. 5) and Hüppe (Mittheilungen, kaiserl. Gesundheitsamt, 2) respectively. Some schizomycetes have the power of utilising the food materials present in the most dilute media, thus in some of the purest natural waters, and even in distilled water; from what sources the necessary carbon and nitrogen are here derived has not yet been ascertained (P. F. Frankland, Pr. 1886; Meade Bolton, Zeitschr. f. Hygiene, 1).

As regards their relationship to free oxygen, Pasteur divided bacteria into two groups—the *aërobic* and the *anaërobic* respectively, according as they require or do not require the presence of free oxygen. The possibility of active bacterial life in the absence of all free oxygen has been disputed by Gunning, but Pasteur's observations on anaërobiosis have been confirmed by Nencki, Prazmowski, Rosenbach, and others. Nencki has, in fact, shown that certain bacteria are capable of flourishing in an atmosphere so free from oxygen that both ferrous ferrocyanide of potash and reduced hæmoglobin are unaffected. The recent investigations of Liborius (Zeitschr. f. Hygiene, 1) have shown that bacteria cannot be sharply divided into aërobic and anaërobic, but that the transition from the one to the other is gradual; thus there are (1) anaërobic bacteria proper, for the growth and multiplication of which the exclusion of free oxygen is essential; in some cases this anaërobic existence can only take place in connection with fermentation, active life ceasing in the absence of fermentable matters; (2) bacteria capable of anaërobic existence, which, although flourishing better in the presence of free oxygen, yet exhibit very considerable activity when the latter is rigidly excluded. In some cases the anaërobic vitality of this group, which includes a very large number of organisms, is increased by, and sometimes actually dependent upon, the presence of fermentable matter; (3) aërobic bacteria proper, the vitality of which, whether in the presence or absence of fermentable substances, is dependent on the access of free oxygen.

As already pointed out, the schizomycetes are more unfavourably influenced by a concentrated medium than the saccharomycetes, and these again more so than the moulds. The precise limit which various forms of bacteria are capable of enduring has, however, not been determined; but solid media containing 80 p.c. of water are still capable of nourishing most forms, whilst, on the other hand, forms are known which can still find the means of subsistence in distilled water.

Unlike most of the saccharomycetes and moulds, the bacteria are much more susceptible to acids than alkalis; some, like the bacillus of typhoid fever, are very indifferent to either, rendering by their growth an acid medium alkaline; others, like the *B. aceti*, require a certain degree of acidity (2 p.c. of acetic acid); whilst others, again, like the *M. ureæ*, endure a very marked excess of alkali (13 p.c. ammonium carbonate). It has been ascertained that some of the bacteria are capable of withstanding enormous pressure; thus putrefaction is not interrupted by a pressure of 350–500 atmospheres, and the *B. anthracis* remained virulent after 24 hours' exposure to a pressure of 600 atmospheres.

The most favourable temperature is, on the whole, higher than in the case of the saccharomycetes and moulds, but the various species exhibit great differences in this respect. Thus the *B. aceti* exhibits but very feeble vitality below 10°C., flourishes between 20 and 30°C., whilst above 35°C. its activity rapidly diminishes (Mayer, Gährungschemie, 178). *B. subtilis*, again, multiplies with greatest rapidity at 30°C. (Brefeld), whilst the *B. tuberculosis* exhibits no vitality excepting between 30 and 41°C., the most favourable temperature being 37–38°C. Recently, a number of micro-organisms growing between 50 and 70°C. have been obtained from soil by Globig (Zeitschr. f. Hygiene, 3, 294); one of these exhibited the power of vegetating under great differences of temperature, viz. 15–68°C.; others, again, exhibited no vitality below 50°C., and some not even below 60°C. These remarkable forms were all found in surface soil, which even in temperate climates may reach a temperature of 50–55°C. under direct solar radiation.

On the other hand, a number of organisms capable of growth at 0°C. have recently been described by Fischer (Centralbl. f. Bakteriol. [4] 1888, 89).

The requisite temperature for sporulation varies greatly with different species; thus in the case of *B. subtilis* spore-formation has not been observed below 6°C., whilst the *B. anthracis* requires 16°C. or upwards, 30–40°C. being the most propitious. Whilst the majority of the schizomycetes, like the moulds and saccharomycetes, require the access of free oxygen for the process of sporulation, it has been shown that some of the anaërobic forms, at any rate the *B. amylobacter* (butyric ferment) can only form spores when oxygen is excluded. In the case of *B. amylobacter*, also, the presence of free oxygen prevents the germination of its spores. It is worthy of notice also that whilst the aërobic bacilli are non-motile during sporulation the *B. amylobacter* remains motile (Prazmowski, Untersuchungen über die Entwicklungsgeschichte und Fermentwirkung einiger Bakterien, Leipzig, 1880).

Methods of Cultivation and Study.

In all investigations connected with micro-organisms it must be always borne in mind that all our surroundings are more or less infested with living forms of the same order as those with which we are dealing, and it becomes, therefore, of paramount importance that all operations shall be conducted in such a way as to preclude the possibility, or at any rate reduce to a minimum, the chance of introducing micro-organisms from foreign sources. In order to secure this end great attention has been bestowed by a number of investigators in perfecting the methods by which these micro-organisms may be accurately studied. It is greatly to be regretted that much laborious, and in many respects carefully conducted work, has been absolutely wasted owing to the imperfection of the means employed by many observers, and it is only since the methods of cultivation and examination have been brought to their present state of excellence that great strides have been made in our knowledge of these important and interesting, though minute forms of life. The modern methods of bacteriology, or the study of micro-organisms, may be divided into two parts: (1) microscopic examination; (2) cultivation. For a complete account of the modern methods of bacteriology the reader is referred to the treatises of Hueppe, Fraenkel, Huber and Becker, Flügge, Klein, and Crookshank.

A brief account only of these methods is within the scope of the present article.

1. *Microscopic examination.*—All the organisms to which we have referred are so minute that the individuals can only be observed by means of the microscope, and in the case of the schizomycetes only with the aid of very high powers, although all these micro-organisms give rise to growths consisting of large numbers of individuals, which are readily visible even with the naked eye.

The simplest mode of examining a liquid or solid object for micro-organisms consists in transferring a small portion of it on the end of a platinum needle, which has been previously sterilised by ignition and allowed to cool, to the surface of a clean microscopic cover-glass, adding a drop or two of distilled water if necessary, and then placing the cover-glass, moist surface downwards, on a glass slip. This is then placed under a high power ($\frac{1}{8}$, $\frac{1}{12}$, or $\frac{1}{20}$), and the micro-organisms will be observed in the living state; but, owing to evaporation from the edge of the cover-glass, disturbing currents in the liquid are produced, and the whole soon becomes dried up and further observation is rendered impossible. In order to obviate these disadvantages, and especially to render observation in the natural state over hours, days, or even weeks possible, the device of cultivation in a suspended drop of nutritive liquid has been introduced. For this purpose a drop of sterile broth, or other suitable nourishing fluid, is placed with a sterile platinum needle in the centre of a sterile cover-glass; into this drop a minute trace of the substance under examination is introduced with the point of a sterile platinum needle, the cover-glass being held with its face downwards during these operations to prevent aërial microbes falling into the drop, and it is then lowered on to an excavated slip (previously sterilised) so that the drop hangs downwards into the centre of the circular excavation without touching the slip itself. The edges of the cover-glass, which must overlap the excavated disc of the slip, are then rendered air-tight by painting with a little vaseline. On now examining with a high power the organisms can be seen in the drop, and if the operations described above have been carefully executed, the growth and development of the forms under examination can be observed over an indefinite period of time without the cultivation becoming contaminated. But although this mode of examination is the best for ascertaining the general character of the micro-organisms in the living state, their motility, mode and rapidity of multiplication, it does not enable us to determine their detailed form with such precision as is possible by the methods of staining, which become specially indispensable when the organisms are sparsely distributed in other substances, such as vegetable fibres, animal tissues, or detritus of different kinds.

The staining of micro-organisms with coal-tar colours was first introduced by Weigert in 1871, and has now been brought to a very high pitch of perfection by Koch, Ehrlich, and others. Although a great number of coal-tar colours have been successfully employed for the purpose, the following are those in most general use:—gentian-violet, methyl-violet, methylene-blue, magenta, and Bismarck-brown, all of which are basic materials and most widely applicable; of acid coal-tar colours, eosin, acid-magenta, and saffranin are sometimes used, whilst of vegetable colours hæmatoxylin has been specially employed for staining the flagella of bacilli and spirilla, and the animal pigment carmine (cochineal) is also used in special cases. All these colouring matters have the property of entering more or less firmly into combination with cellular nuclei in general as well as with the cellular contents of micro-organisms, which, as has already been pointed out, are devoid of nuclei. The pigments in question may thus be regarded as micro-chemical reagents for cellular nuclei and micro-organisms. In employing these pigments they are first dissolved in alcohol to saturation, the alcoholic solution being then diluted with three times its volume of distilled water for actual use. The general method of staining bacteria for microscopic observation consists in transferring by means of a platinum needle a small portion of the liquid or other substance containing them on to a cover-glass and then spreading this over the surface so as to form a very thin coating, and which is then allowed to become perfectly air-dry. The stains may now be applied to the air-dried preparation, provided there are no albuminous matters present; should there be any of the latter, however, as there generally are, these will also combine with the pigment and give rise to very disturbing deposits and precipitations. It is much better, therefore, by exposing the cover-glass to a suitable temperature to so alter these albuminous matters that they will no longer fix the stain. An exposure of twenty minutes to a temperature of 120°C. produces this alteration in the albumen without altering the staining power of the bacteria. The same result may be more rapidly attained by holding the cover-glass with a pair of forceps by one corner and passing it with the prepared surface uppermost three times through the flame of a Bunsen burner, so that it remains about half a second in the flame each time, and about one second elapses between each exposure. Preparations thus scorched can be kept for an indefinite length of time without change, and can then be stained when required. The staining is effected by allowing a few drops of the dilute solution mentioned above to run on to the surface of the cover-glass, moving the latter so that the liquid flows evenly over the surface and remains on for about one minute; the excess is then washed off by means of a gentle stream of water from a wash-bottle, and the preparation is then ready for immediate examination, or it may be allowed to dry for mounting with Canada balsam. By this method of staining, the bacteria appear beautifully distinct and strongly coloured, whilst the remainder of the field is colourless or nearly so. Spores, owing to their tough cell-wall, only stain with great difficulty, so that in preparations made as above they are sharply distinguished as bright highly refracting bodies against the stained bacteria. In order to stain the spores also, the following method may be adopted. The cover-glass is placed for one hour in a hot aqueous solution of aniline and magenta,[1] the colouring matter penetrates into the contents of the spore, from which it is then very difficult again to remove, much more difficult than from the bacterial cells. The cover-glass is then placed in alcohol acidulated with hydrochloric acid (20 c.c. alcohol, 3-4 drops of hydrochloric acid) until the colour appears removed. By this means the colour is withdrawn from everything but the spores. The cover-glass is washed with water and then treated with a dilute solution of methylene-blue, which the bacterial cells now absorb, and on then washing off the excess and examining, the spores will be found coloured red, the bacterial cells blue. It is needless to add that numerous modifications in the above methods have been made by individuals, and that success in staining bacteria can only be attained by actual practice.

2. *Isolation and cultivation of micro-organisms.*—Of the greatest importance in the study of micro-organisms is their isolation and cultivation in a state of purity. In the absence of such pure cultivations it is impossible to identify any particular organism with any particular change. It is no longer sufficient to discover that some form of micro-organism invariably accompanies some process of fermentation or similar change, but modern science demands that the particular organism should be isolated, its characters clearly defined by growing it in a state of purity in various cultivating media, and then showing that the change in question can be actually brought about by introducing the organism from such a pure culture. Then and only then is there indisputable evidence that the microbe is the cause and not the mere concomitant of the change. The great rapidity with which our knowledge of the changes brought about by micro-organisms has progressed during recent years is due to the improvements which have been made in the processes of isolation and culture.

The media employed for cultivation are of two kinds: (1.) Liquid. (2.) Solid.

Until recently liquid media were exclusively employed, and are still preferred by some investigators. The liquids employed are broth prepared from various kinds of flesh, the infusions of various vegetables, including decoctions of yeast itself, extract of malt, and the like, as well as a great variety of solutions prepared by dissolving various salts in suitable proportions, sugar, peptone, or other organic substances being generally added to the latter to increase their nutritive value.

As solid media, on the other hand, are employed slices of potato, hard-boiled egg, broth to which such a proportion of either gelatine or agar-agar has been added that the mixture is solid at the temperatures of culture; finally, for the cultivation of some organisms, like the *B. tuberculosis*, solidified blood serum is used.

These solid media possess the great advantage that the organisms introduced into them are confined to the spot where they are first deposited, and around this spot their progeny grows up without infesting the entire medium, as is the case in a liquid. Another advantage is obtained by conducting all inoculations of such media with the mouth of the containing vessel in an inverted position, by which the possibility of aërial microbes being introduced during the operation is reduced to a minimum, and should any such aërial forms gain access, they will in all probability not fall on the precise spot inoculated, and on growing up into a colony their presence will be at once recognised. The most striking advantage of all, however, is the facility which the solid media afford of obtaining pure cultivations. Thus with liquid media the most satisfactory method of obtaining pure cultivations is that known as '*Fractional Dilution*,' which consists in taking a certain quantity of the liquid containing the micro-organisms and diluting it with water or some other liquid to such an extent that when a number of aliquot parts of this dilution are taken out, each of these shall contain not more than a single organism. By then introducing these aliquot parts into a number of fresh quantities of nutritive liquid one or other of these inoculated portions of liquid will probably yield the organism sought for in a state of purity. The method is on the face of it uncertain, extremely tedious, and troublesome. With solid media, on the other hand, pure cultures are readily obtainable by means of the process of *plate cultivation*, which is due to Koch, and which has been the means of enormously extending the accurate study of micro-organisms. This process consists in taking a portion of the substance containing the microbes under examination and thoroughly mixing it with some of the melted gelatine or agar-agar medium in a test-tube, then pouring this mixture out on a horizontal glass-plate and allowing it to congeal. The plate bearing the solid film is then preserved in a damp chamber at a suitable temperature, and in the course of a few days each organism originally introduced will have given rise to a separate and isolated *colony* visible to the naked eye, and often presenting very characteristic appearances when examined with a low power. Each of these colonies is a pure cultivation, and fresh cultures can be started by inoculating from them. Thus this process of plate cultivation serves a number of highly useful purposes—(1) it enables us to procure pure cultures; (2) to test cultures supposed to be pure; (3) to ascertain the actual number of organisms present in a given quantity of substance; (4) to identify or to differentiate between organisms, through the characteristic appearances of their colonies.

For modifications of the above process, in which the use of plates is dispensed with, and in which the whole operation is conducted in the tube or flask containing the culture-medium,

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[1] Prepared by shaking up some distilled water with an excess of aniline, then filtering through a moist filter. To some of the filtrate placed in a watch-glass a saturated alcoholic solution of magenta is then added until the surface of the liquid shows iridescent colours indicating first it is saturated with magenta.

v. Esmarch (Zeitschr. f. Hygiene, [1] 1886, 293); P. F. Frankland (Tr. 1887, 113); Fraenkel (Centralbl. f. Bakteriologie, [3] 1888, 735 and 763); and Buchner (Centralbl. f. Bakteriol. [4] 1888, 149).

Preparation and sterilisation of the culture media.—The three principal culture media now employed—gelatine, agar-agar, and broth—are so similar in their mode of preparation that one description will serve for the three. The essential principle in each is a neutral or feebly alkaline extract of meat, freed from coagulable albuminoids by boiling, but the nutritive power of which is increased by the addition of peptone (1 p.c.); the gelatine or agar-agar are merely added to give the requisite solidity to the medium at the temperature to be employed in cultivation. The following is the method commonly adopted in the preparation of these media:

1lb. of finely minced lean meat is added to 1,000 c.c. of distilled water in a flask, the mixture being placed in a refrigerator for twenty-four hours. It is then strained through a piece of coarse linen, and to the clarified liquid, after restoring the volume to 1 litre, 10 grams of dry peptone and 1 gram of common salt are added, together with 100 grams of the best French gelatine (sold in thin transparent and colourless leaves), or 10 grams of agar-agar cut up very finely, according as a gelatine or an agar-agar medium is desired, whilst in the case of broth these solidifying ingredients are omitted. The mixture is now placed in the steam-steriliser, in which it is heated for about one hour, when the gelatine &c. will be found to have completely dissolved, whilst the agar-agar may require two, three, or more hours' digestion at 100°C. The liquid will now be found to have a very decidedly acid reaction, which is removed by adding a solution of carbonate of soda until it becomes weakly alkaline. The whites of two eggs may now advantageously be added, and the liquid again heated for about half an hour in the steamer, for by the coagulation of the albumen the clarification of the liquid is greatly assisted. The liquid is then strained through a piece of fine cloth, and is finally filtered through a large ribbed filter. The filtration is most conveniently carried on in the steamer, as by this means the requisite temperature to preserve fluidity can be maintained whilst no concentration by evaporation takes place. In the case of agar-agar, the steamer may be kept at 100°C., or near it, during filtration, whilst with gelatine it should only be at about 50°C., as a prolonged high temperature often renders the gelatine-medium turbid, and also reduces the melting-point of the gelatine. The filtered liquid is collected in a flask which has been sterilised in the steamer, and should be plugged with cotton wool which has been heated in an air-oven until it is slightly browned. The flask and contained medium are then finally sterilised by steaming for ten to thirty minutes, according to the size of the flask and volume of medium, on three or four successive days. In the case of test-tubes containing nourishing material ten minutes' steaming on three to four successive days will be found sufficient. This intermittent sterilisation, which was originally devised by Tyndall, is of great importance, as by this means media can be with certainty sterilised which by a prolonged exposure to a temperature of 100°C. would become altered. Thus milk, blood serum, &c., can be sterilised without coagulating the albumen by heating to 54-56°C. for two hours on eight successive days. The efficiency of this method of sterilisation depends upon the fact that it is only the spores of micro-organisms, excepting those recently found by Globig in soil, which can survive a temperature of 54-56° for any considerable time, so that, by allowing a day to elapse between each heating, an opportunity is afforded to any spores which may be present to germinate into fully developed bacilli, which will then be destroyed when the temperature is next raised.

Although the above media are the ones most commonly used, they are sometimes modified for special purposes. Thus some investigators prefer a gelatine medium containing only 5 p.c. or 7·5 p.c. of gelatine, whilst others add from ·5-2 p.c. of grape sugar. It has been found that an addition of glycerine is very advantageous for the cultivation of some organisms, thus the *B. tuberculosis* which had previously only been grown on blood serum (and with great difficulty on agar-agar) can now be readily cultivated on the agar-agar mixture to which 8 p.c. of glycerine has been added (Nocard and Roux, Centralbl. f. Bakteriol. [2] 1887, 136). Again, in the study of micro-organisms causing the alcoholic fermentation, it is usual to add the requisite quantity of gelatine for solidity to brewers' wort, or to beer itself (Hansen, Methode zur Analyse d. Brauwassers in Rücksicht auf Mikroorganismen, Centralbl. f. Bakteriol. [3] 1888, 377).

As regards the choice of these various media, it may be mentioned that the gelatine-peptone medium is only applicable for cultivations not requiring a temperature above 24°C., whilst for higher temperatures, agar-agar, blood serum, or broth are employed.

Of the numerous artificial solutions which have been employed for culture those of Pasteur and Cohn may be mentioned, which have the following composition respectively:

Pasteur's Solution.

Ammonium tartrate . .	1 part
Sugar-candy	10 parts
Ash of yeast	1 part
Water	100 parts

Cohn's Solution

Potass. phosphate . .	·5 gram
Magnes. sulphate . .	·5 „
Tricalc. phosphate . .	·05 „
Ammon. tartrate . .	1·0 „
Water	100 c.c.

FERMENTATIONS CAUSED BY SACCHAROMYCETES.

The alcoholic fermentation of sugar by yeast is of all fermentations the one which has longest attracted the attention of man, and has also been most closely subjected to scientific investigation.

The substances especially adapted for this fermentation by yeast are the various forms of glucose possessing the general formula $C_6H_{12}O_6$, including dextrose, lævulose, and galactose. Other carbohydrates are, however, also capable of undergoing fermentation by yeast, but they are probably in the first instance invariably converted into glucose, and it is then the latter which really undergoes the process of fermentation. Thus maltose

$$C_{12}H_{24}O_{12} \text{ or } C_{12}H_{22}O_{11} + H_2O$$

undergoes the alcoholic fermentation, the molecule of dextrose which it contains being apparently first attacked, for dextrose is the form of glucose which is most readily fermented: thus if a mixture of dextrose and lævulose is exposed to the action of yeast, the whole of the former is fermented before the latter is touched.[1] This selective property exhibited by the yeast-cell is much more intelligible now that the difference in the constitution of these two forms of glucose has been established. Again, cane sugar or saccharose is apparently fermentable by yeast, but the real fermentation is preceded by a process of conversion into equal parts of dextrose and lævulose which is effected by the yeast itself, for the latter contains a true soluble ferment, *invertase*, possessing this property. Similarly, milk-sugar undergoes conversion into dextrose and galactose through the agency of a soluble ferment formed by some schizomycetes, and the products of this conversion are then capable of undergoing the alcoholic fermentation. Pure galactose, however, is, according to Bourquelot (C. R. 106, 283; Centralbl. f. Bakteriol. [3] 1888, 557), not fermentable by ordinary yeast, but only becomes so in the presence of glucose. Thus whilst milk-sugar is not fermented by pure cultivations of ordinary wine and beer-yeasts (Pasteur, Études sur la bière, 257), a special variety has been discovered by Duclaux (Annales de l'Institut Pasteur, 1887, No. 12; Centralbl. f. Bakteriol. [3] 1888, 525) in milk which directly converts lactose into alcohol and carbonic anhydride.

A ferment resembling the saccharomycetes, and named *Monilia candida*, has been described by Hansen (C. J. (abstr.) 1885, 1168), and differs from all other yeasts in fermenting cane sugar without the formation of intermediate products.

The most available indirect sources of fermentable sugar are the various forms of starch, which, by the action of the soluble ferment diastase, is convertible into maltose and into dextrose either by the action of ptyaline or by treatment with mineral acids. Thus in practice the starch contained in various cereals, notably barley, is converted into fermentable maltose by the diastase contained in malted grain, the starch in potatoes being converted into dextrose by boiling with dilute sulphuric acid under pressure.

From whatever ultimate source, however, the dextrose has been derived, it undergoes the same change when brought in contact with yeast. This change has been shown by Pasteur to consist essentially in the formation of ethyl alcohol and carbonic anhydride, together with a small proportion of glycerin (2·5–3·6 p.c.), succinic acid (·4–·7 p.c.), besides traces of acetic acid and higher homologous alcohols, especially amyl alcohol. The older observers, Lavoisier (Traité élémentaire de Chimie, [1] 150, 1789) and Gay-Lussac (A. Ch. [95] 318, 1815), had omitted to notice the formation of these by-products, and regarded the change as a simple decomposition of the molecule of sugar into two molecules of alcohol and two molecules of carbonic anhydride $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$.

In 1847, however, Schmidt discovered the presence of succinic acid in all fermented liquids, whilst the invariable presence of glycerin was first pointed out by Pasteur (C. R. [46] 857), according to whom the products of fermentation are found in the following proportions:

100 parts of cane-sugar = 105·36 of glucose, yield

Alcohol	51·11
Carbonic anhydride . .	48·89
,, ,, from succinic fermentation	·53
Succinic acid	·67
Glycerin	3·16
Cellulose, fat, and extractive matters, &c. . . .	1·00
	105·36

Pasteur has attempted to formulate the production of these by-products in the following equation:

$$49C_6H_{12}O_6 + 30H_2O = \underset{\text{Succinic acid}}{12C_4H_6O_4} + \underset{\text{Glycerin}}{72C_3H_8O_3} + 30CO_2$$

whilst a simpler equation has been proposed by Monoyer

$$4C_6H_{12}O_6 + 3H_2O = C_4H_6O_4 + 6C_3H_8O_3 + 2CO_2 + O$$

the liberated oxygen serving for the respiration of the yeast-cells. With regard to these by-products, it has been shown by Brefeld that they are especially formed at the close of the fermentation, or when exhausted yeast is employed, and generally when the conditions are unfavourable to the activity of the yeast. More recently it has been found by Borgmann (Fr. [25] 532; Amthor, Centralbl. f. Bakteriol. [3] 1888, 428) that the proportion of these by-products is largely dependent on the purity of the yeast employed. Thus, whilst in a number of ordinary lager beers the proportion of alcohol to glycerin was found to vary between 100 : 5·497 and 100 : 4·140, in beers fermented with yeasts of undoubted purity prepared by Hansen's method, the proportion was found to be 100 : 2·63 with Hansen's No. 1 yeast, and 100 : 3·24 with No. 2 yeast.

Again, in fermentations on the large scale, various homologous alcohols are produced in small quantities, thus propyl (Chancel, C. R. [37] 410), butyl (Wurtz, C. R. [35] 310), amyl (Pelletan, A. Ch. [30] 221), and capryl (Faget, C. R. [37] 730) alcohols. To what extent these secondary products are due to the presence of different kinds of yeast or even to other kinds of micro-organisms present in the fermentation has not yet been determined, but it has been found by Ordonneau (C. R. 1886, 217) that a potato-spirit mash fermented with brewers' yeast yields, amongst other products, the unpleasant isobutyl alcohol, whilst fermented with *Saccharomyces ellipsoïdeus*, the natural ferment of grape-juice, the normal butyl alcohol is produced, the latter imparting the agreeable aroma of cognac. Schwarz, Le Bel, and quite recently Lindet (C. R. [107] 182) have shown that the proportion of higher alcohols

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[1] This point is disputed by Bourquelot (C. R. 100, 1404, 1466; abstract C. J. 1885, 1003).

formed diminishes slightly as the temperature of fermentation is reduced, thus:

32–35°C.	25–27°	19–21°	8–10°
·58 p.c.	·59 p.c.	·54 p.c.	·52 p.c.

of the crude alcohol.

The process of fermentation differs in the course which it takes according to a number of circumstances; it may, however, be generally stated that it takes from 10–20 minutes (Cochin, C. R. [96] 852) after addition of the yeast before active fermentation commences, and if the evolution of carbonic anhydride be taken to indicate the progress of the reaction, the latter may be represented by a steep curve, which with diminishing activity becomes parabolic. In dilute solutions the period of incubation is longer than above mentioned, and a similar period of repose is observed even when the yeast is taken directly from an actively fermenting liquid, so that it cannot be due to the time required for the saccharine liquid to penetrate into the cell. As regards the most favourable strength of the saccharine solution, 2–4 p.c. appears to be the best, whilst 20–25 p.c. (Wiesner, Sitz. W., 1, 1873) is said to be the next most favourable degree of concentration, although this appears extremely improbable. The sugar must, however, not exceed 35 p.c. With regard to the effect of the quantity of yeast employed, the experiments of Dumas (A. Ch. [5] 3, 57) show that 20 grams of yeast decompose 1 gram of glucose in 23–24 minutes at 24°C., cane sugar requiring about twice this time under similar circumstances. Most remarkable is the fact that an excess of yeast does not increase the rate of decomposition of a given weight of sugar; it appears, therefore, that by thus increasing the proportion of yeast beyond a certain limit, each cell has less sugar surrounding it than it is capable of transforming in a given time, and thus the rate of fermentation is not increased. In pure solutions of sugar, on the other hand, active fermentation only takes place when a large quantity of yeast is added, and the yeast remaining, when the fermentation is complete, is poor and exhausted, for in order to carry on fermentation with a relatively small proportion of yeast it is necessary that other food-materials, and especially nitrogenous ones, should be present.

Temperature exerts a powerful influence on the alcoholic fermentation, 25-30°C. being on the whole the most favourable.

When the proportion of alcohol produced amounts to 12 p.c. the further growth of the yeast is prevented, and with 14 p.c. fermentation ceases altogether. In thus resisting the action of alcohol, yeast appears to excel other organisms capable of setting up alcoholic fermentation; thus, certain forms of mucor will only set up fermentation as long as the alcohol is under 3½–4 p.c., and *Mucor stolonifer* is particularly sensitive in this respect, its fermenting power being stopped by 1·3 p.c. of alcohol, active fermentation also only taking place with less than 7 p.c. of sugar (Fitz).

Some salts, like potassium tartrate, do not interfere with the process of fermentation, others retard or arrest it before the whole of the sugar has been converted, others again arrest the fermentation but do not prevent the inversion of cane sugar, whilst others, such as borax, prevent both fermentation and inversion. Again, free alkalis, sulphurous acid, mercuric chloride, and chloroform prevent fermentation, whilst sulphuretted hydrogen, arsenious acid, carbolic, salicylic, and hydrocyanic acids, as well as strychnine, are comparatively inactive.

There has been much discussion as to whether alcoholic fermentation can take place in the total absence of free oxygen, but from Pasteur's experiments there can be no doubt that free oxygen is not essential to vigorous fermentation. Nägeli is of opinion that the access of free oxygen is invariably beneficial, especially in rich solutions, as the multiplication of the yeast-cells is greatly accelerated thereby. Hansen (Meddelelser fra Carlsberg Lab., 1; Buchner, Zeitschr. physiol. Chem. [9] 380 (abstr. C. J.) 1885, 1002) has more recently shown that in the absence of oxygen there is less growth of yeast, and the transformation of a given quantity of sugar requires more time, but that the quantity transformed per single cell is greater than with access of oxygen, in the latter case the production of yeast as well as the rate of fermentation being both increased.

The rate of fermentation may, however, also be greatly increased by exhausting the space above the fermenting liquid, thus removing the carbonic acid and alcohol as they are produced, and preventing their retarding influence upon the activity of the yeast. The normal proportion of glycerin, namely, 2·5 to 2·9 parts per 100 of glucose, was found in fermentations thus carried on *in vacuo* (Boussingault, C. R. [91] 37).

It is usual to distinguish between a number of different varieties of yeast, partly by means of differences in form and mode of development, partly by the differences which they exhibit as regards fermentation. The classification of the yeasts is, however, undergoing revision, as the recent researches of Hansen have shown that probably but few of the older forms were really pure.

The following are the principal recognised varieties:

Saccharomyces cerevisiæ. This is the yeast used in the ordinary fermentation of brewers' and distillers' worts. This fermentation may be of two kinds, viz. (1) 'top' fermentation, as carried on in English breweries and all distilleries; (2) 'bottom' fermentation as employed in the production of lager-beer. Whether the forms of yeast producing these two kinds of fermentation are distinct species or not is still disputed, but they undoubtedly retain their distinctive mode of action through a long series of generations, although Rees affirms, in opposition to Pasteur, that the one form may be transmuted into the other.

The 'bottom' fermentation yeast consists of round or oval cells 8–9μ in diameter, occurring either singly or in short chains, and less branched than in the case of upper fermentation yeast. In sporulation there are 3-4 spores of 4–5μ in each cell. The fermentation to which this yeast gives rise takes place slowly at 4-10°C., temperatures at which other forms of yeast are practically inert. During this fermentation the yeast-cells collect on the *bottom* of the fermenting vessel, and are not even carried to the surface if the temperature rises to 20°C. and fermentation becomes violent.

The top-fermentation yeast consists of cells which are generally somewhat larger and more globular, and give rise to more branched chains. The fermentation to which this yeast gives rise takes place between 14° and 20°C.; the reaction is very violent, and the yeast is carried to the surface of the fermenting liquid by the current of carbonic anhydride. At lower temperatures this yeast is inert.

Saccharomyces apiculatus. This most characteristic form of yeast consists of citron-shaped cells having a small prominence at each extremity, from which points the budding alone takes place. The cells are 6–8μ long and 2–3μ broad. Sporulation has not been observed. This form of yeast is very widely distributed, being found in considerable quantity in active multiplication on ripe fruit, whilst on unripe fruit, leaves, &c., it is not found, nor in winter on any part of the plants. Hansen has shown, however, that it passes the winter in the ground and is carried from there on to the fruit in summer by winds, insects, &c. This yeast almost invariably appears at the outset of the vinous fermentation of grape-juice, but is soon displaced by *S. pastorianus* and *S. ellipsoïdeus.* It is remarkable that *S. apiculatus* does not secrete any invertine. A form of yeast not causing inversion is also described by Roux (C. J. Abst. 1881, 632), and is consequently inert towards cane sugar and maltose (Amthor, Centralbl. f. Bakteriologie, [4], 1888, 650), whilst in solutions of dextrose it sets up a vigorous alcoholic fermentation.

Saccharomyces ellipsoïdeus. This is the form of yeast which takes the most important part in the fermentation of grape-juice and in other spontaneous fermentations. The elliptical cells are 6μ by 4–5μ, 2–4 spores of 3–3·5μ diameter are formed in each mother-cell.

Two varieties have been cultivated in a state of purity by Hansen, for description of which *v. infra.*

The following products were obtained by Claudon and Morin (Centralbl. f. Bakteriol. [2] 1887, 655), by the fermentation of 100 kilos. sugar with a *S. ellipsoïdeus* derived from white wine:

Aldehyde	traces	
Ethyl alcohol . . .	50,615	grams
Propyl ,, (normal) . .	2	,,
Isobutyl ,, ...	1·5	,,
Amyl ,, ...	51	,,
Œnanthylic ether . . .	2	,,
Isobutylene-glycol (Henninger and Sanson, C. R. 106, 208)	158	,,
Glycerin	2,120	,,
Acetic acid	205·3	,,
Succinic ,, ...	452	,,

Saccharomyces pastorianus. This form of yeast takes part in numerous spontaneous fermentations, and in the fermentation of grape-juice usually succeeds the *S. apiculatus*, and gives way itself to the *S. ellipsoïdeus* by which it is displaced. This yeast is highly polymorphous; the cells are oval or club-shaped, the long diameter varying from 6–20μ, the cells often form abundant ramifications. 2–4 spores are formed in a mother-cell.

Three varieties have been cultivated by Hansen in a state of purity, *v. infra.*

Saccharomyces conglomeratus. Spheroidal cells 6μ in length, and disposed in conglomerates around the parent cell. Found on decomposing grapes and occasionally at the commencement of the fermentation of grape-juice.

Saccharomyces exiguus. Small cells 5μ by 2·5μ. Found in the fermentation of fruit juices and also in the after-fermentation of beer.

Saccharomyces sphæricus. Parent cells 10–15μ long by 5μ broad, the bud-cells 5–6μ in diameter and globular. Spores are not known.

Saccharomyces minor. Oval cells 6μ long, singly, in pairs and sometimes in threes. This is stated by Engel to be the yeast employed by bakers to raise the dough, whilst it only slowly transforms sugar into alcohol.

Hansen's experiments.—Six forms of yeast have been obtained by Hansen from fermenting liquids and cultivated in a state of purity. He finds that the form, size, and appearance of the cells are not to be depended on for purposes of differentiation, but, on the other hand, valuable indications are afforded by the temperature at which spore-formation takes place, as well as by the time and temperature required for the formation of a surface-film when each variety is grown in a state of purity under precisely similar conditions in a liquid medium (hopped wort).

The six forms thus examined by Hansen are:—

S. cerevisiæ, I.
S. pastorianus, I., II., and III.
S. ellipsoïdeus, I. and II.

The tables opposite (G. H. Morris, S. C. I. 1887, 119), show the differences exhibited by these several varieties in the formation of spores and films respectively.

For practical brewing purposes Hansen has isolated two forms of *S. cerevisiæ*, both for bottom-fermentation, and known as Nos. 1 and 2; these he has cultivated in a state of purity, and they are not only employed at the Old Carlsberg Brewery in Denmark, but in many other breweries on the Continent. The beers obtained from these two different forms of yeast exhibit considerable differences in their properties, thus:

No. 1 gives a beer well adapted for bottling, and containing less carbonic anhydride than No. 2. The beer should remain bright in bottle for at least three weeks; it has also a lower attenuation than No. 2. This yeast is chiefly employed for home use.

No. 2 gives a good draught beer, containing more carbonic anhydride than No. 1; it is not adapted for bottling, and is much preferred by German brewers to No. 1, and is, therefore, chiefly cultivated for export.

By employing these pure yeasts a number of dangers to which fermentation is ordinarily exposed are obviated, and there can be no doubt that a most important departure in practical fermentation has been inaugurated by the results of Hansen's investigations.

For description of pure yeast-culture on the manufacturing scale according to Hansen's methods, *v.* Zeitschr. f. Bierbrauerei and Malzfabrik, 1887; or Centralbl. f. Bakteriol. [2] 1887, 118; also The Micro-organisms of Fermentation, Jörgensen, edited by G. H. Morris, 1889.

Ascospore Formation.

Temperature	S. cerev. I.	S. past. I.	S. past. II.	S. past. III.	S. ellips. I.	S. ellips. II.
37·5°C.	none	—	—	—	—	—
36–37°	29 hours	—	—	—	—	—
35°	25 „	—	—	—	—	none
33·5°	23 „	—	—	—	none	31 hours
31·5°	—	none	—	—	36 hours	23 „
30°	20 „	30 hours	—	—	—	—
29°	—	27 „	none	none	23 „	22 „
27·5°	—	24 „	34 hours	35 hours	—	—
26·5°	—	—	—	30 „	—	—
25°	23 „	—	25 „	28 „	21 „	27 „
23°	27 „	26 „	27 „	—	—	—
22°	—	—	—	29 „	—	—
18°	50 „	35 „	36 „	44 „	33 „	42 „
16·5°	65 „	—	—	53 „	—	—
15°	—	50 „	48 „	—	45 „	—
11–12°	10 days	—	77 „	—	—	5·5 days
10°	—	80 „	—	7 days	4·5 days	—
8·5°	none	5 days	—	9 „	—	9 „
7°	—	7 „	7 days	—	11 „	—
3–4°	—	14 „	17 „	none	none	none
0·5°	—	none	none	—	—	—

Film Formation.

Temperature	S. cerev. I.	S. past. I.	S. past. II.	S. past. III.	S. ellips. I.	S. ellips. II.
40°C.	—	—	—	—	—	none
36–38°	none	—	—	—	none	8–12 days
33–34°	9–18 days	none	none	none	8–12 days	3–4 „
26–28°	7–11 „	7–10 days	7–10 days	7–10 days	9–16 „	4–5 „
20–22°	7–10 „	8–15 „	8–15 „	9–12 „	10–17 „	4–6 „
13–15°	15–30 „	15–30 „	10–25 „	10–20 „	15–30 „	8–10 „
6–7°	2–3 months	1–2 months	1–2 months	1–2 months	2–3 months	1–2 months
3–5°	none	5–6 „	5–6 „	5–6 „	none	5–6 „
2–3°	—	none	none	none	—	none

S. pastorianus I. has been shown, both by Hansen and by Grönlund (Centralbl. f. Bakteriol. [3] 1888, 300), to be the cause of a bitter taste in beer.

Saccharomyces mycoderma (*Mycoderma vini*). This organism forms a skin on the surface of fermented liquids, without itself producing fermentation; when, however, it is kept artificially submerged in a saccharine solution, it forms a small quantity of alcohol, but no growth takes place. The skin consists of oval or cylindrical cells, which are much ramified, 6–7μ by 2–3μ. In sporulation 1–4 spores are formed in a mother-cell, which may reach 20μ in length. It was formerly supposed that *S. mycoderma* was the cause of the acetous fermentation of alcohol, owing to its appearing on acid wines, beers, &c. According to Hansen, if the skin on such liquids is grey and dull, it will consist principally of *S. mycoderma*, numerous bubbles being distributed amongst its ramifications. If, on the other hand, the skin is shining and slimy, it is composed of schizomycetes, and the liquid beneath will be turbid and discoloured. In fact the liquid beneath skins, consisting exclusively either of *S. mycoderma*, *Mycoderma aceti*, or *Mycoderma pasteurianum* (the two latter are the bacilli of the acetous fermentation), is always clear. A low temperature of about 15°C. is most favourable for the growth of *S. mycoderma* on fermented liquids, whilst at higher temperatures it can with difficulty compete with the schizomycetes, which from 26°C. and upwards practically monopolise the field, 30-40°C. being most suitable for the growth of *Mycoderma aceti* and *pasteurianum*.

It is still a disputed point whether *S. mycoderma* is identical (Rees; Grawitz, Virchow's Archiv, 70) or not with *S. albicans* (*Oïdium albicans*), which is the cause of 'thrush' in infants. The principal differences observed are that *S. albicans* is not known to form spores, and, submerged in saccharine liquids, produces more distinct alcoholic fermentation with abundant growth (Plant).

Fermentation induced by Moulds.

It has been already pointed out that moulds growing in their natural condition flourish only on the surface of nourishing media, in which they do not set up any fermentation but only consume or assimilate the sugar and other nutritive materials. When, however, they are artificially submerged in saccharine liquids, and thus withdrawn from the presence of free oxygen, they undergo a marked morphological change, the ramified mycelium giving place gradually to short oval cells, multiplying by budding and much resembling yeast. *Pari passu* with this morphological change, the organism exhibits the power of transforming sugar into alcohol and carbonic anhydride. These abnormal yeast-like forms of moulds were first observed by Bail (Flora, 1857, 439; Nova Acta, 28, 23, 1861; Mittheil. über Vorkommen und Entwickelung einiger Pilzformen, Dantzig, 1867, 7) in the case of mucor, and were at first regarded by him as distinct from yeast, but subsequently were considered to represent a true transmutation of the mucor into yeast. It was, however, shown by Rees (Botan. Untersuch. üb. Alkoholgährungspilze, Leipzig, 1870), Fitz (B. 1873, 48), and Pasteur (Études sur la bière, 1876, 86–140) that this latter view was erroneous, and that the mucor-yeast, on being again exposed to free oxygen, resumed its ordinary form, whilst the converse transformation of a true yeast into a mucor or other mould-form could not be effected.

The various forms of penicillium and aspergillus only yield very small quantities of alcohol, as they do not appear to be capable of active growth in this submerged state. *Mucor racemosus* and *M. mucedo*, on the other hand, adapt themselves more readily to this modified mode of life, and Pasteur (Études sur la bière, 134) found after a fermentation with *Mucor racemosus* that the liquid contained in 120 c.c., 4·1 grams of alcohol, and only ·25 gram of the dried mould.

According to Gayon (C. J. Abstr. 1881, 480), *Mucor circinelloïdes* ferments glucoses, but leaves the saccharoses unacted upon, and it is suggested that by means of pure cultures of this mould cane sugar may be advantageously recovered from molasses. The fermentation takes place even in the presence of 30 p.c. of saccharose.

Very similar to this alcoholic fermentation induced by moulds in the absence of free oxygen, are certain changes effected by the higher plants under special circumstances, and which also result in the formation of alcohol. Bérard, in 1821, found that picked fruits absorb oxygen during ripening, and give out approximately an equal volume of carbonic anhydride, and further, that if they are placed in contact with a limited volume of air, the evolution of carbonic anhydride continues after the whole of the available oxygen has been absorbed and a decomposition of the sugar present in the fruit is found to have taken place. In 1869 these observations were further extended by Lechartier and Bellamy (C. R. 69, 356, 466; 75, 1203; 79, 949, 1006), who placed the fruit in an atmosphere free from oxygen, and discovered that the decomposition of the sugar had resulted in the formation of alcohol. Fruits of every description, including grain, and the tubers of potatoes, were found to yield alcohol under the same circumstances. These results have been confirmed by Pasteur, and Muntz (A. Ch. [5] 13, 543) has shown that if whole plants are placed in an atmosphere of nitrogen, they similarly yield alcohol. In all these cases it would appear that the vitality of the fruit &c. continues, and in the presence of oxygen the heat necessary for the vital processes is furnished by the combustion of a portion of the constituents, whilst in the absence of free oxygen this heat is generated by the decomposition of the sugar into alcohol and carbonic anhydride.

Amongst the chemical changes effected by moulds must be mentioned the remarkable discovery of Frank (B. 1885), that the nutrition of some trees, notably some of the *Cupuliferæ*, is dependent upon the presence of a mould-mycelium investing their roots, and to which the name of *mycorrhiza* is given.

Of the greatest interest, also, in connection with the chemistry of micro-organisms, is the proof which has been given by Lewkowitsch (B. 1883, 1568, 2722) that ordinary or inactive mandelic acid is composed of equal parts of dextro- and lævo-rotatory modifications, for by growing the common mould, *Penicillium glaucum*, in mandelic acid, the latter becomes dextro-rotatory through the removal by the mould of the lævo-rotatory portion. On the other hand, by means of a specific schizomycetes the dextro-rotatory half can be removed, the lævo-rotatory remaining intact.

In the same way, by means of *Penicillium glaucum*, Pasteur (J. 1860, 250) had previously obtained lævo- tartaric acid from racemic acid, the dextro- tartaric acid being alone removed by the mould. Lewkowitsch further found that the specific schizomycetes which he had employed to obtain dextro-rotatory mandelic acid also yielded dextro-rotatory tartaric acid when growing in racemic acid (*v.* also *Fermentation of Tartaric Acid*, p. 129).

By means of *Penicillium glaucum*, Lewkowitsch (B. 1883, 720) has also obtained a lævo-rotatory glyceric acid and a dextro-rotatory lactic acid from the inactive acids respectively.

The fermentation of dextrin and starch by a form of mucor has been recently observed by Gayon and Dubourg (Ann. de l'Institut Pasteur [1] 1887, No. 11; C. R. 103, 885; Centralbl. f. Bakteriol. [1] 1827, 168). Like the *Mucor circinelloïdes*, however, it has not the power of inverting or fermenting cane sugar.

FERMENTATION INDUCED BY SCHIZOMYCETES.

A very large number of fermentations are induced by the schizomycetes, but unfortunately the majority of these having been studied before the introduction of the modern methods of cultivation and isolation, it is only in comparatively few cases that such fermentations have been carried out with pure cultivations of well-characterised micro-organisms. In fact the subject of fermentation may be approached from two distinct points of view—the biological and the chemical. In the first case the object is to study the changes effected by particular forms of life, whilst in the other the interest is concentrated on the investigation of particular changes brought about by vital agencies. There can be no doubt that the chemical side of the question has hitherto received the most attention, the biological side having been so insufficiently considered, that but a very imperfect picture of these fermentative changes has been obtained.

In considering the numerous processes of fermentation known to be the result of bacterial life, it will be most convenient to arrange them in groups according to the nature of the principal reaction taking place in each case, subdividing these groups again according to the nature of the fermentable substances. The processes of fermentation may thus be divided into the following four groups:

1. Fermentation by hydration.
2. Fermentation by decomposition.
3. Fermentation by reduction.
4. Fermentation by oxidation.

1. **Fermentation by hydration.** The most important instances of this group of fermentative reactions are the conversion of urea into carbonate of ammonium, and that of hippuric acid into benzoic acid and glycocoll, besides numerous cases in which micro-organisms secrete a soluble ferment capable of exerting a diastatic action; these latter cases, however, will be more especially referred to in treating of the soluble or unformed ferments. Similar processes of hydration take place in the phenomenon of putrefaction, to which special reference will be made.

Ammoniacal fermentation of urea.—Normal freshly passed urine is acid and free from ammonia, but contains a large quantity (2-3 p.c. or about 30 grams in 24 hours) of urea, which, however, soon disappears and is replaced by carbonate of ammonium, the urine acquiring an alkaline reaction. This change, which may be represented by the equation

$$\underset{\text{Urea}}{CO(NH_2)_2} + 2H_2O = \underset{\text{Ammonium carbonate}}{CO(NH_4O)_2}$$

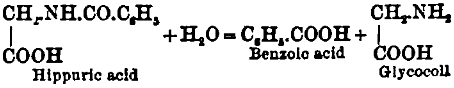
was, according to the older theories of Liebig, supposed to be due to the action of particles of decomposing mucus from the bladder, but Pasteur (C. R. 50; A. Ch. 64; Bullet. de l'Acad. de Méd. 1876, 27) and Van Tieghem (C. R. 58, 210) found that all ammoniacal urine contained micrococci which they regarded as the cause of the above reaction, and to which they gave the name of *Torula urinæ*, now generally known as *Micrococcus ureæ* (Cohn). The micrococci ·8-1·0μ in diameter, are often arranged in pairs, tetrads, and in chains of considerable length. On gelatine plates they produce in 24 hours white colonies with a pearly lustre, which, as they become older, resemble drops of tallow; under a low power the edge of the colony is seen to be granular, the centre quite opaque. In gelatine-tube cultures the needle-path is indicated by a thin thread-like growth; the gelatine is not liquefied (Leube, Virchow's Archiv, 100, 540).

The alkaline reaction resulting from the fermentation does not interfere with the growth of the organism, the latter tolerating as much as 13 p.c. of ammonium carbonate. The most suitable artificial solution for this fermentation consists of urea 3 grams, sodium potassium tartrate 5 grams, dihydrogen potassium phosphate ·12 gram, magnesium sulphate ·06 gram, dissolved in 1,000 c.c. of water (v. Jaksch, Zeitschr. f. physiol. Chem. 1881). The most favourable temperature was found to be 30-33°C. According to v. Jaksch the *M. ureæ* exhibits a great variety of forms, some of them bacillar; his observations were, however, not conducted in such a manner as to exclude the possibility of more than one organism being present, and this polymorphism could not be confirmed either by Leube or Flügge (Die Mikroorganismen, Leipzig, 1886, 169). Polymorphism has, however, also been observed by Limbeck (Centralbl. f. Bakter. [2] 1887, 508).

The above *M. ureæ* is by no means the only organism which is capable of setting up this fermentation with equal vigour, although it appears to be the most frequent cause. Leube has shown that a number of different organisms, including several bacilli, produce the same reaction, and a micrococcus causing liquefaction of the gelatine (*M. ureæ liquefaciens*) has been described by Flügge as similarly active. A number of micro-organisms stated to be endowed with the same power have also been described by Heraeus (Zeitschr. f. Hygiene, 1886) and Warington (C. J. 1888, 727-755). A *Micrococcus ureæ* has been found by Miquel (Bl. 29, 387; 31, 391; 32, 126) to be very widely distributed in the atmosphere, and also a bacillus ureæ in sewage. To obtain the latter the sewage is kept for two hours at 80-90°C., by which treatment the micrococci are destroyed, and on then introducing a few drops into neutral sterilised urine, which then, in nine cases out of ten, is said to undergo the ammoniacal fermentation.

According to Musculus (B. 1871, 124; Archiv f. Phys. 12, 214), the *M. ureæ* secretes a soluble ferment, which he was able to separate by precipitation with alcohol, and which possesses the property of converting urea into ammonium carbonate in the absence of all organisms (Pasteur and Joubert, C. R. 83, 5; B. 9, 1130). This diastatic substance is very unstable, its activity being destroyed by a temperature of 80°C. and by weak acids. It may be made a delicate test for urea by saturating a piece of turmeric paper with its solution; on then treating the paper with a drop of a neutral solution containing urea, the paper at once becomes brown. Leube, however, found that pure cultivations of the *M. ureæ*, when filtered through porous porcelain, were incapable of converting urea; it would appear, therefore, that the soluble ferment obtained by Musculus must have been derived from some other source, possibly from some of the other organisms which convert urea, as there was no guarantee that he was dealing with a single organism.

Fermentation of hippuric acid.—The conversion of hippuric acid into benzoic acid and glycocoll is, according to Van Tieghem (C. R. 58), effected by the same organism as that concerned in the fermentation of urea. This has been confirmed by Rattone and Valenta (Archivo per le scienze mediche, 1886, 10, 311), who also found that another micrococcus capable of fermenting urea, but which liquefies the gelatine, and is perhaps, therefore, identical with Flügge's *M. ureæ liquefaciens*, similarly decomposes hippuric acid. The change is represented by the equation



$$\underset{\text{Hippuric acid}}{\begin{array}{l}CH_2.NH.CO.C_6H_5\\|\\COOH\end{array}} + H_2O = \underset{\text{Benzoic acid}}{C_6H_5.COOH} + \underset{\text{Glycocoll}}{\begin{array}{l}CH_2.NH_2\\|\\COOH\end{array}}$$

Early literature on conversion of urea.—A. Müller (J. pr. 81, 467); Dumas (Traité de Chimie, 6, 380); Jaquemart (A. Ch. [3] 7, 149); Liebig and Wöhler (A. 88, 100; *ibid.* 121, 80).

2. Fermentation by simple decomposition. *Lactic fermentation.*—It is usual to represent the conversion of dextrose into lactic acid by the equation

$$\underset{\text{Dextrose}}{C_6H_{12}O_6} = \underset{\text{Lactic acid}}{2C_3H_6O_3}$$

i.e. as a simple decomposition of 1 molecule of sugar into 2 molecules of the acid. Recent investigations, however, tend to show that the change is in reality more complex than this, inasmuch as the evolution of carbonic anhydride is probably an invariable accompaniment of the reaction, and this fermentation can therefore only provisionally be included in this group.

The souring and coagulation of milk on keeping are phenomena which have long been known to be due to the conversion of the milk sugar into lactic acid, the latter then causing the coagulation of the caseïn. These changes were first attributed to an organised ferment by Remak (Canstads Jahresb. 1841, 1, 7), which was further examined and erroneously described as *Penicillium glaucum* by Blondeau (J. Ph. [3] 12, 244, 336). The systematic investigation of this ferment was, however, first prosecuted by Pasteur (C. R. 45, 913; 47, 224; A. Ch. [3] 52, 404), and later by Lister (Ph. 1877), who appears to have obtained the organism in a state of purity by means of the method of dilution. More recently the lactic fermentation has been carefully studied by Hueppe (Mittheilungen a. d. kaiserl. Gesundheitsamte, 2; Deutsche med. Wochenschrift, 1884, 48), who has further found that a large number of different bacteria are capable of setting up the same change, although one form, probably the same as that described by Pasteur and Lister, appears to be the most frequent spontaneous cause of this change, and may therefore be considered as the lactic ferment *par excellence.*

This lactic ferment consists of short, thick, non-motile bacilli 1–1·7μ by ·3–·4μ, but sometimes reaching 2·8μ in length, generally occurring in pairs, sometimes in strings of four. The bacilli form spores, especially in saccharine liquids, each situated at one extremity of a bacillus. These spores resist a boiling temperature for a few minutes. On gelatine plates the colonies in the depth are seen with a low power to be round, with a sharp edge, and uniformly dark, whilst on reaching the surface they become invested with a lighter zone. In gelatine tubes a thin delicate growth forms along the whole length of the needle canal. The gelatine is not liquefied (Hueppe).

A sarcina (*Pediococcus acidi lactici*) causing active lactic fermentation has been found in malt-worts by Lindner (Centralbl. f. Bakteriol. [2] 1887, 340; Hayduck, *ibid.* 2, 1887, 34).

Amongst the other bacteria which have been ascertained to induce the same reaction (Malapert, Fr. 1886, 25, 39; Marpmann, Ergänzungshefte z. Centralbl. f. allgemeine Gesundheitspflege, 1886, 2, Heft 2, 117), may be mentioned all the micrococci connected with suppuration, and especially the *staphylococci*; also *Bacillus oxytocus perniciosus*, *Bacterium coli commune*, and *Bact. lactis aërogenes*; also a number of microbes obtained by Miller from carious teeth; again, the *B. prodigiosus* and a micrococcus contained in saliva. Most of these forms require the presence of air for active fermentation, but the *Bact. lactis aërogenes* exerts its fermenting action when air is excluded (Escherich, Fortschritte d. Medicin, 1885, 3, 16, 17; Darmbacterien d. Säuglings, 1886), although in the absence of sugar it is incapable of anaërobiotic existence (Flügge, Die Mikroorganismen, Leipzig. 1886, 293).

The pure *Bacillus acidi lactici* of Hueppe sets up the lactic fermentation in solutions of milk and cane sugar, dextrose, and mannite, carbonic anhydride being also invariably liberated (Boutroux, C. R. 86, 1878). The bacilli appear to invert the milk and cane sugar before fermenting it, and they also exert a diastatic action on starch, converting the latter into sugar. Owing to the bacillus being very sensitive to free acid it is necessary, in order to obtain a large yield, to add an excess of carbonate of lime or carbonate of zinc so as to neutralise the free lactic acid as it is formed; otherwise fermentation ceases when the free acid amounts to ·8 per cent. Thus, in the spontaneous lactic fermentation of milk, only a part of the milk sugar is converted, owing to the reaction being interrupted by the free acid formed. The most favourable temperature appears to be 35–42°C., whilst at 45·4°C. it ceases. The presence of free oxygen favours the fermentation (Richet, C. R. 86, 550; 88, 750).

In practice a large number of substances undergo spontaneous lactic fermentation. Thus, besides milk and the various forms of sugar, sorbite, mannite, dulcite, and inosite are all transformed into lactic acid, as is also calcium malate (Schützenberger). The lactic fermentation frequently occurs in the manufacture of starch, and is one of the chief dangers in the preparation of beet sugar; it has also to be contended against in the alcoholic fermentation, and it probably plays an important part in the leavening of bread.

The ferment, which is very widely distributed, may be conveniently obtained either by allowing milk to stand for several days at about 30°C. or by similarly exposing the following mixture: Water 100 parts; cane sugar, glucose, or mannite 10 parts; decomposing cheese 1 part; and chalk 10 parts.

Conversion of cane sugar into cellulose and lævulose.—The only other instance of fermentation by simple decomposition is one recorded by Durin (C. R. 83, 128), in which a ferment discovered in some German molasses was found to convert cane sugar into lævulose and a cellulose-like substance which separated in clots:

$$nC_{12}H_{22}O_{11} = (C_6H_{10}O_5)_n + nC_6H_{12}O_6.$$

As this remarkable result lacks confirmation, it must be received with considerable reserve.

3. Fermentation by reduction. In a very large number of fermentations which the carbohydrates and many fatty acids undergo, a part of the carbon is completely oxidised to carbonic anhydride, whilst the remainder, having lost the oxygen taken up in the formation of the carbonic anhydride, is left as a reduced product of the reaction. In most cases a part of the hydrogen is removed from the fermentable substance as water, whilst in some cases it appears as free hydrogen, which is then capable of producing the various reactions characteristic of hydrogen in the nascent state—*e.g.* the reduction of nitrates to nitrites and ammonia. As, however, these fermentations all take place in an alkaline medium only, the reducing action of the hydrogen is similar to that exerted by sodium amalgam, zinc and caustic soda, and the like. In other cases, again, as in the fermentation of cellulose, a part of the carbon is entirely deoxidised and escapes as marsh gas.

Particularly noticeable amongst these fermentations are those which result in the formation of alcohols, especially ethylic and normal butylic, as showing that these substances may be produced without the action of yeast.

The fermentations by reduction may be subdivided into

(*a*) Polyhydric alcohols.
(*b*) Carbohydrates.
(*c*) Fatty acids.

(*a*) *Fermentations by reduction of polyhydric alcohols.*

Glycerin, erythrite, quercite, mannite, and dulcite have all been found to undergo interesting decompositions by the agency of suitable ferments, which have, however, only in few cases been obtained in a state of purity and adequately characterised.

Fermentation of glycerin.—Fitz has shown that this substance undergoes several distinct decompositions, according as it is acted upon by different micro-organisms. Thus

1. *The Bacillus ethylicus*, or *Fitzianus*, was obtained by Fitz (B. 1878, 49) from infusion of hay, and at first mistaken by him for *B. subtilis*. The fermentation is inaugurated by taking a small portion of the pellicle, which forms on the hay-infusion after standing for several days at the ordinary temperature, and introducing this into a sterilised solution composed of 5 p.c. glycerin, 2 p.c. Liebig's extract of beef, and 10 p.c. carbonate of lime. After inoculation the liquid is boiled for five minutes, as the spores of the ferment resist this exposure and are thus freed from a number of admixed organisms. The liquid is then preserved at 40°C., and the fermentation, which is completed in about seven weeks, results in the formation of ethylic alcohol (25·8 grams from 100 grams of glycerin), along with traces of volatile and fixed acids. The principal reaction may perhaps be thus formulated: $C_3H_8O_3 = C_2H_6O + CO_2 + H_2$.

The *B. Fitzianus* has been characterised by Buchner; the bacilli are very variable in length, from 1·2μ upwards, and 1μ in breadth; they form spores similarly to *B. subtilis*. On gelatine plates the colonies are round, of brownish-yellow tint, with a sharp edge, and almost opaque in the centre.

2. *The Bacillus butylicus*, also obtained by Fitz from hay-infusion, but without subsequently boiling the liquid, as the spores which it forms appear to be less resistant than those of *B. ethylicus*. Owing to the fact that the *B. butylicus* flourishes more luxuriantly in the glycerin solution than the other microbes which accompany it, it is readily obtained in a state of comparative purity after a few cultivations in this medium. The bacillus is much larger than the *B. ethylicus*, being 5–6μ long by 2μ in breadth. During the fermentation they are highly motile, but not before, when free oxygen is still present in the liquid. No zooglœa is formed on the surface of the liquid. The young cells give no reaction with iodine, but before spore-formation it colours them wholly or in part an intense violet. The air-dried spores are not killed by five minutes' ebullition, but the fully developed bacilli succumb at a temperature considerably below 100°C.

The *B. butylicus* gives rise to a very vigorous fermentation above 31°C., the most favourable temperature being 39–40°C., and ceasing at about 45°C. The gaseous products are hydrogen and carbonic acid, giving rise to much frothing, whilst normal butylic alcohol (8·1 grams), butyric acid (17·4 grams), lactic acid (1·7 gram), normal propylic glycol (3·4 grams), are obtained from 100 grams of glycerin, together with traces of ethylic and normal propylic alcohols, whilst according to Schulze phorone is likewise amongst the products. This process is recommended by Fitz, and later by Freund, as a convenient method of obtaining normal butylic alcohol and propylic glycol.

By inoculating fresh cow-dung into a solution of glycerin, Fitz found that ethylic and normal butylic alcohols were formed in about equal proportions, and what appeared to be the *B. ethylicus* and *B. butylicus* were both observed in the solution (Fitz, B., 1878, 48). The same *B. butylicus* sets up fermentations also in solutions of mannite and of cane-sugar (*v. infra*). In the latter case the principal product is butyric acid, which is also produced by the ordinary butyric ferment of sugar (*B. amylobacter*); the *B. butylicus* is, however, sharply distinguished from the latter inasmuch as it does not ferment calcium lactate, whilst *B. amylobacter* converts it into calcium butyrate. *B. butylicus*, however, grows in solutions of calcium or ammonium lactate, as well as in solutions of calcium glycerate, malate, citrate, tartrate, and quinate, also in ammonium tartrate, in erythrite, quercite, and milk sugar, but in none of these does it give rise to a true process of fermentation (Fitz, B. 1876, 1348; 1877, 276; 1878, 42; 1880, 1311; 1882, 867).

The *B. amylobacter* also ferments glycerin with production of butyric acid (Van Tieghem, C. R. 1879, 88).

3. The bacillus inducing the succinic fermentation of calcium malate also ferments glycerin, producing principally ethylic alcohol (21 parts from 100 of glycerin), together with calcium formate (4 parts), and acetate (2 parts), with only a trace of succinate.

This *Bacillus succinicus*, as it may be provisionally termed, closely resembles the *B. ethylicus* (*v. supra*) in its morphological characters, the bacilli being small, slender, and often hanging together in pairs.

4. *The Bacillus pyocyaneus*, which gives rise to the blue-green colouring matter, pyocyanine, frequently present in pus, also induces a fermentative change in glycerin, the principal products of which are ethylic alcohol (11 parts

from 100 of glycerin) and butyric acid, together with smaller quantities of normal butylic alcohol, acetic and succinic acids (Fitz, B. 1878, 55 and 1898).

This organism is one which has been fully characterised by numerous observers (Lücke, Archiv f. klin. Chirurgie, 1862; Girard, Chirurg. Centralbl. 2, 1875; Eberth, Centralbl. f. med. Wissenschaft, 1863; Virchow's Archiv, 72, 1875; Charrin, Communication à la Société Anatomique, 1884; P. F. Frankland, Pr., 1886, 534; Flügge, Die Mikroorganismen, 1886, 286). The bacilli are small and slender, about 1μ in length and about ·3μ in thickness, often hanging together in twos and threes; sometimes thicker bacilli containing spores are also observable. The colonies on gelatine-plates are very characteristic; in a day or two the whole plate exhibits a greenish-blue lustre when viewed by reflected light. With a low power the colonies are seen to consist of a dark-grey centre, surrounded by a lighter zone from the periphery of which numerous delicate filaments or spines extend into the adjacent gelatine. Liquefaction of the gelatine soon takes place, but the individual colonies generally remain distinct and do not become confluent. In gelatine-tube cultivations, the path of the needle is generally indicated after twenty-four hours by incipient liquefaction at the surface, which as growth proceeds undergoes funnel-shaped depression, the fringe of which soon exhibits the characteristic green-blue fluorescence. Ultimately the whole gelatine is liquefied. On potatoes the bacillus forms a yellowish-brown slimy growth. The colouring matter, pyocyanine (Fordos, C. R. 51; Gessard, De la pyocyanine et de son microbe, Thèse de Paris, 1882), is soluble in chloroform, from which it crystallises in long blue needles; it is precipitated by platinic chloride and by phosphomolybdic acid. Acids convert the blue into red, reducing substances into yellow.

Fitz's experiments were not made with pure cultivations of the bacillus, but he attributes the decomposition of the glycerin as above to the action of this particular microbe.

Fitz has also observed the fermentation of glycerin with the micro-organisms present in orange pus (Fitz, B. 1878, 55 and 1898). Both a micrococcus and a bacillus appear to have been concerned in this reaction, the products of which were ethylic alcohol (23·8 parts from 100 of glycerin) and only traces of acids either fixed or volatile. Neither the microbes of green or orange pus effected any fermentation of either calcium malate or lactate.

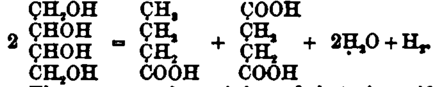
In addition to the above fermentations observed by Fitz, glycerin was found by Hoppe-Seyler (Hoppe-Seyler) to yield butyric, acetic, and succinic acids when suitable solutions were inoculated with decomposing fibrin.

Vigna (B. 1883, 1438) also describes a fermentation of glycerin induced by the addition of some fermenting ammonium tartrate, with the result that ethylic and normal butylic alcohol were obtained, the latter to the extent of 9 p.c. of the glycerin employed. Carbonic anhydride and hydrogen were evolved. Perhaps this decomposition was due to the joint presence of the *B. ethylicus* and *butylicus*.

5. *The Bacillus ethaceticus*, obtained by the writer from sheep-dung, and cultivated in a state of purity, ferments dilute solutions of glycerin (3 p.c.), to which the necessary salts and peptone (·1 p.c.) have been added, the products being ethyl alcohol, acetic and formic acids, together with a trace of succinic acid. The organism also ferments glucose, cane-sugar, milk-sugar, starch, mannite, and calcium glycerate, whilst it has no action on dulcite, erythrite, glycol, or calcium citrate, tartrate, glycollate, and malate. The bacillus is from 1·5μ to 5·1μ in length, and from 0·8μ to 1·0μ in breadth, it forms on gelatine plates colonies, having the appearance of small white dots, which gradually liquefy the gelatine. It has not been observed to form spores (P. F. Frankland and J. Fox, Pr. 1889, 345).

Fermentation of erythrite $C_4H_6(OH)_4$. Several decompositions of this tetrahydric alcohol by the microbes of hay-infusion and cow-dung are described by Fitz.

1. *By the micro-organisms of cow-dung* (Fitz, B. 1878, 1890), the erythrite was found to yield a trace of alcohol, the principal products being succinic and normal butyric acids, with smaller proportions of acetic and caproic acids. In fact the reaction appears to take place according to the equation



$$2\begin{array}{l}CH_2OH\\ CHOH\\ CHOH\\ CH_2OH\end{array} = \begin{array}{l}CH_3\\ CH_2\\ CH_2\\ COOH\end{array} + \begin{array}{l}COOH\\ CH_2\\ CH_2\\ COOH\end{array} + 2H_2O + H_2.$$

The amount of succinic and butyric acids obtained approached the theoretical quantities. The fermenting liquid was, however, occupied by a number of different organisms, so that it is impossible to say which was the active agent. The most conspicuous forms were certain pear-shaped cells 2·7μ by 1·5μ, the broader extremity of the cell inclosing a bright spot. The cell-contents mostly assumed an intensely violet colour on the addition of iodine.

2. *By the micro-organisms of unboiled hay-infusion* (Fitz B., 1879, 475), the erythrite was found to undergo a different change from the above, for only a trace of succinic acid was formed, whilst the principal products were butyric and acetic acids, with traces of alcohol and formic acid. A number of different organisms were present in the liquid. The pear-shaped bacillus referred to above was only observed at the commencement.

Fermentation of quercite (Fitz B., 1878, 45) $C_6H_{12}O_5$. This pentahydric alcohol was fermented by Fitz with the production of practically nothing but normal butyric acid. The ferment was obtained from hay-infusion and appears to be identical with the butyric ferment described by Fitz (*v. Fermentation of calcium lactate, infra*).

Fermentation of mannite $C_6H_{14}O_6$. This hexahydric alcohol has been shown by Fitz and others to undergo several different fermentations. Thus, as already mentioned, it yields lactic acid when submitted to the action of the *B. acidi lactici*. The following fermentations are also known.

1. *By a club-shaped bacillus* (Fitz, B. 1878, 1895), accidentally obtained from boiled hay-infusion, mannite was found to yield in a

fermentation, lasting seven weeks, ethylic alcohol (26·3 parts per 100 of mannite), together with formic acid (5·6 parts), and a trace (·04 part) of succinic acid.

2. *The Bacillus ethylicus* grows in dilute solutions of mannite, but the nature of the fermentation is unknown.

3. *The Bacillus butylicus* was inoculated by Fitz (B. 1882, 875) into a solution consisting of 6 litres water, 180 grams mannite, ·1 gram potassium phosphate, ·02 gram magnesium sulphate, 1 gram ammonium chloride, and 45 grams calcium carbonate, and kept at 37–40°C. The fermentation commenced in eleven days' time, and continued for fifteen days. The products calculated on 100 parts of mannite taken were: normal butylic alcohol, 10·2 parts, butyric acid, 35·4 parts, lactic acid, ·4 part, and a trace of succinic acid (·01 part).

4. *The Bacillus amylobacter* also produces butyric acid from mannite (Van Tieghem).

5. A fermentation of mannite is described by Fitz (B. 1883, 845) occasioned by a microbe obtained from cow-dung, and supposed to have been a pure cultivation. The products were from 200 grams mannite, after six weeks, 22·2 grams ethyl alcohol, together with acetic and formic acids (13·5 grams, calculated as acetic acid), and a trace of succinic acid, but the fermentation was very incomplete. The products are thus very similar to those obtained with the club-shaped bacillus above. The organism is described as a bacillus 2–2·5μ by ·9–1μ, often resembling a micrococcus. Spore-formation was not observed. The same organism ferments sugar, including milk sugar, but neither starch nor cellulose; the fermentation which it induces in calcium glycerate was studied by Fitz (B. 1883, 845), and is described below (*v. Fermentation of calcium glycerate*).

6. *The Bacillus ethaceticus* (*v. supra*) ferments mannite with formation of the same products as from glycerin, *viz.* ethyl alcohol, acetic and formic acids, together with a trace of succinic acid. It differs in several important points from the description given by Fitz of the organism mentioned above (P. F. Frankland and J. Fox, *l.c.*).

(*b*) *Fermentations by reduction of carbohydrates.*

Glucose, saccharose, and lactose.—The various kinds of sugar take part in a great number of reactions brought about by micro-organisms, some of the most important of which, the alcoholic and lactic fermentations, have been already described. In these as well as in those about to be detailed, it appears that only the glucoses (dextrose and lævulose) are directly fermentable, and in order to render the disaccharates—cane and milk sugar—fermentable, they must previously undergo hydration. This hydration is, however, frequently accomplished by means of a diastatic ferment secreted by the micro-organisms themselves, and thus at first sight it appears as though the milk or cane sugar underwent direct fermentation.

As already pointed out, the lactic fermentation of glucose is probably not such a simple reaction as it is usually represented to be (*v. supra*) and inasmuch as it is always accompanied by evolution of carbonic acid, it more properly belongs to the processes of fermentation by reduction, and should be included in the present group. The other important decomposition of this type is the butyric fermentation, which may be effected by the *Bacillus amylobacter*, by Fitz's *B. butylicus*, and probably by other organisms.

1. *Butyric fermentation by Bacillus amylobacter.*—Our knowledge of the butyric fermentation is at present in a rather unsatisfactory state in consequence of the difficulty of obtaining some of the organisms producing it in a sufficiently pure state for accurate study. This difficulty arises principally from the fact that one at least of the butyric ferments is a strictly anaërobic form, and cannot, therefore, be handled with the same facility as the ordinary aërobic microbia. Of this anaërobic character is the *B. amylobacter* described by Pasteur (C. R. 52, 344) and Van Tieghem, which is probably identical with the *B. butyricus* more recently described by Prazmowski (Untersuchungen üb. d. Entwickelungsges. und Fermentw. einiger Bakterien, Leipzig, 1880), and possibly also identical with the anaërobic butyric ferment which has been studied more recently still by Liborius, possibly also with the *B. butyricus* of Fitz.

On the other hand, sharply distinguished from the above by their aërobic mode of life are a butyric ferment obtained from milk by Hueppe, and another from cow-dung described by Fitz (B. 1884, 1188).

The *B. butyricus* of Prazmowski is 3–10μ by about 1μ in breadth, frequently found in chains and threads; generally very motile, but also forming zooglœa. The bacillus is coloured blue or violet by iodine, not, however, when grown in solutions of sugar or dextrin. Sporulation is preceded by the bacillus becoming thickened in the middle, thus giving rise to a spindle-form (clostridium). The oval spore is 2–2·5$\mu \times 1\mu$. The spores are less resistant than those of *B. subtilis*, being destroyed by five minutes' boiling. The bacillus is extremely sensitive to free oxygen, its growth, sporulation, and germination only taking place in the almost entire absence of this gas.

The butyric fermentation is an extremely common phenomenon in nature, usually occurring after an antecedent lactic fermentation. The cause of this sequence appears to be dependent partly upon the anaërobic requirements of the *B. amylobacter*, which thus finds the suitable conditions for its growth in a liquid the free oxygen of which has been exhausted by the previous lactic fermentation, and partly to the hydrating action of the lactic ferment on the lactose or milk sugar, which power of hydration is probably not possessed by the *B. butyricus*. The fermentation is accompanied with the liberation of carbonic anhydride and hydrogen. When milk is kept, the butyric fermentation sets in after the lactic fermentation is over, and, as in the latter, the addition of carbonate of lime is necessary in order to obtain a considerable yield, otherwise the free acid formed checks the further growth of the organism. The most favourable temperature is 35–40°C.

Butyric ferments of the *Bacillus amylobacter* type are very widely distributed in nature, but whether they are all one and the same organism or not is quite uncertain. Thus old milk and cheese, hay, decomposing vegetable infusions of various kinds, and notably soil (Déhérain and Maquenne, Bl. [2] 39; C. R. 97) are all capable of exciting the butyric fermentation in solution of sugar. The ferment has also been found within the cells of lactiferous plants, and according to Van Tieghem the *B. amylobacter* can be discerned in the conifers of the carboniferous epoch (C. R. 89, 1102).

The *Bacillus butyricus of Liborius* (Liborius, Zeitschr. f. Hygiene, 1 (1886, 160) has been isolated and cultivated by the aid of modern methods, and the characters which it exhibits are, therefore, of great importance for the purposes of future comparison. The organism, which in its morphological characters does not differ from the amylobacter of Prazmowski, is also essentially anaërobic and may be cultivated most advantageously in the depth of solid media such as gelatine or agar-agar mixture, the addition of grape sugar being beneficial. It may also be grown on the surface of these materials if the air is displaced from the containing vessels by some indifferent gas such as hydrogen. The colonies in the depth of the gelatine appear after 24–48 hours as small white spherules which soon become surrounded by a gradually increasing sphere of liquefaction; bubbles of gas are also formed which find their way through the upper layers of the medium, and by their displacing the air prepare the way for an extension of the growth and liquefaction from below. In agar-agar the colonies exhibit more characteristic branchings from the centre, and evolution of gas also takes place. A systematic examination of the products of fermentation with this undoubtedly pure ferment is unfortunately still wanting.

The *Bacillus butyricus of Hueppe*, again, resembles Prazmowski's *B. amylobacter* in its morphological characters, but is aërobic, requiring for its cultivation none of the special precautions mentioned above. It was accidentally discovered in imperfectly sterilised milk. It does not ferment lactose, as it has no power of hydrating the latter; it appears, however, to secrete a ferment coagulating the caseïn of milk, and it subsequently decomposes it with formation of peptone, leucine, tyrosine, ammonia, and other products. Similarly the bacillus grows in gelatine, producing rapid liquefaction. Glucose, hydrated lactose, and lactates undergo butyric fermentation through the action of the bacillus.

The *Bacillus butylicus* of Fitz, which has already been described above (*v. Fermentation of glycerin*) also resembles the *B. amylobacter* as far as its morphological characters have been determined, but differs essentially from the latter in its incapacity to transform calcium lactate. The bacillus hydrolyses saccharose, but not lactose, and the latter is consequently not directly fermentable by it. Unfermentable also are calcium and ammonium lactates, calcium glycerate, calcium malate, calcium and ammonium tartrate, calcium citrate and quinate, erythrite, and quercite.

Comparative experiments with this organism were made by Fitz (B. 1882, 876) on glycerin, mannite, and invert-sugar,[1] the following very striking differences being obtained for 100 parts of each of these substances employed:—

Products	100 parts glycerin	100 parts mannite	100 parts invert-sugar
Butyl-alcohol (norm.)	8·1	10·2	·5
Butyric acid "	17·4	35·4	42·5
Lactic acid . .	1·7	·4	·3
Succinic acid . .	—	·01	trace
Trimethylene alcohol	3·4	—	—
	30·6	46·0	43·3

Especially in the case of the sugar there were also found traces of acetic and caproic acids. The fermentation lasted 21 days in the case of the glycerin, whilst in the case of the mannite it only began on the 11th day and then continued for 15 days, and in that of the cane sugar it began on the 8th day and then lasted 25 days.

Fitz found that the *B. butylicus* lost its power of fermenting by exposure to a high temperature, and also by long cultivation in the presence of an abundant supply of air.

The *new butyric ferment of Fitz* (B. 1878, 51; 1884, 1188) will be described below under the fermentation of calcium lactate. It is an aërobic form, and appears to ferment all carbohydrates, excepting cellulose and starch.

Three butyric ferments, two anaërobic and one aërobic, the latter doubtless identical with Hueppe's, have been recently carefully described by Gruber (Centralbl. f. Bakteriologie, [1] 1887, 367).

Fermentation of dextrin and starch.—Besides glucose and cane-sugar the carbohydrates—starch, dextrin, and inulin, are also capable of undergoing butyric fermentation, a preliminary conversion into glucose doubtless taking place first through the agency of a diastatic ferment secreted by the micro-organism. Whether this preliminary conversion is effected by the butyric ferment itself, or by some other micro-organisms simultaneously present, has not been with certainty ascertained, owing to the fact that but few of these butyric fermentations have been conducted with pure cultures.

It has already been pointed out in the butyric fermentation of the sugars that both the *Bacillus butylicus* of Fitz and the *B. butyricus* of Hueppe are incapable of acting on milk sugar, whilst the latter is said to be fermentable by the *B. amylobacter*. Similarly the *B. amylobacter* is said to ferment starch and also arabin and lichenin, whilst the *B. butylicus* was found by Fitz to be without action on these carbohydrates. It must, however, be remembered that the purity of the fermentations with *B. amylobacter* is extremely doubtful, whilst in the case of those with *B. butylicus* it is at any rate very pos-

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[1] The liquid employed for fermentation contained sugar, glycerin, or mannite, 180 grams; potassium phosphate, ·1 gram; magnesium sulphate, ·02 gram; ammonium chloride, 1·0 gram; with calcium carbonate, 30 grams (for glycerin), 45 grams (for mannite), 70 grams (for cane sugar), with 6 litres of water.

sible that Fitz was dealing with a single organism.

A remarkable and important butyric fermentation of starch with the *B. ethylicus* is described by Fitz. Remarkable because the *B. ethylicus* does not ferment calcium lactate, and it is, therefore, probable that the carbohydrate is directly converted into butyric acid without passing through the intermediate lactic acid stage, as is generally supposed to be the case in ordinary butyric fermentation. This fermentation is of practical importance also as the most convenient method of preparing butyric acid. The above explanation given by Fitz must, however, be received with reserve, and it would appear to be far more probable that the result was obtained through a mixed fermentation owing to the possible use of an impure cultivation.

Thus Fitz (B. 1878, 44 and 53) found that 100 parts of starch, suspended in a solution containing the necessary salts, yielded with the *B. ethylicus* at 40°C., 34·7 parts of butyric acid, 5 parts acetic acid, ·3 parts succinic acid, 1 part ethylic alcohol, and a trace of normal butyric alcohol.

Inulin is probably similarly converted.

The new butyric ferment of Fitz (*v. Butyric fermentation, supra*) does not attack starch.

Fermentation of cellulose.—That cellulose may undergo dissolution by fermentation was first shown by Mitscherlich in 1850; he found that if slices of potato were left immersed in water for several days the parenchymatous tissue suffered a process of disaggregation, accompanied by disappearance of the cell walls, which could be readily followed with the aid of the microscope.

Experiments of Haubuer, Von Henneberg, and Stohmann also showed that a considerable amount of cellulose disappears in its passage through the alimentary canal of the herbivora, and this disappearance was at first supposed to be due to a soluble ferment, which Hofmeister believed to have discovered in the saliva of sheep. It has, however, been shown by Tappeiner (B. 1881, 2375; 1882, 999; 1883, 1734; 1884, 142 [2], 262 [2], 587 [2]) that a very extensive process of fermentation by micro-organisms takes place in the stomach and intestine of these animals, which results in the destruction of cellulose with evolution of large volumes of gas, principally carbonic acid and marsh gas, and, in the horse's stomach, also hydrogen. These fermentations have been artificially imitated by Tappeiner outside the animal body by inoculating flasks containing cellulose and nutritive solution with the contents of different portions of the alimentary canal of herbivorous animals. In this manner he was able to cause cellulose to undergo two distinct types of fermentation, one of which was characterised by the evolution of marsh gas, and the other by that of hydrogen.

The *marsh-gas fermentation* may be induced in a neutral 1 p.c. solution of extract of meat containing cellulose (cotton-wool or paper-pulp) in suspension, by inoculation with the contents of a ruminant's paunch. Fermentation commences in the course of a few days, and continues from 1 to 4 weeks, the liquid being kept at blood-heat. The following is the composition by volume of the gas evolved:

Fermentation of paper.

Commencement.		End.	
CO_2 SH_2	85·48	CO_2 SH_2	76·98 p.c.
H	·03		
CH_4	11·86	CH_4	23·01
N	2·73		
$CH_4 : CO_2 = 1 : 7{\cdot}2$		$CH_4 : CO_2 = 1 : 3{\cdot}4$	

Upwards of 50 p.c. of the cellulose disappears, and amongst the non-gaseous products were found aldehyde, large quantities of the lower fatty acids, especially acetic acid and butyric acid. This is the fermentation which appears to take place in the first stomach and colon of ruminants, as well as in the colon of the horse.

The *hydrogen fermentation* takes place when the neutral solution of extract of meat is replaced either by a weakly alkaline one or by one diluted with its own volume of water containing Nägeli's salts K_2HPO_4 ·2 p.c., $MgSO_4$ ·04 p.c., $CaCl_2$ ·02 p.c., or, thirdly, by a similar solution containing, in addition, either ammonium acetate ·35 p.c., acetamide ·3 p.c., or asparagine ·6 p.c. In all other respects the conditions are similar to those described above for the marsh-gas fermentation, and the inoculation is also made with the contents of a ruminant paunch. The gases evolved were—

½ p.c. extract of meat solution		Solution of asparagine		Solution of acetamide	
CO_2 SH_2	55·39	CO_2 SH_2	86·47	CO_2 SH_2	78·14 p.c.
H	42·71	H	5·73	H	13·68 „
N	1·90	N	7·80	N	8·18 „

The non-gaseous products appear, as far as they have been studied, to be similar to those obtained in the marsh-gas fermentation.

In neither of these fermentations is there any reliable information concerning the nature of the micro-organisms to which they are due.

Opinion is divided as to whether the whole or only a part of the cellulose disappearing in the alimentary tract of herbivora is disposed of by fermentation as above. Thus Tappeiner considers that practically the whole of the cellulose deficit is thus transformed into non-nutritive products, whilst according to Wilsing (Zeitschr. f. Biolog. 20) and Henneberg and Stohmann (Zeitschr. f. Biolog. 21) a part undergoes other changes.

The fermentation of cellulose doubtless takes place also on a very large scale in nature, outside the animal organism. Thus Hoppe-Seyler (B. 1883, 122; C. J. 1886 (Abstr.), 577, 932) was able to induce its fermentation by means of sewage-mud, and with any kind of soil; the gases evolved consisted of carbonic anhydride, upwards of 50 p.c.; marsh-gas, about 45 p.c.; and hydrogen several p.c. Déhérain (C. R. 98) and Gayon (C. R. 98) have shown that a similar fermentation takes place in manure. Similar fermentations of cellulose as well as of albuminoids have also been observed by Tappeiner (B. 1883, 1740). The marsh-gas fermentation of sewage-mud has also been observed by Popoff (Archiv f. Physiol. 10, 129).

According to van Tieghem (88, 205) it is the *B. amylobacter* which causes the fermentation of cellulose.

(c) *Fermentations by reduction of the salts of the fatty acids.*

The lower members of the fatty series of acids readily enter into fermentation when they are presented to certain micro-organisms in the condition of neutral salts, most conveniently as calcium salts. Thus formic and acetic acids are capable of decomposition by fermentation, whilst the higher members, from propionic acid upwards, are not known to ferment. On the other hand, if hydroxyl groups are likewise present in the molecule the fermenting capacity is greatly increased; thus lactic acid (oxypropionic acid) undergoes several different fermentations, as do also glyceric, malic, tartaric, and citric acids. In all these decompositions carbonic anhydride is split off from the carboxyl group, whilst a fresh carboxyl group is formed from another carbon atom, giving rise to the production of a new acid, and this change is much more readily effected if the atom of carbon in question is already in combination with hydroxyl.

Fermentation of calcium formate and acetate. Both these salts undergo fermentation through the addition of sewage-mud (Hoppe-Seyler, Zeitschr. physiol. Chem. 2, 561; C. J. (Abstr.), 1887, 1135), the products being calcium carbonate, carbonic anhydride, and hydrogen in the case of the formate, whilst the acetate yields the same products, with the exception that the hydrogen is replaced by marsh-gas.

Fermentation of calcium lactate.—This salt is said to undergo no less than four different fermentations, thus:—

1. *By the Bacillus amylobacter.*—That calcium lactate is converted by the butyric ferment into calcium butyrate was first observed by Pasteur (C. R. 52, 344; Études sur la bière, 282). The change may be represented thus:

$$2(CH_3.CH(OH).COO)_2Ca + H_2O$$
$$= CaCO_3 + 3CO_2 + 4H_2$$
$$+ (CH_3.CH_2.CH_2.COO)_2Ca.$$

Fitz (B. 1880, 1309) obtained in this fermentation from 500 grams of Ca-lactate, about 182·4 grams of Ca-butyrate, besides 3·76 grams of ethylic and butylic alcohols, and no succinic acid.

2. *By two new butyric fermentations of Fitz* (B. 1878, 51).—This fermentation was discovered by inoculating cow-dung into a solution containing calcium lactate. The decomposition into calcium butyrate takes place with great rapidity and almost quantitatively $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$, thus from 100 grams of Ca-lactate 35·5 grams of Ca-butyrate were obtained besides traces of caproic and acetic acids and ·04 gram succinic acid.

The organism producing this change is described as a large micrococcus consisting of round cells 1·6–1·7μ in diameter arranged in chaplets; the cells in which division is taking place by constriction are 2–2·4μ in length.

Another organism capable of transforming calcium lactate into butyrate, and obtained from cow-dung, is described by Fitz in his last publication (B. 1884, 1188); it is a bacillus 1·8-2·4μ long by ·7-1μ broad, motile, and growing in the absence of air. Spore formation was not observed, and the bacilli were destroyed by fifteen minutes' exposure to 59°C. The substances fermented by this microbe are: glucose, cane sugar, milk sugar, mannite, and the calcium salts of lactic, malic, tartaric, and citric acids. Erythrite, dulcite, and quercite are not fermented, whilst glycerin and calcium glycerate are only slowly attacked. The bacillus does not hydrolyse either starch, cellulose, or albumen.

This ferment is, therefore, sharply distinguished both from the *B. amylobacter* and the *B. butylicus*, amongst the properties of which should be mentioned hydrolysis of albumen.

It is especially noticeable that in the fermentation of calcium lactate by this microbe an appreciable quantity of propionic as well as a little acetic acid are formed; the proportion of butyric to propionic acid is about 8 : 1.

3. *The propionic fermentation* of calcium lactate was observed by Strecker (A. 1854, 92, 80; C. R. 39, 56) in endeavouring to prepare butyric acid in the ordinary way. After two or three months the fermenting mass contained calcium lactate and mannite, both of which had at the end of a year disappeared, but instead of butyric acid he found chiefly propionic acid together with some valeric and acetic acids.

A similar fermentation is described by Fitz (B. 1878, 1898; 1879, 479; 1880, 1309) as taking place through the agency of a long slender bacillus, often forming long and curved chains, the products being principally propionic acid with some acetic acid and a trace of alcohol, but no butyric acid. Thus in one case 50 grams of calcium lactate gave 20·3 grams of the calcium salt of the volatile acid. The decomposition may be represented thus:

$$3C_3H_6O_3 = 2C_3H_6O_2 + C_2H_4O_2 + CO_2 + H_2O.$$

It is probable that Pasteur (Études sur la bière, 297) must have also accidentally met with this reaction, as he mentions that in a case of supposed butyric fermentation of Ca-lactate, the evolved carbonic anhydride was not mixed with hydrogen.

4. *A combined propionic and valeric fermentation* of calcium lactate was also observed by Fitz (B. 1880, 1309; 1881, 1084). The organisms inducing this fermentation are not described, but they are stated to have been derived from another source than those causing the previous fermentation. The products were principally propionic and normal valeric acids (126 grams of the former and 101 grams of the latter from 3,000 grams of Ca-lactate, but a part of the acids was accidentally lost, and the actual amount formed must, therefore, have been greater), together with a little ethylic alcohol, 3·31 grams.

Fermentation of calcium glycerate (Fitz, B. 1879, 474). Two decompositions of this salt have been described by Fitz; in both cases, however, a palpable mixture of organisms was present in the fermenting liquid. In one case, with organisms from cow-dung, the products were principally acetic acid, with a trace of ethylic alcohol and some formic acid. In another case, with organisms from unboiled hay-infusion, the result was again principally acetic acid, with traces of alcohol and succinic acid. The decomposition is approximately represented by the equation:

$$\underset{\text{Glyceric acid}}{C_3H_6O_4} = \underset{\text{Acetic acid}}{C_2H_4O_2} + CO_2 + H_2.$$

Subsequently Fitz (B. 1883, 845) reinvestigated the decomposition of calcium glycerate, using a purer ferment (*v. Fermentation of mannite* (5)) from cow-dung, with the result that after nine weeks only partial decomposition (40 p.c.) of the glycerate was found to have taken place, the products from 100 grams being a trace of alcohol (·23 gram), acetic and formic acids (12·7 grams calculated as acetic acid), and a considerable quantity of succinic acid (3·66 grams). The interesting synthesis of succinic acid may possibly be represented thus:

$$2C_3H_6O_4 = C_4H_6O_4 + 2CO_2 + 3H_2.$$

Calcium glycerate is also fermented by the *B. ethaceticus* (P. F. Frankland and J. Fox, Pr. 1889, 345), the products have not yet been fully investigated, but the proportion of succinic acid formed is much less, and that of alcohol greater, than in the case of Fitz's organism referred to above.

Fermentation of calcium malate.—This salt is liable to several distinct and interesting decompositions by fermentation.

1. *Succinic fermentation* (Fitz, 1878, 1896; 1879, 481).—Is occasioned by the same bacilli as have already been described in the fermentation of glycerine (3). The fermentation is very vigorous and is concluded in five days; from 53·6 grams malic acid there were obtained 10·8 grams of calcium acetate and 30·8 grams of succinic acid, thus almost quantitatively harmonising with the equation:

$$3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + H_2O.$$

Maleïc acid is also said to be occasionally formed in the succinic fermentation of malic acid (Gehling, A. 67, 300).

2. *Propionic fermentation* (Fitz, 1878, 1896).—Takes place through the agency of short cylindrical bacilli, and results in the formation of 18 grams propionic acid (from 53·6 grams malic acid), 6 grams acetic acid, ·07 grams succinic acid, and ·5 grams alcohol. The probable equation is:

$$3C_4H_6O_5 = 2C_3H_6O_2 + C_2H_4O_2 + 4CO_2 + H_2O.$$

3. *Butyric fermentation* (Fitz, 1878, 1898). In the succinic fermentation with impure cultivations, butyric acid is sometimes obtained, its formation being attended with evolution of hydrogen. Nothing is known concerning the inducing organisms; it was formerly supposed that this deviation from the ordinary fermentation was due to a higher temperature or to the addition of an excess of yeast or putrid cheese.

4. *Lactic fermentation.* — According to Schützenberger (Die Gährungserscheinungen, 1874), calcium malate may also be transformed into lactate and carbonic anhydride.

Fermentation of tartaric acid.—Several fermentations, both spontaneous and induced, have been observed, the spontaneous ones varying apparently according to the base with which the tartaric acid is combined.

Thus calcium tartrate is subject to the following decompositions:—

1. *Propionic fermentation.*—Pasteur (Études sur la bière, 274) describes a spontaneous fermentation taking place in a mixture composed of calcium tartrate 100 grams, ammonium phosphate 1 gram, magnesium phosphate 1 gram, potassium phosphate ·5 gram, ammonium sulphate ·5 gram, in 2,500 c.c. of water. The inducing cause is a bacillus which grows at the bottom of the liquid, and the result acetic and propionic acids according to the equation,

$$3C_4H_6O_6 = 2C_2H_4O_2 + C_3H_6O_2 + 5CO_2 + 2H_2O.$$

Very remarkable was the discovery made by Pasteur (C. R. 46, 615) that only the dextro-tartrate was capable of fermentation, the lævo-tartrate remaining unacted upon by the ferment. It was by taking advantage of this fact that Pasteur succeeded in obtaining lævotartaric acid from the inactive racemic acid (*v.* also *Fermentations induced by moulds*, p. 120).

Acetic fermentation.—Fitz (B. 1879, 475), on the other hand, describes a fermentation produced by a mixture of organisms from cow-dung, which resulted in the production of 45 grams calcium acetate (from 100 grams tartaric acid), besides traces of butyric and succinic acids, and alcohol. The probable equation is:

$$C_4H_6O_6 = C_2H_4O_2 + 2CO_2 + H_2.$$

Butyric fermentation.—There is also some evidence that calcium tartrate may be transformed into butyrate. In fact, the older investigators obtained an acid which was variously interpreted as a modification of acetic acid, as a compound of acetic and butyric acids, or as a mixture of the two acids (Fitz, B. 1879, 476).

König (B. 1881, 215, 1717) also obtained in the fermentation of calcium tartrate with a mixture of organisms (appearing spontaneously in solutions of ammonium tartrate), carbonic, acetic, formic, propionic, and a little butyric acid.

The fermentation of ammonium tartrate has also been studied by König (B. 1881, 211, 1717; 1882, 172). The microbes producing the reaction appeared spontaneously in a 1 p.c. solution of tartaric acid neutralised with ammonia, and to which the necessary salts had been added. Portions of this weak solution were then introduced into a solution of five times the strength, and the action allowed to go on for six to eight weeks at 25-30°C. with exclusion of air; carbonic anhydride was evolved and a very large quantity of succinic acid obtained (500 grams from 2,000 grams tartaric acid), together with acetic and some formic acid. The change may be represented thus:

$$3C_4H_6O_6 = C_4H_6O_4 + 2C_2H_4O_2 + 4CO_2 + 2H_2O.$$

It is especially noteworthy that no succinic acid whatever was obtained in the fermentation of the calcium salt, although the inoculation was made from a fermenting solution of the ammonium salt.

Fermentation of calcium citrate.—A fermentation of this substance was obtained by Fitz (B. 1878, 1895) through inoculation with unboiled hay-infusion, and continued over thirteen days. In the fermenting liquid a micrococcus and a thin bacillus were visible during the earlier stages, the former, however, almost entirely disappeared towards the end of the reaction, and it was to the presence of the bacillus that the actual fermentation was attributed by Fitz. The products from 100 grams of anhydrous citric acid were 4·75 grams of ethyl alcohol and 55·4 grams of acetic acid, along with ·41 gram of succinic acid.

Fermentation of calcium quinate.—Two interesting decompositions of quinic acid have been observed by Loew (B. 1881, 450) to take place through the agency of micro-organisms appearing spontaneously in solutions of calcium quinate.

The solution employed contained 1 p.c. of calcium quinate, 1 p.c. asparagine, ·1 p.c. dipotassium phosphate, ·01 magnesium sulphate, and was freely exposed to the air in a large flask loosely plugged with cotton-wool. An abundant bacterial growth soon made its appearance, and after four weeks there were obtained protocatechuic acid $C_6H_3(HO)_2(COOH)$ (1, 3, 4) and succinic acid, the latter doubtless from the asparagine employed. The reaction is, therefore, essentially a process of oxidation similar to that which takes place when bromine is added to quinic acid, thus:

$$C_6H_7(HO)_4.(COOH)+O$$
$$=C_6H_3(HO)_2.(COOH)+3H_2O.$$

A second decomposition, in this case by reduction, was observed when a similar solution (with ·2 p.c. peptone instead of the asparagine) was kept for five weeks without access of air. The products in this case were propionic, acetic, and a little formic acid. This result is peculiarly interesting as showing that the benzene-nucleus may be torn asunder by the agency of a microbial ferment, thus:

$$C_6H_7(HO)_4(COOH)=CO_2+2CH_3.CH_2.COOH.$$

Whilst the formation of acetic and formic acids may be thus represented:

$$C_6H_7(HO)_4(COOH)+2H_2O$$
$$=3C_2H_4O_2+H_2CO_2+H_2.$$

Fermentation of calcium mucate.—When this salt is placed in contact with meat and water, it undergoes fermentation, carbonic anhydride, hydrogen, acetic acid, and a little butyric acid being formed (Rigault, J. 1860, 263). Thus:

$$C_4H_4(HO)_4(COOH)_2=2C_2H_4O_2+2CO_2+H_2.$$

Fermentation of asparagine.—It has been long known that this substance undergoes fermentation with formation of ammonium succinate (Piria, A. Ch. 68, 343; Dessaignes, J. 1850, 414). More recently Miquel (Bl. 31, 101) has isolated an organism from water, to which he has given the name of *Bacterium commune*, which in the presence of air decomposes asparagine, yielding ammonium succinate and a little carbonate, together with a mucilaginous substance, whilst one-half of the carbon is given off as carbonic anhydride. The change is complete in 8–10 days at a temperature of 30–36°C., the action being assisted by aspirating a current of filtered air through the liquid. The bacilli are described as 1·5μ in length by ·5μ, motile, and occurring singly or in chains of two, or more rarely in a longer series.

Viscous fermentation.—Saccharine juices, including wine and beer, are subject to a form of fermentation which is very troublesome in practice, and is known as 'ropiness,' 'vin filant,' 'fadenziehende Milch' &c. The products of this fermentation are carbonic anhydride, mannite, and a dextrinous substance for which the name of '*viscose*' has been proposed by Béchamp (C. R. 93). The fermentation was first attributed by Pasteur (Bl. 1861, 80) to the presence of a small micrococcus ·2μ diameter, and generally arranged in chains. Pasteur represents the reaction thus:

$$\underset{\text{Glucose}}{50(C_6H_{12}O_6)}$$
$$=\underset{\text{Gum}}{24(C_6H_{10}O_5)}+\underset{\text{Mannite}}{24(C_6H_{14}O_6)}+12CO_2+12H_2O$$

Monoyer (Thèse, Strasbourg, 1862, 624 [2]) pointed out in 1862 that the gum and mannite were probably the result of separate fermentations, and as a matter of fact the production of a larger proportion of the viscose is sometimes observed, and in such cases considerably larger micrococci are found. More recently it has been shown by Schmidt-Mülheim (Pflüger's Archiv, 1882, 27, 490, that in ropy milk ('fadenziehende Milch') there are present large micrococci of 1μ diameter and arranged in chaplets of 15 or more segments, and that gum is produced but neither mannite nor carbonic anhydride, as would in fact be indicated by Monoyer's equation

$$n(C_6H_{12}O_6)=n(C_6H_{10}O_5)+nH_2O.$$

In this case, however, the gum produced reduces Fehling's solution, whilst in the former it does not.

The viscous fermentation is readily induced by adding to a saccharine solution a filtered aqueous decoction of brewers' yeast, starch, barley, or rice, and allowing it to stand in a warm place (30°C.), which is the most favourable temperature for the 'vin filant' fermentation, whilst the 'fadenziehende Milch' is most favoured by a temperature of 30–40°C.

Dextrane-fermentation.—In the manufacture of beet sugar there not unfrequently appear in the saccharine solutions and molasses large quantities of a gelatinous substance ('*dextrane*'), (Scheibler, Wagner's Jahrb. Chem. Techn. 1875, 790; Zeitschr. f. Rübenzuckerindustrie, 1874), the composition of which is represented by the formula $C_6H_{10}O_5$, and which in its glutinous appearance resembles a mass of frog's eggs. The production of this body has been found to be due to the presence of chains of micrococci (*Leuconostoc mesenterioïdes*) (Van Tieghem, Ann. Sc. Nat. [6] 7), which are surrounded with a thick and tough gelatinous envelope. The organism contains a sugar-inverting ferment by means of which it readily prepares cane sugar for the fermentative process, and, owing to the great rapidity with which it multiplies, large quantities of sugar-solution may be destroyed in a very short time; hence it is regarded as a very dangerous enemy in beet-sugar factories. On slices of beet it grows in thick gelatinous masses of a cartilaginous consistency.

The substance obtained in this fermentation differs from 'viscose,' referred to above, in its insolubility in water; it is converted into the soluble form, however, by treatment with alkalis.

Denitrification.—It was first shown by Meusel (B. 8, 1215), that nitric may be reduced to nitrous acid by the agency of bacteria; thus well-water containing nitrates was found on standing for some days to give a definite reaction for nitrous acid. The reduction was prevented by the addition of antiseptics, and much increased by adding carbohydrates. Gayon and Dupetit (C. R. 95, 644, and 1365), as well as Déhérain and Maquenne (C. R. 95, 691) further found that nitrates are powerfully reduced by certain organisms present in soil, the products being, according to circumstances, nitrites, ammonia, nitrous oxide, or even free nitrogen.

Several micro-organisms, employed in a state of purity, were also found by Heräus (Zeitschr. f. Hygiene, 1886, 297) to reduce nitrates to nitrites or ammonia, and upwards of thirty different forms obtained from air and water by the writer of this article were examined for their action on nitric acid (P. F. Frankland, C. J. 1888, 373), with the result that sixteen or seventeen were found to reduce the latter to nitrous acid more or less completely, whilst fifteen or sixteen were quite destitute of this power. It was further found that this difference in reducing power may in certain cases be of great value in distinguishing between micro-organisms morphologically very similar. The action of the various microbes in question on nitric acid was not altered by preventing the access of air to the solutions in which they were cultivated, and in no case did the reducing action lead to the formation of any considerable amount of ammonia. Similar results have also been obtained by Warington (C. J. 1888, 727–755).

Reduction of sulphur-compounds.—The remarkable pleomorphic organisms generally grouped together under the name *Beggiatoa*, of which the commonest form is the *B. alba* or 'sewage-fungus,' possess the remarkable power of reducing sulphates with evolution of sulphuretted hydrogen, and with deposition of granules of free sulphur within the substance of their cell-contents. These forms are very widely distributed in marshes, sewers, hot sulphur-springs, and in the shallows of the sea-coast; they endure a very high temperature, exhibiting vigorous growth even at 55 C. (Cohn, Beiträge zur Biol. d. Pflanzen, 1, 173; Winogradski, Ueber Schwefelbakterien, Centralbl. f. Bakteriol. [2] 1887, 590).

Miquel (Bl. 32, 127; B. 1879, 2152) has described a micro-organism occurring in sewage, potable and even rain water, which converts the sulphur of albuminoids, of vulcanised india-rubber, and even free sulphur itself into sulphuretted hydrogen. The reaction is very vigorous; thus, in four or five days the solution may contain as much as 30 c.c. of sulphuretted hydrogen per litre, whilst when the latter reaches 60–70 c.c. per litre the fermentation ceases; in the presence of a base a corresponding quantity of sulphide is formed (Quantin, Reduction of Calcium Sulphate by certain Anaërobic Ferments, C. J. Abst. 1886, 573).

4. Fermentation by oxidation.—There are two highly important processes of fermentation belonging to this group, viz. the conversion of alcohol into acetic acid, and that of ammonia into nitrous and nitric acids. In addition to these, however, there are a great number of processes of oxidation effected by micro-organisms, the ultimate products of whose action in the presence of air are generally carbonic anhydride and water; these are in fact also the ultimate products in the acetic fermentation of alcohol, the acetic acid occurring merely as an intermediate stage in the process.

Acetic fermentation of alcohol.—The conversion of alcohol into acetic acid is a phenomenon which has been long known as taking place when wine is left exposed to the air, and in the manufacture of vinegar. In 1864, Pasteur (Mémoire sur la Fermentation acétique; Wurm, D. P. J. 235, 225; C. J. Abst. 1881, 128) showed that this conversion was due to the presence of an organism which, owing to its forming a skin on the alcoholic liquid, he termed *Mycoderma aceti*, and which formerly had been known as 'flowers of vinegar.' Pasteur further showed that the microbe acts as the oxygen-carrier in the reaction, and that if its vitality is impaired aldehyde makes its appearance, whilst, if the fermentation is allowed to continue after the alcohol has been wholly transformed, the acetic acid itself is further oxidised to carbonic anhydride and water. Succinic acid in small quantity is also stated to form a by-product of the reaction.

The morphological characters of the *Mycoderma aceti* have been studied by Cohn (Biol. d. Pflanzen, 2, 173), Hansen (Meddelelser fra Carlsberg-Laboratoriet) and Brown (C. J. 1886, 174), but their observations have been chiefly confined to the appearances under the microscope and in fluid media. When growing vigorously on the surface of a liquid the bacilli are seen to be about 2μ in length, slightly contracted in the middle so that they somewhat resemble the figure 8, and the cells being often completely divided in the middle, they then present a micrococcus-like form. The bacilli hang together in chains of various length. More especially in old cultivations abnormal forms are observed attaining a length of 10–15μ or upwards, and often swollen into irregular shapes. The free cells of normal shape are motile. Treated with iodine, the bacilli are stained yellow. Another acetic ferment has been described by Hansen which only differs from the ordinary *B. aceti* in being stained blue by iodine; to this form the name of *B. pasteurianus* has been given.

The chemical action of pure cultures of *B. aceti* has recently been very completely studied by Brown, whose results entirely accord with those previously obtained by Pasteur. Traces of a body resembling aldehyde were obtained when the bacillus was grown with a deficiency of air, whilst acetic acid was in every case the principal product, a trace of succinic acid being also formed. The further oxidation of the acetic acid to carbonic anhydride and water was also confirmed. The solution employed in these experiments was a 5 p.c. one of pure ethylic alcohol in clear yeast decoction (7 p.c.), the fermentation being carried on for ten days at 28°C. in a flask plugged with cotton-wool.

Brown has extended his observations to the action of *B. aceti* on other alcohols and aldehydes. Normal propylic alcohol was found to be oxidisable to propionic acid, whilst methylic, isoprimary butylic, and amylic (fermentation) alcohols proved refractory.

By the action of *B. aceti* on dextrose, Brown, as also Boutroux (C. R. 91, 236), found gluconic acid to be the sole product: thus,

$$\underset{\text{Dextrose}}{CH_2OH.CHOH.CHOH.CHOH.CHOH.COH} + O = \underset{\text{Gluconic acid}}{CH_2OH.(CHOH)_4.COOH}$$

This change was effected in Pasteur's mineral solution containing 2 p.c. of dextrose, and with 10 grams of carbonate of lime added to 3 litres of solution. The liquid was kept at 28°C. for thirty-nine days. *B. aceti* was found unable to attack cane sugar, whilst with mannite it yielded lævulose as the principal product without any accompanying acid. Lævulose also is unacted upon by *B. aceti*. The formation of lævulose from mannite is extremely remarkable, as in all purely chemical oxidations mannite yields an inactive sugar, mannitose (Gorup-Besanez, A. Ph. 118, 273; Hecht and Iwig, B. 14, 1760; Dafert, B. 17, 227).

The resistance of lævulose to oxidation by *B. aceti* also points to an essential difference in its molecular constitution from that of dextrose, and is quite in accord with Kiliani's (B. 18, 3066) ketonic formula for lævulose. Thus

$$\underset{\text{Mannite}}{CH_2OH.(CHOH)_4.CH_2OH} + O = \underset{\text{Lævulose}}{CH_2OH.CHOH.CO.(CHOH)_2.CH_2OH} + OH_2$$

By means of this fermentation of mannite it is now possible to convert dextrose into lævulose, for dextrose can be converted into mannite by the action of sodium amalgam (Dewar, P. M. 4, 39; Brown, C. J. 1887, 642), from which mannite lævulose can then be obtained by the action of *B. aceti*.

Dulcite (Brown, C. J. 1887, 638), the isomeride of mannite, and erythrite were both found to be insusceptible of oxidation by *B. aceti*. Glycol was found to yield glycollic acid; glycerine was decomposed into carbonic acid and water, with a very small amount of acid of an undetermined nature.

Bacillus xylinus.—In the manufacture of vinegar a tough gelatinous mass is often observed on the vessels employed, and is known as the 'vinegar-plant' or 'mother.' This has been shown by Brown (C. J. 1886, 432) to be a distinct acetic ferment, differing essentially from the *B. aceti* in its power of producing this jelly-like membrane which binds the individual bacilli together. The morphological characters are very similar to those of *B. aceti*, but the swollen forms referred to above have not been observed. Brown describes in old cultivations the appearance of highly refracting nuclei which he regards as spores, but as he also states that they stain deeply with aniline dyes this appears highly improbable, at least if the usual methods of staining were adopted. The membranous jelly gave the usual reactions of cellulose, and on analysis yielded figures corresponding almost exactly with the formula $(C_6H_{10}O_5)_n$, whilst its solubility in ammonio-cupric oxide shows it to be cellulose proper like cotton-wool; the meta-cellulose found in fungi and the envelopes of yeast is insoluble. The *B. xylinus* produces the same fermentations as have been described for *B. aceti*, but in addition it converts dextrose, and more especially lævulose, into cellulose: with mannite it also yields cellulose more abundantly than with dextrose, but as already mentioned, lævulose is formed by its action on mannite, and it is doubtless this lævulose from which the cellulose is actually formed.

Acid fermentation of glucose.—Boutroux (C. R. 102, 924) has recently described a fermentation of glucose resulting in the formation of an acid $C_6H_{12}O_8$, and to which he gives the name '*oxygluconic*.' The *M. oblongus* to which the conversion is attributed yields no acid with cane sugar.

Nitrification of ammonia.—The important and long-known process of oxidation occurring in soils and natural waters, resulting in the transformation of organic nitrogen into nitrous and nitric acids, was first shown by Schloesing and Müntz (C. R. 84, 301; 86, 392; 89, 891, 1074; Soyka, Zeitschr. f. Biolog. 1878, 449) to be due to the action of bacterial life. These chemists found that nitrification did not take place in soil which had been either sterilised by heat or treated with suitable antiseptics, such as chloroform. A very large number of experiments on the conditions under which nitrification takes place have been recorded both by Schloesing and Müntz, as well as by Warington (C. J. 1879, 429; 1884, 637), who has entirely confirmed their results. Unfortunately these careful and very laborious observations were all made before the modern methods of isolation and study had been introduced, and, owing to the impurity of the cultivations employed, they are deprived of much of their permanent value. Schloesing and Müntz, indeed, claim to have isolated a nitrifying organism from the soil which they describe as a micrococcus; there is, however, no guarantee that it was obtained in a state of purity. It has, however, been shown by these investigators that it is only ammoniacal nitrogen which can undergo nitrification, and that the organic nitrogen in the soil undergoes a preliminary transformation into ammonia, also through the agency of micro-organisms. They have further shown that a faint alkalinity, preferably that due to bicarbonate of lime, is necessary for nitrification, whilst an excess of alkali is distinctly prejudicial and ultimately prohibitive. It is on this account that urine will not undergo nitrification unless largely diluted with water. Similarly excessive concentration of the ammoniacal solution prevents nitrification. Again, nitrification is greatly accelerated by the addition of a large quantity of the nitrifying organisms, and by free exposure to the air. Only an excessively minute proportion of organic carbon is requisite for the adequate nourishment of the organisms concerned, and its presence in any quantity materially retards the process (Warington, C. J. 1884, 653).

Nitrification is also assisted by the presence of calcium sulphate (Warington, C. J. 1885, 758; (later) 1887, 118).

More recently the process of nitrification has been studied by Heräus (Zeitschr. f. Hygiene, 1886 [1] 193) and Leone, both claiming to have worked with pure cultivations of nitrifying organisms. Thus Heräus cultivated two species ('ρ and σ') from soil, and another from urine, which rapidly gave the reaction for nitrous acid. The species 'ρ' is a small bacillus, 'σ' a streptococcus, both of which give rise to leaf-like expansions on gelatine, whilst the third form is a small bacillus growing as a thick white knob on gelatine. In all three cases he found that the oxidation took place both in the presence and absence of organic matter (sugar), According to Heräus also, a number of well-known pathogenic and other organisms are capable of producing small quantities of nitrous acid in ammoniacal solution, but as these experiments were made in solutions of urine, which normally contains nitrates in appreciable proportions, it is highly probable that in all cases the nitrite was formed by reduction of pre-existing nitrate, and not by oxidation of ammonia. It should be pointed out further that Heräus has in no case quantitatively determined the amount of nitrate or nitrite produced by these pure cultivations, and there is, therefore, no conclusive evidence that but little more than traces of these products were formed (Warington, C. J. 1888, 754). There is, in fact, no satisfactory evidence that a nitrifying organism has yet been obtained in a state of purity.

According to Leone (Gazzetta Chim. 16, 505; C. J. Abst. 1887, 615), one and the same organism may under varied circumstances either convert ammonia into nitrous and nitric acids, or reduce the latter to ammonia.

The oxidation of organic carbon to carbonic anhydride which takes place in the soil has also been shown by Wollny (Landwirth. Versuchsstat. 1880, 390; Journ. f. Landwirthsch. 1886, 213), Fodor, and Déhérain (C. R. 98, 877; 99, 45), to be due to the action of micro-organisms.

Fermentation of indigo, *v.* Alvarez, Sur un nouveau microbe, déterminant la fermentation indigotique et la production de l'indigo bleu (C. R. 105, 286; Centralbl. f. Bakteriol. [2] 1887, 441).

Some fermentations due to mixtures of micro-organisms.

Production of cheese.
  Duclaux. Le lait. Études chimiques et microbiologiques. Paris, 1887 (C. J. Abst. 1882, 436.
  Vieth. Micro-organisms and their Action on Milk and Milk-products (Agric. Soc. Journ. 1887).
Panary fermentation.
  Arcangeli. Sulla fermentazione panaria. Centralbl. f. Bakteriol. [3] 1888, 717.
  Chicandard (C. R. 96, 97).
  Marcano (C. R. 96, 97).
  Boutroux (C. R. 97).
  Moussette (C. R. 96).
  E. Laurent (C. J. Abst. 1887, 70).
Koumiss.
  Kern. Ueber ein neues Milchferment aus dem Kaukasus (Bl. Soc. Imp. des Naturalistes, Moskau, 1881).
  Kern. Dispora caucasica, eine neue Bakterienform (Biolog. Centralbl. [2] 137).
  Krannhals. Ueber das kumysähnliche Getränk Kephir (Deutsch. Archiv f. klin. Med. 35, 1884).
Japanese koji.
  Marcano (C. R. 95).

Putrefaction.

This term is generally employed to indicate those complex processes of decomposition which nitrogenous organic substances, and notably albuminoids, spontaneously undergo, and which are accompanied with the evolution of foul and fœtid odours. These putrefactive changes are now known to be entirely due to the action of micro-organisms, although there is still but little precise information as to the particular forms which play a part in these important reactions. The putrefactive fermentation of albumen appears essentially to consist of decomposition into simpler products, accompanied by hydrolysis, and, according to Gautier and Étard (C. R. 94, 1357), the products formed are almost precisely similar to those obtained by the action of caustic alkalis on albumen at a high temperature (250°C.).

The first step appears to be the peptonisation of the albumen, which may take place through the agency of a great variety of micro-organisms. The peptones then undergo further decomposition, the principal products being amido-compounds of the fatty acids (leucine and tyrosine), which are in turn decomposed with formation of the fatty acids themselves, ammonia, and carbonic anhydride; there are further formed complex amido- bodies, oxalic, lactic, phenylacetic and phenylpropionic acids, phenol, scatol, and indol, besides organic bases, such as methylamine, trimethylamine, and the ptomaïnes.

The process of putrefaction differs essentially according as the materials undergoing change are exposed to, or protected from, the access of free oxygen. This difference was first clearly pointed out by Pasteur, who considered the absence of free oxygen as an essential factor in this, as in other processes of fermentation. More recent researches, however, have shown that some bacteria are capable of setting up putrefactive changes in albuminous substances irrespectively of the presence or absence of free oxygen. In the absence of free oxygen the products of the putrefactive process are preserved from further decomposition, for not only are they unacted upon by the hydrogen which is evolved in so many fermentations, but the want of oxygen prohibits the growth of aërobic micro-organisms capable of attacking them. In the presence of an abundant supply of free oxygen, on the other hand, the putrefactive products undergo further change, which, according to Hoppe-Seyler, is due to the nascent hydrogen of the fermentation breaking up the free molecules of oxygen, the latter in its atomic or active condition then effecting oxidations which in its molecular condition it is incapable of. The hydrogen, sulphuretted hydrogen, and other products of deoxidation which characterise ordinary putrefaction thus disappear when a plentiful supply of air is provided; but it must be remembered that this supply of air also invites the growth and activity of numerous aërobic bacteria capable of further decomposing and oxidising the putrefactive products, so that the difference in the final products obtained, according as air is freely admitted or not, may receive either a purely chemical or a purely biological explanation. It is usual to distinguish this decomposition of albuminous substances in the presence of free oxygen by the name of *decay*, but under ordinary natural circumstances the two processes go on side by side; thus, in the depth of a liquid, putrefaction may be taking place whilst the process of decay may be at work on the surface.

Of great importance in connection with the process of putrefaction is the production of certain basic nitrogenous bodies, known as *ptomaïnes* (πτῶμα, a corpse), some of which are possessed of intensely poisonous properties. The poisonous character of many substances in a state of putrefaction has been long known, and the similarity in their action to that of some of the vegetable alkaloids, notably coniine, had been frequently observed; Nencki (J. pr. 1882, 47), however, first isolated and determined the composition of one of these bases, which he obtained from putrid gelatine. The base in question $C_8H_{11}N$ is isomeric with collidine, and probably the same substance was afterwards obtained by Gautier and Étard (C. R. 94, 1601) from putrid fish, together with another $C_9H_{13}N$. Another base $C_{10}H_{15}N$, resembling curarine in its action, was obtained from putrid fibrin by Guareschi and Mosso, whilst a base having the composition $C_5H_{11}NO_2$ or $C_7H_{13}NO_2$ was prepared by Salkowski from putrid meat and fibrin. A number of these basic bodies have been isolated by Brieger (Die Ptomaïne, Berlin, 1885 and 1886; Sitz. k. preuss. Akad. d. Wissenschaften zu Berlin, 1889, 5), some being poisonous, others innocuous, or nearly so. Thus

Non-poisonous or nearly so.

Neuridine $C_5H_{14}N_2$.
Gadinine $C_7H_{17}NO_2$.
Cadaverine $C_5H_{16}N_2$.
Putrescine $C_4H_{12}N_2$.
Saprine $C_5H_{16}N_2$.
Choline $C_5H_{15}NO_2$, or $(CH_3)_3.N.(OH).C_2H_4(OH)$.

Poisonous.

Peptotoxine.
Neurine $C_5H_{13}NO$, or $\begin{matrix}(CH_3)_3\\(C_2H_3)\end{matrix}N.(OH)$.
Ethylenediamine $C_2H_4(NH_2)_2$.
Muscarine $C_5H_{15}NO_3$.
Mydaleïne.

All the above bases were obtained from putrifying meat, fish, or other albuminous substances, and the discovery of poisonous products of the vitality of micro-organisms has completely revolutionised the views which had previously been entertained as to the pathogenic action of certain micro-organisms. Thus, formerly it was generally supposed that the mere presence of these organisms in the blood or in the tissues occasioned the characteristic disturbances, whilst now the cause of these morbid processes is believed to reside in the production of certain specific alkaloidal poisons by the micro-organisms in question. There has, moreover, long been evidence that certain forms of blood-poisoning may follow upon putrid wounds without any micro-organisms being present in the blood, a phenomenon which receives a ready explanation on the hypothesis that the microbes flourishing on the surface of the wound generate poisons which are absorbed into the system and give rise to a general intoxication.

Attempts have more recently been made to isolate the basic products resulting from the growth of organisms known to be possessed of pathogenic properties. These attempts have, however, so far met with but partial success. Thus cultures of the *B. anthracis* were examined by Nencki and Marmé without any basic products being discovered. The *Staphylococcus aureus* (the commonest organism in abscesses) again was found to yield only a non-poisonous base. On the other hand, a poisonous base, *typhotoxine* $C_7H_{17}NO_2$, was, on two occasions, obtained by Brieger from cultures of the typhoid bacilli, another from cultures of the bacilli of tetanus, the symptoms produced by the latter poison presenting the strongest resemblance to those resulting from actual inoculation of the bacilli. To this base, $C_{13}H_{30}N_2O_4$, Brieger has given the name of *tetanine* (Die Ptomaïne [3] 1886, 95).

It has also been ascertained that the pathogenic effect of inoculating certain organisms is greatly increased by simultaneously introducing a quantity of the sterilised products of their growth, clearly indicating the poisonous nature of the latter. In some cases also it has been found that a previous intoxication induced by such poisonous but sterile products of a pathogenic micro-organism is capable of conferring subsequent immunity towards the disease which the particular micro-organism is capable of setting up (D. E. Salmon and Theobald Smith, The Production of Immunity by Hypodermic Injection of Sterilised Cultures, Centralbl. f. Bakteriol. [2] 1887, 543; Hueppe, Fortschritte d. Medicin [6] 1888, 289; Centralbl. f. Bakteriol. [4] 1888, 122; Wooldridge, *ibid.* [4] 1888, 342; Bouchard, C. R. 106, 1582; Roux and Chamberland, Centralbl. f. Bakteriol. [3] 1888, 769, 770).

There can be no doubt, therefore that these ptomaïnes are bodies of the greatest importance from a hygienic point of view, and that their study, which hitherto has been but begun, is calculated to throw light on many unexplained phenomena of disease.

2. Soluble Ferments, or Enzymes.

Under this term are understood a number of highly complex organic bodies, of an albuminoid character, which possess the power of bringing about chemical changes on a scale altogether out of proportion to their own mass. These changes are in all cases processes of hydrolysis, in which the products formed contain less potential energy than the bodies from which they are derived. The mode of action of these soluble ferments is not fully understood, but it would appear to resemble the action of sulphuric acid in the process of etherification, in which a given quantity of acid is theoretically capable of transforming an indefinite amount of alcohol, and, similarly, a small quantity of acid can transform large quantities of starch into glucose and dextrin without itself undergoing any change. In the case of papaïn, Wurtz (C. R. 90, 91, 93) has shown that this ferment, in the first place, actually enters into combination with albuminoids; the compound formed can be isolated and washed with water, but on digesting with pure water at 40°C., the albuminoids pass into solution as peptones, whilst the papaïn is regenerated and can then act on a further quantity of albuminoids.

These soluble ferments, or *enzymes*, are very widely distributed both in the vegetable and animal kingdoms, and play a most important part in the process of nutrition, for by their action insoluble bodies incapable of assimilation are rendered soluble and diffusible through vegetable and animal membranes. It has already been pointed out in the first part of this article that soluble ferments are frequently produced by micro-organisms; thus yeast generates *invertase* which transforms cane sugar into dextrose and lævulose, the lactic acid bacillus again secretes a diastatic ferment, which renders starch soluble, whilst numerous forms convert albuminoids and gelatin into soluble peptones. It is, in fact, through the assistance of these enzymes that the field of activity for the various fermentative microbes is greatly extended.

Hueppe (C. J. Abst. 1882, 317) has shown that the soluble ferments in the dry state may be heated to 100°C., and in some cases to 170°C., without losing their activity.

In a number of cases a diastatic action has been found to be exerted by micro-organisms (Marcano, C. R. 95; Hueppe, Mittheil. kaiserl. Gesundheitsamte, 2; Miller, Deutsche med. Wochenschr. 1885, No. 49; Wortmann, Zeitschr. f. physiol. 6), although the soluble ferment has but rarely been isolated.

Thus, in the preparation of 'saké,' the national alcoholic beverage of Japan, the rice-starch is converted into sugar by allowing a fungus to vegetate over the surface of the steamed rice (R. W. Atkinson, Pr. 32, 299; C. J. Abst. 1881, 1059). The same agent also renders soluble the albuminoids of the rice.

It has been shown by Brown and Morris (C. S. J. 1885, 527-570) that when the action of malt-extract on starch-paste is limited, there is always found amongst the products, besides maltose and dextrin, a third body, *maltodextrin*, more soluble in alcohol than the dextrins, and which, from its specific rotatory and reducing powers, corresponds to an apparent composition of 34·6 p.c. maltose, and 65·4 p.c. dextrin. It is completely hydrated to maltose by the action of malt-extract at 50°-60°C.; it is untouched by *Sacch. cerevisiæ* of the 'high fermentation,' but may be fermented by the saccharomycetes which cause the secondary fermentation of beer (*S. ellipticus* and *pastorianus*), and which also act on ordinary dextrin.

The soluble ferments are divisible into the following groups:—

1. *Diastatic.*—These transform starch into dextrin and glucose (maltose, dextrose, &c.).

$$\underset{\text{Starch}}{6C_6H_{10}O_5} + 4H_2O = \underset{\text{Dextrin}}{2C_6H_{10}O_5} + \underset{\text{Maltose}}{2(C_{12}H_{22}O_{11} + H_2O)}$$

(Dubrunfaut, Jahrb. d. Chem. 1847-8, 793; O'Sullivan, *ibid.* 1872, 771; 1874, 884; B. 9, 949; Schulze, B. 7, 1047; Brown and Heron, A. 199, 201; Musculus and Mering, Zeitschr. f. physiol. Chem. 2, 413; v. Mering, *ibid.* 5, 185; Herter, C. J. Abst. 1882, 753).

The diastase of malt is capable of converting no less than 2,000 times its weight of starch (Payen and Persoz, A. Ch. 53, 73; 56, 237; 60, 441; 61, 351); diastatic ferments are also found in many other vegetable organs. In animals, the principal diastatic ferments are the ptyalin of saliva, the pancreatic secretion, and that of the liver, the latter converting glycogen into glucose, as well as certain ferments present in urine. These several diastatic ferments present considerable differences amongst themselves in their mode of action; thus the diastase of malt is most active at a temperature of about 66°C., and in a neutral or faintly acid medium (Kjeldahl, C. J. Abst. 1881, 115); ptyalin and pancreatic juice, on the other hand, entirely lose their power at 60°C. (Roberts, Pr. 32, 145; C. J. Abst. 1881, 1051), and perform their functions in an alkaline medium. The diastatic ferment of the pancreas produces principally maltose, and not glucose, as was formerly supposed, but only a small proportion of the latter, as well as some achrodextrin. 1 gram of pancreatic juice converts 4·672 grams of starch at 35°C.; it is without action on inulin and cane sugar.

The influence of various reagents on diastatic action has been investigated by Bouchardat (A. Ch. [3] 14, 61).

2. *Inverting.*—This class of ferments comprises those bodies which are capable of converting the disaccharates (cane sugar, milk sugar, maltose), into glucoses (dextrose, lævulose, galactose). The term *invertase* is applied to these ferments because in the conversion of cane sugar into equal proportions of dextrose and lævulose, the action on polarised light is inverted, becoming changed from dextro- to lævo-rotatory. Ferments of this kind are widely distributed throughout the alimentary canal in animals, whilst in the higher plants there must be similar agencies at work, as cane sugar is found in the stems, whilst the fruits contain dextrose, always mixed with an equivalent quantity of lævulose and sometimes along with some cane sugar. The conversion of the cane sugar into invert-sugar in fruits appears, moreover, to be quite independent of the acid which the latter contains. Thus even in the sourest fruit of the lemon, one-fourth of the total sugar is in the condition of sucrose (Buignet, A. Ch. [3] 61, 233; J. 1860, 539). The presence of an invertase has been proved in certain moulds, penicillium and aspergillus (Gayon, Bl. 35 and 58), and in the case of *Aspergillus niger*, Bourquelot (C. R. 97) actually succeeded in isolating a ferment which transformed both cane sugar and maltose. As far as is known, the various forms of mucor do not contain an invertase, thus *Mucor racemosus* neither inverts nor ferments milk sugar (Fitz, B. 9, 1352).

An invertase is secreted by ordinary brewers' yeast; the inversion of cane sugar by yeast was first observed by Dubrunfaut and Persoz, by whom it was attributed to the natural acidity of the yeast. Berthelot (Chim. organique fondée sur la synthèse [2] 619), however, showed that the reaction could also take place in a solution rendered alkaline with bicarbonate of soda, and that the inverting agent was not removed by filtration, but could be precipitated with alcohol. One part of the precipitated ferment was found to be capable of inverting from 50-100 parts of cane sugar. The invertase of yeast has no action on milk sugar, maltose, inulin, dextrin, or starch (Kjeldahl, Meddelelser fra Carlsberg-Labor. 1;

Donath, B. 1875, 795; Barth, B. 1878, 474). Invertase attains its maximum activity at 53–56°C. in slightly acid solution.

A form of yeast has been recently discovered by Duclaux (Centralbl. f. Bakteriologie, 3, 525), which ferments milk sugar, but whether the latter is previously inverted or not was not ascertained. Some varieties of yeast appear to be destitute of inverting power, although fermenting glucose in the ordinary way (Roux, Bl. 35). The schizomycetes are frequently endowed with an inverting ferment, thus, according to Hueppe, milk and cane sugar are hydrolysed by the *B. lactis* prior to the lactic fermentation, whilst Bourquelot's experiments appear to indicate that these substances undergo lactic fermentation directly. The bacilli of the butyric fermentation, on the other hand, are generally admitted to be without inverting power.

3. *Peptonising ferments.*—These ferments convert coagulable albuminoids into soluble and diffusible albuminoids or *peptones*, which are neither precipitated on boiling, nor by copper sulphate, ferric chloride, mineral acids, nor alkaline salts; precipitable, however, by chlorine, tannin, mercuric chloride, silver nitrate, and lead acetate, neutral or basic.

Of the several peptonising ferments, *pepsin*, which is contained in gastric juice, exerts its action in an acid (hydrochloric, phosphoric, or lactic) solution only, whilst the pancreatic ferment *trypsin* (Roberts, Pr. 32, 145; C. J. 1881, 1053; A. Gautier, Soluble and Insoluble Modifications of the Gastric Ferment, C. R. 94, 652; Béchamp, C. R. 94, 582; Duclaux, C. R. 94, 736), as well as the vegetable ferment *papaïn* (from the latex of *Carica papaya*), act especially in an alkaline solution, but also, though with less energy, in a neutral or an acid one.

According to Kühne and Chittenden (Zeitschr. f. Biolog. 19, 159, 1883), the process of peptonisation is not to be regarded as a series of simple hydrolyses, but the molecule of albumen appears in the first instance to undergo decomposition into two equal halves, one of which, the *hemialbumose*, is readily converted by pepsin into *hemipeptone*, the latter being further converted by trypsine into leucine, tyrosine, &c. The other semimolecule, *anti-albumose*, is only slowly acted upon by pepsine, but more rapidly by trypsin, with formation of *antipeptone*; the latter, unlike the hemipeptone, undergoes no further change through trypsin. According to this view ordinary peptone is a mixture of antipeptone and hemipeptone.

Peptonising ferments appear to be frequently secreted by micro-organisms, a large number of which cause liquefaction of the gelatine medium on which they are cultivated. These ferments have hitherto received but little attention; from the fact, however, that this liquefaction generally takes place in an alkaline medium, the ferments in question would appear to be more closely allied to trypsin and papaïn than to pepsin. According to Liborius (Zeitschr. f. Hygiene, 1, 115) many organisms are deprived of their peptonising powers when cultivated in the absence of free oxygen.

4. *Ferments causing coagulation of caseïn.*—A ferment possessing the property of curdling milk is contained in rennet (A. Mayer, The Action of Rennet under various conditions, C. J. Abst. 1881, 1183), and made use of in the preparation of cheese. Similar ferments appear to be formed by numerous micro-organisms, the curdling taking place in some cases with an acid, in others with an alkaline, and in others with a neutral reaction (Duclaux, C. R. 91); frequently the coagulated casein is subsequently peptonised. Of micro-organisms causing such curdling may be mentioned the butyric bacillus, the *B. pyocyaneus*, *Sarcina aurantiaca*, &c. (Hueppe, Mittheilungen a. d. kaiserl. Gesundheitsamte, 2; Deutsch. med. Wochensch. 1884, Nos. 48 and 49).

5. *Ferments causing the decomposition of glucosides.*—The numerous glucosides found in the vegetable kingdom are resolved into their proximate constituents, of which one is invariably glucose, by the action of certain soluble ferments, the most familiar of which is *synaptase* or *emulsin*. Thus, amygdalin when brought in contact with a small quantity of emulsin, which is contained in an aqueous extract of sweet almonds, is decomposed according to the equation

$$\underset{\text{Amygdalin}}{C_{20}H_{27}NO_{11}} + 2H_2O = \underset{\text{Benzaldehyde}}{C_7H_6O} + \underset{\text{Hydrocyanic acid}}{HCN} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

(Liebig, Wöhler, A. 22, 17).

Other instances of the same type of decomposition are those of potassium myronate, salicin, arbutin, coniferin, &c. Thus:

$$\underset{\text{Potassium myronate}}{K.C_{10}H_{18}NS_2O_{10}} = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Allyl mustard-oil}}{C_3H_5.N.CS} + KHSO_4.$$

This change is effected by the ferment known as *myrosin*, which is present along with the potassium myronate in the seeds of black mustard; it is, however, more abundant in the white mustard seed.

$$\underset{\text{Salicin}}{C_{13}H_{18}O_7} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Saligenin}}{C_7H_8O_2}.$$

The above is effected by emulsin (Piria, A. 56, 36), as well as by the salivary ferment (Staedeler, J. 1857, 559),

$$\underset{\text{Arbutin}}{C_{12}H_{16}O_7} + H_2O = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Hydroquinone}}{C_6H_6O_2}$$

also by the action of emulsin, as well as the following:

$$\underset{\text{Coniferin}}{C_{16}H_{22}O_8,2H_2O} = \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Coniferyl alcohol}}{C_{10}H_{12}O_3} + H_2O.$$

Emulsin is best obtained from sweet almonds, which are first skinned, bruised, and squeezed to express the greater part of the oil; the cake is then mixed with three times its weight of water and again pressed. In this manner an emulsion is obtained which on being kept at 25–30°C., separates into two layers, of which the upper is creamy and the lower one clear and transparent. The latter contains the ferment, which can be precipitated with absolute alcohol. In order to further purify the emulsin, this precipitate should be dissolved in a little water acidulated with acetic acid, and then submitted to a stream of carbonic acid gas, which causes the precipitation of albuminous matters. The process is continued until the solution ceases to give a precipitate with potassium ferrocyanide and acetic acid, after which it is precipitated with alcohol, again dissolved in water, and the solution evaporated *in vacuo*. The emulsin is thus obtained as a white hygroscopic powder. Its solution is lævorotary. In the dry state it is unaltered by a temperature of 100°C. Emulsin is precipitated from aqueous solution by the chlorides of iron and mercury, ferrous sulphate, and the sulphate of copper and zinc, as well as by silver nitrate. Its solution in glycerin is without action on amygdalin. A very small proportion of hydrochloric acid (Falk, Virchow's Archiv, 93) (·15 per 1,000) interferes with the ferment, whilst chloroform has no action on it (Müntz, C. R. 1875).

The composition of emulsin, as given by Bull (A. 69, 145), is carbon 43·5, hydrogen 6·96, nitrogen 11·64, sulphur 1·25, and oxygen 36·56 p.c.

6. *Ferments causing the conversion of urea into ammonium carbonate.*—The evidences of the ammoniacal fermentation of urea being occasioned by soluble ferments have already been dealt with in treating of the micro-organisms which bring about this chemical change.

In addition to the soluble ferments already referred to, it is probable that there also exist some capable of dissolving cellulose; thus it would appear that in the butyric fermentation of cellulose it is such a ferment which acts in the first instance, and renders the material available for the subsequent butyric fermentation. This cellulose-dissolving ferment is apparently secreted by *B. butyricus*, and especially by *Spirillum rugula* (Prazmowski, Untersuchungen, Leipzig, 1880, 44).

The secretion of the pancreas possibly also contains another ferment, besides diastase and trypsin already referred to, for pancreatic juice saponifies fats with formation of fatty acid and glycerin, which decomposition is according to Wassilieff (Zeitschr. physiol. Chem. 6, 112) not interrupted by a large proportion of calomel; it is, however, destroyed by alcohol, and cannot be extracted with glycerin, so that it must be extremely unstable. P. F. F.

FERONIA GUM *v.* Gums.

FERRATES *v.* Iron.

FERRIC ACETATE *v.* Acetic acid.

FERRIC SALTS *v.* Iron.

FERROCYANIDES *v.* Cyanides.

FERROMANGANESE *v.* Iron.

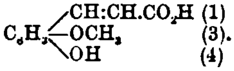
FERROTYPE *v.* Photography.

FERROUS ACETATE *v.* Acetic acid.

FERROUS SALTS *v.* Iron.

FERULAIC ACID. An acid found in asafœtida, *v.* Gum resins.

FERULIC ACID. *Metamethoxy-parahydroxy-cinnamic acid*



$$C_6H_3\begin{cases} CH:CH.CO_2H & (1) \\ OCH_3 & (3) \\ OH & (4) \end{cases}$$

Occurs in asafœtida resin (Hlasiwetz and Barth, A. 138, 64). The alcoholic extract of the resin is precipitated with lead acetate, and the precipitate, consisting of lead ferulate, is decomposed with sulphuric acid. It has been prepared artificially by means of Perkin's reaction by heating together vanillin, acetic anhydride and dry sodium acetate, and decomposing with potash the acetyl-ferulic acid thus formed (Tiemann and Nagai, B. 11, 647).—Rhombic needles, melting at 168–169°, almost insoluble in cold water, readily soluble in alcohol, less soluble in ether. The solution gives with lead acetate a yellow flocculent precipitate, and with ferric chloride a yellowish-brown precipitate. Fusion with caustic potash converts it into acetic and protocatechuic acids. Sodium amalgam reduces it to hydroferulic acid $C_{10}H_{12}O_4$. F. R. J.

FIBRIN *v.* Albuminoids.

FIBRINOGEN *v.* Albuminoids.

FICETIN *v.* Fustic.

FICHTELITE. Fichtelite occurs together with retene in the turf beds of Redwitz in the Fichtel Mountains, and is found in the fossil stems of the sporadic bog-fir, *Pinus uliginosa* N. It was found by Bamberger on the high-lying turf moor, near Rosenheim, in Upper Bavaria. It occurs on the stumps of fossil pine-trees which project above the surface of the turf in the shape of a white efflorescence or crystals. It is easily isolated by extracting the wood with petroleum spirit, from which it separates on concentration in large crystals. From alcohol it crystallises in glassy prisms. Bamberger's experiments show that the formula $C_{40}H_{70}$, proposed by Clark (A. 103, 236) is inadmissible. Its vapour density is 8·6; it contains 87 p.c. of carbon and 12·9 p.c. of hydrogen. Hence its formula is $C_{18}H_{32}$. It boils at 355·2° under 719 mm. Derivatives of fichtelite are very difficult to obtain, owing to the great stability of this singular hydrocarbon. It can be distilled over red-hot lead oxide without decomposition. When fichtelite is heated with iodine, hydriodic acid is given off and a syrupy yellow liquid is left. On distillation under 270 mm. pressure the bulk goes over at 290–295°C. as a thickish liquid, nearly colourless, and possessing a splendid blue-violet fluorescence. This body is *dehydrofichtelite*, differing from fichtelite in having two atoms of hydrogen less (E. Bamberger, B. 22, 635–637; B. 22, 3364). It is best separated from retene by repeatedly recrystallising from a mixture of alcohol and ether; it forms long prismatic crystals, melting at 46°. The mother-liquors yield, on further evaporation, first retene and finally a brown soft mass, with a strong smell of vanilla. Vapour-density determinations by V. Meyer's method, at 440°, show that it has the formula $C_{18}H_{30}$. Dehydrofichtelite is identical with retenedodecahydride. Fichtelite is in all probability *perhydroretene* (Bamberger and Strasser, B. 22, 3361; also L. Spiegel, B. 22, 3069).

Fichtelite is acted on extremely slowly when boiled with fuming sulphuric acid; potassium bichromate, and sulphuric acid, or a 10 p.c. solution of potassium permanganate; but when treated with chromic acid in glacial acetic acid solution it seems to be oxidised to carbonic acid. It is not acted on by cold fuming nitric acid, but when boiled with nitric acid of sp.gr. 1·32 it yields oxalic acid. Bromine acts on it very readily, but the products could not be obtained free from unchanged hydrocarbon (C.

Hell, B. 22, 498–502; S. C. I. 8, 382; Trommsdorff, A. 21, 126; Bromeil, A. 37, 304; Clark, A. 103, 236).

FIELD'S CARMINE, MADDER CARMINE, *v.* Pigments.

FIELD'S LAKE, MADDER LAKE, *v.* Pigments.

FIELD'S PURPLE, PURPLE MADDER, *v.* Pigments.

FIELD'S RUSSET, PURPLE MADDER, *v.* Pigments.

FIG WAX *v.* Wax.

FILICIC ACID *v.* Filix mas.

FILITANNIC ACID *v.* Filix mas.

FILIX MAS. Male fern; *Rhizoma filicis*; *Racine de fougère mâle*, Fr.; *Farnwurzel*, Ger. The rhizome of male fern, *Aspidium filix mas* (Swartz), has been a favourite anthelmintic medicine since the times of Theophrastus, Dioscorides, Pliny, and Galen. For botanical characters *v.* Woodville (Med. Bot. 271), Moore a. Lindley (Ferns of Great Britain, 14–17), and Bentl. a. T. 300.

The early chemical investigations of the rhizome, of which Pereira gives a summary (Mat. Med. 3rd ed. 2, 959) show that, besides the constituents common to plants, it contains a peculiar *green fixed oil*, *tannin*, and a crystalline compound, first analysed by Luck (J. 1851, 558) and named by him *filicic acid*. These constituents are all found in the ethereal extract or 'oil of male fern,' in which form alone the drug is made use of in medicine. Further analytical details are given by Geiger (Handb. Pharm. 1829), Bock (Ar. Ph. [2] 65, 257), Spiess (C. C. 1860, 766), Kruse (Ar. Ph. [3] 9, 24).

The green fixed oil is composed, according to Luck, of the glycerides of the non-volatile *filixolinic*, and the volatile *filosmylic acids*. These compounds were analysed, and their barium salts described. The same observer regards the tannin to be composed of two compounds, the one 'tannaspidic acid' insoluble, and the other 'pteritannic acid' soluble in ether. Malin, however (A. 143, 276), shows that there exists but one form of tannin, which he isolates and names *filitannic acid*. This is a glucoside, breaking up through the agency of water (dilute acids) into a kind of *glucose* and dark brick-red flocks of *filix red*, $C_{20}H_{15}O_{12}$. The latter compound when treated with caustic potash yields phloroglucin and protocatechuic acid. The tannaspidic acid of Luck was probably filix red.

The therapeutic value of male fern appears, however, to belong to the *filicic acid* of Luck. Several derivatives were prepared and analysed, and the acid itself is described by its discoverer as a light-yellow crystalline powder, melting at 161° (180°, Daccomo). In water it is insoluble, in alcohol only slightly soluble; but ether, especially in presence of the green fixed oil, dissolves it readily. According to Grabowski (A. 143, 279) filicic acid is *dibutyryl-phloroglucin* $C_6H_5(OH)(OC_4H_7O)_2$. Treated with alkalis it takes up the elements of water, forming *butyric acid* C_4H_7O,OH, and *monobutyryl-phloroglucin* $C_6H_3(OH)_2(OC_4H_7O)$, which latter, in the further progress of the reaction, yields *phloroglucin* $C_6H_3(OH)_3$ and another molecule of butyric acid. Grabowski attempted to prepare filicic acid from phloroglucin and butyryl chloride, but the compound obtained was of a different character. Daccomo (C. C. 1887, 1357; B. 21, 2962) has re-examined filicic acid and prepared several alkoyl and alkyl derivatives. The evidence of these leads to the formula $C_{14}H_{18}O_5$. By the action of water he obtains *isobutyric acid* and not phloroglucin, but a *new substance* $C_{20}H_{18}O_7$, which on oxidation yields *phthalic acid*. Daccomo suggests that filicic acid is *isobutyryl-oxynaphthoquinone* (Luck, B. 21, 3465, and Paternò, B. 22, 463). A wax-like constituent, two resins and *aspidol*, m.p. 136·5°, are also stated to exist in *filix mas* (Daccomo). The 'aspidin' of Pavesi (Ar. Ph. [2] 108, 142) seems to have been impure filicic acid. A. S.

FILIX RED *v.* Filix mas.

FILOSMYLIC ACID *v.* Filix mas.

FILTER PUMPS. The filter pump is a recent invention, and is generally some form of dynamic air-pump. Sprengel in 1865 (C. J. 9) showed how a very perfect vacuum could be obtained by the fall of mercury or other liquids, and Bunsen, in 1868 (A. 148, 277), showed how the difference of pressure so obtained could be utilised in greatly improving the ordinary process of filtration.

This application has given a name to all these instruments, though they are applicable to nearly all the purposes for which any ordinary air-pump or aspirator might be used. Many of them, with a continuous supply of falling liquid or of steam or other gas, under pressure, are almost automatic in their working, and far more convenient than any piston air-pump.

The pumps used in laboratories are of three kinds:

1. Barometer or weight-pumps.
2. Momentum or pulsation-pumps.
3. Injection or pressure-pumps.

1. Barometer pumps. Of these there are two varieties, the statical or Geissler pump, and the dynamic or Sprengel pump.

The Geissler pump was invented about 1855 by Geissler, and in it air is exhausted by the alternate emptying and filling with mercury of a vessel forming the upper part of a barometric column. It is simply an application of the Torricellian vacuum. Geissler used this pump in the production of his vacuum tubes, and since his time it has been modified and improved by many inventors; Töpler (D. P. J. 1862, 423), also Poggendorf, Mitscherlich, Pflüger, Joule, and others.

The Sprengel pump, in its simplest form, is a plain tube of small but uniform bore, and of a length rather greater than that of the barometric column of the liquid used in it. It is furnished with a side tube near its upper extremity. The continuous falling of the liquid, generally mercury or water, produces the exhaustive effect, which is slow at first, but can be made to give a more perfect vacuum than is possible by any other means. The improvements of the Sprengel pump have been chiefly towards quickening its action, and have been described by McLeod, Swan and Stearn, Gimingham, Weinhold, and others. Crookes' experiments on the radiometer and radiant matter were rendered possible by the use of the Sprengel pump, and in the manufacture of incandescent electric-lighting lamps these barometric pumps have had a considerable industrial application. The Sprengel pump, worked by water, was that used by Bunsen in his improved mode of filtration, and this application—the most important to the chemist—gave rise to the many inventions described below in this paper.

2. The Momentum or Pulsation pump. This was described by Jagn in 1872 (P. 148, 817). It consists of a plain tube of moderate length, with side tube near the upper end. In action the soft india-rubber tube connecting the apparatus with the water supply (of a very moderate fall or pressure) is ingeniously made to act as a valve by which the water is alternately admitted and shut off. We have thus an action similar to that of the hydraulic ram, in which the momentum of a column of liquid comes into play. In the ram, water is raised in front by the momentum; in this pump air is pulled in behind. Modifications of the Jagn pump have been described by Thorpe (P. M. 1872, 249), also by Foote, Linnemann, and O. Witt. As these pumps are intermittent in their action they work more slowly than others which are continuous, and have been superseded by them.

3. Injector or pressure-pumps. These consist of tubes of various forms, but generally furnished with a jet or narrow neck in front of a wider neck or expanding mouthpiece. Any liquid or gas under pressure, such as water or steam, may be used to work them, and in any position.

They are similar in principle and construction to the water-pump (fig. 1) described by Professor James Thomson (B. A. 1852–3) or the Giffard steam-injector, patented in 1858. The principle of the injector was, however, partially known long before. Hawksbee, in 1719, found that on blowing through a tube into a small box, the air escaping by another tube opposite the first, the pressure in the box became less than that of the atmosphere; and D. Bernouilli, in 1738, found that water from a higher source flowing towards the wide end of a conical tube could lift water from a lower level through a side tube attached near the narrow part of the conical tube. More recently, 1830–1850, the steam-jet aspirator was used by Carson, G. Stephenson, and others. MM. Clement and Desormes, in 1855 (A. Ch. 36, 69) showed that a light plate brought near a small orifice in the side of a reservoir of compressed air was attracted, and remained rapidly oscillating near the opening. This effect can be shown by blowing between the fingers against a piece of paper, or by blowing between two cards, as described in Weinhold's Physics, 812. All these experiments are examples of the passage of a fluid through an expanding mouth-piece, causing a diminished pressure as compared with that in front, which in each case is that of the atmosphere.

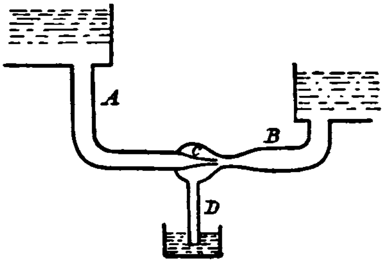


FIG. 1.

The first injector air-pump for laboratory use was that of Christiansen, described in 1872 (P. 196, 155). In fig. 2, A is a piece of thick-walled india-rubber tubing, perforated at B by a hot wire, and constricted at C by a ring drawn over the tube. On inserting at B a short piece of bent glass tubing, drawn out to a jet and connecting the top end of A with the water supply under moderate pressure, air is drawn in through the bent tube and a considerable vacuum obtained.

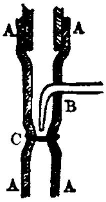


FIG. 2.

Other early forms of injectors were described by Lovett (C. N., May 1874, 209); Casamajor (Am. Ch., April 1874, and C. N., June 27, 1875, 33), and soon after these dates numerous forms were invented for the use of chemists, dentists, &c.

The experiments of Mr. W. Froude (B. A. 1875), though made for a different purpose, afford an excellent explanation of the action of injectors.

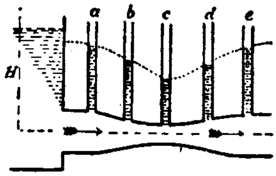


FIG. 3.

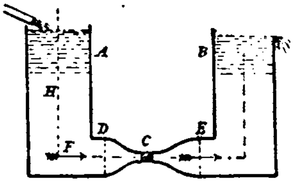


FIG. 4.

Mr. Froude showed that water under any head H, fig. 3, passing through a contracted pipe, does not exert an excess of pressure on the converging surface, which it meets, as is frequently stated, but that the pressure is least at the contracted part, as shown by the levels in the gauge glasses *a*, *b*, *c*, *d*, *e*. If the pipe be much contracted the pressure can be still more reduced, so that if two cisterns A and B, fig. 4, be connected by such a contracted pipe, a portion of the pipe at C may be removed without the flow of the liquid being interfered with; the water rising in the cistern B only slightly below its level in A. At F, in the central line of the connecting pipe, the full head of pressure H is exerted, but there is practically no movement, while at C there is no pressure, but very rapid movement. The pressure and velocity of movement are therefore convertible and complementary, and the differences of pressure at any two points vary as the differences of the squares of the velocities at those points. In any given case the pressure observed, *plus* that which has been lost in producing velocity, is constant and equal to the total head of water H, figs. 3, 4, 5. If we modify Mr. Froude's experiment and cut off the pipe at E, figs. 4, 5, the pressure at E is simply the general pressure of the atmosphere, and all the pressure due to the head of water in A has been changed into velocity, but the velocity at C must be greater than the velocity at E by as many times as the sectional area of the pipe at C is contained in its area at E. The velocity at C being so much greater than at E, the pressure must be less, and therefore less than that of the atmosphere. The tube G, fig. 5, may be regarded as a gauge to show the minus pressure, and if this gauge be supplied with mercury the latter may rise to near the height of the barometer. In place of water or liquid under pressure, air, steam, or any gas under pressure may be used, and injector air-pumps worked by steam have been proposed by Lovett, Kochinke, Teclu, and others.

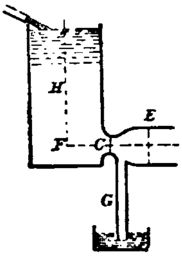


Fig. 5.

Injector air-pumps worked by water may be classified:

a. As in figs. 6, 7, where the water enters by a jet placed over a constricted tube or neck, the air being drawn in on all sides round the jet of water. The ratio of the areas of the jet and neck in this form is generally 1 : 2, or their respective diameters 1 : 1·4.

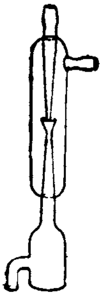


Fig. 6.

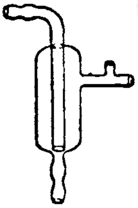


Fig. 7.

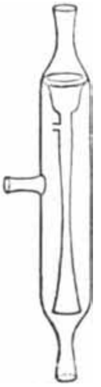


Fig. 8.

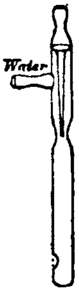


Fig. 9.

b. As in fig. 8, where the jet and neck are continuous and the air enters on one side only.

c. As in fig. 9, where the general form is similar to *a*, but the air enters by a very narrow jet and the water filling the body of the pump enters all round the jet.

These differences in construction are of little importance in the practical working of the instruments, but by altering the width of the apertures pumps suited to different pressures can be obtained. Pumps with very narrow apertures work best with a small quantity of water at very high pressures, whereas pumps with wider apertures require much more water at a low pressure. As the water passing through these instruments is practically a falling body, on multiplying the weight of water in pounds used per minute by its head or pressure in feet, we obtain in foot-pounds the power required to produce the exhaust in one minute's working of the pump. Compared in this manner the low-pressure pumps are less efficient than those working at higher pressures.

In using these injectors care should be taken to have a sufficient and constant water supply. The water tap turned full on should supply in one minute twice to three times the quantity required by the pump in the same time. In towns and large buildings where many persons are using the water at different levels, the pressure is often very variable, and a reservoir of water under pressure is necessary. A simple form devised by the author is a strong iron bottle (or an iron boiler) capable of standing a greater pressure than is likely to be required, say up to or over 100 pounds per square inch. This bottle A, fig. 10, has one tube passing to the bottom connected by a T piece with the water supply pipe, and it may carry a pressure gauge if desired. The connection with the water tap may be made with lead pipe and soldered joints, or with sound rubber tubing encased in a double thickness of strong canvas sewn over it, the connections being well bound with copper wire. The bottle being air-tight and water-tight under pressure, and full of air when connected with the supply pipe, the air cannot escape, but is compressed by the pressure of the water. Thus, at 15, 30, or 45 pounds' pressure the bottle becomes half, two-thirds, or three-fourths full of water, and with a variable pressure in the supply-pipe keeps the pressure more constant, and maintains the supply for some time, depending on the size of the bottle or reservoir. Passing from this reservoir, the supply-pipe is next led to the pump B, which may be conveniently fixed out of the way on a board against the wall behind the laboratory table. The board carries a barometric gauge to show the vacuum obtained.

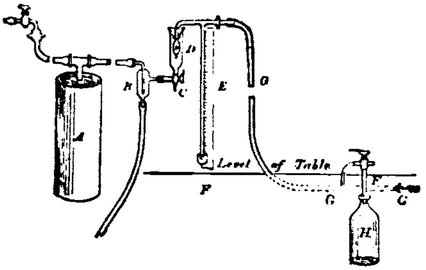


Fig. 10.

Passing from the pump, the water used runs into the sink on the laboratory table, or if desired it may be connected with a box or drum provided with an overflow at a certain height, so as to give a blast of air under pressure suitable for general blowpipe work. The vacuum tube from the pump is connected by means of the tap C (fig. 10) with the safety tube D, having a Bunsen valve fitted inside to the end of the vacuum tube, thence with the barometric gauge E and the laboratory vacuum tube G.

Table of the First Minute's Working of the Pumps.

Name of pump	(a) Exhausting the receiver of 2·2 litres capacity											(b) Blowing power			
	Water pressure in pounds per square inch										Ratio of volume of air pumped out to water used	Water pressure in pounds per square inch	Litres per minute		Ratio of air to water
	5	10	15	20	25	30	35	40	45	50			Air blown	Water used	
	Vacuum obtained in one minute														
	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.	mm.					
Alvergniat Frères (glass), fig. 6	—	302	395	442	481	515	564	577	—	—	Varies from 0·27 to 0·29	40	5·9	6·32	0·93
„ „ (brass)	—	182	240	322	385	426	452	468	—	—	„ 0·21 to 0·29	40	4·35	5·08	0·85
Arzberger and Zulkowsky (brass)[1]	221	286	374	468	530	—	—	—	—	—	„ 0·14 to 0·16	25	4·36	9·52	0·46
„ „ with outflow tube in lowest position	—	330	419	507	562	—	—	—	—	—	„ 0·14 to 0·16	20	4·51	10·8	0·42
„ „ in highest position	—	156	213	273	342	478	497	512	—	—	„ 0·17 to 0·28	40	3·90	5·44	0·79
Bendix (brass)	—	226	299	356	406	442	468	478	—	—	„ 0·22 to 0·25	40	4·65	5·92	0·79
Bulk (glass)[2], fig. 9	—	160	226	286	338	395	426	458	—	—	„ 0·24 to 0·32	40	2·65	4·26	0·62
Finkener (glass)[3]	—	—	—	—	447	551	582	—	—	—	„ 0·21	35	6·38	8·24	0·77
Fischer (glass)[4], fig. 7	—	203	247	286	322	380	408	419	—	—	„ 0·33 to 0·35	40	5·15	3·52	1·46
„ (brass, by Dreyer & Co.)	—	135	205	268	312	351	390	421	—	—	„ 0·35 to 0·54	40	3·21	2·26	1·48
„ (brass, by Desaga)	—	226	261	364	390	416	439	491	—	—	„ 0·36 to 0·37	40	4·73	3·80	1·22
„ (brass, copy by ?)	—	143	226	265	283	312	346	380	—	—	„ 0·30 to 0·40	40	2·90	2·75	1·05
Geissler (glass)[5]	—	117	162	179	205	234	252	307	329	—	„ 0·21 to 0·25	40	1·76	3·53	0·50
Knecht (brass)	—	—	—	161	252	278	286	296	299	—	„ 0·35 to 0·54	40	0·90	1·73	0·52
Körting (brass)[6]	195	333	426	499	546	582	—	—	—	—	„ 0·15 to 0·23	30	4·15	8·32	0·50
Mawson and Swan (No. 1 glass)[7], fig. 8	—	182	239	273	320	331	439	458	—	—	„ 0·23 to 0·28	40	3·00	4·88	0·62
„ „ (No. 2 glass)[8]	—	138	179	202	247	289	432	447	—	—	„ 0·16 to 0·28	40	2·95	4·96	0·59
„ „ (No. 3 glass)[9]	—	130	192	229	266	309	335	376	—	—	„ 0·28 to 0·36	40	2·25	3·01	0·75
Muencke (No. 971 glass)	—	276	338	395	429	458	486	—	—	—	„ 0·18 to 0·19	35	3·30	8·52	0·39
„ (No. 970 glass)	234	307	398	473	515	—	—	—	—	—	„ 0·14 to 0·16	20	2·76	8·60	0·32
„ (No. 948 small brass)	—	—	—	—	—	356	390	413	432	453	„ 0·53 to 0·56	50	2·75	2·86	1·12
„ (No. 952 adjustable brass with three-way tap)	—	—	—	356	426	486	507	535	—	—	„ 0·31 to 0·34	40	4·00	4·72	0·85

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[1] Ann. d. Chem. u. Pharm. Bd. 176, p. 327, 1875.

[2] Ber. d. deutsch. chem. Ges. 1876, p. 1871.

[3] Winkler's Industrie Gaze, i. p. 23.

[4] Dingl. Poly. Jour. 1877, 221, p. 136 and 225, p. 342.

[5] Sent out about 1876.

[6] Sent out about 1880.

[7] Sent out about 1876.

[8] Sent out about 1877.

[9] Sent out about 1879.

Fig. 11 shows the tap in full size which is fitted C (fig. 10) to the bottom of the safety tube and to the laboratory vacuum tube at each working place on the tables F (fig. 10). An ordinary good gas tap, which should be specially ground so as to be as air-tight as possible, has the little screw and washer at the bottom of the plug removed and a hole bored from C into the ordinary through hole of the tap, the latter being soldered up at one side at D, so that the hole is from the bottom to one side only, and the plug is then trimmed and reground. A piece of tubing FF is then soldered on to the body of the tap and a pointer E soldered on to the top of the plug to point which way it is open. When the plug is turned across in the ordinary position of a closed tap, it is closed to both A and B; when the pointer points to A it is open towards A, and if towards B to B. The tube FF is fitted air-tight by means of a stopper in the bottle H (fig. 10).

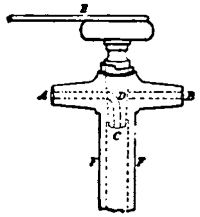


FIG. 11.

By means of these taps (devised by the author in 1883) one pump can do all the exhaustion work in an ordinary laboratory for a number of filtrations going on simultaneously. The pump is connected with a main-pipe of soft lead tubing passing along or under the laboratory tables, and at each worker's place is a bottle like H (fig. 10) fixed below the table, the tube FF from it rising above the table. One end of the tap, say A, is connected with the vacuum main-pipe by soldered lead tubing; the other end of the tap is connected by a flexible tube with the filtering apparatus or other vessel to be exhausted.

In using this arrangement all the vacuum supplied at B must come from the bottle below FF, and not from the main pipe, which is then shut off. When the vacuum is not required at B the tap is turned towards A to raise the degree of exhaustion in the bottle. As these bottles are of half-gallon or 2·2 litres capacity, a moderate vacuum in one of them (say half to three quarters the height of the barometer) is sufficient for a filtration on the small scale, and as there are a number of such bottles in the laboratory they form together a vacuum reservoir of some magnitude available at once without waiting. If well fitted the taps retain the vacuum for several days. A lute made by dissolving india-rubber in vaseline at as low a temperature as possible is of good service for these taps and connections.

The author has made a series of comparative tests of the pumps in common use (S. C. I. 1877, 69–76). With a supply and pressure of water suited to each pump, and exhausting receivers of the above capacity, 2·2 litres, vacua corresponding to from half to three quarters of the height of the barometer could generally be obtained in one minute's working; such vacua are quite sufficient for ordinary filtrations.

As the apparent size of these instruments is somewhat misleading, the quantity of water used is the real test of size; pumps of the same construction but of different sizes would exhaust a receiver at different rates but in proportion to the water used.

The annexed table gives the results in brief of tests made with the pumps most frequently found in use, first, in exhausting a receiver of 2·2 litres capacity; and second, in blowing air, with the exhaust tube of the pump open to the atmosphere. The results of the first minute's working only are given, though the tests were carried out to ten minutes. In each case those pumps which worked best during the first minute continued to do throughout, and came nearest to the height of the barometer at the end of the exhaustion.

The blowing power of each pump is also a test of its exhaustive power, as in blowing with the pump open to the atmosphere, it is practically exhausting an infinitely large receiver.

Of the high-pressure pumps, those of Fischer, Bulk, Knecht, and Muencke's brass pumps give good results, and of the low-pressure pumps, which use more water, those of Arzberger and Zulkowsky, Finkener, and Körting are good. Alvergniat's glass and brass pumps are intermediate in character, and work well through a considerable range of pressure.

Given abundance of water at sufficient pressure the pumps which give the most rapid exhaustions are those of Finkener, Körting, Alvergniat, Arzberger and Zulkowsky, but where economy of water is desired the high-pressure pumps ought, if possible, to be used. Though considered as machines doing work for the power put into them none of these injectors are very perfect, yet they are exceedingly convenient, and it will be observed that all those tested give *at some particular* pressure in one minute's working sufficient vacua for filtrations and similar laboratory work.

In choosing an instrument for laboratory use, one should ascertain the average quantity of water per minute delivered by the fully open water tap and also the average pressure in the closed water pipes. The pump selected should require not more than half the quantity of water delivered by the open tap, and should work well at from half to two-thirds of the pressure in the closed pipes. T. F.

FILTRATION. The process of filtration consists in the separation of solid particles from a liquid or gas by allowing the fluid to percolate through some porous material, as paper, sand, or cloth, the solid particles being left behind. This process of filtration is carried on naturally during the percolation of water through the soil to supply underground reservoirs and springs. In a similar way it is made use of to purify the water supplied to towns by passing it through beds of sand and gravel, and on the domestic scale by filtration of water through animal charcoal, sponges, iron, &c. This special branch of the subject, however, is treated separately, the following article being confined to the application of filtration in the arts and manufactures, and more especially in the preparation of various chemicals used in these processes.

In the laboratories it is customary to use filter paper (unglazed paper specially prepared, to be free of impurities) folded into a cone and slipped into a glass funnel. The precipitate is then paired into the funnel and the liquid passes through the paper, leaving the solid precipitate behind. For filtering larger quantities a square frame of wood is used, over which a piece of calico sufficiently close in texture is loosely stretched. This is placed over a basin and the precipitate poured on to the cloth. In many cases the process of filtration on a commercial scale is carried on in this way, without any more elaborate mechanism.

Pressure filtration.—When it is desirable to hasten the process, arrangements are made whereby a partial vacuum can be maintained beneath the filter paper, thus pouring the liquid through at a more rapid rate. For this purpose many forms of filter pump are used in the laboratory. Most of these are varieties of the injector or pressure pumps, which depend on the laws relating to the flow of liquids through an expanding mouthpiece. When water, under any head, is passing through a contracted pipe, the pressure is least at the contracted part, where the velocity is greatest. The pressure at any point varies inversely as the square of the velocity at that point. If the pipe below the constriction opens into the air, the pressure there is the pressure of the atmosphere. But the velocity of the water at the constriction is greater than the velocity at the opening by as many times as the sectional area of the pipe is greater at the one place than the other. Consequently, the pressure at the constriction is below that of the atmosphere. By taking advantage of this a pump for sucking air is constructed. The water entering by a jet just over a constricted tube draws in air along with it. As a rule, the diameter of the jet is to that of the constricted portion as 1 : 1·4. Fairley has made a large number of experiments with different pumps to test the vacuum produced, the quantity of air sucked through in the first minute, and the quantity of water and pressure required. By examining his tables it is possible to pick out the pump best suited for special work or for a special water supply. As mechanical machines doing duty for energy supplied, none of these pumps are very efficient; but those of Fischer, Körting and Muencke seem the best (*v.* FILTER PUMPS).

On the large scale the suction is applied by means of pumping engines drawing away the filtered liquid. For instance, in order to drain off the caustic liquor still held in the precipitate of lime and carbonate of lime formed during the conversion of carbonate into caustic soda, the lime sludge is run into shallow tanks with false bottoms covered with powdered chalk, and suction applied underneath the cloth by means of pumps.

To obtain 12 tons of lime sludge, a vessel 28 feet by 14 feet is required, and about 48 hours are occupied in filtering and washing. The sludge contains about 40 p.c. of water, and the cost is 2*s.* per ton.

Upward filtration.—In certain cases, instead of filtering downwards, filtering upwards is resorted to; the filtering cloth, stretched on a suitable frame, being dipped down into the liquid and suction applied behind or pressure applied in front of it. This arrangement is advantageous in certain cases, as it prevents the accumulation of a mass of precipitate over the filtering surface, but is obviously only applicable when the liquid to be filtered is supplied for a considerable period, the precipitate accumulating at the bottom of the vessel.

The nature of filtration.—If we examine under the microscope a piece of filtering cloth or filter paper, we see it to be made up of fine hairs loosely interlaced, having the appearance of a network of interwoven sticks with considerable holes between. These holes are enormous as compared with the size of the particles of a precipitate when first thrown down, and, consequently, the process of filtration does not depend on using as filtering mediums a substance sufficiently porous for the passage of liquid but too fine in texture to allow the passage of precipitate. It seems rather to depend on the property of most precipitates of coalescing into larger masses. This coalescence is assisted by the filtering cloth or paper, as it forms a scaffolding or skeleton upon which these larger masses of precipitate are built up by the coalescence of the smaller particles. A remarkable example of this process is the filtration of Prussian blue. Although this precipitate is in so fine a state of division that a grain will colour two or three gallons of water, yet, after the first liquor has passed through, there is no difficulty in filtering it. The precipitate thus forms its own filter bed, only using the filter paper or cloth as a skeleton on which to build.

In the case, however, of certain precipitates the particles refuse to stick together, and (as in the case of the sulphide of cobalt) require prolonged boiling to assist this process before they can be filtered.

Further, there are precipitates which, instead of forming a bed through which the liquid can percolate, form a gelatinous layer over the filtering surface practically impervious to water. Any attempt to filter such substances is quite hopeless. As an example, precipitated sewage sludge to which insufficient lime has been added, or 'finings' in beer, may be taken. The only hope in such cases is to devise some different mode of preparing the precipitate, or some method of treatment which will modify this property, as no machine yet in the market is capable of dealing with such substances. It will be seen from the above remarks that filtration depends upon certain obscure and little-investigated properties of freshly-formed precipitates, and that it is therefore impossible to tell beforehand whether a given precipitate can be filtered, or what is the best method for treating it.

Filtering machines.—Innumerable varieties of filtering machines have been invented, but these inventions can easily be classified. We have:

First. Filter presses.

Second. Centrifugal machines.

Third. Machines in which the surface of the cloth is scraped to keep it clean.

Fourth. Machines in which the cloth is an endless band, one portion being used for filtration while another portion is being cleaned.

The two first types of machine we shall consider in detail.

Of the two second types it is sufficient to state that they have never come into general use, and therefore are of no special importance from the point of view of an article of this kind.

Filter Presses.

The earliest known filter press is described in a patent taken out by Bramah about 1790. Numerous patents are taken out every year for so-called improvements in filter presses; but the machines have already been reduced to the simplest possible construction, and consequently these patents are of little, if any, importance.

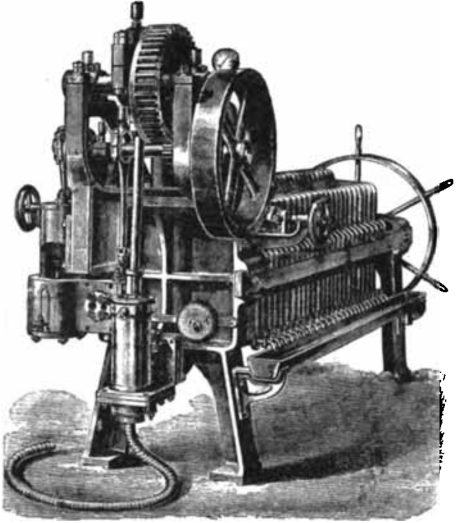


Fig. 1.

Construction of the press.—The filter press consists of a series of cells lined with filtering cloth into which the substance to be filtered is pumped under pressure. The liquid passing through the cloth is drained away, so that at the end of the process each cell is filled with a hard cake of precipitate. They are then opened, the cakes of precipitate allowed to fall out, the cells closed up again, and the machine is then ready for another filtering operation.

Types of machine.—The presses in use consist of three varieties, known respectively as *recessed plate*, *flush plate*, and *washing machine.*

Recessed plate machine.—The recessed plate machine may first be described as giving the essential points in all such machines. The following is a description of the different parts of the machine. It consists, first, of a series of circular or flat plates of cast iron, with a flange at back and front, resembling on each side a shallow soup plate in appearance. Each of these plates has a hole in the middle, and it is covered on each side with a series of fine grooves, so arranged as to communicate with a hole near the bottom of the plate and passing outside. Second, of a frame consisting of two end pieces rigidly bolted together by long tie-rods. The cast-iron plates hang by means of hooks, cut in them, from these tie-rods, and can be slid backwards and forwards upon them. Through one of the end pieces a powerful screw passes. Third, of a pump attached to the frame. Fourth, of a series of pieces of filtering cloth, each consisting of two pieces of cloth, cut the same size as the cast plates, and sewn together round a hole in the middle.

To prepare the machine for use one of these pieces of cloth is drawn through the hole in one of the plates, leaving the other piece on the other side. The plate is thus covered with cloth on both sides, the cloth being continuous through the hole. Each plate having been thus prepared they are all shoved up against each other, the cloth forming a washer between each, and screwed up tight by means of the screw. We have then a series of cells communicating by a central tube with the pump, and lined with filter cloth. The precipitate is then pumped in and the liquid passes through the cloth, runs down the grooves on the plates and passes out through the holes in the plates either into a continuous tube or through a series of taps into a trough placed below the machine.

When the cells are filled with precipitate, the screw is run back and the end plate moved along the tie-rods. The cake of precipitate falls out, and the next plate is then moved up to it, and so on. until all the plates have been shifted. They are then shifted back into their old positions, screwed up again, and the machine is ready for a new filtering operation.

The flush plate machine differs slightly in construction. Instead of having a raised edge round the plates, they are cast flat, and a frame is placed between every two plates. The liquid is introduced by a tube in one corner of the plate, made by drilling holes facing each other through the plates and frames. The hole in the frame has a slot cut into it to admit the liquid into the space between the plates. A piece of cloth is used twice the length of the plates, which is simply hung over the frame, falling down on each side of it.

This machine is the simplest in working, as the cloth does not require to be cut and sewn, and can easily be removed, but it is not suitable for high pressures on account of the multiplication of joints. It is consequently used for pressures between 70 lbs. and 200 lbs. on the square inch; the recess plate machine being used for higher pressures.

The washing machine is a modification of the flush plate machine. It is designed for the washing of the cake after it has been formed in the press, the method being to force the washing liquid in behind one filtering cloth and cause it to pass through the cloth and the cake and the opposite cloth, and so into the discharge pipe. For this purpose the usual feeding tube is closed and the washing liquid forced in by a tube communicating with the space behind every alternate filtering cloth, the tap in connection with that cloth being turned off. In the case of a machine discharging into one outlet, two tubes are formed in the two bottom corners of the plates, communicating with alternate chambers. During ordinary filtering, both are left open. During washing, one is connected to the pump supplying the washing liquid and the other is left open. In these machines two supply tubes are also used communicating with alternate chambers.

Sizes of machine.—Filtering presses are made of various sizes according to the work they have to do, from those suitable for laboratory operations up to machines with plates four feet each way, such as those constructed for the Metropolitan Sewage Works, and holding from 10 lbs. up to 4 or 5 tons of cake at a charge. The actual process of opening, cleaning, and closing occupies about 15 minutes. The time occupied in filtering varies directly as the square of the thickness of the cakes and the rate of filtration varies with the substance to be filtered. In some cases a 4 or 5 ton machine gets through 200 tons of stuff in a day.

Filter cloths.—The substances used as filter cloths are made of cotton, linen, woollen, jute, or paper, built on a fine net. Asbestos cloth is also being experimented upon. Woollen cloth is best for acids. These cloths are usually especially manufactured for the purpose. For filtering wines and liquids where a very clear effluent is required, 'raised' cotton cloth is used, that is cloth which after weaving has had the surface teased up so as to cover it with a soft down of cotton fibre. Messrs. Johnson & Hutchinson have invented a press in which no filter cloth is used, the filtering surface being made up of bars laid together, with or without sand, &c., in the slits between them (Pat. 4,766, 1888).

Filtering machines are used for the following special kinds of work:—

Use of filter presses.—1st. For the obtaining of a plastic mass from a liquid mud, as in the preparation of china clay, the thin mud or slurry being passed through presses to make it fit for the potter.

2nd. For filtering suspended matter from liquids where a clear effluent is the object, as in filtering the lees from wine and yeast from beer, or filtering the effluent from works before admitting it to a stream.

3rd. For partially drying a precipitate and thus saving fuel, as in the preparation of paints and the treatment of sewage sludge from the precipitating tanks. In the case of sewage sludge the water present is reduced from 90 p.c. to 50 p.c., or from 1 : 9 of water to 1 : 1, so that $\frac{8}{9}$ths of the water is eliminated and the sludge reduced to $\frac{1}{5}$th of its weight.

4th. For washing precipitates.

5th. For the filtration of oils.

For instance, linseed, rape, and cotton oils, after expression, are pumped warm from the spell tank through a filter press, thus saving the time and space necessary for the months of settling formerly necessary.

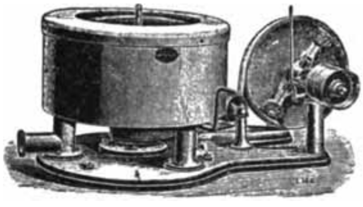
Also in the preparation of cod liver oil, it is cooled to 12°F. to crystallise out stearine, and pumped at this temperature through a filter press, and thus prepared, remains liquid during the winter.

The following figures will give some idea of the work turned out by these machines. They are taken from 'Engineering' and apply to the Leyton Sewage Works. Two of Johnson's machines turn out 50 tons of sewage cake a week, reducing the water from 90 p.c. to 50 p.c., at a cost of 2*s.* 6*d.* per ton for labour, lime, and fuel, and 1*s.* per ton for interest on capital, wear of cloth, &c.

CENTRIFUGAL MACHINES.

The two types of centrifugal machines in common use are known respectively as under-driven and over-driven machines.

Construction of machines.—They consist essentially of a perforated cylindrical cage, fixed to a central shaft, and surrounded by a case. On spinning this cage at a high rate of speed, anything contained in it is driven to the circumference, and if of sufficiently fine texture, passes out through the perforations in the case, and flies off tangentially. Consequently, if we wish to separate, say, crystals from their mother liquor, on placing them in a centrifugal machine, the mother liquor escapes through the perforations in the case, leaving the crystals behind.



(UNDER-DRIVEN TYPE)

FIG. 2.

Improvements.—The following sketch gives a sectional representation of such a machine. Given the centrifugal machine, the only improvement of first-class importance was first that of Weston of America, which was designed to get over the difficulty that the crystals, &c., do not necessarily distribute themselves evenly round the centre of revolution. This is a serious matter with machines running at so high a speed, tending to the injury of the bearings. Weston therefore devised an arrangement whereby the shaft was enabled to adjust itself to the centre of gravity of the cage *plus* its contents, by making a flexible connection between the portion of the shaft carrying the cage and the portions running in the bearings.

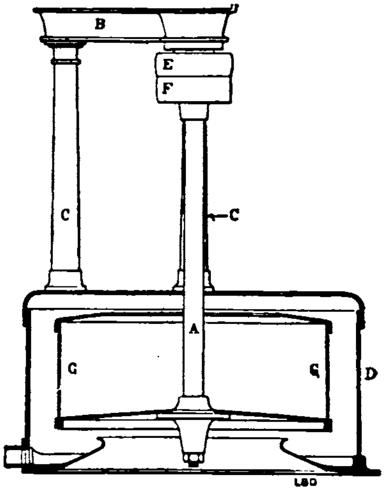


FIG. 3.

The same advantage was afterwards secured by the Hepworth patent. In the Hepworth machine the outer casing as well as the inner cage is hung from a flexible support, so that while the cage always remains in the centre of the case, the whole cage and case adjust themselves to the new centre of gravity. These machines are manufactured by Messrs. Manlove, Alliots, Fryer & Co.; the Weston patent being adopted by Messrs. Laidlaw and Watson.

Application of centrifugals.—It is unnecessary to say anything in detail of the various arrangements for supplying power to these machines, and the next matter of importance is the application of the machines to manufacturing processes, and the different types of machine made to suit different kinds of work. These applications may be stated under three heads.

1st. The treatment of coarse-grained solids, such as crystals, for the separation of the mother liquor.

2nd. The treatment of fine-grained but heavy solids, such as paint, for a separation of a portion of the liquid in which they are immersed, to facilitate drying.

3rd. The treatment of mixtures of liquids of different specific gravity, or liquids and semi-solids, for their separation from each other.

First application.—The largest application of centrifugal machines is in class 1. They are used to separate the syrup from sugar crystals, and in the preparation of ammonia soda by the Solvay process. In fact they can be advantageously used in most operations where the removal of mother liquor from crystals is required. They are often used when the solid substance to be separated is sufficiently coarse-grained, as in the treatment of fish refuse for making into manure, and have obviously many useful applications. Steam is often introduced to wash the crystals.

Second application.— Figure 4 shows in section machines of the second class for the treatment of heavy precipitates. They differ from the ordinary machines in having perforations in the top and bottom of the cage as well as the sides. When in use they are completely lined with filter cloth. This machine has been brought out by Messrs. Laidlaw and Watson, of Glasgow, and the patent is No. 16,014, 1885.

It is used among other places by Messrs. Freeman & Co., of Battersea, in the manufacture of their non-poisonous white lead, for partially drying a precipitate produced in the presses. On introducing the precipitate as a thin mud, and starting the machine, all the solid particles plaster themselves against the side of the cage, and the water escapes through the top and bottom openings. In this way the percentage of water is reduced in a few minutes from 25 p.c. to 11 p.c., the precipitate being removed in a stiff state, just breakable by wooden spuds. The precipitate has a sp.gr. of 5·5–6. For very light flocculent precipitates these machines are not so successful.

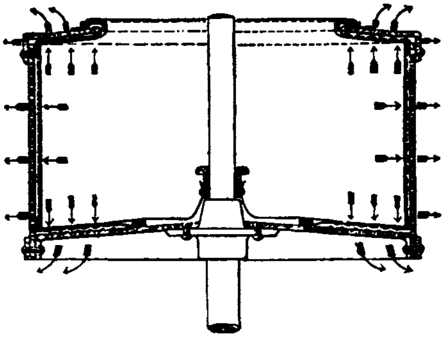


Fig. 4.

Third application.—The third type of machine is used principally as a cream separator. The cage has no perforation. The milk is introduced at the top and the skim milk and cream drawn off respectively by tubes connected to the circumference and the centre of the cage. In this way the process is carried on continuously.

New applications of the centrifugal machine are continually suggesting themselves. One of the latest is in the preparation of gelatine emulsion for dry plates.

Statistics.—The following table gives an accurate statement of the work done by the ordinary machines. Soda crystals may be taken as equal to the second quality of sugar.

Diameter of basket in inches	Indicated horse power	Sugar cured in tons per day of ten hours, and per each machine — In refinery—Qualities		
		1st	2nd	3rd
12	·5	·55	·40	·280
18	·7	1·56	1·25	·830
24	1·7	5·00	4·00	3·00
30	3·0	10·00	8·00	6·00
36	3·7	12·5	10·0	7·5
42	5·0	13·75	11·00	8·25
48	6·0	15·0	12·0	9·0
54	7·5	16·25	13·0	9·75
60	8·5	17·5	14·0	10·5
66	10·0	20·0	16·0	12·0
72	11·0	22·5	18·0	13·5

In conclusion reference may well be made to a very interesting problem in filtration at present being experimented on. This is the filtration of sewage sludge, more than once referred to during this article. The late Metropolitan Board of Works decided to precipitate the London sewage, and the treatment of all this sludge is a practical problem of immense difficulty. If successfully solved we may expect to see all the large towns building sewage precipitation works, and converting the sludge into a portable form suitable for manure by passing it through some form of filtering machine to reduce the percentage of water it normally contains. A. P. L.

FINE BLUE, GENTIAN BLUE 6B, SPIRIT BLUE, OPAL BLUE, BLEU DE NUIT, BLEU LUMIÈRE. The hydrochloride, sulphate, or acetate of triphenyl rosaniline and triphenyl pararosaniline *v.* ANILINE BLUE and TRIPHENYLMETHANE COLOURING MATTERS.

FIRE-CLAY. A refractory clay capable of withstanding a very high temperature without fusion or perceptible softening, and hence largely used for the manufacture of fire-bricks, gas-retorts, crucibles, and glass-house pots. The best fire-clays are obtained from the coal-measures, the most celebrated in this country being that of Stourbridge in Worcestershire. This clay is remarkable for the small amount of contraction which it undergoes when fired, the shrinkage of the unrefined clay being in some cases as low as 1 p.c. (G. Maw). In order to reduce shrinkage, the fire-clay is often mixed with ground potsherds to the extent of about one-third of its weight. The comparative infusibility of fire-clays depends on their high percentage of silica, and on the small proportion of alkalis present. Many highly-siliceous substances, which are not true clays, have come to be used in the preparation of certain fire-bricks: thus the so-called 'Dinas clay,' from the Vale of Neath in Glamorganshire, largely employed in the copper-smelting furnaces of South Wales, is really a disintegrated sandstone, containing as much as 98 p.c. of silica. Another highly-siliceous rock is the *ganister*, which forms the seat-stone beneath certain coal-seams in the lower coal-measures of Yorkshire, and is extensively used, when ground and mixed with water, for lining Bessemer converters. The following analyses represent the composition of certain fire-clays:—

—	I.	II.	III.
Silica . . .	65·10	67·12	68·12
Alumina . .	22·22	21·18	26·69
Ferric oxide . .	—	1·85	2·00
Potash . . .	0·18	2·02	1·17
Lime . . .	0·14	0·32	1·15
Magnesia . .	0·18	0·84	0·59
Ferrous oxide .	1·92	—	—
Water, combined .	7·10	4·82	0·20
„ hygroscopic	2·18	1·39	—
Organic matter .	0·58	0·90	—
	99·50	100·44	99·92

I. Stourbridge, by C. Tookey. II. Dowlais, by E. Riley. III. Better-bed fire-clay, Bowling, Yorkshire, by J. W. Westmorland. No. I. contained 0·06 p.c. P_2O_5; III. contained 0·87 p.c. TiO_2. Riley has found as much as 1·05 p.c. TiO_2 in a Stourbridge fire-brick (S. C. I. 15, 1862, 311). For a large series of analyses of British and foreign fire-clays, *v.* Percy's Metallurgy; Fuel, 1875, 87. F. W. R.

FLAGSTONE. A stratified rock which may be split along the planes of bedding into smooth-faced slabs, suitable for use as paving-stones. If the stone is too absorbent, or finely laminated, the surface is apt to flake off by the action of frost. As hardness and durability are essential in a flagstone, sandstones are superior to calcareous or argillaceous rocks. The flaggy sandstones are generally micaceous; and their fissility may be partly due to the presence of mica along definite planes. The best English flagstones are derived from the lower coal measures, the millstone grit, and the Yoredale rocks. Most of the flags used for paving the streets of London are obtained from the Yorkshire coal-field. The Elland flagstone, which is extensively worked, is a fine-grained micaceous sandstone from the lower coal measures, or ganister series, extending with persistence through the coal-fields of Yorkshire, Lancashire, and Derbyshire. In Scotland, the lower old red sandstone yields paving slabs of very large size, the best-known being the dark-grey flagstones of Caithness and the Arbroath pavement of Forfarshire.

F. W. R.

FLAKE WHITE. A variety of white lead, *v.* LEAD. The term is also applied to basic bismuth nitrate.

FLAVANILINE *v.* QUINOLINE.

FLAVAURIN. A yellowish-red powder consisting of either the ammonium or sodium salt of dinitrophenolsulphonic acid, and obtained by boiling mononitrophenol, ortho- or para-sulphonic acid with dilute nitric acid (Leipziger Anilinfabr. Beyer and Kegel, Germ. Pat. 27,271, June 8, 1883, expired October 1886). Flavaurin dissolves readily in water, forming a yellow solution, and was introduced as a yellow dye for silk and wool.

FLAVENOL *v.* QUINOLINE.

FLAVIN *v.* QUERCITRIN BARK.

FLAVOLINE *v.* QUINOLINE.

FLAVOPHENIN *v.* AZO- COLOURING MATTERS.

FLAVOPURPURIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

FLAX. This term, as applied to the fibre of commerce, designates the product of the plant *Linum usitatissimum*, belonging to the Nat. order *Linaceæ*, a group consisting of herbs and small shrubs indigenous to all temperate climates. *Linum usitatissimum* now only occurs in its cultivated condition. It has solitary erect stems attaining a height of from twenty to forty inches. The cultivation of flax is of insignificant extent in England and Scotland, but is of much greater importance in Ireland. It forms also an important crop in some parts of Belgium, Holland, France, and Russia.

The plant having attained about two-thirds of its full height is ready for gathering; as when allowed to grow to maturity a coarser and less valuable fibre results. The stem consists of an internal woody core, an external cortex, and an intermediate cellular tissue (the bast) from which the flax is prepared. The operations necessary in the preparation of the fibre for the purposes of the spinner are (1) Pulling; (2) Rippling; (3) Steeping, Retting, or Watering; (4) Grassing; (5) Breaking; (6) Scutching; (7) Heckling. Of these 'pulling' is a distinctive method of gathering the flax-plant, which is always torn up by the roots and not cut down like other crops. A fine day is selected for this purpose, and the stems are as far as possible arranged in sizes by the pullers; those also being assorted which may have been damaged by wind and rain. 'Rippling' is the process of removing the seed-balls by drawing the heads through a species of comb set up usually in the field wherein the flax is being harvested. 'Retting' consists in immersing the stems in pools or streams of water in such a position as that they shall stand almost erect, although weighted down so as to be quite submerged. The object of this is to induce fermentation, which dissolves the glutinous matter and disintegrates the fibres. Pure soft water and great judgment in the proper length of time to be allowed, which may be ten days to a fortnight, are essentials in this part of the treatment. Retting is followed by 'grassing,' whereby the separation of the flax fibre from the ligneous portions of the stalk is further facilitated. It consists in spreading the stems on the grass for a week or a fortnight, during which time they are occasionally turned. The flax during this operation becomes somewhat bleached. 'Breaking' and 'scutching' are the means employed to strip off the hard epidermis, and are effected either by hand or machinery. 'Heckling' is a still further combing, which arranges the fibres in parallel order, ready for the manufacture of yarn.

According to Kolb, retting sets up a peculiar fermentation which results in pectose or its analogous bodies being changed into pectin and pectic acid; of which the former being soluble is left in the water, whilst the latter being insoluble remains attached to the fibre until its treatment with hot alkaline ley in bleaching, when it is changed into soluble metapectic acid.

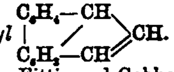
Under the microscope, flax fibre has the appearance of a cylindrical tube, not continuous as in the case of cotton, but broken up by septa or knots at irregular distances through the length of the fibre, varying from four to six times the diameter of the tube. This diameter is from about $\frac{1}{1100}$th to $\frac{1}{1800}$th of an inch. The adhesive power of the fibres, which gives the strength when spun into yarn, appears to depend on the twist given by the spindle as well as by the tenacity of the rough cellular sheath, which remains always more or less incrusted with the characteristic resinous deposit. Advantage is taken of the presence of this gummy deposit to detect the admixture in fabrics of cotton with linen; as, although the ultimate basis of both is cellulose, cotton exists in a much purer state than flax. The difference in the reaction upon them by caustic alkalis points out such admixture. When immersed in a boiling solution of caustic potash and water for about a minute, and then pressed between folds of filter paper, flax exhibits a dark-yellow colour, whilst cotton when similarly treated either remains white or becomes a very bright yellow. The same solution of potash employed cold, colours raw flax orange-yellow, whilst cotton becomes grey, a result which Kuhlmann believed to be due to the pectic substances contained in flax. For an account of the culture and manufacture of flax and a description of Schenck's method of retting in water of 27° to 32°, whereby the duration of the process is curtailed, and for statistics, *v.* Ency. Brit. articles AGRICULTURE and FLAX.

FLINT. (Fr. *Silex*; Ger. *Feuerstein*.) A variety of chalcedonic silica, found chiefly in the Upper Chalk, where it occurs either as irregular nodules or in tabular masses, and more rarely in veins. It appears to be generally a mixture of opaline silica with microlites of quartz: hence it is acted upon unequally by solvents, the colloid silica being more soluble than the crystalline part. Organic remains, especially sponge-spicules, are frequently inclosed in flint, and much of it seems to have been formed by the deposition of gelatinous silica around sponges: in other cases it may represent a silicified chalk-ooze. The nodules of flint are often hollow, sometimes lined in the interior with crystals of quartz, or with mammillated chalcedony, and inclosing fossils. Flint varies in colour from yellow and brown to black: according to Professor Judd the black colour is due to all the interstices of the flint being filled with colloid silica, while the white surface of an exposed flint is produced by removal of this interstitial silica in solution; the opaque white character of a calcined flint results from the formation of innumerable fissures throughout the mass (Proc. Geol. Assoc. 10, 1888, 219).

Flint differs from most other natural forms of silica by breaking with a conchoidal fracture, the fragments having sharp edges well suited for cutting. This character led to its extensive employment, before the introduction of metals, as a material for the implements and weapons of prehistoric man. Although brittle when first taken from its bed, it gradually loses moisture and acquires toughness. In many chalk districts, flint is used as a building stone and as a road-material; while in the form of flint gravel and shingle it is largely employed elsewhere on roads. When struck with steel, or with iron pyrites, sparks are elicited; whence the former use of flint in the tinder-box and in flint-locks. Gun-flints are still made to a limited extent, chiefly for the African market; the art of 'flint knapping' surviving at Brandon in Suffolk. When calcined and thrown suddenly into cold water, flint may be easily pulverised; and the snow-white powder thus produced is used, as a pure form of silica, in the manufacture of pottery and glass. F. W. R.

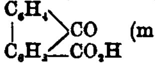
FLUID GELATIN *v. Aluminium oleate*, art. ALUMS.

FLUORANTHENE *Idryl*



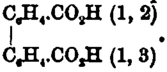
$$\begin{matrix} C_6H_4-CH \\ | \qquad\quad CH \\ C_6H_3-CH \end{matrix}$$

Discovered independently by Fittig and Gebhard (B. 10, 2143; A. 193, 142; *v.* also Fittig and Liebmann, A. 200, 1) in coal-tar, and by Goldschmiedt in 'stupp,' a mixture of hydrocarbons obtained in distilling mercury ores at Idria (B. 10, 2022; Goldschmiedt and Schmidt, M. 2, 1). Best obtained from the fraction of coal-tar boiling higher than anthracene by redistilling it under reduced pressure and collecting the fraction passing over at 250° under a pressure of 60 mm. This fraction, which consists of a mixture of fluoranthrene and pyrene, is treated in alcoholic solution with picric acid; the picric acid compounds of the two hydrocarbons are separated by crystallisation, and the fluoranthene compound $C_{15}H_{10},C_6H_2(NO_2)_3OH$ (long reddish-yellow needles, melting at 182–183°) is decomposed with ammonia.—Slender needles or monoclinic plates, melting at 109–110°. Boils at 250–251° under a pressure of 60 mm. Sparingly soluble in cold, readily soluble in boiling alcohol; soluble in ether, carbon disulphide, and glacial acetic acid. Chromic acid oxidises it to a quinone $C_{15}H_8O_2$ (red needles, m.p. 187–188°), which on further oxidation yields *diphenyleneketone-carboxylic acid*



$$\begin{matrix} C_6H_4 \\ | \qquad\quad CO \\ C_6H_3-CO_2H \end{matrix}$$

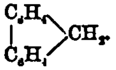
(m.p. 191–192°). This last is converted by heating with lime into *diphenylene-ketone* (*v.* FLUORENE), and by fusion with caustic potash into *isodiphenic acid*



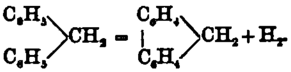
$$\begin{matrix} C_6H_4.CO_2H\ (1,2) \\ | \\ C_6H_4.CO_2H\ (1,3) \end{matrix}.$$

F. R. J.

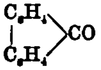
FLUORENE *o-Diphenylene-methane*



Discovered by Berthelot in coal-tar (C. R. 65, 465; A. Ch. [4] 12, 222). Obtained by Gräbe (A. 174, 194) by passing the vapour of diphenylmethane through a red-hot tube



By the reduction of diphenylene-ketone



either by distillation with zinc-dust (Fittig, B. 6, 187) or by heating with hydriodic acid and amorphous phosphorus to 150–160° (Gräbe, B. 7, 1625).—The tar oils of high boiling-point are allowed to deposit their naphthalene and anthracene, and the liquid portion is then submitted to fractional distillation, collecting in the first distillation from 290 to 350°, and in the second from 300 to 320°. The latter portion, when cooled in a freezing mixture, deposits its fluorene, which is purified by redistillation and subsequent recrystallisation, first from a mixture of benzene and alcohol, and afterwards from glacial acetic acid. A still better plan is to dissolve the redistilled fluorene in ether, precipitate it by the addition of picric acid, and decompose the picric acid compound with aqueous ammonia. —Lustrous laminæ melting at 112–113°. Boils at 294–295° (cor.). Sparingly soluble in cold, readily soluble in hot alcohol; readily soluble in ether, carbon disulphide, and benzene. Chromic acid oxidises it to *diphenylene-ketone* (*v. supra*) (yellow prisms, melting at 84°, boiling at 337°, which by further oxidation with potassium permanganate yields phthalic acid and by fusion with caustic potash *o*-phenylbenzoic acid

$$C_6H_5.C_6H_4.COOH).$$

Nitric acid converts fluorene into *di-paranitro-fluorene*, melting at 199–201° (Fittig and Schmidt), or at 255–260° (Barbier and Goldschmiedt), which on reduction yields the corresponding diamido-compound. From this latter, azo-dyes have been prepared (Ger. Pat. 39,756, of 22 May, 1886) which, like those from benzidine, dye unmordanted cotton; but they have not been employed on a practical scale. With the halogens and sulphuric acid, fluorene also yields substitution compounds.

Isomeric diphenylene-methanes have been described by Carnelley (C. J. 1880, 708). They were obtained by passing the mixed vapours of benzene and toluene through a red-hot tube.

F. R. J.

FLUORESCENT BLUE or **RESORCIN BLUE** $C_{18}H_3Br_6N_2O_3(NH_4)$. A colouring matter obtained in 1880 by Weselsky and Benedikt by treating a solution of diazoresorufin in potassium carbonate with bromine, and precipitating with an acid. Soluble in boiling water, giving a reddish violet solution with green fluorescence. On the addition of hydrochloric acid the aqueous solution gives a yellowish-brown precipitate. With zinc-dust and caustic soda solution rapidly becomes colourless, but again becomes blue on exposure to air. Soluble in concentrated sulphuric acid with blue colour which becomes violet on addition of water and eventually gives a reddish-brown precipitate. Dyes silk and woollen blue with brownish fluorescence (Brunner and Krämer, B. 17, 1847, 1867, 1875; Weselsky and Benedikt, Monats. f. Chem. 5, 605, B. 18, ref. 76); *v.* PHENOL AND ITS HOMOLOGUES.

FLUORSPAR *v.* CALCIUM.

FLUORESCEÏN *v.* PHTHALEÏNS; TRIPHENYL METHANE COLOURING MATTERS.

FLUORINE. Symbol F. At. w. 19. Ampère, in 1810, first pointed out the analogy between hydrochloric acid and the gas evolved from a mixture of fluorspar and sulphuric acid; he assumed the existence of an element similar to chlorine, and further that the acid obtained from fluorspar was a hydrogen compound. Berzelius and Davy a few years later more fully established this view.

The name fluorine was given to the supposed element on account of its being a constituent of fluorspar. Many fruitless attempts have been made to isolate the element, but, owing to its great affinity for other elements, none could be regarded as successful until Moissan, in 1886, announced his results.

Occurrence.—Fluorine occurs in the combined state only, and generally as fluorspar CaF_2, crystallising in cubes and octahedrons; this compound is found in abundance in Derbyshire, where it is known as Derbyshire-spar, and 'Blue John;' it is also found in Northumberland, Durham, Yorkshire, and Cornwall, and from it most of the preparations of fluorine are made. Cryolite, a double fluoride of aluminium and sodium, $3NaF.AlF_3$, or $Al_2F_6.6NaF$, found in Greenland, is a mineral containing fluorine (*v.* CRYOLITE). Fluorine is widely but sparingly diffused, occurring in small amount in conjunction with aluminium and silicon in *topaz*: with cerium and yttrium in *fluocerite* and *yttrocerite*; it occurs also in *apatite*, *wavellite*, *wagnerite*, and other minerals. It is also found in the idiocrase of Vesuvius, Christiansand in Norway, and in the variety from the River Wilni in Siberia (Jannasch, J. M. 1883 [2] 123). Traces of it exist in sea-water, and in the water of many mineral springs and rivers. Traces of fluorine have been detected by Wilson in the silicious stems of grasses and equisetaceous plants. Bones, both fossil and recent, contain fluorine, and it is found in the enamel of the teeth. It is said to occur in the blood, the brain, and in milk, also in human urine.

Isolation of fluorine.—Davy concluded, from his experiments on the compounds of fluorine, that the latter was an extremely active element. Since his time many chemists have endeavoured to obtain fluorine in the free state. It has been known since the time of Faraday that strong hydrofluoric acid is a very bad conductor of the electric current, and Moissan in his experiments found that the current from 50 Bunsen cells was not able to effect a passage through the anhydrous acid; by dissolving a little hydrogen potassium fluoride, HF.KF, in the acid, it was at once rendered a conductor. The apparatus employed consisted of an iridio-platinum

U-tube 9·5 centimetres high and 1·5 centimetre diameter. At the side and near the top of each limb was a small exit tube of platinum F and H; each limb of the U-tube was provided with a hollow cylinder screwed into it, and the hollow part of each cylinder was closed by a stopper of fluorspar through the axis of which passed the terminals of iridio-platinum; these terminals were 2 mm. square in section and side, 12 mm. long, and passed to within 3 mm. from the bottom of each limb. The whole apparatus was first entirely freed from moisture by drying at 120°C., then about 6 grams of the double fluoride of hydrogen and potassium were introduced, the stoppers screwed in and covered with shellac, and then placed in a methyl chloride bath, a constant supply of which at −23° was maintained in the bath. The delivery tubes, hitherto kept in communication with desiccators of fused potash, are now connected with the vessel containing anhydrous hydrofluoric acid, and about 16 grams are gently aspirated into the apparatus. On now passing a current from 20 Bunsen cells through the solution a continuous evolution of gas took place. To demonstrate its effects upon other bodies they were placed in small glass tubes, and brought to the delivery tube at the positive side.

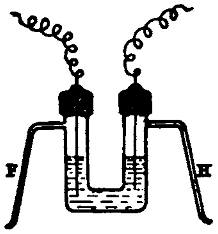


FIG. 1.

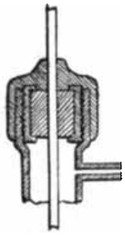


FIG. 2.

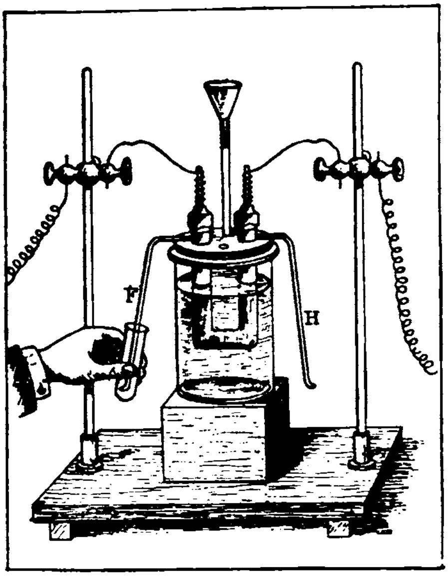


FIG. 3.

On taking the apparatus to pieces after each experiment, the hydrofluoric acid remaining was found to contain a small quantity of platinum fluoride in solution, and a black mud consisting of a mixture of iridium and platinum in suspension. The negative electrode was not attacked, but the platinum rod forming the positive pole was eaten away to a point, so that one rod only served for two experiments. The average delivery of gas was about 1·5 to 2 litres per hour.

It is probable that potassium fluoride is first decomposed, fluorine being evolved at the positive pole, and potassium, which decomposes hydrofluoric acid, liberating its equivalent of hydrogen at the negative pole, reforming potassium fluoride which may be again electrolysed. Hence a small quantity of the double fluoride can serve for the decomposition of a comparatively large amount of hydrofluoric acid.

To prepare the pure anhydrous acid a known volume of commercial acid was treated with sufficient potassium carbonate to neutralise about a fourth part, and was then distilled in a leaden retort over an oil bath at 120°C. Fluosilicate of potassium, formed from the hydrofluosilic acid contained as impurity. was not decomposed on distilling, and the distillate was therefore free from silica. The distillate was divided into two parts, one of which was neutralised by potassium carbonate and then added to the other half, thus forming the double fluoride, HF.KF. This was dried at 100°C., and kept for several days in vacuum in the receiver of the air-pump, over sulphuric acid and sticks of potash. When perfectly dry this compound falls to powder, and is then ready for the preparation of the anhydrous acid. The dry fluoride thus obtained was introduced into a platinum retort and gently heated; the first portions of distillate are rejected, as they contain traces of water. A platinum receiver is then adapted and placed in a freezing mixture of ice and salt; on increasing the temperature, pure hydrofluoric acid passes over and is condensed in the receiver as a limpid liquid, which boils at 19°·4, is very hygroscopic, and fumes in air (A. Ch. [6] 12, 472–537).

The double fluoride is very soluble in hydrofluoric acid, forming with it a crystallisable compound richer in hydrofluoric acid than the double fluoride itself, and which gives off no acid vapour at the boiling-point of the anhydrous acid (19·4°).

Moissan electrolysed the double fluoride itself, which fuses at 140°C. to a colourless liquid. The experiment was done, as before, in a U-tube of platinum, but the latter was strongly attacked. On dipping the platinum terminals of the battery into the fused double fluoride contained in a platinum dish, gas was freely evolved at each pole, detonation occurring on bringing the terminals together, even in the dark. The wire at the end where the fluorine was evolved was strongly corroded.

Properties of fluorine.—Fluorine is a light-greenish-yellow gas of a penetrating and disagreeable odour, similar to that of hypochlorous acid; it has an irritating effect on the eyes, and upon the mucous membrane. It decomposes water with formation of hydrofluoric acid, and the oxygen which is set free is ozonised. It corrodes glass, and attacks with violence all organic compounds, cork being at once carbonised and inflamed; alcohol, ether, benzene and turpentine take fire immediately in contact with it. Fluorine combines with hydrogen, even in the dark, the combination is attended with detonation, and is effected at a temperature as low as −23°C. Iodine burns in fluorine with a pale-blue flame, and, in an atmosphere of iodine vapour, fluorine burns with a similar flame. Vapour of bromine loses its colour in fluorine, and the combination is sometimes attended with detonation. Fluorine at once releases chlorine from cold potassium chloride; chlorine is also expelled from its combination with carbon in carbon tetrachloride.

Sulphur and selenium, on being placed in fluorine, at once melt and inflame, as also does tellurium with incandescence and formation of fumes and a coating of solid fluorides. Phosphorus burns in it with formation of fluoride and oxyfluoride; arsenic in powder becomes incandescent, and forms liquid drops of the trifluoride; antimony also becomes incandescent. Silicon in crystalline form, and cold, burns with brilliancy, and sometimes with scintillations. Adamantine boron also burns in the gas.

Metals are all attacked, but with varying energy, and formation of fluorides. Sodium and potassium in the cold are rendered incandescent. Calcium, magnesium, and aluminium become incandescent when slightly warmed. Iron and manganese in a state of powder, with slight warming, burn with bright scintillations; lead is attacked in the cold, and tin on slightly warming. Mercury is entirely converted into a yellow protofluoride. Silver at a gentle heat becomes coated with a satin-like deposit of fluoride soluble in water. Gold and platinum, when heated to between 300–400°, become converted into their respective fluorides, which are decomposed again at a red heat with evolution of free fluorine (**A. Ch.** [6] **12**, 472-537).

The majority of the metallic compounds of fluorine are easily fusible, and when ignited in a current of steam many of them are converted into the corresponding oxides, whilst hydrofluoric acid is formed. The fluorides of silver and tin are easily soluble in water, while those of sodium, potassium, and iron are only sparingly soluble. They are all decomposed by sulphuric acid when heated, with evolution of hydrofluoric acid, but nitric does not so easily attack them. Heated in a current of chlorine they are all decomposed with formation of corresponding chlorides. Solutions of the soluble fluorides corrode glass, and they give no precipitate with silver nitrate, as the fluoride of silver is soluble. Lead, barium, magnesium, and calcium salts produce insoluble precipitates. The precipitate of calcium fluoride is so transparent as to be perceived with difficulty, but is rendered more opaque by heating.

Many metallic fluorides combine with hydrofluoric acid and form compounds obtainable in crystals soluble in water. The double fluorides of the alkali-metals with the fluorides of the electro-negative metals which form acids with oxygen may be obtained with facility, and are analogous in composition to the double fluoride of hydrogen and potassium. They are all decomposed by sulphuric acid, yielding hydrofluoric acid and a sulphate. A mixture of hydrofluoric acid and nitric acid dissolves silica which has not been previously ignited, but the mixture has no action on gold or platinum.

Hydrofluoric acid or Hydrogen fluoride HF. The corrosive action of this compound on glass was known to Schwankard of Nuremberg as early as the year 1670. Scheele, in 1771, first recognised that fluor-spar is a compound of lime and a peculiar acid, and he prepared the latter in both the aqueous and gaseous form by distilling in a tin retort. Priestley was the first to collect the gas over mercury. It was regarded by Gay-Lussac and Thenard, in 1808, as an oxygen compound. Ampère, however, in 1810, pointed out its similarity to hydrochloric acid, a view which was subsequently supported and confirmed by Davy and Berzelius.

The anhydrous acid is best prepared from the double fluoride of potassium and hydrogen, as previously described. Fremy obtained the anhydrous acid by decomposing plumbic fluoride with dry hydrogen.

Anhydrous hydrofluoric acid is a colourless, mobile liquid of density 0·9879 (Gore). It boils at 19·4°, and solidifies at −102·5° to a white crystalline transparent mass, becoming white and opaque at a lower temperature, and melts at −92·3° (Olszewski, M. 7, 371). Its vapour tension at 15·5° is equal to a pressure of 7·58 pounds per square inch. The anhydrous acid does not attack glass even if left in contact with it for weeks; but if the least trace of moisture be present, this action is apparent at once. The acid has little action on the metalloids and the noble metals, and below 20° the other metals are not attacked. Basic oxides unite readily with it, some of them dissolving; on peroxides it has no effect.

Potassium, when thrown into the anhydrous acid, decomposes it with explosion. It combines eagerly with phosphoric and sulphuric anhydrides, with evolution of great heat, in this respect resembling water, and not its more obvious analogue, hydrochloric acid. It also combines energetically with the fluorides of potassium and sodium, just as water combines with the oxides of these metals.

The anhydrous acid decomposes carbonates with effervescence and with the formation of fluorides. Solid organic bodies immersed in it are for the most part disintegrated. Gutta-percha, caoutchouc, and numerous gums and resins dissolve to red liquids. Gun-cotton, silk, paper, cotton-wool, calico, &c., are converted into glutinous substances, and generally dissolve. Wood-spirit, alcohol, and ether, but not benzol, mix with it, and oil of turpentine, when mixed with it, forms a red liquid (Gore, Pr. 17, 256).

Thorpe and Hambly (C. J. 1889, 163) find that the vapour density of hydrogen fluoride varies rapidly with the temperature and pressure. The following table gives the results of their experiments at temperatures varying between 26·4° and 88·1°:—

Temperature	Pressure mm.	V.D. air = 1	Mol. weight
26·4°	745	1·773	51·18
27·8	746	1·712	49·42
29·2	750	1·578	45·54
32·0	743	1·377	39·74
33·1	750	1·321	38·12
33·8	753	1·270	36·66
36·3	739	1·115	32·20
38·7	751	1·021	29·46
39·2	743	1·002	28·94
42·8	741	0·910	26·26
47·3	745	0·823	23·76
57·5	750	0·737	21·28
69·4	746	0·726	20·96
88·1	741	0·713	20·58

These numbers show that the process of dissociation of the vapour of hydrogen fluoride is perfectly continuous, and that there is no direct evidence of the existence of a molecule corresponding to H_2F_2. It is also found that the vapour density is lowered by diminishing the pressure of the gas at a constant temperature. The following table shows the vapour density of hydrogen fluoride under varying pressures at the constant temperature of *circa* 32°:—

Temperature	Pressure mm.	V.D. air = 1	Mol. weight
32°	743	1·377	39·74
32·2	686	1·239	35·78
31·8	655	1·177	33·98
32·0	603	1·068	30·82
32·5	545	0·963	27·78
32·3	493	0·920	26·54
31·9	354	0·797	23·00
32·3	353	0·789	22·78

Similar results were obtained by mixing the hydrogen fluoride with air so as to lower the partial pressure of the gas.

The anhydrous acid, on addition of water, is changed in sp.gr. from 0·988 to as much as 1·25, further dilution causing a regular decrease in sp.gr. The acid of sp.gr. 1·15 may be distilled unchanged; it boils at 120°, and contains about 36 to 38 p.c. of the anhydrous acid, but does not thus form a definite hydrate; when allowed to evaporate over caustic lime in the air, the aqueous acid attains a constant composition containing 32·6 p.c. of the anhydrous acid (Roscoe).

A small quantity of hydrofluoric acid lowers the freezing-point of water, and when the aqueous acid is electrolysed with platinum for the positive electrode, ozone is evolved, and, with acid of 30 p.c., the platinum is attacked.

The dilute acid dissolves all the metals except platinum and some of the metals associated with it—gold, silver, lead, and mercury—with evolution of hydrogen. On this account it is kept in platinum vessels when concentrated, and in leaden or gutta-percha vessels in the dilute form.

Aqueous hydrofluoric acid may be kept in glass bottles lined with a film of gutta-percha as follows. Gutta-percha is dissolved in carbon disulphide and the solution put in a bottle, every part of the interior of which must be brought in contact with the solution; the excess, if any, is then poured out and the bottle laid aside until the solvent has volatilised. Caoutchouc stoppers are required (C. N. 49, 201).

On mixing one part of finely-powdered and pure fluor-spar with about twice its weight of strong sulphuric acid no evolution of gas takes place at ordinary temperatures, but a transparent gelatinous mass is formed, and, on gently heating, dense and highly irritating fumes arise, somewhat similar to those produced in the manufacture of hydrochloric acid: $CaF_2 + SO_4H_2 = SO_4Ca + 2HF$. For ordinary purposes the decomposition is effected in a leaden retort, divided into two halves for convenience in cleaning, which, when in use, are accurately fitted together by an overlapping grooved joint. The receiver may be a leaden U-tube, blind at one end, and fitted by grinding at the other to the neck of the retort; the retort is heated on a sand-bath, and the acid is condensed in the receiver, which is surrounded by a freezing mixture.

To prepare the aqueous solution on the large scale, a leaden retort, on the upper part of which a leaden head can be cemented, is used; the neck of the retort fits into the side of a leaden receiver or chamber, in which is placed a basin of water. The acid vapours are absorbed by the water, and air, with any excess of acid vapours, is conducted through an escape pipe into the atmosphere.

The impure commercial acid may be purified by passing an excess of hydrogen sulphide through the liquid, neutralising the sulphuric and silicofluoric acids present with potassium carbonate, then decanting and adding silver carbonate to remove excess of hydrogen sulphide, filtering, distilling the filtrate from a leaden retort with a platinum receiver, and finally rectifying.

Tests for hydrofluoric acid.—For the detection of this compound its corrosive action on glass is utilised. The compound suspected to contain a fluoride is reduced to powder and moistened with strong sulphuric acid in a platinum or leaden capsule. A watch-glass is thinly coated with wax, and, after tracing some design with a sharp-pointed instrument, is inverted over the capsule. The capsule is then gently warmed and the watch-glass placed over it, a little water being put in to prevent the melting of the wax. On removing the watch-glass after a few minutes' exposure, and cleaning off the wax with a little oil of turpentine, the parts exposed will have become etched if fluorine was present in the mixture. When the etching is very faint, a good plan is to breathe upon it, which makes the markings more apparent.

Use of hydrofluoric acid.—The chief use of this compound is in etching glass. In making the graduations on a thermometer the tube is first coated with engravers' etching varnish; the divisions are then accurately traced with a fine pointed instrument through the varnish. The tube is then plunged for a short time into a long tube containing dilute hydrofluoric acid, when, after cleaning the thermometer tube, it will be found to be permanently engraved. If the engraving is done by the vapour of hydrofluoric acid the tracings are white and opaque, whereas if the liquid acid be employed, the lines are transparent.

There are three processes in use for the preparation of opaque etchings on glass: viz. (*a*) the application of solutions of acid fluoride of the alkalis; (*b*) a mixture of fluorspar with sulphuric acid; and (*c*) hydrofluoric acid gas. The first of these always contains uncombined hydrofluoric as well as an indifferent salt as shown in the following recipes:—

—	I.	II.		III.	
	grams				
Water	1,000	100	1,000	1,000	1,000
Acid potassium fluoride	250	—	—	—	—
Sodium fluoride	—	—	40	250	—
Ammonium fluoride	—	—	—	—	1,000
Alkali fluoride	—	8	—	—	—
Hydrochloric acid	250	—	—	160 to 175	—
Sulphuric acid	—	1	—	—	250
Glacial acetic acid	—	—	50	—	—
Potassium sulphate	140	—	—	200	—
Ammonium sulphate	—	—	—	—	100

The first of these recipes is recommended by Tessié du Mothay and Maréchal; the two under heading II. by Siegwart, and those under heading III. by J. B. Miller. In practice, however, an acetic solution of sodium fluoride is much used, and is prepared by dissolving 25 parts of sodium carbonate crystals in 5 parts of fuming hydrofluoric acid, and adding to 1 litre of this solution after clarifying, 1 litre of glacial acetic acid. For light shades of etching a single application of the acid is sufficient, but for deeper shades repeated applications are necessary, as is the case in etching landscapes &c. on glass. An etched glass surface viewed by the microscope has the appearance of an aggregation of crystals, hexagonal in shape, and agrees with those of silicon-sodium fluoride, and in addition there are some longer in shape, which much resemble those of silicon-calcium fluoride. Small crystals are formed from concentrated solutions, and the smaller the crystals the more delicate is the etching. The strength of an etching solution must be varied according to the compound used, and regard must also be paid to the kind of glass to be operated upon. The application of gaseous hydrofluoric acid does not produce a uniform opacity, and is, therefore, not suitable for the production of opaque plates (S. C. I. [5] 669).

It has been suggested to employ hydrofluoric acid in the purification of beet-root sugar; the alkalis present in the juice being effectually removed by the acid, whilst the organic matter remains unaffected.

Silicofluoric acid or **Hydrofluosilicic acid** H_2SiF_6. This compound is prepared by heating a mixture of sulphuric acid and fluorspar, sand, or powdered glass in a flask and passing the evolved fluoride of silicon into water $3SiF_4 + 2OH_2 = SiO_2 + 2(H_2F_2.SiF_4)$. The tube from which the fluoride escapes must dip into mercury at the bottom of the vessel of water, otherwise it would soon be stopped up by the deposition of silica. The bubbles of gas as they rise through the water are decomposed, and a gelatinous mass accumulates. The solution of acid is strained through linen to separate the silica, and is then filtered, and concentrated at a low temperature. The acid is obtained more easily when required in quantity by dissolving silica in dilute hydrofluoric acid. The saturated solution fumes strongly and has a very sour taste. It does not attack glass, but if allowed to evaporate on it the glass is attacked, especially on heating; silicon fluoride is volatilised, and the free hydrofluoric acid attacks the silica of the glass. The salts are called silicofluorides or fluosilicates, are generally soluble in water, and may be obtained well crystallised. The potassium salt is one of the least soluble salts of potassium, and the copper salt one of the most soluble of copper salts. Silicofluoric acid is sometimes employed as a test for potassium.

Antiseptic properties of fluorine compounds.—W. Thompson found the compounds of fluorine, such as hydrofluoric acid, the acid and neutral fluorides of sodium, potassium, and ammonium, and the fluosilicates of those bases, were effectual as antiseptics. Of these compounds the last-mentioned appeared most powerful. They are not poisonous, possess no smell, and are sparingly soluble in water. As they have only a very slight alkaline taste, they may be employed for preserving food without communicating any taste to it.

They have been used in surgical operations. A solution containing 0·61 p.c. of ammonium fluosilicate is not irritating to wounds, whilst it possesses greater antiseptic power for animal tissues than 1 part of chloride of mercury in 1,000 of water, which latter is a stronger solution than that which can be generally employed for surgical purposes without producing poisonous effects (C. N. 56, 132) (*v.* DISINFECTANTS).

FLUX. This term is applied in metallurgy to bodies used to assist the fusion of mineral substances. Fluxes also frequently act by combining with a portion of the substance under treatment, and thus breaking up or preventing formation of an alloy or compound which could not easily be separated into its constituents. Thus, silicate of zinc yields no zinc on reduction with carbon unless a flux capable of combining with silica be present. Metallic iron, free from manganese, may be obtained by the reduction of a mixture of the oxides of iron and manganese in presence of a flux capable of combination with the latter metal; whereas, in the absence of a flux, the manganese and iron would be simultaneously reduced with production of an alloy.

Among the fluxes employed in manufactures are alkalis and oxides of lime, lead, aluminium, and iron, used to render silica and silicates completely fluid in glassmaking; potash-felspar, used to produce an incipient fusion of clay in the manufacture of pottery, and limestone and other substances used in iron smelting. The proportion of flux employed should be sufficient to unite with all the earthy matter in the ore, but not to unite with the metallic oxide undergoing reduction. The silicates of potassium and sodium are the most fusible slags produced by fluxing. Silicates of lime and most other oxides are sluggish at a red heat. A mixture of silicates is usually far more fusible than the mean fusibility of the constituents, and frequently is more fusible than any constituent. An example of this is seen in iron slag, which consists essentially of a mixture of lime and aluminium silicates.

When iron ore contains silica, alumina, and iron oxide, the amount of lime required to render the whole fluid is not great, on account of the tendency of the iron and alumina to form a mixture of fusible silicates, but a larger proportion of lime is employed when the alumina is wanting. In that case argillaceous limestone, or limestone mixed with clay, is usually added. On the other hand, clayey ores may sometimes be more readily fluxed after addition of silica. When the ores contain excess of earthy bases, silica and alumina are sometimes added. Alumina may be added as bauxite and silica in the form of forge cinder (ferrous silicate), but the two are usually added together as clay slate or shale.

When charcoal or other non-sulphurous fuel is used, the amount of limestone added is such that the weight of lime in the limestone is about six times the weight of alumina in the ore. When the fuel contains sulphur, more lime is added.

The value of limestone for this purpose depends principally upon its freedom from silica, refractory silicates, and metallic sulphides. The best fluxing limestones are those of the Silurian and Carboniferous formations. For smelting foundry iron the presence of magnesia is objectionable. Dolomite cannot therefore be used for that purpose, although it is of value in the manufacture of forge and manganiferous pig. Lime removes the sulphur introduced into the material from the fuel, but magnesia has not that power.

The following list shows the more important fluxes used in assaying, some being also employed in reductions on the manufacturing scale.

Borax is one of the most valuable of fluxes on account of its power of forming a highly fluid combination when fluxed with silica and most metallic oxides. On account of the intumescence of ordinary borax when heated, only the fused variety, known as *glass of borax*, should be employed.

Glass (finely powdered) is used, frequently to economise borax, in the assay of ores containing lime and other earthy bases and but little silica. Window or plate glass, free from lead, is the best.

Lime, preferably prepared from marble and free from moisture, is used to flux silica, aluminium silicate, &c.

Fluorspar should be free from copper pyrites, blende, and galena, and, if possible, from quartz. Derbyshire spar is the best. It fluxes sulphates of calcium, lead, barium, phosphate of calcium, silica, silicates, &c., with formation of a very fusible slag. According to Berthier, it has no action on sulphides. A mixture of fluor spar and calcspar is used for smelting galena containing lead carbonate and barium sulphate.

Potassium or **sodium nitrate** is used to oxidise certain sulphides with formation of metallic oxides.

Sodium chloride is used, mixed with another flux or placed above it, to prevent access of the atmosphere, and should be thoroughly dried by ignition before use. When used for copper assaying it should be free from sulphates, which would cause it to retain copper.

Sodium carbonate or bicarbonate, or potassium carbonate, or a mixture of potassium and sodium carbonates, especially in presence of carbon, forms the most fusible slag with silica. They act also as powerful desulphurising agents.

Iron pyrites (ferric sulphide), or ferrous sulphide, or a mixture of hæmatite and sulphur, is used for fluxing copper ores. That occurring in the coal measures is preferred on account of its freedom from copper.

Potassium cyanide is used, on account of its tendency to become oxidised into cyanate, as a reducing flux. It acts also as a desulphuriser.

Red lead and **litharge** are employed as oxidising agents, and to furnish a supply of lead, in the assay of silver. That prepared by the Pattinson process is preferred on account of its freedom from silver. Two to five parts of litharge mixed with one part of oxide of iron, copper, bismuth, antimony, or arsenic, fuses readily. Other oxides require more litharge. It also readily fluxes silica and silicates and lead sulphate.

Metallic lead (granulated) is used in the assay of silver by scorification, its oxidation in the muffle furnishing the litharge necessary to flux the earthy matters in the ore.

Silicate of lead (glass of lead), prepared by fusion of a mixture of 1 part of sand and 4 parts or more of litharge, is used in preference to litharge for fluxing substances containing no silica and no oxides capable of combination with litharge.

Borate of lead, or a mixture of borax, glass, and litharge, is used in preference to the silicate when free earths are contained in the substance assayed. That containing 90·56 p.c. of litharge is one of the best.

White or **refining flux** is prepared by plunging a red-hot iron rod into a mixture of 3 parts by measure of potassium nitrate, 2 parts tartar, and 1 part sodium chloride contained in a large crucible. The mixture is stirred until deflagration ceases. With these proportions a porous grey or reddish-grey mass is produced. The strength, *i.e.* the oxidising power of the flux, may be varied by the addition of tartar or of potassium nitrate. That containing most nitre is used for refining very coarse copper buttons. It may be replaced by potassium carbonate with or without addition of nitre.

Black flux is prepared by heating a mixture of 2 parts of tartar and 1 part or less of nitre to redness in a closed crucible. The resultant mixture of potassium carbonate and carbon is much used in copper and lead assaying. It should be kept in bottles to prevent absorption of moisture. When great reducing power is required, black flux is prepared by heating the argol alone, but the excess of carbon thus produced reduces the fusibility of the slag. A mixture of carbonate of potassium, or sodium and charcoal (preferably lamp-black), is frequently used instead of black flux, the three following proportions being frequently employed:

Sodium carbonate .	47	22	272
Charcoal . . .	3	3	61

Potassium bisulphate, *Acid potassium sulphate*, is used as a flux when the action of sulphuric acid is required at a high temperature, as in the decomposition of some aluminous and ferruginous materials for analysis.

FOND ROUGE (Castelhaz), or **ORCELLIN** (Henriet, Roman, and Vignon), *Picraminic acid-azo resorcin* $C_6H_2.OH.(NO_2)_2N_2.C_6H_3(OH)_2$. A colouring matter obtained by Nölting, Boasson, and Bohlen in 1877. No longer used.

FORCITE *v.* EXPLOSIVES.

FORMALDEHYDE *Formic aldehyde* CH_2O. Known only in solution or in the gaseous state. Obtained by the partial oxidation of methyl alcohol. Hofmann (A. 145, 357; B. 2, 152) passes a mixture of methyl alcohol vapour and air over a heated platinum spiral. Loew (J. pr. 33, 321) finds that a much better yield is obtained by substituting for the platinum spiral a roll of superficially oxidised copper gauze gently heated in a glass tube through which the mixed vapour is passed: by leading the product into water a solution containing from 15 to 20 p.c. of formaldehyde may be obtained (*v.* also Tollens, B. 19, 2133). The aqueous solution has a pungent smell, gives with an ammoniacal silver solution a specular deposit of silver, and on treatment with sulphuretted hydrogen yields crystals of *trithiomethylene* $(CH_2S)_3$ (Hofmann, A. 145, 360), the vapour density of which corresponds with the trimolecular formula. With ammonia formaldehyde yields the monacid base *hexamethylenamine* $C_6H_{12}N_4$ which crystallises from alcohol in rhombohedra (Butlerow, A. 115, 322; Legler, B. 16, 1333).

Formaldehyde polymerises when its solution is evaporated over sulphuric acid, forming *trioxymethylene* $(CH_2O)_3$, a crystalline mass fusing at 171-172°, but subliming below 100°; insoluble at ordinary temperatures in water, alcohol and ether, but soluble when heated with water at 130°, under which circumstances it appears to be converted into formaldehyde or paraformaldehyde (*v. infra*) (Tollens and Mayer, B. 21, 3504). When trioxymethylene is volatilised it dissociates completely into formaldehyde (V.D. 15·3 Hofmann), and the trimolecular formula assigned to it is based merely on the analogy of trithiomethylene. When boiled with lime-water it yields formic acid and an amorphous saccharine substance—*methylenitan* (Butlerow, A. 120, 295).

When dry trioxymethylene is heated in a sealed tube with a trace of sulphuric acid at 115° it is converted into the isomeric *a-trioxymethylene* $(CH_2O)_3$, which crystallises in needles melting at 60-61° and sublimes at ordinary temperatures. The vapour-density agrees with the trimolecular formula. Soluble in water, alcohol, and ether (Pratesi, G. 14, 139).

According to Tollens and Mayer (B. 21, 3507) formaldehyde exists in three distinct forms, without counting Pratesi's *a-trioxymethylene*: (1) as mono-molecular formaldehyde CH_2O, in dilute solutions; (2) as di-molecular formaldehyde (*paraformaldehyde*) $(CH_2O)_2$, in concentrated solutions; (3) as oxy-methylene or *metaformaldehyde* (probably trimolecular) in the solid state, almost insoluble in water. The foregoing molecular weights of formaldehyde and paraformaldehyde in aqueous solution were determined by Raoult's method.

By careful treatment with bases, such as calcium hydroxide or lead oxide, formaldehyde may be polymerised into a mixture of saccharine substances (*v.* FORMOSE). F. R. J.

FORMAMIDE $CHO.NH_2$. First obtained by Hofmann (J. pr. 91, 61) by heating ethyl formate with ammonia in a sealed tube at 100°. Best by heating crystallised ammonium formate in a sealed tube at 230° for five hours (Hofmann, B. 15, 980).—Liquid, boiling under reduced pressure without decomposition. Under atmospheric pressure it boils at 192–195° with partial decomposition into carbon monoxide and ammonia. Phosphorus pentoxide converts it into water and hydrocyanic acid: $CHO.NH_2 = HCN + H_2O$. Strong caustic potash decomposes it, even in the cold, into potassium formate and ammonia.

F. R. J.

FORMAMIDINE *Methenylamidine*

$$CH(NH)(NH_2).$$

This compound, the lowest member of the amidine series, may be regarded as formamide $CHO.NH_2$ in which the oxygen atom has been replaced by imidogen. Obtained by acting on the double compound of hydrocyanic acid and hydrochloric acid with absolute alcohol:

$$2HCN,HCl + 2C_2H_5.OH$$
$$= CH(NH)(NH_2),HCl + C_2H_5Cl + CHO_2.C_2H_5$$

(Gautier, C. R. 65, 410; *cf.* Claisen and Matthews, C. J. 1882, 265). From the hydrochloride of formimido-ether

$$CH(NH)(OC_2H_5),HCl$$

and alcoholic ammonia.—Formamidine hydrochloride crystallises from alcohol in hygroscopic granules, melting at 81°, and decomposing at 100° into hydrocyanic acid and ammonium chloride: $CH(NH)(NH_2)HCl = HCN + NH_4Cl$. When liberated from its salts by caustic potash formamidine is at once decomposed into ammonia and potassium formate. Its salts crystallise with difficulty: $(CH_4N_2,HCl)_2PtCl_4$ forms very soluble, orange-red, quadratic pyramids.

F. R. J.

FORMANILIDE $CHO.NH.C_6H_5$. First obtained by Gerhardt (A. 60, 310) by heating aniline oxalate. Best prepared by heating together molecular proportions of aniline and strong formic acid on the water-bath under reduced pressure to remove the water, then distilling under ordinary pressure until the thermometer registers 250°, and finally pouring out the undistilled portion, when it solidifies on standing (Wallach and Wüsten, B. 16, 145).—Long four-sided prisms melting at 46°, moderately soluble in water, readily soluble in alcohol. Dilute acids decompose it into aniline and formic acid.

F. R. J.

FORMIC ACID v. FATTY ACIDS.

FORMOSE. The first saccharine substance from formaldehyde was obtained by Butlerow (A. 120, 295) by boiling trioxymethylene (v. FORMALDEHYDE) with milk of lime or baryta water. After removing the formate of the alkaline earth and evaporating the solution, an uncrystallisable syrup remained, having a sweet taste and a smell resembling that of caramel. To this substance, which he termed *methylenitan*, Butlerow assigned the formula $C_7H_{14}O_6$. It reduces Fehling's solution, but is optically inactive and is not fermentable with yeast. It was afterwards examined by Tollens (B. 15, 1632; 16, 919), who also obtained it by the action of alkalis on formaldehyde; according to him it has the composition of a carbohydrate of the formula $C_6H_{10}O_5$. He found that its power of reducing Fehling's solution was only one quarter that of glucose, and that when boiled with mineral acids it did not yield lævulic acid.

The subject of the condensation of formaldehyde under the influence of bases was afterwards taken up by Loew (J. pr. 33, 321). By saturating a 3·5 to 4 p.c. solution of formaldehyde with slaked lime in the cold, and allowing it to stand, he obtained an uncrystallisable sugar which he termed *formose*, and to which he gave the formula of a glucose, $C_6H_{12}O_6$. He declared Butlerow's methylenitan to be a saccharine transformation-product of formose, containing some unaltered formose. Like methylenitan, formose was optically inactive, had a sweet taste, reduced Fehling's solution, and appeared to be non-fermentable with yeast. On oxidation it yielded oxalic acid, but no mucic or saccharic acid.

Wehmer and Tollens (A. 243, 334) were unable to obtain lævulic acid from Loew's formose by boiling it with mineral acids, and therefore concluded that formose was not a true carbohydrate. Wehmer (B. 20, 2614) was further confirmed in this opinion by the fact that leaves of plants, which had been previously deprived of starch and which have the property of generating starch from dextrose, lævulose, and various other soluble carbohydrates, failed to produce starch when left in contact with solutions of formose. Wehmer and Tollens considered that formose did not differ essentially from methylenitan, and proposed to retain the latter name for the substance.

E. Fischer (B. 21, 989) found that phenylhydrazine yielded with formose a mixture of osazones, thus proving that formose was not, as Loew had supposed, a homogeneous substance. One of these osazones was afterwards shown by E. Fischer and Passmore (B. 22, 359) to be identical with the osazone of α-acrose, the artificial fermentable glucose obtained by Fischer and Tafel both from acroleïn dibromide and from glycerose. Fischer and Passmore therefore assumed that formose contained, along with other substances, α-acrose, a conclusion which, as Loew pointed out (B. 22, 478), was not unassailable, inasmuch as distinct glucoses, such as dextrose and lævulose, may yield the same osazone.

Loew (B. 22, 475), independently of Fischer, isolated from formose a fermentable sugar of the formula $C_6H_{12}O_6$, to which he gave the name *methose*. By acting with granulated lead upon a dilute solution of formaldehyde to which a small quantity of magnesia and magnesium sulphate had been added, he obtained a formose containing, on an average, 20 p.c. of fermentable sugar. By fermentation with yeast, this product yielded ethyl alcohol, recognisable by the iodoform test and by forming aldehyde on oxidation. This was the first occasion on which alcohol had been actually obtained from a synthetic sugar, Fischer and Tafel having been compelled, owing to the smallness of the quantity of α-acrose at their disposal, to accept the evolution of carbon dioxide as a proof of fermentation.

Lastly, E. Fischer has shown (B. 23, 388) that methose is identical with α-acrose. As regards the constitution of this latter compound he proves (B. 23, 386) that it is *inactive lævulose*—a combination of two opposite optically-active lævuloses of the mannite series, each having the formula

$$CH_2(OH).CH(OH).CH(OH).CH(OH).CO.CH_2(OH)$$

(v. LÆVULOSE).

As Loew and Fischer both point out, the formation of a true sugar from formaldehyde is an argument in favour of Baeyer's theory of the assimilation of carbon by plants (B. 3, 66), according to which the carbon dioxide of the air is reduced by the chlorophyll of the plant in sunlight to formaldehyde, this latter being then polymerised to glucose in the plant cells.

F. R. J.

FOSSIL RESINS v. RESINS.

FRACTIONAL DISTILLATION v. DISTILLATION.

FRANCEÏNS. Benzene and its chloro-, nitro-, and other derivatives, yield a *franceïn* when heated with strong sulphuric acid, the proportion of franceïn obtained increasing with the proportion of chlorine in the benzene derivative. All the franceïns are soluble in strong sulphuric acid and some are soluble in water. With two exceptions, they dissolve in alkalis and form neutral salts very soluble in water. They are all more or less soluble in alcohol, forming highly coloured and strongly dichroic solutions. They dye cotton, linen, and especially silk, with shades varying from rose-colour to maroon. The depth of colour and the tinctorial power of the franceïns increase with the proportion of chlorine.

The franceïns from benzene, methylbenzene, and mono- and di-chlorobenzene are black, but they become redder and acquire a conchoidal fracture and a dark-green metallic lustre, as the proportion of chlorine increases.

The action of sulphuric acid on pentachlorobenzene yields two franceïns. The first has a deep-green metallic lustre, and dissolves in potash, methyl, ethyl, and amyl alcohols and glycerin, but is insoluble in water. Its solution shows intense red-green dichroism, and dyes silk a rose-colour. The second is formed in much smaller quantity and is soluble in warm water, but is almost insoluble in potash, and is much less soluble in alcohol than the first franceïn.

It dyes silk a peach colour. The first franceïn forms salts which differ in their solubility in water and alcohol, and also in their dichroism. Both franceïns have the composition $C_{18}HCl_{9}O_{5}$ and seem to have the functions of a phenol and a diquinone.

By the action of sulphuric acid on the halogen derivatives of benzene a migration of halogen atoms results, and this determines the formation from the initial compound of franceïns, whose chlorine values differ. Thus from 1:2:4-trichlorobenzene, three franceïns resulting from the oxidation of di-, tri-, and tetra-chlorobenzene sulphonic acids are produced, and these are accompanied by a small quantity of 1:2:4:5-tetrachlorobenzene. From 1:2:4:5-tetrachlorobenzene, a franceïn is obtained which is separable into five franceïns of varying solubilities and composition. From comparative experiments on the formation of franceïns from 1:2:4-trichlorobenzene, it is found that the yield of franceïn is dependent on the temperature, and varies inversely as the amount of sulphonic acid remaining in the mixture at the close of the operation. It is further found that when a mixture of excess of sulphuric acid and a sulphonic acid or sulphonate is heated, regeneration of hydrocarbons with formation of water and of pyrosulphuric acid respectively occurs, while sulphobenzide is formed as a condensation-product, and a decomposition of the sulphonic acid into sulphurous anhydride, hydrocarbon and oxygen determines the formation of a franceïn by the oxidation of unaltered sulphonic acid (C. Istrati, C. R. 106, 277; C. J. Abstr. 1888, 591; Bl. [3] 1, 481, 488, 492; C. J. Abstr. 1890, 51).

FRANGULIN *v.* Glucosides, also Cascara sagrada.

FRANGULINIC ACID *v.* Frangulin.

FRANKINCENSE *v.* Gum resins.

FRANKLINITE *v.* Zinc.

FRAXETIN *v.* Horse chestnut.

FRAXIN *v.* Horse chestnut.

FREESTONE. A rock which admits of being freely worked in any direction for use as a building stone. Many stratified rocks may be readily sawn when freshly quarried, and while holding the 'quarry-water,' but acquire considerable hardness on exposure to the atmosphere. Most freestones are either limestones or sandstones. In the inferior oolite there are certain beds known to geologists as the lower and upper freestones, which are largely quarried as building stones near Cheltenham. The Bath stone from the great oolite, and the Portland stone from the upper oolites, are also well-known oolitic freestones. Many of the coal-measure sandstones admit of being readily cut and tooled, and being without any marked tendency to split in definite directions are valuable freestones; such, for instance, are the sandstones of Craigleith, near Edinburgh, and of Darley Dale in Derbyshire. F. W. R.

FREIBERGITE. An argentiferous fahl-ore, occurring typically at Freiberg in Saxony, whence the name. It is generally known to German miners as *Weissgültigerz.* An analysis of a crystallised specimen from the Habachtfund mine, Freiberg, by H. Rose, yielded—sulphur, 21·17; antimony, 24·63; silver, 31·29; copper, 14·81; iron, 5·98; and zinc, 0·99. Silver fahl-ore is also sometimes known as *Polytelite* (πολυτελής, valuable), a name given to it by Glocker, and revived by D. Forbes for a silver-ore from the Foxdale mine in the Isle of Man (Phil. Mag. [4] 34, 1867, 350; 35, 1868, 171). F. W. R.

FRENCH CHALK. A variety of steatite, or soap-stone, used for marking cloth and for removing grease from silk. It is a hydrated silicate of magnesium, with a smooth unctuous feel. In a powdered state it is sprinkled inside new gloves and in the heels of boots to produce a smooth surface and enable them to be readily slipped on.

FRENCH GREEN, EMERALD GREEN, *v.* Pigments.

FRENCH POLISH. A solution of shellac in alcohol; occasionally containing gum elemi and copal.

FRIT or **FRITL.** The calcined mixture of the materials for the manufacture of glass (*v.* Glass).

FUCHSIA. The chlorides of α and β diamyl saffranines are met with in commerce under this name (*v.* Azines).

FUCHSIACIN. Impure aniline red *v.* Fuchsin.

FUCHSIN, ANILINE RED, RUBIN, ROSEIN, MAGENTA, *v.* Triphenyl methane colouring matters.

FUCOSOL. This product which Stenhouse obtained by the distillation of certain *algæ* with dilute sulphuric acid (Pr. 20, 80), and which he considered as isomeric with furfurol, has been shown by Bieler and Tollens (B. 22, 3062) and by Maquenne (C. R. 109, 571) to be a mixture of furfurol and methyl-furfurol derived from pentaglycoses contained in the *algæ*.

FUEL. This term is applied to substances which may be burned by means of atmospheric air with sufficient rapidity to evolve heat capable of being applied to economic purposes. Fuels may be divided into (*a*) solid fuels, including—1. Natural fuels, consisting of woody tissue in an unaltered (wood) or an altered form (peat, lignite, coal, anthracite); 2. Carbonised fuels (charcoal, coke); 3. Compressed fuels (patent fuel, briquettes); 4. Powdered fuels. (*b*) Liquid fuels (petroleum). (*c*) Gaseous fuels, including—1. Natural gas; 2. Gases produced by the incomplete combustion of solid fuels (waste gases of blast-furnaces, producer-gases). All fuel consists of vegetable matter, or of the products of its alteration. The elementary constitution of fuel is consequently much the same (C, H, O, N, and inorganic matter that constitutes the ash). The gradual passage of woody tissue into anthracite is shown by the following analytical results:

	C	H	O
Wood . .	100	12·18	83·07
Peat . .	100	9·85	55·67
Lignite . .	100	8·37	42·42
Bituminous coal	100	6·12	21·23
Anthracite .	100	2·84	1·74

The calorific power, or total amount of heat obtainable on combustion, of various fuels has been determined by Rumford, Lavoisier, Andrews, Favre and Silbermann, and others. The general principle of their methods consisted in the use of an apparatus (calorimeter) in which the entire heat of combustion was absorbed by a known weight of water, the increase in the temperature of the latter being ascertained by the indication of thermometers suspended in it. The value of such determinations is simply relative. The imperfect nature of furnaces and boilers, and the large quantity of unconsumed fuel passing into the ash-pit, give rise to a great loss of calorific power. In expressing the calorific power of fuel, the amount of heat generated by the combustion of C to CO_2 is taken as the standard of comparison. This calorific power of carbon is expressed by the number of parts by weight of water capable of being heated from 0° to 1° by the combustion of 1 part of carbon. This is found by direct experiment to be 8080 units. The unit of heat varies with the thermometric scale and the unit of weight employed. The metric unit of heat, or calorie, is the quantity of heat required to raise 1 gram of water from 0° to 1°C., whilst the British unit is the amount of heat required to raise 1 pound of water from 39° to 40°F. Thus 1 calorie = 3·96832 British units, and 1 British unit = 0·251996 calorie. The calorific power of a fuel may be determined by experiment on a small scale in a calorimeter, or on a large scale by estimating the amount of water converted into steam in a steam-boiler. It may also be calculated from the results of an organic analysis. In this calculation, the O must be considered to be in combination with sufficient H to form H_2O. It is thus only the excess of C and of H (disposable H) after this deduction that is available for the generation of heat. Such calculations have been found by Scheurer-Kestner and Meunier (A. Ch. 8, 267) to only approximate to the truth; coals, excluding lignites, giving a higher calorific power with the calorimeter than that obtained on calculation. In the erroneous belief that the amount of heat evolved on combustion was in proportion to the amount of O consumed, Berthier determined the calorific power of fuel by burning it by the O in PbO and ascertaining the weight of the resulting button of lead. The calorific powers of various fuels are as follows:—

	Calories
Air-dried wood with 20 p.c. H_2O	2800
Charred wood	3600
Wood charcoal with 20 p.c. H_2O	6000
Dry charcoal	7050
Peat with 20 p.c. H_2O . .	3600
Dried peat	4800
Peat charcoal	5800
Average bituminous coal . .	7500
Good coke	7050
Coke with 15 p.c. ash . .	6000
Air-dried lignite . . .	4360-5410
Hydrogen	34462
Carbon burnt to CO . .	2473
Carbon burnt to CO_2 . . .	8080
CO burnt to CO_2 . . .	2403
Marsh gas	13063
Olefiant gas	11858

The calorific intensity or pyrometric effect of a fuel is the highest temperature the fuel is capable of producing when burnt. It may be determined (1) by calculation, on the assumption that the calorific intensity of a simple combustible body burnt in O is equal to its calorific power expressed in heat-units divided by the product of the relative weight of its products of combustion into the specific heat of those products; (2) By direct experiment by means of the pyrometer. Pyrometers are based on various principles: (*a*) change in the volume of bodies (*e.g.* Daniell's, with an expanding bar of Pt as indicating agent; Wedgwood's, based on the principle that china-clay contracts when heated); (*b*) the known melting-points of metals and alloys (*e.g.* Ducomet's, J. Iron & Steel Inst. 1884, 240); (*c*) calorimeter methods, similar to the determination of specific heat by the method of mixtures; (*d*) production of thermo-electric currents: (*e*) change in the electrical resistance of conductors (*e.g.* Siemens', in which are applied the principles that there is an increase in the electrical resistance of a metallic conductor when heated, and that when two branches or conductors are substituted for a single conductor in part of a circuit the intensities of the separate currents in the two branches are inversely proportional to the resistance offered by each branch, *v.* Brit. Assoc. Rep. 1872, 134); (*f*) other pyrometers. In Krupp's modification (J. Iron & Steel Inst. 1886, 207) of Hobson's hot-blast pyrometer, the temperature is measured by calculating the value of a mixture of hot air from the stove and of outside cold air sucked in by the passage through an injector nozzle. The pyrometer of Mesuré and Nouel depends on the partial rotation of polarised light by a quartz plate (Industries, 6, 331). Most pyrometers, however convenient they may be for measuring relative temperatures, are useless for measuring temperatures absolutely. (On pyrometry, consult Barus, Bull. U. S. Geol. Survey, 1889.)

In order to estimate the value of a fuel, it is necessary to determine the moisture, volatile matter, fixed carbon and sulphur. In the metallurgical laboratory of the Normal School of Science and Royal School of Mines, these assays are performed in the following manner:—1. *Hygroscopic moisture.* In a water-bath heat for an hour 20 grains of powdered sample placed in a watch-glass; weigh repeatedly until the result is constant. 2. *Coke.* Heat 1,000 grains of finely-powdered sample in large covered earthen crucible in furnace until no flame is evolved; weigh when cold, or, better, heat 50 grains in platinum crucible with lid on, the loss of weight giving the volatile matter. 3. *Ash.* Heat 20 grains of finely-powdered sample in platinum capsule until no trace of carbon is left. 4. *Sulphur.* Deflagrate in platinum crucible 20 grains of powdered sample with 500 grains of a mixture of salt and nitre (2 : 1), dissolve in water, dilute to ½ pint, add HCl in slight excess, heat for twenty minutes, filter, and to filtrate add $BaCl_2$; allow to stand for twelve hours, filter, weigh precipitate. Complete analysis of fuel is seldom required in practice. The economic value of a fuel cannot be determined entirely from the assay or analysis and calorific power; attention must be directed to the way in which it burns and to its mechanical condition, in particular to the length of flame when large inclosed spaces are to be heated.

Literature.—The principal treatises on fuel are: J. Percy, Metallurgy, Fuel, 155-577, 2nd ed., London, 1875; R. Galloway, Treatise on Fuel, London, 1880; F. Schwackhöfer, Fuel and Water, edited by W. R. Browne, London, 1885; B. Kerl, Metallurgy, edited by W. Crookes and E. Röhrig, vol. 3, London, 1870; J. A. Phillips and H. Bauerman, Elements of Metallurgy, 16–107, 2nd ed., London, 1887; E. J. Mills and F. D. Rowan, Fuel and its Application, London, 1889; R. Krüger, Lehre von den Brennmaterialen, Jena, 1883; F. Fischer, Chemische Technologie der Brennstoffe, Leipzig, 1887; C. A. M. Balling, Metallurgische Chemie, 135-248, Bonn, 1882; L. Gruner, Traité de métallurgie, vol. 1, Paris, 1875.

A. Solid Fuels.

1. *Natural fuels.*

Wood consists of 96 p.c. of organic tissue (cellulose $n(C_6H_{10}O_5)$), 4 p.c. of sap, containing a small proportion of inorganic matter. When recently felled, all wood also contains a large proportion of water. The mean composition of well-dried wood, exclusive of ash, is 50 C, 6 H, 42 O, 2 N, or 50 C and 50 combined H_2O. Inclusive of ash, the composition is 49·5 C, 6 H, 43·5 O, 1 ash. Air-dried wood contains 40 C (including ash), 40 combined H_2O, and 20 hygroscopic H_2O. This large percentage of hygroscopic H_2O renders wood unsuitable as fuel where high temperatures are required. Though the calorific intensity of wood is small, its combustibility is greater than that of any other solid fuel, and it gives more flame. The sp.gr. of woods varies considerably. Air-dried woods with 20 p.c. H_2O, having a sp.gr. of more than 0·55, are classed as hard; with a lower sp.gr. they are classed as soft. After complete expulsion of air from the pores, the sp.gr. is the same (1·5) in all woods. For domestic purposes wood is a serviceable fuel when it can be obtained cheaply. The demolition of forests, however, gradually increases its cost in towns, and its place must be taken by cheaper and less bulky fuels. In Europe, Russia is the country richest in timber; its forests occupy an area of 476 million acres, or 64 p.c. of the total woodland area of Europe. Then follows Austria-Hungary with 44 million acres, Sweden with 43, Finland with 35, Germany with 34, Norway with 25, Spain with 21, France with 20.

Literature.—Chevandier, Wertheim, and Exner, Mechan. Eigenschaften des Holzes, Vienna, 1871.

In countries where wood is scarce, vegetable refuse (*e.g.*, cotton-stalks, brushwood, straw, woody residue of sugar-canes) is used as fuel. According to J. Head (Proc. C. E. 48, 75), the evaporative values of these substances when burnt in a tubular boiler compare as follows:—8 lbs. of water will be evaporated by 1 lb. of good coal, 2 lbs. of dry peat, 2·25 to 2·3 lbs. of dry wood, 2·5 to 3 lbs. of cotton-stalks or brushwood, or 3·25 to 3·75 lbs. of straw.

Peat (or turf) is the product of the decay of plants under special conditions of air and moisture. It consists of the fossil remains of moss, chiefly *sphagnum* and *hypnum*, mixed with other plants. It may be classified (1) according to the localities where it has been formed, as lowland and mountain-peat; (2) according to its age, as recent peat with distinct vegetable structure, and old peat of a dark-brown or black colour with mere traces of organic texture; (3) according to the mode in which it has been extracted, as cut-peat or dredge-peat. Peat bogs are of frequent occurrence in all parts of the world. In Europe, the most considerable are in Russia, Ireland, Germany, Scandinavia, and Austria. In France, Italy, and Spain, peat is of less frequent occurrence. Peat consists of—(*a*) peat-substance proper, which according to Websky (Erdm. J. pr. 83, 65) contains 49·6 to 63·9 C, 4·7 to 6·8 H, 28·6 to 44·1 O, 0 to 2·6 N; (*b*) inorganic constituents, which vary from 0·5 to 20, or even 50 p.c., according to the elevation at which the peat was formed; the average percentage of ash-giving constituents is 6 to 12, and, unlike that of wood, the ash is poor in alkalis, and consists chiefly of a mixture of argillaceous sand (up to 35 p.c.), and magnesia-bearing gypsum (40 p.c. and more), with ferric oxide (up to 30 p.c.), alkalis (up to 3 p.c.), phosphoric acid, and chlorine; (*c*) water (90 p.c. in peat fresh from the bog, 15 to 20 in air-dried peat). The mean composition of well-dried peat is 52·94 C, 5·24 H, 31·55 O and N, 10·27 ash; that of air-dried peat is 44·5 C, 4·5 H, 26·5 O and N, 8·5 ash, 16·0 H_2O. The sp.gr., and consequently the tenacity and suitability for transport, varies with the proportion of ash and the mode of preparation from 0·113 to 1·039. The sp.gr. of compressed peat is 0·9 to 1·8. The calorific power of peat (3,000 when air-dried to 5,230 calories when completely dry) is rather higher than that of wood. Air-dried peat is used for heating boilers, evaporating pans, pottery kilns, and for domestic purposes. Even when dried, peat cannot be economically substituted for coal on account of its bulky nature, and consequent cost for carriage, its want of uniformity, and its large percentage of water and ash.

Literature.—S. W. Johnson, Peat and its Uses, New York, 1866; Sir R. Kane, Industrial Resources of Ireland, Dublin, 1845; Lencauchez, Traité sommaire concernant la tourbe, Paris, 1876; and monographs in German by A. Vogel, Brunswick, 1859; Seydel, Berlin, 1873; Nöggerath, Berlin, 1875; H. Stiemer, Halle, 1883.

Lignite. Under this general term, Percy includes those varieties of coal which form the intermediate stage between peat and true coals of carboniferous age. The word lignite is used by British and American writers as synonymous with the brown coal of the Germans. According to their geological age, brown-coals have either a distinct ligneous texture (true lignite, fibrous brown-coal), or are without organic structure and earthy in fracture (earthy brown-coal), or black, shining, with conchoidal fracture. The organic substance consists of 60 C, 5 H, 35 O, in fibrous brown-coal, and 75 C, 5 H, 20 O, in conchoidal brown-coal. The ash is usually 5 to 15, sometimes 50 p.c.; in composition it is similar to that of true coal, and differs from that of peat in the low percentage of P_2O_5 (0 to 1·6). Usually it is rich in sulphur (as gypsum, iron pyrites, and sometimes as free sulphur). Freshly mined lignites may contain 50 p.c. hygroscopic H_2O. In air-dried fibrous lignite, the percentage is 10 to 15, in conchoidal lignite 10 to 5, in earthy lignite 22. Dried lignite, on exposure to air, absorbs the quantity of water it lost. Lignite burns with a very long smoky flame. Its calorific power varies greatly, from 4,000 to 6,000 calories. It is generally non-caking, *i.e.*, its powder, when heated, does not yield a coherent coke. Raw lignite is largely used for heating steam-boilers, evaporating pans, and for domestic purposes, with successful results, especially when burnt on step-grates. The better qualities are sometimes used in Austria and Germany for metallurgical purposes (J. Iron & Steel Inst. 1882, 96, 461). The annual production of lignite is—in Austria (1888), 12,860,255 tons; in Hungary (1887), 1,723,440 tons; in Prussia (1888), 13,207,868 tons; in Saxony (1887), 766,732 tons; in Bavaria (1887), 6,026 tons; in France (1888), 438,312 tons.

Literature.—C. Zincken, Physiographie der Braunkohle, 1867, supplement, 1878.

Bituminous coal. This term, a misleading one, is applied to coal which burns with a more or less smoky flame, and chemically occupies a place between lignite and anthracite. 'Flaming' is suggested by Percy as a good substitute for the word bituminous. Bituminous coal is the product of the decomposition of vegetable matter, and was formed previously to or in the cretaceous period. For economic purposes, Percy classes bituminous coal as (1) non-caking or free-burning, rich in O; (2) caking; (3) non-caking, rich in C. This classification of coals is based on their chemical composition, and therefore on their calorific powers. Gruner's researches have led to the following classification: 1. Anthracitic or lean coals, burning with a short flame; composition 90 to 93 C, 4 to 4·5 H, 3 to 5·5 O + N. Having a black colour, and a sp.gr. of 1·33 to 1·4, these coals form the transition to true anthracite. On coking they yield 82 to 90 fritted or pulverulent coke, and 12 to 8 p.c. gases. Calorific power 9,000 to 9,500 calories; evaporative factor (or number of times its weight of water evaporated by a unit weight of coal starting at 100°) 9 to 9·5. Adapted for domestic use. 2. Caking coals (fat coals) burning with a short flame, with 88 to 91 C, 4·5 to 5·5 H, 4·5 to 6·5 O + N; black, shining, often with lamellar structure; sp.gr. 1·30–1·35. Yields 74 to 82 fairly hard coke, caked together very densely, and 12 to 15 p.c. gases. Calorific power 9,300 to 9,600 calories; evaporative factor 9·2 to 10. Adapted for coking and for heating steam-boilers. 3. Caking coals proper, or furnace coals, with 98 to 89 C, 5 to 5·5 H, 5·5 to 11 O + N, black, shining lustre more marked, flame longer, and intumescence greater than in preceding class. Sp.gr. 1·30. Yields 68 to 74 caked fairly dense coke, and 13 to 16 p.c. gases. Calorific power 8,800 to 9,300; evaporative factor 8·4 to 9·2. Adapted for coking and smithy use. 4. Caking coals, burning with a long flame (gas coals) with 80 to 85 C, 5 to 5·8 H, 10·0 to 14·2 O + N; hard and tough, dark colour, high lustre; sp.gr. 1·28 to 1·30. Yields 60 to 68 caked but very friable coke, and 17 to 20 p.c. gases. Calorific power 8,500 to 8,800 calories; evaporative factor 7·6 to 8·3. Adapted for gas manufacture, and for reverberatory furnaces. 5. Dry coals, burning with a long flame, with 75 to 80 C, 4·5 to 5·5 H, 15·5 to 19·15 O + N; hard, conchoidal fracture (splint coal), intense black colour; sp.gr. 1·25. Yields 50 to 60 pulverulent coke, and 20 p.c. gas. Calorific power 8,000 to 8,500; evaporative factor 6·7 to 7·5. Adapted for reverberatory furnaces. The passage from one class to another is gradual. The ash-forming constituents of coal vary from 0·5 to 30 p.c., averaging 4 to 7 in the best coals, 8 to 14 in medium, and upwards of 14, with 0·5 to 2 of sulphur, in the worst. Cannel coal is a variety of bituminous coal rich in disposable H, whence it is especially valuable as a gas-coal.

The word coal is a popular rather than a scientific term, being applied not solely to beds of fossilised vegetation, but to any mineral substance capable of being used as fuel. For information concerning localities and modes of occurrence of coal in all parts of the world, consult E. Hull's Coalfields of Great Britain, 4th ed., London, 1881.

Literature.—Lectures delivered at the Yorkshire College on Coal, its history and uses, London, 1878; F. Muck, Chem. Aphorismen über Steinkohlen, Bochum, 1873; Chem. Beiträge zur Kenntniss der Steinkohlen, Bonn, 1876; *idem*, Grundzüge der Steinkohlenchemie, Bonn, 1881.

Anthracite is the ultimate product of the conversion of vegetable matter into coal. Its average composition is 91·29 C, 2·91 H, 2·75 O + N, 3·05 ash. The percentage of N varies from 0·58 to 2·85; that of sulphur from 0·63 to 1·0. Anthracite is hard and brittle; it has a sub-metallic lustre, a conchoidal fracture, a sp.gr. of 1·35 to 1·7. It burns with a smokeless flame. Some varieties (*e.g.* Welsh anthracites) decrepitate considerably, even when gradually heated. This property is not exhibited by the anthracites of Pennsylvania.

Literature.—C. A. Ashburner, Trans. Amer. Inst. M.E. 14, 706; H. M. Chance, Report on Coal Mining, Pennsylvania 2nd Geol. Survey, Philadelphia, 1885.

The world's annual production of coal, excluding lignite, is estimated at 405 million tons; the production of the principal coal-producing countries being as follows:—United Kingdom (1888), 169,935,219 tons; United States (1888), anthracite, 35,273,442 tons; total coal 110,727,906 tons; Germany, 65,321,834 tons; France, 22,513,628 tons; Belgium, 19,185,181 tons; Austria, 8,274,461 tons; Hungary (1887), 786,405 tons; Russia (1886), 4,434,816 tons. When not otherwise described, the figures refer to the year 1888.

2. *Carbonised fuels.*

Wood-charcoal. When wood is heated to 200° without access of air, it remains unaltered, at 220° it becomes brown, and at 270° to 300° it suffers decomposition, torrefied wood or *Rothholz* being formed. At 350° it is resolved into volatile products and a fixed residue of charcoal. Good charcoal produced at 350° to 400° is porous, black, sonorous when struck, has a conchoidal fracture and a ligneous texture. It burns without smoke, and in separate pieces without flame. Its sp.gr., exclusive of pores, is 1·5 to 2, inclusive of pores, 0·2 to 0·35 in soft charcoal, and 0·35 to 0·5 in hard. Dry charcoal contains on an average 90 C, 3 H, and 7 O. After storing, it contains 70·45 C, 1·68 H, 13·1 O, 1 ash, 13·76 moisture and gases. The usual percentage of ash is 3 to 4. The carbonisation or dry distillation of the wood may be effected in the open air in circular piles or stacks (Meiler), provided with a yielding cover, in rectangular piles, in pits (the most primitive method), in kilns of brick or stone, or in iron retorts heated externally (method used in the manufacture of gunpowder and of pyroligneous acid). The yield of charcoal varies with the nature, age, and condition of the wood, and with the method of carbonisation, from 31 p.c. by volume (branchwood of fir) to 80 (logs of the same). In Sweden 67 p.c. of the volume of the wood was obtained in piles in which the wood was stacked vertically, and 75 when stacked horizontally. The yield by weight ranges from 15 to 28 p.c. The more slowly the charring is effected, the greater will be the yield of charcoal. Charcoal is an excellent fuel for metallurgical purposes on account of its low percentage of ash and its high calorific power. Where wood is still plentiful, as in the United States, Sweden, and Austria, charcoal furnaces are largely used for iron-making.

Literature.—Gillot, Carbonisation du bois, Paris, 1873; G. Svedelius, Handbook for Charcoal Burners, New York; W. J. L. Nicodemus, Handbook for Charcoal Burners, translated by R. P. Anderson, New York; T. Egleston, Trans. Amer. Inst. M. E. 8, 373.

Peat charcoal is very friable and porous, and consequently difficult to use in metallurgical operations. When sufficiently coherent, and when the percentage of P_2O_5 is low, it may be used in low, small furnaces. The carbonisation may be effected in open kilns, in pits, or in ovens in which the air for combustion passes from above downwards, or by external firing in close vessels, in order to enable the volatile products of distillation to be collected. Peat-charcoal is easily kindled, and has a calorific power of 6,500 to 7,000 calories. It is not adapted for iron-making, but may advantageously be used for gas-furnaces, on account of the large size of the lumps, absence of clinker, and the fact that the ash readily falls through the bars.

Coke is the solid product of the carbonisation of coal. It varies considerably in external characters. For metallurgical purposes, the best coke is compact, heavy, homogeneous, with bright light-grey surface. It contains up to 93 C. Coke from Dukinfield colliery, dried at 100°, contained 85·8 C, 0·5 H, 1·4 O + N, 0·9 S, 11·4 ash. The ash varies from 1 to 30 p.c.; cokes with more than 5 are unsuited for iron-making. The ash has the same composition as that of coal, with 0·0025 to 0·05 p.c. P. Coke rarely contains more than 2 to 3 p.c. hygroscopic H_2O, occasionally 5 to 6 p.c. The sp.gr. varies from 1·2 to 1·9. The calorific power is nearly 8,000 calories, and the evaporative factor 7·34 with undried coke, and 7·81 with dried coke. The suitability of a coal for coke-manufacture depends on its caking power and its chemical composition. The ash-giving constituents lower the calorific power, retard the coking, form adherent clinker on the bars, and introduce deleterious elements (*e.g.* sulphur) into the product. A ready means of lowering the proportion of sulphur and ash is to wash the coal and separate from it the inorganic substances (shale and iron pyrites) that are not essential constituents. All systems of coal-washing depend upon the difference between the sp.gr. of coal and that of its accompanying impurities. The sp.gr. of shale is often double that of coal. The earliest system, that of trough-washing, consists in placing the mixture in a current of water sufficiently powerful to carry away the coal but not powerful enough to transport the shale. The process of separating the coal from impurities by machinery consists in screening with a view to taking out the larger lumps for domestic purposes, crushing when coarse coal has to be washed, and washing the crushed coal, the particles of which have been separated according to their sizes, by causing an upward current of water to pass through the coal, or by allowing the coal to fall through a greater depth of still water. The use, in intermittent upward-current machines, or jiggers, of a layer of felspar (a mineral that has a lower sp.gr. than the impurities but greater than coal) as a medium for separating the coal and impurities, enables the finest coals to be effectively cleansed. A highly perfect plant with machines of this kind (Lührig-Coppée type) has been erected at Dowlais, in South Wales, and treats 1,000 tons per day of ten hours. (On coal-washing, consult T. F. Harvey, Proc. Inst. C.E. 70; Althaus, Entwickelung der mechan. Aufbereitung, Berlin, 1878; Haton de la Goupillière, Exploitation des mines, [2] pt. 10, Paris, 1884; J. Callon, Lectures on Mining, Engl. trans. [3] London, 1886; R. Lamprecht, Kohlenaufbereitung, Leipzig, 1888.) Coking is conducted in the open air in piles, in kilns open at the top, and in closed ovens of brick or stone. The last is the best method; in the first two methods too much carbon is burnt, so that the coke remaining is very rich in ash. Since 1842 numerous modifications of coke-ovens have been brought forward with a view to increasing the yield and improving the quality of the coal, and, recently, to collecting the by-products. Experience soon showed that the best way to employ the combustible gases evolved was to use them for heating the oven itself, and, in consequence, small coal was coked in ovens heated exteriorly by the products of the combustion. The idea of using the heat produced for heating the oven walls continued to be followed; the ovens were greatly reduced in width, several were combined to form one system so arranged that the gas passing through the flues heated two adjacent ovens simultaneously. Partly with the object of increasing the output and partly to avoid loss of heat when the oven was emptied, attempts were made to accelerate as far as possible the charging and emptying of the ovens. In order to burn the volatile matters evolved from the coal, without burning the coke produced, air is employed. It is admitted through adjustable apertures in the door, and through apertures leading to the gas flues. All coke-ovens are regarded by Watson Smith (J. Iron & Steel Inst. 1884, 486) as developments of three typical forms: 1. The beehive, a sort of covered-in pile or meiler; 2. the Coppée; 3. the Knab and Pauwels-Dubochet ovens. He arranges the principal coke-ovens in the following way:—

I. Those in which the by-products are not recovered: (A) Air is admitted, consequently there is partial combustion in the coking space itself, thus some coke is burnt. Examples: 1.

The Meiler or circular pile; 2. Beehive oven; 3. Lürmann's. (B) No air is admitted into the coking space but into the side flues, so as to mix with the gaseous products passing through openings in the oven-walls into side-flues; thus there is complete combustion of all the products, and the ovens are heated without any coke being burnt. Examples: 1. Jones' (Brit. Pat. 1858, No. 2,738); 2. Appolt's (Percy, *op. cit.* 444); 3. Coppée (Brit. Pat. 1868, No. 2,152); in Müller and Wintzek's ovens (modified Coppée ovens), heated air is admitted into side or bottom flues.

II. Those in which the by-products are recovered. (C) Air is admitted into the coking space, so a partial combustion ensues; gases are not saved nor utilised. Examples: 1. Jones' adapted meiler. In 2. Jameson's adapted beehive, and in 3. Hutchinson's, the gases are saved after condensation but are not utilised in the ovens. In some cases the gases, after condensation, return for combustion and are burnt in flues to heat the ovens. Examples: 1. Lürmann's (Germ. Pat. suppl. 1881, 17,203); 2. Aitken's adapted beehive; 3. Jameson's. (D) No air is admitted into the coking space, but at certain stages of the process, the volatile products can pass through spaces in the walls of the ovens into side flues, and, mixing there with air, be burnt to heat the oven, or this passage can be cut off at will, and the volatile products be drawn off by an exhauster and condenser, the pure gas being returned into flues and burnt with air as in Otto's adapted Coppée oven (J. Iron & Steel Inst. 1884, 517). In some cases air is admitted into the coking space towards the close of the process; in this finishing stage the half-burnt gases are burnt in the flues, as in R. de Soldenhoff's oven (Germ. Pat. 1883, 25,824). Or the air admitted to burn the half-burnt gases may receive a previous heating, as in Klonne's adapted beehive (Germ. Pat. 25,673, D. P. J. 252, 256). (E) No air is admitted into the coking space, and in all cases the volatile products are drawn off by an exhauster, and subjected to cooling and condensation for the sake of the tar and ammonia. The gases are returned to the ovens and burnt in the flues with air admitted cold, or with air previously heated (recuperated) as in the Simon-Carvès oven and its modifications, the Hüssener, Semet and Solvay, and Seibel. Or the gases are returned and burnt in conjunction with a small fireplace and solid fuel, as in Pernolet's oven, Carvès' modified Knab oven, the more recent forms of Otto oven, or in conjunction with the fire of gas-producers, as in Herberz and Otto's recent ovens. Or, lastly, the gases are not returned to the ovens at all, but are used as illuminating gas or otherwise, the ovens themselves being heated by solid fuel or by fire from gas-producers, as in the Pauwels-Dubochet (1854), and Herberz oven. In 1884, in Great Britain 50 ovens utilising by-products were in operation, 150 in France, and 190 in Germany. Good coke may be obtained by coking together a mixture of non-caking coal-slack and caking-coal. In Wales, anthracite is coked with caking coal and pitch in the proportion of 60 : 35 : 3. In Pennsylvania, anthracite is coked with an equal quantity of bituminous coal. In metallurgical operations where coke is burnt in contact with the metal, the coke must be as free as possible from sulphur. Various methods of desulphurisation have been proposed, *e.g.* heating the coke to redness in a current of steam, or in a current of air at ordinary pressure, or heating coke to a lower temperature than redness in a current of compressed air, or coking coal in admixture with common salt. None of these methods are thoroughly satisfactory. It is best, therefore, to free the coal from iron pyrites by washing. In 1885 the make of coke in Great Britain amounted to 11,017,375 tons. During the same year, in the United States, there were 20,116 coke ovens with a total production of 5,106,696 tons; in Germany 9,035 ovens, production 4,310,851 tons; in Belgium 3,733 ovens, production 1,678,475 tons. The production of coke in France, Austria-Hungary, Russia, and Spain is estimated at 1,500,000, 446,000, 10,000, 10,000 tons respectively.

3. *Compressed fuels.*

Patent fuel (briquettes). Numerous patents have been taken out for producing a good fuel by mixing various substances with small coal in proportions sufficient to enable the mixture to be pressed into a coherent block. Various binding materials have been tried, *e.g.* soluble glass, asphalt, turpentine. Meal made from potatoes was abandoned because the blocks were not water-tight. Coal tar (Warlick's process) was tried at Swansea, the blocks being baked after compression, whereby a quantity of tar was recovered. On the Continent, cellulose (Germ. Pat. 1879, 7,590) and treacle (Germ. Pat. 1884, 31715) have been tried. Pitch made from coal-tar has been used for many years with great success. Two modes of manufacture are in vogue in South Wales. In the dry process, small coal is carried by an elevator into a large bunker, whence it is lifted by another elevator to a shoot into which it is tipped with the contents of a small elevator containing pitch. The mixture then passes into a Carr's disintegrator, and the resulting product, containing 8 to 12 p.c. of pitch, passes to heaters, and finally to the presses, which turn out 100 to 200 blocks, weighing 10 to 30 lbs. per day of 12 hours. In the steam process, there is used a large vertical iron cylinder with arms revolving inside, constantly kept full of the mixture of pitch and coal. High pressure steam is injected near the bottom, and allowed to percolate up through the mass, whilst the arms expose every portion to its action. Attempts have been made to utilise peat by mixing it in a state of powder with small coal and sawdust, and pressing the mixture into blocks.

Literature.—E. Preissig, Presskohlenindustrie, Freiberg, 1887.

4. *Powdered Fuels.*

In the system of burning powdered fuel worked out by Crampton (J. Iron & Steel Inst. 1873, 91), the coal is pulverised until it passes through a 30-sieve, and fed into the furnace by a kind of injector, air being supplied in measured quantities by a fan, so that intense heat is generated. This method has been successful as regards economy and regularity of high temperature. (On powdered fuel, consult Isherwood, Proc. Inst. C.E. 44, 289; W. G. McMillan, J. Soc. Arts, 34, 527.)

B. Liquid Fuels.

Petroleum. This is a general term under which is included a series of natural mineral oils. Being cheap, and developing great heat on combustion, petroleum is largely used as fuel in America and Russia. Crude petroleum has an average composition of 85 C and 15 H. Its boiling-point is 110 to 280°. According to Deville (C. R. 66, 442; 68, 349) the calorific power of the crude oil is 10,000 calories; it is greater than that of refined oil. Various varieties gave the following calorific powers, in calories: Heavy oil from West Virginia 10,180, light oil from same State 10,223; light oil from Pennsylvania 9,963; heavy oil from Ohio 10,399; oil from Java 10,831; fom Alsace (Schwabweiler) 10,458; from E. Galicia 10,005; from W. Galicia 10,235; from Autun 9,950. The oil is used by burning it in a trough or gutter, by effecting its combustion in a spray by the aid of a jet of steam or air, or by converting it into gas before combustion. Under many circumstances, liquid fuel is an economical fuel. It occupies less space than coal; a ton of coal occupying 40½ cubic feet, oil 33 cubic feet. It also presents the advantages of greater efficiency of evaporation per unit measure of heating surface, more equable generation of steam, greater cleanliness and freedom from ash, avoidance of loss of heat caused by frequent opening of furnace doors, and instantaneous extinction of furnace fires. The oil regions of Pennsylvania have a productive area of 364 square miles, the total production from 1859 to 1884 having been 260,990,035 barrels each of 42 gallons. The production of crude petroleum at Baku in Russia in 1886 is estimated at two million tons.

Literature.—B. J. Crew, Treatise on Petroleum, Philadelphia and London, 1887; H. Aydon, Proc. Inst. C.E. 52, 177; B. Redwood, S. C. I. 6, 405; C. A. Ashburner, Trans. Amer. Inst. M.E. 14, 419.

The crude residue, hitherto a waste product, left after extracting oil from bituminous shale was applied to heating purposes at the Forth Bridge. In appearance, the residue resembles butter, and will not burn on the application of a light. By melting it and forcing it in jets with superheated steam against previously heated fire-clay surfaces with an induced current of air, it burns freely and develops great heat.

C. Gaseous Fuels.

Natural gas. In the petroleum districts of Pennsylvania and adjoining States, natural gas issues from the strata at a depth of 500 to 2,000 ft. below the surface, and when bore-holes are sunk to this accumulation, the gas rises under a mean pressure of 150 to 200 lbs. per square inch. When first reached the tension of the gas is very high, 1,000 lbs. per square inch being not unusual. Since 1821 natural gas has been used in a limited and irregular way for illuminating and heating purposes. Since 1883, however, it has attained an extraordinarily rapid development for industrial purposes. The composition of the gas varies in different wells, and even in the same well after a short lapse of time. The mean volumetric composition is 67 CH_4, 22 H, 0·8 O, 3 N, 5 C_2H_6, 1 C_2H_4, 0·6 CO_2, 0·6 CO. The composition is said to vary within the following limits: 60–80 CH_4, 5–20 H, 1–12 N, 1–8 C_2H_6, 0–2 C_2H_4, 0·3–2 CO_2, trace CO. Its density is 0·45 to 0·55. Natural gas has a calorific power of 14,000 to 15,600 calories, and a calorific intensity of 2,745 to 2,765°. For generating steam 1,000 cubic feet of gas is equal to 80 to 133 lbs. of coal. The neighbourhood of Pittsburg, Pennsylvania, is the most important locality for natural gas. Six companies (1887) supply the gas for that city; they have 107 wells, and transport the gas through 500 miles of pipes, delivering 250 million cubic ft. of gas in one day. No record is kept of the yield of natural gas in the U.S. The amount of coal displaced by gas in 1886 was 6,353,000 tons. It has been found that the supply of gas in a reservoir is limited; some of the smaller ones have already been exhausted. On the other hand, a gas-well at Cambia, Ohio, has been blowing for twenty years without any apparent diminution in the supply.

Literature.—J. Iron & Steel Inst. 1885, 168; Reports of the 2nd Geol. Survey of Pennsylvania; Mineral Resources of the United States, published annually; Use of Natural Gas in the Blast Furnace, Trans. Amer. Inst. M.E. 15, 661.

Producer gases. The only system of heating that offers a remedy for the imperfections of the ordinary fire and of various fuels, is that of heating by gases generated from the fuel by a process resembling distillation. These gases, being collected and conducted to the place where the heat of combustion is to be utilised, are mixed with air, ignited, and consumed. There is no cinder and no ash, so that the surface of the bodies receiving the heat is not altered; the heating is effected by radiation as well as by conduction, and inferior classes of fuel may be used. A higher calorific power may be obtained with gaseous fuel on account of the smaller quantity of air required for combustion, and the consequently lessened dilution of the heat by inert N and CO_2. The investigations of W. Foster (Proc. Inst. C.E. 77, 162) on the N contained in coal have added to the advantages of the use of gaseous fuel the consideration of the recovery of the ammonia and other by-products. The most successful method of applying gaseous fuel is the well-known producer of the brothers Siemens (Brit. Pat. 1861, 167). The principle is the transfer of the waste heat of the products of combustion to the air and combustible gases before entering the furnace by means of regenerators. In a separate gas-producer, the fuel is converted into a mixture containing 30·5 C, 2·5 H, 4 CO_2, 59·5 N, 3·5 CH_4. The producer is a rectangular chamber, 6 ft. wide, 6 ft. deep, 3 ft. from front to back, the front part sloping outwards from the grate, which is formed on the model of the continental step-grate. The sides are of fire-brick, and through an aperture at the top of the brick-wall the gas escapes into an upright chimney and thence into the gas-main. In the top of the producer, which is arched over with fire-brick, charging-holes are placed. Four producers are usually placed side by side, working into one chimney, whence the gas is carried by the gas main to the furnace. Connected with this are 4 regenerators, chambers filled with loose brickwork. The waste heat from the furnace passes through two of these chambers to the chimney, leaving most of the heat stored up in the brick-work. The current is then reversed by valves, and the gas passes up through one regenerator and the air through the other. When the air and gas meet in the furnace itself, combustion ensues and intense heat is produced. Formerly it was considered necessary to bring the flame into contact with the substance to be heated by contracting the furnace chamber and inclining the roof, but F. Siemens (J. Iron & Steel Inst. 1884, 434) thinks that the heat should be transmitted by radiation alone. He has therefore designed a radiation furnace in which the roof is very high, and the ports horizontal, so that the flame travels across the furnace without touching the bed, roof, or sides. It is claimed that there is thus a great saving of fuel and very little wear and tear. Numerous modifications of the Siemens producer, fitted with atmospheric or steam blasts, have been introduced, the Wilson circular producers (Brit. Pat. 1882, 4,697) being perhaps the most successful. Another class of gas-producers consists of apparatus in which incandescent coke or anthracite is used to decompose steam for the production of so-called *water-gas*, either continuously by the use of externally heated retorts containing the C in contact with which the steam is decomposed, or intermittently by the use of generating chambers in which the C is first brought into a state of incandescence by an air-blast, and into which steam is passed through the carbon, the air-blast being cut off; or the heat produced by the combustion of the C, or of gases from the generating chamber, is stored up in brick-work, and subsequently used to decompose steam. The manufacture of water-gas is described by Sir L. Bell (J. Iron & Steel Inst. 1889 [2], 139). The various types of producer are fully described by F. L. Rowan (Proc. Inst. C.E. 84, 2). Since the Siemens furnace has been in use, attempts have been made to regenerate the waste heat without complicated valves and reversing currents. In some cases the waste heat is made to pass through or around fire-clay tubes, the air passing around or through the tubes in the opposite direction. The most successful furnaces of this type are the Gorman and the Ponsard. In Price's retort furnace the waste heat is partly used to heat the air for combustion, and partly to heat the fuel itself. The Boetius furnace, which has no regenerators, is provided with a gas-producer instead of the ordinary grate, thus there is a saving in plant and expense, and loss of heat by radiation is prevented. The air for combustion is heated before its admission by circulating through flues in the wall and roof. This is also the case with the Casson-Bicheroux furnace (J. Iron & Steel Inst. 1884, 60). The gas from producers worked by internal combustion contains 25 to 45 p.c. of combustible ingredients, and has a calorific intensity of 1,575 to 2,200°. Water-gas and ordinary illuminating gas contain 86 to 97 p.c. of combustible matter.

Furnace waste gases may be used instead of producer gas when very high temperatures are not required and where variations in temperature are permissible (*e.g.* heating steam-boilers, hot-blast, brick burning, ore roasting, drying fuel). Blast furnace gases rarely contain 30 p.c. CO, usually 25 to 29.

Other modes of producing heat.

1. In the Cowles electrical furnace (Am. S. 1885, 308) a continuous high temperature is obtained by introducing a material of high resistance to conductivity (coarsely pulverised carbon) into the path of an electric current. A mixture of C and the oxide to be reduced is subjected to the current of a powerful dynamo, and in this way Al, Si, B, Mn, Mg, Na, K, have been reduced from their oxides. 2. Certain elements serve as heat producers, which in special cases replace the ordinary fuel when once the necessary heat has been produced, *e.g.* sulphur in roasting ores, silicon in the Bessemer process. B. H. B.

FULLER'S EARTH. A term originally applied to a sandy loam or argillaceous earth occurring in association with the chalk and oolite, and used in *fulling* or cleansing of cloth. Found in Surrey, Kent, Bedfordshire, &c.

Specimens from Nutfield, Surrey, analysed by Sanford (Geol. Mag. [3] 1889), were found to have the following composition:—

No. 1. Blue Earth.

Dried at 100°C.				Insoluble residue.			
Insoluble residue	=	69·96	per cent. =	SiO_2	=	62·81	per cent.
Oxide of iron, Fe_2O_3	=	2·48	Soluble in acid.	Al_2O_3	=	3·46	,,
Alumina, Al_2O_3	=	3·46		Fe_2O_3	=	1·30	,,
Lime, CaO	=	5·87		CaO	=	1·53	,,
Magnesia, MgO	=	1·41		MgO	=	0·86	,,
Phosphoric acid, P_2O_5	=	0·27				69·96	
Sulphuric acid, SO_3	=	0·05					
Sodic chloride, NaCl	=	0·05					
Alkalis, K_2O	=	0·74					
Combined water	=	15·57					
		99·86					

No. 2. Yellow Earth.

Insoluble residue	=	76·13	per cent. =	Silica	=	59·37	per cent.
Iron, Fe_2O_3	=	2·41	Soluble in acid.	Al_2O_3	=	10·05	,,
Alumina	=	1·77		Fe_2O_3	=	3·86	,,
Lime, CaO	=	4·31		CaO	=	1·86	,,
Magnesia, MgO	=	1·05		MgO	=	1·04	,,
P_2O_5	=	0·14				76·18	
SO_3	=	0·07					
Salt, NaCl	=	0·14					
Alkalis, K_2O	=	0·84					
Combined water	=	13·19					
		100·05					

FULMINATING MERCURY v. Explosives.

FULMINATING SILVER v. Explosives.

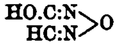
FULMINIC ACID $H_2C_2N_2O_2$, has not been obtained in a free state. Scholvien (J. pr. [2] 32, 161) obtained an ethereal solution of the acid by heating sodium fulminate with dilute sulphuric acid, keeping the mixture cool, and dissolving the yellow oil thus obtained in ether. The solution was very unstable, and the fulminic acid was rapidly converted into the two isomeric acids, isocyanuric acid, $C_3N_3H_3O_3$, and isocyanilic acid HCNO. Howard (T. 1800) first showed that when silver nitrate or mercuric nitrate was heated with alcohol and excess of nitric acid, a crystalline, detonating precipitate—fulminating silver or fulminating mercury, was produced. Analyses of these substances (Liebig, A. Ch. [2] 24, 298; A. 24, 546; Gay-Lussac, A. Ch. [2] 25, 285; Divers and Kawakita, C. J. 1884, 17) show that they are salts of an acid possessing the formula $H_2C_2N_2O_2$. The constitution of this acid has given rise to much discussion. Berzelius wrote fulminating silver as

$$Ag_2O.(AgN)_2.C_4N_2O_2.$$

This formula accounted for the fact that in many of its reactions only half of the metal is separated, also that the double fulminate of potassium and silver detonates as violently as fulminating silver itself, the detonation being attributed to the decomposition of the compound AgN. Laurent and Gerhardt next proposed the constitution $C_2N(NO_2)Ag_2$, assigning the explosive nature of the body to the presence of a nitro-group, and the subsequent experiments of Kekulé (A. 101, 200; 105, 279) and Schischkoff (A. 101, 213) apparently confirmed this view. These chemists found that fulminating mercury treated with chlorine or bleaching powder yielded chloropicrin, $C(NO_2)Cl_3$, and with bromine, bromopicrin, or dibromonitracetonitrile, according as bromine or fulminating mercury was in excess. Isocyanuric or fulminuric acid, $C_3N_3H_3O_3$, a body produced by the action of alkaline chlorides or iodides on fulminating mercury, was also found by them to yield chloropicrin on treatment with bleaching powder and tri-nitracetonitrile, with strong nitric acid.

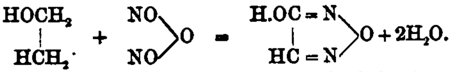
Kekulé then formulated fulminic acid as $CH_2(NO_2)CN$. This constitution is in accordance with the preceding reactions, and accounts in some measure for the explosive character of the fulminates. It shows why cyanogen derivatives are so readily formed from them, and represents half the nitrogen as oxidised, and able to be converted into hydroxylamine. But it makes a nitroxyl group to be introduced by nitrous acid, which it should not do. It entirely fails to account for the two kinds of acid properties which the fulminates possess, and allows of only half the nitrogen becoming hydroxylamine, whereas Divers and Kawakita have shown that all the nitrogen is so convertible (C. J. 1884, 16). Schischkoff (C. R. 52, 99) doubles Kekulé's formula for fulminic acid, and writes it as $C_4(NO_2)_2H_4Cy_2$, in order to explain its formation, which he supposes is due to the union of dinitroethylene and hydrocyanic acid, produced by the action of nitric acid on alcohol. From the fact that mercuric fulminate yields hydroxylamine on treatment with hydrochloric acid (Carstanjen and Ehrenberg, J. pr. [2] 25, 232), Steiner (C. 16, 1484) proposed HON:C:C:NOH as the formula of fulminic acid. This formula, however, does not make the explosive character of the fulminates apparent, nor the production of cyanogen compounds probable, and represents the two hydrogen atoms of equal value.

Divers (C. J. 1884, 19) writes the acid as



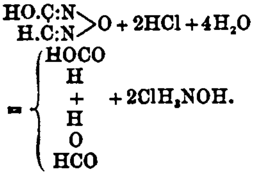
$$\begin{matrix}\text{HO.C:N}\\ \text{HC:N}\end{matrix}\!>\!O$$

and its formation from alcohol, thus—



$$\begin{matrix}HOCH_2\\ |\\ HCH_2\end{matrix} + \begin{matrix}NO\\ NO\end{matrix}\!>\!O = \begin{matrix}H.OC=N\\ |\\ HC=N\end{matrix}\!>\!O + 2H_2O.$$

This constitution readily explains the behaviour of the fulminates towards reagents, and accounts for their producing formic acid and hydroxylamine on treatment with hydrochloric acid, thus—



$$\begin{matrix}\text{HO.C:N}\\ \text{H.C:N}\end{matrix}\!>\!O + 2HCl + 4H_2O = \left\{\begin{matrix}HOCO\\ H\\ +\\ H\\ O\\ HCO\end{matrix}\right. + 2ClH_3NOH.$$

The formula was, however, subsequently modified by Divers (C. J. 1886, 582) to $\underset{\displaystyle H}{HOC\dot{N}ONC}$, the carbon atoms being disconnected, and having along with the nitrogen atoms the same valencies as they have in the carbamines, either C^{II} and N^{III} or C^{IV} and N^{V}. This constitution more clearly explains the action of chlorine and iodine on the fulminates. It accounts for the non-production of di-carbon derivatives, and represents the atom of silver in silver fulminate, which is not displaceable by potassium, as joined to nitrogen and not to carbon.

Armstrong, in pointing out that a fulminate is not the immediate product of the action of nitrous acid on alcohol in presence of a silver or mercury salt, regards the fulminate as due to the simultaneous or, it may be, consecutive action of nitrous acid and hydroxylamine on hydroxyethaldehydrol $CH_2(OH).CH(OH)_2$. This last body he considers is formed as shown by Debus by the action of dilute nitric acid on alcohol, the hydroxylamine being produced from the nitric or nitrous acid by the reducing action of ethaldehydrol on the higher hydroxylated derivatives of alcohol. In this way he deduces $N\!<\!\begin{matrix}COH\\ C(NOH)\end{matrix}$ or $\begin{matrix}N.CH\\ O.C(NOH)\end{matrix}$ as probable formulæ for fulminic acid (C. J. 1884, 26; 1885, 79).

Whether either of these formulæ or that finally proposed by Divers represents the constitution of fulminic acid, in the present state of knowledge it is impossible to say.

Mercuric fulminate or **fulminating mercury** $C_2HgN_2O_2$. To prepare this substance on a small scale, 3 parts of mercury are dissolved in 36 parts nitric acid of sp.gr. 1·34, without warming. The solution is then poured into a flask capable of containing eighteen times the quantity, in which there has been placed 17 parts alcohol of from 90–92 volumes p.c. The liquids are well mixed, poured back into the first vessel, which is of the same size, shaken to absorb nitrous fumes, and the whole then allowed to stand. In a short time gas is given off and a highly refracting liquid separates at the bottom of the flask. On shaking the flask to mix this liquid with the rest, the whole becomes black, metallic mercury separates, and a violent reaction takes place, which is moderated by the gradual addition of 17 parts of alcohol. Crystals of mercuric fulminate separate on cooling (Liebig).

On a large scale 1 part mercury is dissolved in 10 parts nitric acid of sp.gr. 1·33, and to every kilogram of acid 1 litre of alcohol of sp.gr. ·833 is added. The reaction begins either spontaneously or on slightly warming. The operation is carried out either in a tubulated retort, in which case the evolved gases escape into a flue, or in glass balloons placed in an open wooden shed. As soon as the alcohol has been added, the operator does not approach the shed till the reaction is complete (*v.* EXPLOSIVES). Mercuric fulminate may also be produced by using mercuric oxide for mercury in the above preparation, by boiling silver fulminate with mercury and water or by precipitating the zinc salt with mercuric chloride.

It crystallises from hot water in white or greyish silky needles of sp.gr. 4·42. It is insoluble in cold water.

When heated to 180° or when forcibly struck, mercuric fulminate detonates with great violence. The electric spark or the spark from flint and steel, or contact with nitric or sulphuric acids also bring about explosive decomposition. When moist it may be handled without danger, and when heated to 100° it does not explode if the crystals contain no inclosed mother liquor. The disruptive force of the explosion within a small space is greater than that of gunpowder, but too sudden for its use in guns. The pressure exerted by the gases evolved in the decomposition of the fulminate is less than that caused by the explosion of an equal weight of gun-cotton, the greater action of the former being attributed to the density of the compound and the great rapidity of the decomposition. Fulminate of mercury is used in the manufacture of percussion caps and of the various detonators used for exploding gun-cotton, dynamite, and other nitro-glycerin compounds (*v.* EXPLOSIVES).

Concentrated hydrochloric acid reacts with perfectly dry mercuric fulminate to produce formic acid and hydroxyammonium chloride. Thus: $C_2H_2N_2O_2 + 4H_2O = 2H.COOH + 2NH_2O$.

If the fulminate is moist, or the acid dilute, hydrocyanic acid is also a product of the reaction; no oxalic acid is produced in either case (Divers and Kawakita, C. J. 1884, 13).

Moderately dilute sulphuric acid decomposes mercuric fulminate without explosion; hot nitric acid converts it into mercuric nitrate, acetic acid, and carbon dioxide. If sulphuretted hydrogen be passed through ether in which mercuric fulminate is suspended, ammonium thiocyanate and a body having the formula $C_2H_4N_2O_2S$ is produced. This latter substance may be regarded as nitro-acethiamide, and is decomposed by sulphuretted hydrogen into ammonium thiocyanate, oxalic acid, and sulphur (Steiner, B. 7, 1244; 8, 518; 9, 779). Heated with aqueous ammonia, mercuric fulminate yields urea, guanidine, and complex nitrogenous substances; with alcoholic ammonia, fulminuric acid is the main product (Steiner).

Potash, lime, and strontia decompose mercuric fulminate on boiling, with the separation of mercuric oxide and the formation of double salts, which detonate on percussion (Liebig).

Finely divided zinc, copper, or silver (the last in contact with platinum) displace mercury from the fulminate, forming salts of zinc, copper, or silver. Mercuric fulminate readily forms double salts with potassium cyanide and potassium and ammonium thiocyanates (Steiner).

Silver fulminate, *Fulminating silver*

$$C_2Ag_2N_2O_2.$$

In preparing this substance 1 part silver is dissolved in 20 parts nitric acid of sp.gr. 1·36 and 27 parts of 86 p.c., spirit of wine added, and the whole gently heated till it froths up. The liquid is then removed and 27 parts or more of spirit added in order to moderate the action. Fulminate of silver separates out on cooling (Liebig).

Silver fulminate is not formed, as was stated by Liebig (A. 5, 287), when nitrogen trioxide is led into an alcoholic solution of silver nitrate (Divers and Kawakita, C. J. 1884, 27), and is only produced by the energetic oxidation of alcohol by nitric acid in presence of silver nitrate. Great caution must be exercised in the preparation of this substance. Capacious vessels must be used, so that the liquid may not boil over, as in that case the salt might dry on the outside and then explode; all flame must be kept at a distance lest the vapours should take fire; and the mixture should be stirred with wooden rods, not with glass rods or other hard bodies. When dry it should be transferred on paper shovels, and kept in paper or card-board vessels, loosely covered, to prevent explosion from the friction of stoppers or lids.

Silver fulminate crystallises in white opaque glistening needles, scarcely soluble in water, and having a bitter metallic taste. Given in certain doses it produces violent convulsions (Pagot-la-Forêt), while in doses of ·3 gram it acts as a narcotic (Ittner).

Fulminate of silver is an exceedingly dangerous body, as it explodes much more violently than the mercury salt, by the action of heat, by the electric spark, by friction or percussion, or by contact with oil of vitriol. It even explodes in the moist state, sometimes under water, by friction with a glass rod. It may be rubbed to powder in a mortar with the finger or with a cork. The light accompanying the explosion, which is best seen in the dark, is reddish white with a tinge of blue (Liebig). When ignited under a pressure of about 2 or 3 mm. it burns slowly with a visible flame. If fulminate of silver be thrown into a bottle containing chlorine it deflagrates before it reaches the bottom, and does not fracture the bottle (E. Davy). Silver fulminate dissolves in hot aqueous ammonia, and the solution, on cooling, deposits crystalline grains of ammonium silver fulminate

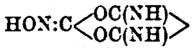
$$C_2Ag(NH_4)H_2O_2.$$

This salt is sparingly soluble in water, and explodes with much greater violence than the silver salt, even under liquid, when touched with a glass rod (Liebig). Aqueous solutions of the hydrates of the metals of the alkalis or alkaline earths, or of the sulphides or chlorides of the alkalis, yield similar double salts when boiled with silver fulminate. Copper or mercury can displace silver wholly or in part from silver fulminate. Zinc, even on boiling for several days, displaces only half of the silver, forming silver zinc fulminate. The normal zinc salt is prepared by the action of zinc on mercuric fulminate. By acting on this salt with baryta water, and exactly precipitating the barium from the zinc barium fulminate thus produced with sulphuric acid, zinc hydrogen fulminate is obtained. By saturating this salt with metallic bases, many double salts of zinc fulminate are obtained.

FULMINURIC ACID *Isocyanuric acid* $C_3H_3N_3O_3$. This compound was discovered independently by Liebig (A. 95, 282) and Schischkoff (A. 97, 53; 101, 213). It is produced by boiling a solution of a metallic chloride or iodide with water and mercuric fulminate

$$2C_2H_2N_2O_2 + H_2O = C_3H_3N_3O_3 + CO_2 + NH_3.$$

Sixty to seventy-five grams of well-washed mercuric fulminate are boiled with 700 to 800 c.c. of water, 60 c.c. of a saturated solution of ammonium chloride are then added, and the whole heated to the boiling-point. As soon as a yellow deposit of oxydimercuric ammonic chloride separates, the flame is removed, and ammonia added till all the mercury is precipitated. On filtering, evaporating the filtrate, and recrystallising the first crop of crystals, pure ammonium fulminurate is obtained. On converting this into the basic lead salt by treating with lead acetate and precipitating with sulphuretted hydrogen, an aqueous solution of fulminuric acid is obtained. This, on evaporation and standing in a warm place, solidifies to an indistinctly crystalline mass, which, dissolved in alcohol, deposits on evaporation colourless prisms of fulminuric acid. The potassium or ammonium salt may be converted into the silver salt, which may be decomposed by hydrochloric acid yielding free fulminuric acid. The acid decomposes on heating, with slight deflagration, and has an acid taste and reaction. Its aqueous solution is decomposed by mineral acids. It appears to be monobasic. The constitution of fulminuric acid is still uncertain. It is probably represented by the formula



$$HON{:}C\left\langle\begin{matrix}OC(NH)\\OC(NH)\end{matrix}\right\rangle$$

(Ehrenberg, J. pr. [2] 32, 97).

Ammonium fulminurate forms anhydrous monoclinic crystals which blacken on heating and give off hydrocyanic acid, ammonia, and cyanic acid, which latter partially unite to form urea (Liebig).

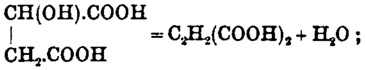
Potassium fulminurate. To prepare this body two parts of mercuric fulminate are gradually added to a saturated solution of one part of potassium chloride and the mixture gently boiled till the whole is dissolved. The liquid is filtered through a hot funnel from a yellowish precipitate which appears, and the compound of mercuric oxide and potassium fulminurate, which separates in the filtrate, is freed from mercury by sulphuretted hydrogen. On recrystallising from water, potassium fulminurate separates in long glistening prisms, which decompose with incandescence when heated to 225° (Schischkoff).

Silver fulminurate may be obtained by heating ammonium or potassium fulminurate with silver nitrate. It is almost insoluble in cold water, but may be recrystallised from boiling water in long very thin needles. Heated with concentrated hydrochloric acid, in sealed tubes, at 110°, traces of the oxides of carbon are produced; one-third of the nitrogen goes to form hydroxylamine hydrochloride, and the other two-thirds ammonium chloride (Ehrenberg). Under ordinary pressures at 100° the action is complicated.

The fulminurates of calcium, barium, strontium, iron, and lead may be obtained by double decomposition from ammonium or potassium fulminurates. On heating an ammoniacal solution of copper sulphate with fulminuric acid, dark-blue prisms of ammonium copper fulminurate are deposited on cooling. By passing hydrochloric acid gas through alcohol containing potassium fulminurate in suspension, Schischkoff obtained an oil which he considered to be ethyl fulminurate. This body is, however, not an ethyl salt of fulminuric acid, but has the composition $C_4H_6EtNO_5$. It readily forms additive compounds with ammonia and the amines (Ehrenberg, *l.c.*).

FUMARIC ACID and **MALEIC ACID**
$C_2H_2(COOH)_2$.

These two unsaturated dibasic acids may be obtained by heating malic acid:



$$\begin{matrix}CH(OH).COOH\\|\\CH_2.COOH\end{matrix} = C_2H_2(COOH)_2 + H_2O;$$

maleic anhydride $C_4H_2O_3$ distils over, and fumaric acid remains behind in the retort. By rapid distillation maleic anhydride is obtained as chief product; by long heating to 150° fumaric acid is mainly formed.

Both acids when treated with nascent hydrogen yield succinic acid. Both unite with hydrobromic acid to form monobromsuccinic acid. But fumaric acid unites with bromine to form dibromosuccinic acid, whilst maleic acid gives isodibromosuccinic acid. Potassium permanganate oxidises fumaric acid to racemic acid; maleic acid is converted into inactive tartaric acid.

The difficulty of explaining these and other reactions of fumaric and maleic acid by means of ordinary constitutional formulæ has led to the adoption of stereometric (tridimensional) formulæ for these compounds, a subject which, however, cannot be discussed here.

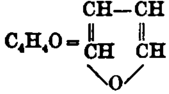
Fumaric acid occurs in various plants, thus in the common fumitory (*Fumaria officinalis*), in Iceland moss, and in some fungi. Small prisms, very sparingly soluble in water. Sublimes at 200° without decomposition, but by distillation is converted into maleic anhydride and water. Fumaric acid forms no anhydride of its own: all processes of dehydration convert it into maleic anhydride, which unites with water to form maleic acid.

Maleic acid forms large prisms or tabular crystals, very soluble even in cold water. It melts at 130° and boils at 160°, decomposing for the most part into anhydride and water.

Heating for some time to 130°, or boiling with dilute mineral acids converts it into fumaric acid. F. R. J.

FUMARINE *v.* VEGETO-ALKALOIDS.

FURFURAN *Tetrol, Tetraphenol*



$C_4H_4O =$

Obtained by the distillation of barium pyromucate with soda-lime:

$$C_4H_3O(COOH) = C_4H_4O + CO_2$$

(Limpricht, B. 3, 90; A. 165, 281). Appears to be contained in the volatile portions of pinewood tar.—Colourless liquid, boiling at 32°. Insoluble in water, readily soluble in alcohol and in ether. Acids convert it into pyrrhole-red. F. R. J.

FURFURINE $C_{15}H_{12}N_2O_3$. By the action of ammonia on furfurol furfuramide is obtained, and this, by boiling with dilute caustic potash (Fownes), or by heating to 110-120° (Bertagnini, A. 88, 128), is converted into the isomeric furfurine.—Needles, melting at 116°. Sparingly soluble in water, readily soluble in alcohol and ether. Monacid base. F. R. J.

FURFUROL *Furfuraldehyde, Pyromucic aldehyde* $(C_4H_3O)CHO$. First obtained by Doebereiner by distilling sugar with manganese dioxide and dilute sulphuric acid. Best by distilling bran with dilute sulphuric acid (Fownes). An aqueous solution is obtained, from which the furfurol may be separated by fractional distillation.—Colourless liquid, boiling at 161°, smelling like benzaldehyde and cinnamaldehyde. Moist silver oxide converts it into pyromucic acid. F. R. J.

FURNACES FOR GENERAL LABORATORY USE. Fig. 1 shows a Fletcher's muffle furnace which, while intended principally for cupellation, will be found invaluable for general laboratory use in the ignition of precipitates, fusions, roasting ores, &c. This little furnace, the smallest and most generally useful size of which has a muffle of 2 × 2½ × 4½ in. internal dimensions, may be maintained at a clear yellow heat with the solid flame burner shown, or may be arranged to work with a blast for more elevated temperatures. When crucibles which have to be weighed are heated, a sheet of asbestos cloth or platinum foil should be placed on the floor of the muffle, and it is advisable, in general work, to keep a layer of bone ash or other absorbent on the muffle floor to avoid the injury to the muffle in case of accident to the crucible.

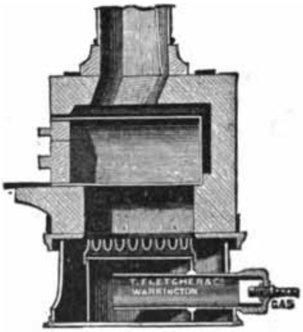


FIG. 1.

A Fletcher's 'injector' furnace, used with a foot blower for the production of temperatures sufficiently high for the fusion of nickel, is shown in fig. 2.

FIG. 2.

Where gas is not obtainable, or cannot be used on account of the sulphur contained, the injector furnace may be worked at its full power with air gas as shown in fig. 3. A branch pipe from the blast tube is connected with the lower regulating tap A of a generator which is charged with *benzoline*, or preferably with *gasoline*, and from whose upper tap B passes a tube to the side tube of the injector burner. The flame in this type of furnace is very liable to become suddenly extinguished.

FIG. 3.

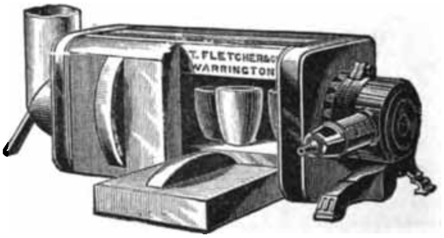


FIG. 4.

Fig. 4 shows a Fletcher's reverberatory furnace available for all general laboratory work, and capable, when working with a draught, of producing a clear yellow heat above the fusing-point of fine silver, and when worked with a blast, for which the same burner is employed, of melting cast steel. It may be employed as shown, or one or both doors may be arranged to receive a muffle, so that the furnace may be used for muffle or crucible operations, or for both simultaneously. Perrot's furnace for heating crucibles by gas is described fully in the Bl. 7, 1867, 332.

A furnace designed by Rössler (Fr. 1886, 95; D. P. J. 253, 79; S. C. I. 1884, 512) for intensely heating the small crucibles employed in chemical analysis is shown in fig. 5. Cold air admitted in carefully regulated quantity at *e* to the burner *a* becomes heated during its passage around a jacket *d*. Combustion takes place within a muffle *c*, surrounding the crucible *b*, and the combustion products pass out through the cover of the muffle and through a chimney *g*, the draught in which is assisted and regulated by a second burner.

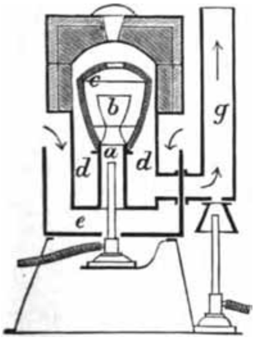


Fig. 5

A somewhat similar arrangement has been described by Hempel (Fr. 1877, 454).

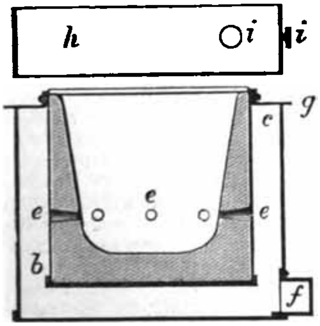


Fig. 6.

Sefström's well-known portable furnace for use with charcoal is shown in fig. 6. It consists of an outer cylinder forming an air chamber around a cylinder *b*, fixed in position by a flange *g*. The cylinder *b* is formed with holes containing small tapering nozzles *e*, and is lined with fire-clay shaped as shown. When greater space is required for fuel &c., a hoop *h* may be placed around the top of the cylinder *b*. It consists of a strip of sheet iron in one end of which are two holes *i*, while in the other end is a button which may be inserted in either of the holes so that the hoop may fit over the cylinder *b*, or, when not in use, over the outer cylinder. The blast is supplied at *f* by a small bellows.

Deville's blast furnace, in which he has melted platinum, is somewhat similar. The crucible, surrounded by fuel, is placed on a stand in a fireclay-lined metal cylinder, above a perforated plate forming the top of a hemispherical chamber into which the blast is admitted.

Furnaces employed for special purposes will be found described under special headings as Assaying; Arsenic; Aluminium; &c. &c.

FUSEL OIL. *Fermentation amyl alcohol, Potato oil, Grain oil, Marc brandy oil.* (Ger. *Fuselöl*; Fr. *Huile de pommes de terre.*) The mixture of alcohols constituting this substance is produced in comparatively small quantity in the alcoholic fermentation of most bodies containing sugar, the largest proportion being contained in the alcohol prepared from potatoes, while in the alcohol from the 'marc' of grapes and from beetroots, grain, &c., smaller quantities are found.

Fusel oil consists mainly of two alcohols, one of which, iso-butyl carbinol, or iso-amyl alcohol, or inactive amyl alcohol $(CH_3)_2CH.CH_2CH_2HO$, is optically inactive, while the other, secondary butyl carbinol or active amyl alcohol

$$C.C_2H_5.CH_3H.CH_2.H.O,$$

rotates the plane of polarised light to the left sufficiently to render fusel oil strongly lævo-rotatory. Several other alcohols, together with fatty acids, ethereal salts, aldehydes, &c., are also found. The following list shows the *alcohols* which are said to have been separated from fusel oil:

Ethyl alcohol . .	$MeCH_2HO$.
Normal propyl alcohol	$MeCH_2CH_2HO$.
Isopropyl „	$(Me)_2CHHO$.
Normal butyl „	$MeCH_2CH_2CH_2HO$.
Isobutyl „	$(Me)_2CHCH_2HO$.
Tertiary butyl „	$(Me)_3CHO$.
Active amyl „	$C.Et.Me.H.CH_2HO$.
Inactive amyl „	$(Me)_2CHCH_2CH_2HO$.
Methyl normal propyl carbinol . .	$MeCH_2CH_2C.MeHHO$.
Normal primary amyl alcohol . .	$Me.CH_2CH_3CH_2CH_2HO$.
A primary hexyl alcohol.	
„ heptyl „	

Formic, acetic, valeric, caproic, œnanthic, caprylic, and margaric acids have been found in fusel oils, and ethyl acetate and other ethereal salts and various aldehydes are also present.

The composition of fusel oil depends on the source of production. That from grain or potatoes consists largely of amylic alcohols with ethyl alcohol, the inactive amyl alcohol being the principal constituent. The fusel oil prepared in the South of France from the marc of brandy contains normal propyl alcohol in considerable quantities, while that obtained from the beet contains a larger proportion of isoprimary butyl alcohol.

The proportion of fusel oil obtained during fermentation is also modified by the condition of the mash. Alkaline liquids, particularly when warm and containing large quantities of sugar, promote its formation, while acid liquids, especially when containing tartaric, racemic, or citric acids are said to prevent its production. The presence in any quantity of tartar or certain bitters such as that of hops also prevents its formation, so that wines &c. are usually free from fusel oil. According to Le Bel (C. R. 96, 1368) pure sugar fermented with beer yeast yields less of these alcohols than wine or beer.

Fusel oil is contained principally in the alcoholic distillates commencing to come off at 105–125° and ending at 132–137°C. Between 105° and 120° most of the isobutyl alcohol is obtained, while the amyl alcohols distil principally between 128° and 132°.

According to Rabuteau (C. R. 87, 500), the following represents the percentage by volume of the principal constituents of *potato oil*:

Isopropyl alcohol	15·0
Propyl „	3·0
Normal butyl alcohol	6·5
Isobutyl „	5·0
Inactive amyl „	27·5
Active „ „	6·0
Products boiling above 132° and retaining amyl alcohol	17·0
Water	12·5
	92·5

The remaining 7·5 volumes contained ethyl alcohol, ethyl acetate, and aldehyde.

According to Ulex, the distillation of fusel oil produced from (1) beet, (2) potatoes, (3) grain, gives (roughly) the following percentage by volume:

	1	2	3
80–100°C. (principally propyl alcohol)	13	13	31
100–130°C. (butyl and amyl alcohols)	53	30	26
Above 130°C. (amyl alcohol)	34	57	43

By careful fractional distillation of wine brandy 25 years old, Ordonneau (C. R. 1886, 102, 217) has obtained the following substances:

		p.c. by volume
Aldehyde		0·003
Ethyl acetate		0·035
Acetate		traces
Œnanthylic ether	about	0·004
Propionic, butyric, and caproic ethers		0·003
Normal propyl alcohol		0·040
„ butyl „		0·218
'Amyl alcohol'		0·0838
Hexyl alcohol		0·0006
Heptyl alcohol		0·0015
Amine bases (probably of the pyridine series)		traces

Commercial alcohols from maize, beets, and potatoes showed the presence, in addition to other substances, of propyl alcohol, active and inactive amyl alcohol, pyridine, a base which appeared to be collidine, and *isobutyl* alcohol, without a trace of *normal* butyl alcohol. Ordonneau attributes the disagreeable difference in flavour between wine brandy and that from a mash to the presence in the former of normal butyl alcohol, while the latter contains the disagreeably smelling isobutyl alcohol but no normal butyl alcohol. He recommends that the fermentation of a mash should be performed with the elliptic *wine* yeast instead of the globular *beer* yeast, as he finds by experiment that the former produces the normal butyl alcohol while the latter tends to form the iso- variety.

The iso-amylic alcohol (inactive amyl alcohol) may be separated from fusel oil by agitation with a saturated solution of common salt. The amyl, butyl, and propyl alcohols, which are less soluble in that medium than in water, separate as an oily layer, while the ethyl alcohol remains in the brine. The separated oil is distilled, the portion coming off between 105° and 120° consisting principally of iso-butyl alcohol, while that distilling between 125° and 140° contains the amyl alcohols. This is collected separately, agitated with hot milk of lime, dried over calcium chloride and re-distilled, the portion coming off between 128° and 132° being collected separately. In this way the iso-amyl alcohol is obtained almost free from butyl alcohol and from valeric aldehyde. The amyl sulphate of barium produced from active amyl alcohol is 2½ times as soluble in water as that from the inactive variety, so that these salts may be separated by careful fractional crystallisation and afterwards treated for reproduction of the alcohols.

The injurious effect of raw or recently manufactured spirits is principally attributable to the presence of fusel oil produced during the fermentation and not thoroughly separated. The actual adulteration of alcoholic liquors with fusel oil is improbable, but spirits containing 0·3 p.c. of that substance are distinctly injurious.

Samples of spirits examined by Dupré (Analyst, 1, 6) contained for 100 parts by weight of ethyl alcohol:

Scotch whisky containing 54·5 p.c. of alcohol	0·19 p.c. amyl alcohol
Cape smoke	0·24 „
Common Samshoe	0·18 „
Fine „	0·13 „

According to Le Bel (C. R. 96, 1368), natural white wine contains 0·2 p.c. amyl alcohol per litre, and according to Hamberg (Schmidt's Jahrb. der Medicin, 201, 27, 1885) beer contains about 0·00114 p.c. of fusel oil.

Beer recommends a maximum permissible limit to the fusel oil in brandy, liqueurs, &c. of 0·3 p.c., but Bödlander and Traube (Rep. Anal. Chem. 7, 167), who have examined a number of commercial spirits, propose a limit of 0·1 to 0·15 p.c.

The separation of fusel oil from spirit is extremely difficult. Among the various substances proposed or used for its destruction or removal, are charcoal, soap, oil and fatty substances, potash ('grey salts') pearl ash ('white salts') lime, sulphuric, nitric, and hydrochloric acids, bleaching powder, and permanganate of potassium.

Charcoal, soap, and oil, are supposed to separate the fusel oil unchanged. When rectified over potassium permanganate or bleaching powder, the amyl alcohols are converted into valerates, but a portion of the ethyl alcohol is also decomposed. Bleaching powder, when used, is made into a milk at the ordinary temperature and permitted to digest for a time, after which the spirit is drawn off and rectified. According to Klezensky, if the spirit be distilled from *hard soda soap*, the fusel oil remains with the soap, from which it may be separated by subsequent distillation at a more elevated temperature.

The most approved method of separation, however, is by well-burnt granulated vegetable charcoal or bone-black. The charcoal is placed upon perforated trays in a vessel surrounded by a cooling jacket, and the spirit, usually diluted to about 160° Tr., is caused to pass through several layers. The operation should not be performed above the ordinary temperature, as the fusel oil is again dissolved from the charcoal near the boiling temperature. From 3 to 5 vols. of charcoal is required for the successful treatment of 100 vols. of brandy. The whole of the fusel oil is evolved from the charcoal on treatment by superheated steam, and the charcoal may be repeatedly used after heating to redness to drive off the occluded gases &c. It is noticeable that the fusel oil obtained by steaming the charcoal does not represent the whole of that removed from the spirit, nor are sufficient compounds which might be produced by the decomposition of the fusel oils found to account for this loss.

Raw brandy, produced in Switzerland from potatoes, maize, and the residues from breweries, by the continuous process, has been found to contain 1·32 p.c. of fusel oil. Raw Swiss brandy filtered through charcoal showed 0·2 p.c. of fusel oil, that rectified by distillation 0·06, and that filtered through charcoal and afterwards rectified, contained none.

Remarks by F. Pampe on the above processes will be found in the Chem. Zeit. 11, 313.

The amyl alcohols of fusel oil dissolve in about 40 parts of cold water. According to Balbiano (B. 9, 1437) the inactive variety is soluble in about 50 parts of water at 14°C. and is less soluble at 50°. Isobutyl alcohol dissolves in 10 parts of water at 15°C. ,One part of inactive amyl alcohol takes up about 0·08 parts of water, while isobutyl alcohol dissolves nearly twice that amount.

Fusel oil dissolves freely in ether, chloroform, alcohol, and benzene.

It is largely used for the manufacture of amyl acetates (for their preparation and applications *v.* Acetic Acid). It is also used in toxicology as a solvent for alkaloids, for which purpose it should be carefully purified by agitation with dilute acid to remove an alkaloidal body which it is liable to contain. On account of its strong affinity for chlorine it has been employed in chlorine generators for laboratory purposes as an absorbent for that gas, to prevent its escape into the atmosphere when the supply is no longer required.

Detection of fusel oils. When a sample of spirit is poured on filter paper or on the hand and allowed to evaporate spontaneously, the characteristic suffocating odour of fusel oil may be recognised towards the close of the evaporation. So small a quantity as $\frac{1}{2000}$ part of amyl alcohol in gin may thus be detected.

On dissolving 1 gram of caustic potash in 150 c.c. of the spirit, concentrating slowly to 15 c.c. and adding an equal volume of dilute sulphuric acid, a powerful odour is given off which is frequently sufficiently distinctive to show the nature of the mash from which the spirit was obtained. Betali (B. 8, 72) adds to the alcohol 6 to 7 volumes of water, and agitates with sufficient chloroform to produce a small layer on subsidence. This layer is drawn off and evaporated, and the residue is tested by digestion with potassium acetate and sulphuric acid. In presence of fusel oil the characteristic pear-like odour of amyl acetate is observable.

Marquardt dilutes 40 c.c. of the spirit with sufficient water to raise the density to about 0·980 and agitates the mixture with 15 c.c. of pure chloroform, which, after settlement, is drawn off, shaken with an equal volume of water, and evaporated spontaneously. The residue is treated with a little water, one or two drops of sulphuric acid, and sufficient of a strong solution of potassium permanganate to ensure that the liquid shall remain red after standing for twenty-four hours in a closed tube. The odour of valeric aldehyde is frequently noticeable shortly after the addition of the permanganate, but the characteristic smell of *valeric acid* on which this very delicate test is based, is not appreciable until after standing.

Determination.—Fusel oil containing less than 15 p.c. of proof spirit is admitted duty free into England. In preference to the erroneous method employed by the Excise, in which the spirit is agitated with an equal volume of water and the amount of ethyl alcohol taken up by the water is ascertained by determining its specific gravity, Ulex recommends the following: Heat 100 c.c. of the spirit in a retort until 5 c.c. have distilled over, and shake the distillate with an equal volume of a saturated solution of common salt. If the fusel oil which separates after standing represent not less than half the distillate, the sample contained less than 15 p.c. of ethyl alcohol, but if less separates, at least that proportion must be present. In that case, a known volume of the sample is shaken up with an equal volume of a saturated common salt solution, and the proportion of ethyl alcohol is estimated by distilling, and determining the specific gravity of the distillate from the aqueous liquor which separates beneath the fusel oil and which contains the whole of the ethyl alcohol.

The accurate estimation of fusel oil in spirits is extremely difficult. The most certain method appears to be that of Marquardt (B. 15, 1661). Sufficient water is added to 150 grams of the spirit to raise its density to about 0·980, and the mixture is agitated for about a quarter of an hour with 50 c.c. of *pure* chloroform (free from impurities which produce valeric and other volatile fatty acids on oxidation). The aqueous layer is separated and treated with a second quantity of chloroform, the aqueous layer from which is treated a third time. The 150 c.c. of chloroform thus produced contains the whole of the amyl alcohol, and is treated in a strong flask with 2 grams of sulphuric acid and a solution of 5 grams of potassium bichromate in 30 c.c. of water, and the closed flask is kept at 85°C. for six hours, with frequent agitation. The liquid is distilled until only about 20 c.c. remain, and to this residue 80 c.c. of water is added, and the distillation is continued until only about 5 c.c. remain. The distillates are digested with barium carbonate for thirty minutes in a flask having an inverted condenser, after which the chloroform is distilled off and the aqueous residue is evaporated to 5 c.c. The solution is filtered from the remaining barium carbonate, and is evaporated to dryness on the water-bath. The residue is weighed, dissolved in water, and diluted to 100 c.c., and exactly half of it is acidulated with nitric acid and precipitated with silver nitrate. The precipitated silver chloride is filtered off, washed, dried, and weighed to ascertain the amount of chlorine in the liquid. The remaining half of the solution is mixed with sulphuric acid, and the barium sulphate precipitated is collected and weighed to ascertain the amount of barium in the solution. The difference between the sum of the weights of barium and chlorine found in the 100 c.c. of solution and the weight of the residue dissolved to form the solution gives the weight of the valeric radicle contained, and this weight, when multiplied by 0·871, gives the weight of amyl alcohol in the spirit taken. This method, like other chemical methods, estimates the amyl alcohol and not the fusel oil itself. The differences produced in the result of the analysis by other substances in the fusel oil, however, tend to neutralise each other, so that the result may be taken as representing the percentage of *fusel oil*. Marquardt obtained 1·02 grams of fusel oil from 1,000 grams of spirit to which 1·00 gram of fusel oil had been added.

A very rapid and simple process introduced by Traube is said to give satisfactory results. The specific gravity of the spirit having been determined, sufficient water is added to reduce the proportion of alcohol to 20 p.c. An error of one-half per cent. in the strength of the diluted spirit is not of great importance. The liquor is sucked up and allowed to fall a few times in a carefully dried, thin-sided capillary tube about 0·8 mm. in diameter, fastened to a scale divided into half millimetres, and terminating at the zero in two points which are set by a stand moved upon screws, to the surface of the liquid in the vessel into which the capillary tube dips. The height to which the liquid rises decreases with a rise in the proportion of fusel oil. The following table shows the result of tests made with various samples of fusel oils:

Height in tube	p.c. of fusel oils in a 20 p.c. volume of water
50·0	0·0
49·1	0·1
48·1	0·2
47·5	0·3
46·7	0·4
46·4	0·5
45·9	0·6
45·1	0·7
44·5	0·8
43·6	0·9
43·3	1·0

This process is said to be largely affected by accidental conditions such as temperature, moisture in the tube, &c., and by the presence of nitrobenzene, oils of peppermint, fennel, orange, and carraway, acetate of amyl, &c.

Further information on this process is given in Traube (Bied. Centr. 15, 559; B. 19, 892; C. N. 53, 302; Rep. Anal. Chem. 6, 659); Stulzer and Reitmair (Rep. Anal. Chem. 6, 606); and in D. P. J. 268, 126.

An improved apparatus, which he calls a *stalagmometer*, has been introduced by Traube (B. 20, 2644) for this estimation. The liquid, diluted as above to 20 p.c., is filled to a mark in a vessel and is allowed to fall drop by drop through a capillary tube at the base of the vessel, the number of drops in a certain time being noted and compared with the number of drops of pure alcohol of the same strength falling in the same time from the same apparatus. A smaller proportion of fusel oil than 0·05 p.c. may thus be determined.

Another process introduced by Rŏse (Pharm. Centr. 1886, 9), which depends on the alteration produced by the presence of fusel oils in the solubility of 50 p.c. alcohol in chloroform, is said to be scarcely affected by the bodies which influence the results obtained by Traube's *capillarimeter*. 20 c.c. of chloroform is introduced into a stoppered tube drawn out and graduated in fifths of a cubic centimetre in the lower part, and having a total capacity of about 180 c.c., and a capacity of about 50 c.c. in the graduated portion. The spirit to be tested is diluted to exactly 50 p.c. by volume of absolute alcohol, and 100 c.c. of the liquid is carefully poured upon the chloroform. The stopper, lubricated with vaseline, is inserted, and the whole tube is immersed for thirty minutes in water at 15°C., after which the tube is violently shaken, replaced in the water, and again allowed to settle, aided by tapping, and after one hour the volume of chloroform is read off. Pure ethyl alcohol would give a layer of 37·1 c.c.; but if 1 p.c. by volume of amyl alcohol be present, the layer measures 39·1 c.c.—*i.e.* an increment of 1 c.c. for each half per cent. of fusel oil. As raw spirits contain propyl and isobutyl alcohols &c., which have less tendency to pass into the chloroform, the results are liable to be rather low.

Stulzer and Reitmair (Rep. Anal. Chem. 6, 335; Chem. Zeit. 8, 1879, and 9, 1156) recommend a modification of Rŏse's process. To 200 c.c. of the spirit add a few drops of potash and distil off 160 c.c. Make up the distillate to 200 c.c., and place 50 c.c. of it in a 100 c.c. flask and dilute until its strength is exactly *thirty* p.c. of absolute alcohol, and then fill to the mark with pure *thirty* p.c. alcohol. Place 20 c.c. of chloroform in the dry apparatus, and add the 100 c.c. of alcohol and 1 c.c. of sulphuric acid (1·286 sp.gr.), and shake and allow to subside. Incline the apparatus several times, so that the chloroform passes from the graduated to the upper part of the apparatus, and after a few minutes read off the volume of chloroform at 15°C. The following table gives the quantity of fusel oil in 50 c.c. of the diluted alcohol, so that the number must be doubled to obtain the actual percentage. Pure 30 p.c. alcohol at 15°C. would give 21·4 as the volume of the chloroform.

Volume increase of chloroform	Percentage volume of fusel oil	0·01 c.c. increase of volume of chloroform corresponds to volume p.c.
0·2	0·1	0·005
0·35	0·2	0·0057
0·50	0·3	0·0060
0·65	0·4	0·0062
0·80	0·5	0·0063
0·95	0·6	0·0063
1·10	0·7	0·0064
1·25	0·8	0·0064
1·40	0·9	0·0064
1·55	1·0	0·0065

FUSIBLE METAL *v.* Bismuth, alloys of.

FUSTET, YOUNG FUSTIC. This is the wood of the Venetian sumach shrub *Rhus Cotinus*, belonging to the natural order Terebinthaceæ, and grown in the West Indies and in Southern Europe. The colouring principle it contains was first isolated by Chevreul and named by him fisetin (frequently called also fustin). J. Koch (B. 15, 285) assigned to it the formula $C_{15}H_{10}O_6$. J. Schmid (B. 15, 285) confirms the views of Koch as to the non-identity of quercetin and fisetin in opposition to the opinion of Bolley (Schweiz, Polyt. Zeitschr. 9, 22). He finds also that fisetin is unaccompanied by red and brown coloured substances as stated by Chevreul and others, but that it is present in the wood as a glucoside of fisetin combined with tannic acid, and hence he names it *fustin-tannide*. This substance is obtained by first adding a little lead acetate and acetic acid to a decoction of the wood in order to precipitate impurities. After filtering and removing lead from the filtrate by means of hydrogen sulphide, the filtered solution is concentrated by evaporation. After precipitating the tannic acid present by means of common salt, the filtrate is extracted with acetic ether, and this on evaporation yields the fustin-tannide in the form of pale-yellow needles. If fustin-tannide is heated with acetic acid and exposed to air it undergoes decomposition, pale-yellow needles of the glucoside of fisetin crystallise out and the mother liquor contains tannic acid. The glucoside itself has been named *fustin*, its composition being $C_{46}H_{42}O_{21}$. If it is heated with dilute sulphuric acid further decomposition takes place and it yields fisetin and a sugary matter supposed to be isodulcit.

Fustin, the glucoside, is readily soluble in water, alcohol, and ether. Its aqueous solution gives with lead acetate a white precipitate, with stannous chloride also a white precipitate but which soon changes to yellow.

Fisetin $C_{23}H_{10}O_3(OH)_6 + 6H_2O$, the true colouring matter of young fustic, forms pale yellow lustrous needles almost insoluble in cold water, little soluble even in hot water and also in ether, but readily soluble in alcohol. With the alcoholic solution lead acetate gives a bright orange-red precipitate, stannous chloride an orange-yellow precipitate. It sublimes with partial decomposition in the form of microscopic needles. The following compounds have been prepared: Hexacetylfisetin $C_{23}H_{10}O_3(C_2H_3O.O)_6$, colourless needles, m.p. 200–201°C.; Hexabenzoylfisetin $C_{23}H_{10}O_3(C_6H_5CO.O)_6$, colourless needles, m.p. 184–185°C.; Hexaethylfisetin $C_{23}H_{10}O_3(O.C_2H_5)_6$, pale-yellow needles, m.p. 106–107°C.; Hexamethylfisetin $C_{23}H_{10}O_3(O.CH_3)_6$, pale-yellow needles, m.p. 152–153°C.; $C_{23}H_{10}O_3(ONa)_2(OH)_4$ yellow lustrous needles.

Under the influence of melting caustic potash fisetin yields protocatechuic acid and phloroglucin. Reduction with sodium amalgam in acid alcoholic solution yields a brown substance soluble in alcohol with a red colour, and giving a green precipitate with lead acetate. On exposure to air, especially in alkaline solution, fisetin is readily reproduced. The composition of this reduction product of fisetin is at presen unknown.

The colours derived from young fustic are all fugitive to light, hence this dyestuff is rapidly losing its importance. In silk dyeing it was formerly used for dyeing brown, the silk being mordanted with alum and afterwards dyed with a decoction of young fustic, peachwood, and logwood. In wool dyeing it is still occasionally used in conjunction with stannous chloride for dyeing a brilliant but fugitive orange, and along with cochineal for dyeing scarlet. With the various metallic salts as mordants young fustic yields colours similar to those obtained from old fustic, the chromium colour is, however, much redder, being a reddish-brown, and the aluminium yellow is much duller; stannous chloride on the contrary gives an incomparably more brilliant orange, not unlike that obtainable from flavin or from Persian berries. J. J. H.

FUSTIC, OLD FUSTIC. This yellow dyestuff is the wood of *Morus tinctoria* or *Maclura tinctoria*, a tree belonging to the natural order Urticaceæ. It is a native of the West Indies, the best quality being imported from Cuba. Fustic contains two useful principles, *morin* and *maclurin*, only the first of which is to be considered as the true colouring matter.

Morin is prepared as follows (A. 127, 351). The ground wood is extracted with boiling water, and the decoction obtained is well concentrated by evaporation and left to stand for several days A yellow crystalline substance is thus deposited, consisting of a mixture of morin and maclurin, partly as calcium compounds. This precipitate is collected, washed slightly with cold water and strongly pressed. It is extracted twice with boiling water and filtered hot. The filtrate contains the maclurin. The insoluble residue of crude morin is heated with a little water slightly acidified with hydrochloric acid in order to remove the lime, again collected, washed well with water and crystallised from hot alcohol containing a little water. When purified by repeated crystallisation it forms pale-yellow lustrous needles.

According to Lŏwe the formula of morin is $C_{15}H_{10}O_7 + 2H_2O$ (Fr. 14, 119). Hlasiwetz gives it as $C_{12}H_8O_5 + H_2O$. It is readily soluble in alcohol, less so in ether, very little soluble in boiling water, and almost insoluble in cold water. Alkalis dissolve it readily with a deep-yellow colour; from such solutions the morin is reprecipitated by acids. Its yellow alcoholic solution is coloured a deep olive-green by ferric chloride. Its aqueous solution becomes fluorescent on the addition of alum. It forms monobasic salts, those of the alkalis being very soluble, those of calcium, aluminium, lead, and zinc being little soluble.

By the action of sodium amalgam, and also of melting caustic potash, morin yields phloroglucin, which in the latter case is accompanied by oxalic acid. When incompletely reduced with sodium amalgam in an alcoholic solution acidified with hydrochloric acid, a purple solution is obtained which on evaporation yields purple crystals of *isomorin*, a body having the same composition as morin, and readily changing into morin by heating, especially under the influence of alkalis.

Treated with bromine morin yields a tribrom-morin. Submitted to dry distillation morin yields resorcinol, and paramorin in small quantity. This last-mentioned body ($C_{12}H_8O_5$) forms pale-yellow woolly needles very soluble in boiling water and in ether. Ferric chloride colours its aqueous solution but slightly.

The chemical constitution of morin is unknown; Hlasiwetz considers it to be closely related to quercetin, because both colouring matters give similar reactions under various influences.

Maclurin ($C_{13}H_{10}O_6$) is prepared by evaporating the filtrate from the crude morin referred to above, and allowing the concentrated solution to cool. The crystalline deposit is purified by repeated crystallising from water slightly acidified with hydrochloric acid. It forms pale-yellow, or, if quite pure, colourless needles soluble in alcohol, ether, and boiling water, and fairly soluble even in cold water. Ferric chloride colours its aqueous solution a deep bluish-green colour; it is not rendered fluorescent by addition of alum. Heated with caustic alkalis maclurin yields phloroglucin and protocatechuic acid. By reduction with zinc and sulphuric acid it gives phloroglucin and *machromin*

$$(C_{14}H_{10}O_5.3H_2O).$$

This latter body may also be obtained by the reduction of protocatechuic acid as a colourless crystalline substance, which both in the solid state and in neutral or alkaline solution, rapidly becomes blue by oxidation. The oxidation product may be separated from the solution as an amorphous indigo-blue precipitate having the composition $C_{14}H_8O_5$. Its blue alcoholic solution is decolourised by reducing agents. A solution of maclurin in concentrated sulphuric acid deposits, on standing, brick-red crystals of *rufimoric acid* which appears to be related to rufigallic acid. Maclurin reacts in alkaline solution with diazobenzene chloride and its homologues, forming orange-red precipitates. The diazobenzene compound is at present sold as a dyestuff under the commercial name 'Fustin.'

The relationship which very probably exists between morin and maclurin is at present unknown.

In silk and cotton dyeing fustic is employed to a comparatively limited extent, but in wool dyeing it is the most important natural yellow dyestuff. The olive-yellow or old-gold colours which fustic yields when used with chromium mordant, and the greenish-olives obtained with the use of copper and iron mordants are all fast to light and milling, but the yellow colours yielded in conjunction with aluminium and tin mordants possess only a moderate degree of fastness with respect to light. Fustic is chiefly employed in wool-dyeing with bichromate of potash as the mordant, and it is for the most part used along with other dyestuffs, *e.g.* logwood, alizarin, &c., for the production of various compound colours: olive, brown, drab, &c.

Literature.—Chevreul, Leçons de chim. à la teinture, 2, 150; Fr. 14, 119; J. pr. 51, 82; 89, 491, 493; A. 127, 353; B. 8, 606; 17. 194; D. P. J. 171, 457.

J. J. H.

G

GABONINE, GABORANDINE, *v.* JABORANDI.

GABORIC ACID *v.* JABORANDI.

GABORIDINE, GABORINE, *v.* JABORANDI.

GADININE *v.* PTOMAÏNES.

GADOLINITE *v.* CERIUM METALS AND EARTHS.

GAHNITE. *Zinc aluminate v.* ZINC.

GALACTIN *v.* GUMS.

GALACTOSE $C_6H_{12}O_6$. By hydrolysis of milk sugar with dilute hydrochloric or sulphuric acid a mixture of two isomeric glucoses is produced, both of which are dextro-rotatory, the rotatory power of the solution increasing from 52·7 to 67·5. These glucoses are dextrose (sucro-dextrose) and *galactose*.

The latter body was termed *lactose* by Pasteur, its discoverer, but the name *galactose*, given to it by Berthelot, is now usually employed, the term lactose being confined to milk sugar.

Galactose has also been prepared from the lime sludge obtained in the manufacture of sugar (Von Lippmann, B. 20, 1001); and Muntz (C. R. 102, 624, 681) states that it may be obtained from gum-arabic and other gums, Iceland moss and like substances, and from pectous bodies, and that the substances from which it may be produced are widely distributed, as in cereals, leguminous and other fruits, edible roots, bulbs, vegetables, &c.

For the preparation of galactose, milk sugar is boiled with 4 parts of water, containing 5 p.c. of sulphuric acid, for 6 hours, and the solution is neutralised with baryta and concentrated. On addition of a few crystals of *grape sugar* the galactose crystallises out, leaving the dextrose in solution. The mass is incorporated with 80 p.c. alcohol, and the brown liquid is removed by filtration and pressure, the treatment being repeated until the mass is white. This is then dissolved in 70 p.c. alcohol and crystallised (Soxhlet, J. pr. [2] 21, 262).

According to Bourquelot (J. pr. [5] 13, 51) the following process yields pure galactose. Stoppered flasks of 600 c.c. capacity are charged with 100 grams milk sugar and 9 grams of sulphuric acid, and are filled up with water. The stoppers are tied down and the flasks are heated to 105°C. for one hour, and the solution is cooled, neutralised with barium carbonate, filtered and evaporated until an amount of the solution which contains 500 grams of milk sugar weighs 640 grams. The syrup is set aside with a few crystals of galactose to induce crystallisation, and after four or five days is washed with 80 p.c. alcohol and drained. The treatment with alcohol is repeated until the mass is perfectly white, 120–135 grams of galactose, dried at 108°, being thus obtained from 500 grams of milk sugar. By heating 250 grams of the crystals in 180 c.c. of water and 1,000 c.c. of alcohol at 90°C., in a reflux apparatus, the crystals are dissolved. The filtered solution on crystallisation yields 150 grams of pure galactose in hexagonal plates, having a specific rotatory power, after repeated crystallisation, of 80° 14′ at 19° for the sodium line, and fusing at 163–164°C., after drying at 100°. According to Rindell its specific rotatory power in 10 p.c. solution is 81° 27′ at 15°C. for the sodium line. Galactose is less sweet than cane sugar. Its reducing power on Fehling's solution is 0·737, taking that of dextrose as unity.

According to Bourquelot (C. R. 106, 283), galactose is not fermented by yeast until addition of glucose, lævulose, maltose, or other food for the plant. This statement is supported by Kiliani, F., Koch, and others, but according to Pasteur, Von Lippmann, and others, it is fermentable. Tollens and Stone (B. 21, 1572) state that *pure* galactose is decidedly, though slowly fermentable.

Galactose yields mucic acid on oxidation by nitric acid.

GALANGA ROOT contains the following yellow colouring matters: *Kämpherid*: $C_{16}H_{12}O_6.H_2O$ crystallising in yellowish needles (m.p. 221°), slightly soluble in water, ether, and benzene, freely soluble in alcohol, soluble in alkalis, forming an intensely yellow solution, and in concentrated sulphuric acid forming a yellow solution with a strong blue fluorescence; *Galangin* $C_{15}H_{10}O_5H_2O$ crystallising from its solution in aqueous alcohol in yellowish-white needles (m.p. 214°) the reactions of which are very similar to those of kämpherid; its solution in concentrated sulphuric acid, however, is non-fluorescent; *Alpinin* $C_{17}H_{12}O_6$ crystallising in yellowish needles (m.p. 173°). Its reactions are similar to those of galangin (S. C. I. 1, 315).

GALBA *v.* Resins.

GALBANUM *v.* Gum resins.

GALENA. Native lead sulphide *v.* Lead.

GALIPOT *v.* Resins.

GALL or **BILE.** The secretion of the liver of animals, is occasionally used in the arts. It is employed for cleansing woollen goods and by artists to ensure the uniform spreading of water-colours on paper. It is a transparent ropy liquid of sp.gr. 1·02, of yellow, brown, or green colour, of a bitter taste and peculiar aromatic smell. It has usually a neutral or feebly alkaline reaction. It is miscible with water, but not with alcohol which occasions a precipitate of *mucin*, coloured with the pigmentary matter of the bile.

The chemical composition of bile varies somewhat with the nature of the animal from which it is derived, but in general it may be said to consist of the sodium salts of *glycocholic acid* $C_{26}H_{43}N_2O_6$ and *taurocholic acid* $C_{26}H_{45}NSO_7$; of biliary pigments, among which may be named *bilirubin* $C_{16}H_{18}N_2O_3$ and *biliverdin* $C_{16}H_{20}N_2O_5$ (Städeler), $C_{16}H_{20}N_2O_4$ (Maly); *cholesterin*, *mucin*, *lecithin*, *urea*, and *fats*.

The composition of human bile may be thus stated:—

1,000 parts of bile	Frerichs		Gorup-Besanez	
	Youth 18 years	Man 22 years	Man 68 years	Boy 16 years
Water	860·0	859·2	908·7	828·1
Solid matter	140·0	140·8	91·3	171·9
Alkaline salts of biliary acids	72·2	91·4	73·7	148·0
Cholesterin	1·6	2·6		
Mucin	26·6	29·8	17·6	23·9
Inorganic salts	—	—	—	—

GALL OF GLASS *v.* Glass.

GALLEÏN. *Anthracene violet* *v.* Alizarin and allied colouring matters; also Phthaleïns.

GALLIC ACID *v.* Hydroxy- acids and Tannins.

GALLIPEÏNE *v.* Cusparia bark.

GALLIPOLI OIL *v.* Oils.

GALLISIN $C_{12}H_{20}O_{10}$. A substance found in commercial glucose. It may be obtained as a white amorphous deliquescent powder, by treating the unfermentable syrup, after evaporation, with absolute alcohol, and finally with ether-alcohol. Has a slight sweet taste; is insoluble in ether, slightly soluble in absolute ethyl alcohol, more easily soluble in methyl alcohol and acetic acid. It reduces silver nitrate, and Fehling's solution; the cupric reducing power of 10·98 grams = that of 5 grams of glucose. It gives no precipitates with solution of lead acetate, mercuric chloride, ferric chloride, or barium chloride. On boiling with dilute acids it is converted into glucose.

GALLIUM. Ga. At. w. 69·86 (Boisbaudran). Gallium occurs in certain zinc blendes, the richest being that from Bensberg, containing about 1 part in 60,000. It was discovered by Boisbaudran by means of the spectroscope in the blende of Pierrefitte in the Pyrenees.

Gallium is a bluish-white, hard, tough slightly malleable metal, of sp.gr. 5·9. It fuses at 30·1° forming a silver-white liquid, resolidifying very slowly even at very low temperatures, but rapidly solidifying into octahedra if touched by a crystal of the metal. It oxidises superficially, but does not volatilise at a red heat.

In air or air-free water it is permanent, but slowly tarnishes in ordinary water. Chlorine attacks it powerfully in the cold; bromine and iodine act less energetically. In hydrochloric acid and potash solution it dissolves rapidly, but only slowly in nitric acid.

Gallium belongs to the aluminium group of elements, being identical with the ekaluminium predicted by Mendeléef. It forms a white oxide Ga_2O_3 and two chlorides $GaCl_2$ and $GaCl_3$, a sulphate and other salts, and an ammonium alum $Ga_2(SO_4)_3(NH_4)_2SO_4 24H_2O$, but no alum with potassium or sodium.

GALL-NUTS or **GALLS** (*Noix de Galle*, Fr.; *Galläpfel*, Ger.) are excrescences found upon the leaves and leaf-stalks of *Quercus infectoria*, which grows in the Levant. They are produced in consequence of the puncture of the female of the gall-wasp (*Cynips folii quercus*), made in order to deposit her eggs, round which the juice of the tree exudes, and dries in concentric portions. When the insect is fully formed, it eats through the nut and flies away.

The Levant galls are of two different appearances and qualities; the first are heavy, compact, imperforated, the insect not having been sufficiently advanced to eat its way through the shell, prickly on the surface, of a blackish or a bluish-green hue, about the size of a musket-ball. These are called *black*, *blue*, or *Aleppo galls*. The second are light, spongy, pierced with one or more holes; smooth upon the surface, of a pale greyish or reddish-yellow colour, generally larger than the first, and are called *white* galls; but they are inferior to the former, and are often dyed by dishonest traders to imitate the best blue Aleppo galls, but the fraud may be detected by the small hole made by the insect in the white galls. Besides the galls of the Levant, others come from Dalmatia, Illyria, Calabria, &c.; they are found upon the *Quercus cerris*; they are smaller, of a brownish colour, and of inferior value. The further south the galls are grown, the better they are reckoned. The galls of the *Quercus cerris* and common oak (*Galles à l'épine*, Fr.; *Knoppern*, Germ.) are of a dark-brown colour, prickly on the surface, and irregular in shape and size. They are used chiefly for tanning in Hungary, Dalmatia, and the southern provinces of the Austrian States, where they abound (Ure).

GALLOCYANINES. Blue or violet colours, obtained by the action of nitrosodimethylaniline on the tannins, or on gallic acid. The colour from gallic acid is made by Durand & Huguenin, under the name of solid violet D. H., as a cake of small green crystals with metallic reflections. The cake contains 10 p.c. dry product. The gallocyanines from gallic acid give blue solutions with water, strong sulphuric acid, aniline, methylaniline, aldehyde, and glycerin; violet with alcohol, alkalis, and acetic acid; and red with strong hydrochloric acid. That from catechin gives violet solutions with water, alcohol, acetic acid, aniline, and glycerin; and blue with strong hydrochloric acid; red with methylaniline; reddish-violet with alkalis and aldehyde; and greenish-blue with strong sulphuric acid; and that from morintannic acid gives green solutions with boiling water, strong sulphuric acid, alkalis, strong hydrochloric acid and glycerin; violet with alcohol (red fluorescence), acetic acid, aniline, and aldehyde (red fluorescence), and red with methyl aniline. The best commercial solvents for gallic acid gallocyanine are ammonia or $\frac{1}{30}$ of its volume of caustic soda of 38 p.c., or the same proportion of sodium bisulphite, the latter requiring 24 hours. It dyes silk and wool blue-violet. To dye wool a little potassium chlorate must be added to the vat, for calico-printing a chrome mordant is necessary, and for calico-dyeing tin, chromium, nickel, or cobalt salts may be used. One of the formulæ given by Koechlin is 4 kilos. starch, 2 litres water, 16 litres gum-dragon thickening, 18 litres D. H. violet prepared by maceration in $\frac{1}{32}$ of its volume sodium bisulphite, 2 litres oil, $1\frac{1}{3}$ litres acetate of lime 18°, 6 litres acetic acid, 9 litres acetate of chromium. This composition keeps well for months. Pale tints may be thickened with gum. After printing, the fabric is steamed for two or three hours, washed and soaped. A mordant for cotton-dyeing is water 10 litres, tin salts 1 kilo., perchloride of tin 55°, 250 cub. centimetres. A violet is obtained with alumina and a black with iron salts, but they will not withstand soap. Gallocyanine from catechin gives redder shades than that from gallic acid, and with alumina and iron yields violets that withstand boiling soap-solution. Gallocyanine from morintannic acid gives with chromium, alumina, tin and iron mordants, green shades which are very fast (S. C. I. [2] 377); *v.* Oxazine colouring matters.

GALLOFLAVIN. This dye, which can be fixed on mordanted fibre like alizarin, is obtained by the action of air—*i.e.*, oxygen—on alkaline solutions of gallic acid. The process of oxidation depends on the amount of alkali present. In practice, 5 parts of gallic acid are dissolved in 80 parts of alcohol of 96°Tr. and 100 parts of water. The cooled solution is gradually mixed with 17 parts of caustic potash solution of 30°B., stirring all the while, and never allowing the temperature to rise above 10°C. It is then exposed to the action of oxygen, either by blowing air through it or by agitating it briskly. The progress of the oxidation shows itself by the liquor assuming at first an olive-green or greenish-brown colour, until finally a crystalline precipitate separates out. When the amount of this precipitate no longer increases, the operation is finished. The mass of crystals is quickly filtered, dissolved in warm water, decomposed with hydrochloric or sulphuric acid, and boiled, when the dye is precipitated in the state of glittering greenish-yellow plates. These are washed, and can then be applied for dyeing or printing. Galloflavin dyes cotton mordanted with alumina greenish-yellow, which turns into a very brilliant yellow by treatment with tin crystals. The chromium-lake of galloflavin is distinguished by being especially proof against soap, air, or light. Galloflavin has probably the composition $C_{13}H_6O_9$. It crystallises in greenish-yellow leaflets, is sparingly soluble in water, alcohol, and ether, more readily soluble in glacial acetic acid and aniline. The potassium salt $C_{13}H_4O_9K_2$ is a crystalline body which is insoluble in alcohol and cold water. The acetyl compound crystallises from benzene in white needles, melting at 230°. It is freely soluble in glacial acetic acid and chloroform, but does not dissolve readily in alcohol and ether (R. Bohn and C. Graebe, B. 20, 2327–2331; D. P. J. 263, 205; S. C. I. [6] 285, 722).

GALLOTANNIC ACID *v.* *Digallic acid*, art. Hydroxy- acids.

GALVANISED IRON *v.* Zinc.

GAMBINE. *Nitroso-β-naphthol* v. Naphthalene colouring matters.

GAMBIR or **GAMBIER.** The Malayan name of an extract obtained from the *Uncaria Gambier.* It is the *Terra japonica* of tanners.

Two methods of obtaining gambir are described: one consists in boiling the leaves in water, and inspissating the decoction; the other, which yields the best gambir, consists in infusing the leaves in warm water, by which a fecula is obtained which is inspissated by the heat of the sun and formed into cakes. The best gambir is made at Rhio, in the Isle of Brittany, in the Eastern Archipelago, and the next best is that of Lingin. It is principally imported from Singapore, and is used mainly for tanning (Ure).

GAMBOGE v. Gum resins.

GAMMAM. A Tunisian dyestuff of unknown origin.

GANNISTER. The name of a bed of highly silicious fire-clay used for the lining of the Bessemer converter and for similar purposes. When crushed, and if necessary mixed with plastic clay, it produces a highly refractory firebrick.

GARANCEUX and **GARANCINE** v. Madder.

GARNET v. *Aluminium silicates*, art. Alums.

GAS-CARBON v. Carbon; also Gas, coal.

GAS, AIR. This gas consists of an explosive mixture of air and the vapour of a highly volatile, inflammable liquid, such as the lighter petroleum spirit of sp.gr. 0·642–0·702, known as *gasoline.*

The proportion of gasoline which is capable of remaining in the vaporous condition in air depends entirely upon the temperature: thus 100 volumes of air will retain of the vapour of gasoline (0·650 sp.gr.) 5·7 p.c. at 14°F., 10·7 p.c. at 32°F., 17·5 p.c. at 50°F., and 27·0 p.c. at 68°F.

Air gas is usually made for immediate use by blowing air through the gasoline, or by passing air over porous material saturated with that liquid. It is said to be used in America for various purposes, principally being supplied, under considerable pressure, to the hearths of forges &c. (Journal of Gas Lighting &c. 46, 1102).

The gasoline may be permanently gasified by passage through a strongly heated retort before admixture with air. Such a gas is prepared in the 'Excelsior' gasoline machine (C. O. Thompson, Journal of Gas Lighting, &c., 26, 552).

GAS, COAL. The first idea of manufacturing coal gas specially for lighting purposes seems to have occurred to William Murdoch in 1792, and in 1798 Messrs. Boulton & Watt's factory, at Soho, near Birmingham, was lighted by him with the new illuminant. In 1802, Lebon, who had been working at the subject of coal distillation for some time, had an installation in Paris which was seen by Winsor, who immediately came to London to introduce gas lighting to the notice of the English public. He met with a little opposition, but more support, for in 1815, as Accum states, there then were in use in London more than 4,000 of Argand's gas lamps, to supply which there were twenty-six miles of gas mains laid in the streets.

Since then the progress of gas manufacture has been rapid, and though it has been threatened with many competitors at various times, it has managed to hold its own and to become an important and prosperous industry. An idea of its magnitude and extent may be gathered from the following table, which is drawn from the Board of Trade Return relating to all Authorised Gas Undertakings in the United Kingdom belonging to Local Authorities for the year ending the 25th day of March, 1886 (in continuation of Parliamentary Paper No. 124, of Session 1884–5), and the Return relating to all Authorised Gas Undertakings in the United Kingdom other than those of Local Authorities in the year 1885 (in continuation of Parliamentary Paper No. 238, of Session 1884–5).

—	Amount authorised	Paid up and borrowed	Tons of coal carbonised	Number of cubic feet of gas made	Number of cubic feet of gas sold	Length of gas mains in miles	Number of consumers	Number of public lamps lighted
Companies' Return:—	£	£						
Share capital and loan authorised	49,091,377	35,513,570	5,595,371	56,903,060,785	52,192,002,288	12,806	1,115,223	250,404
Local Authorities' Return:—								
Loan authorised .	22,771,890	19,619,416	2,783,533	27,734,666,850	25,201,667,909	6,161½	979,802	151,670
Total . . .	71,863,267	55,132,986	8,378,904	84,637,727,635	77,393,670,197	18,967½	2,095,025	402,074

Though this table does not include certain very small undertakings not authorised by any special Act of Parliament, it fairly indicates the extent of the industry.

The position likely to be occupied by the gas industry in the near future is open to considerable discussion, as there are many who consider that its extinction by the electric light is only a question of time; but it must not be forgotten in these discussions that a gas works is a manufactory of a large number of chemical products not fully utilised now, but likely to play an important part in the future, and, further, that though coal gas might be partially supplanted in popular favour as a lighting agent, it is still a convenient, efficient, cleanly, and, for many uses, an economical fuel. It is not likely that this manufacture will readily die out, though it must be admitted that the monopoly of gas-tar and gas-liquor as sources of certain valuable substances has been rudely shaken by the immense improvements in processes for the recovery of liquid products from coke ovens, and is menaced by the knowledge gained in the recent efforts to carbonise coal for the benzene, tar, ammonia, coke, it can produce, without regard to the manufacture of illuminating gas.

The Raw Material Employed.

In this country the only material used for gas making is some form of coal. Of the many varieties of coal found, there are some especially adapted to the manufacture of coal gas on account of the large quantities of illuminating gas yielded on their destructive distillation, together with other valuable primary products, such as coke, tar, ammonia, &c., and only those are in use which yield at least a certain money value in these primary products of distillation. Of the lignites or materials allied to coal occurring out of the coal measures or carboniferous rocks, such as the Bovey Tracey mineral, it does not appear that there can be made an economical use.

Broadly, there are two classes of coal employed for gas making—viz. the caking coals and the cannels. Each class has tolerably distinctive characteristics from the gas maker's point of view, as well as microscopical and chemical differences.

There are several classifications of coal, some very extensive, arranged in classes more or less suitable to the purposes of their authors. Thus the classification of fossil coals according to their internal and external properties to be found in *Die Steinkohlen Deutschlands und anderer Länder Europas* von Geinitz, Fleck und Hartig, is very complete; but it must be recollected that many of the kinds enumerated therein are found mixed and interstratified together so closely in the same parts of the same seam as to render their practical separation impossible. Thus thin layers of soot coal, hard and soft bituminous coal, and cannel coal are often found stratified together in bituminous seams of coal. This German classification, effected under three principal groups, of

Black Coal,
Anthracite Coal,
Brown Coal, and
Peat,

specifies fifteen different varieties, and is a lithological or mineralogical arrangement rather than chemical or technological.

The French classification is more simple, and comprises five different varieties, distinguished by their coking property and behaviour on burning.

1. *Poor coals with long flame*, which burn with a long flame and much smoke, and, on distillation, do not exhibit any signs of melting, but retain their original form, with, however, numerous cracks or clefts due to contraction. If the coal is coked in the powdery form, the coke is powdery.

2. *Rich coals with long flame, or gas coals*, which burn with much flame and smoke, are easily ignited, and then burn quickly. On coking, the pieces change their form and then melt. If coked in the powdery form the coal melts together and forms a more or less porous coke. Between this and the first class there is a kind of coal (*charbons limités*) which, on coking, yields a cindery residue partially retaining the original form of the coal.

3. *Rich coals or smithy coals.*—These burn with a shorter and less brilliant and less sooty flame than the two former kinds. In the fire they soften, melt, and the small coals cake together to form compact masses of coke..

4. *Rich coals with short flame or coking coals.* These are not so inflammable as the former kinds, and burn with a shorter, brighter, whiter, but less sooty flame on distillation; the coal cakes together, intumesces, and yields a hard and strong coke.

5. *Anthracites.*—These ignite with difficulty, and burn with a short, nearly smokeless flame of little duration. On distillation they yield a powdery coke with the smallest possible sign of having been coked.

Grüner (Annales des Mines, 1873, 4) elaborated this classification by the addition of the range of elementary composition of the groups, ratio of hydrogen to the oxygen, and yield of coke and specific gravity of the coal.

Type	Elementary composition			Ratio $\frac{O}{H}$	Yield of coke per cent.	Properties and appearances of coke	Specific gravity of coal
	C	H	O				
1. Poor coal with long flame . .	75–80	5·5–4·5	19·5–15	4–3	50–60	Powdery, very friable	1·25
2. Rich coal with long flame or gas coal	80–85	5·8–5	14·2–10	3–2	60–68	Melted, but full of clefts	1·28–1·3
3. Rich coal or smithy coal . . .	84–85	5–5·5	11–5·5	2–1	68–74	Melted, moderately compact	1·3
4. Rich coal with short flame or coking coal	88–91	5·75–4·5	6·5–5·5	1	74–82	Melted very compact	1·3–1·35
5. Poor or anthracite coal . . .	90–93	4·5–4	5·5–3	1	82–90	Powdery	1·35–1·4

Schondorff (Preuss. Zeitschr. 1875) has shown the want of validity of Grüner's classification for the German Saar coals, and Muck (Grundzüge u. Ziele d. Steinkohlen-Chemie, Bonn, 1881) its want of applicability to the Westphalian coals. The attempt to apply it to English coals is not more successful. The first type would include two such entirely opposite coals as the following:—

Nottinghamshire top hard cannel, carbon 78·24, hydrogen 5·45, with 52·9 p.c. of non-caking residue, and yielding 9,800 cubic feet per ton of 21 candle gas, and Derbyshire Silkstone caking coal, carbon 76·92, hydrogen 4·84, with 62 p.c. of excellent gas coke.

Further, it is difficult to find a coal that will match with all the various qualities of the group such as elementary composition, ratio of $\frac{O}{H}$, &c.

Fleck's classification, founded on the relative amounts of available and combined hydrogen on the assumption that all the oxygen is combined with hydrogen to form water, the remaining hydrogen being capable of otherwise combining more usefully with other bodies, is, according to Muck, also of no value in the case of German coals, and the writer has not been able to apply it to English varieties. A classification number obtained from the proportion between a number found by direct analysis and another, viz. oxygen, a difference containing the unavoidable error of the analysis, and ignoring the nitrogen and sulphur of the coal altogether, is hardly likely to be a certain basis of operation. Considering the nature of coal, its complete want of homogeneity, owing to its being made up in a majority of cases of layers of heterogeneous substances deposited under differing circumstances, it cannot well be expected that an elementary analysis will disclose any of its special technical properties. A study of the elementary analysis of coals brings out certain very broad points, such as the general occurrence of a highly luminous gas from coals containing 6 or 7 p.c. of hydrogen or the anthracitic character of coals containing 90 p.c. of carbon; but it is quite possible to find two coals of approximately the same elementary composition possessing entirely different characters.

A fatal objection to the use of any method of comparison based upon the assumption that the oxygen in the coal would all go to form water with an equivalent portion of the hydrogen is the fact that on the distillation of organic substances containing carbon, hydrogen, and oxygen, &c., the oxygen is divided between the hydrogen and the carbon, forming water and carbon monoxide and dioxide and other oxygenated bodies, and that the relative amount of these oxygen compounds varies with substances of the same stoichiometric composition. Starch and dextrin have the same elementary composition, but on destructive distillation the atoms of the original substances arrange themselves in a different manner.

Thus the nature of the original substance and the original grouping of the atoms is a factor in the re-arrangement of the atoms set up by the action of a high temperature.

All efforts to discern the important and valuable coking property of coal in its composition have been unsuccessful, and it is evident that this coking property is determined by some substance or substances occurring largely in some coals and not at all in others.

In this country coals are classed simply by what they can do or what they are like. Thus we have cannel (candle) coal, because pieces of it burn like a candle, steam coal, hard coal, soft coal, house coal, smithem, &c. The gas maker, whose chief concern is with those that can make illuminating gas, groups the varieties useful to his needs into two classes—common or gas coal and cannel coal.

The common or gas coal prized by the gas maker is found in most of the coal fields of Great Britain, but principally in the Newcastle, Yorkshire, Derbyshire, Wigan, and North Staffordshire coal fields. The richest and finest gas coal is brittle and easily broken into small pieces and dust. It has a greyish-black, shining, resinous lustre, and if examined is seen to be made up of laminations of varying but limited thickness of coals differing in degrees of brightness, and when the fracture parallel to the plane of stratification is smooth, disclosing charcoal or dull thin shaly partings. When heated it breaks up into smaller pieces, and then on the melting of these, and the expulsion of large quantities of gas, the coal agglomerates and forms a hard and compact coke, altogether differing in shape and appearance from the original coal. When the coal is burning on a grate this melting property renders frequent stirring with a poker necessary to enable the air to penetrate its mass, and it is therefore not suitable for many purposes until it has been converted into coke.

The cherry or soft coal found in the Glasgow coal fields is very soft and friable, and does not cake when heated. It is slaty in fracture, and possesses a peculiar shining lustre, which appears in some way to have suggested its name of 'cherry.' It is easily ignited, and burns swiftly.

The splint or hard coal is the variety prized for smelting and manufacturing purposes. The Scotch splint coals and those of the Barnsley seam are representative of this class, which, however, exhibits differences, some coals being very much harder than others, and others exhibiting the long splinty fracture more prominently than others. It is not generally so bright as the first two mentioned kinds of coal, but looks duller. There are some very fair gas-making coals amongst the hard coals, but the coke as made in the gas retort is not of very good quality, and is not hard, bright, and metallic like the coke from the finest gas coals. Some of the hard coals give a very excellent oven coke. On the fire they burn clearly with great heat, and are not swift like the soft coals or so agglomerating as the caking coals.

All the above varieties of coal are built up of parallel laminations and horizontal stratifications of various kinds of coal more or less approximating to the following.

Charcoal, or 'mother of coal,' or 'smut.' This is vegetable matter that has been partially consumed or carbonised by fire before its deposition, and presents the fibrous structure of woody matter in a very marked manner.

Pitch coal. This is bright, lustrous, and breaks with a conchoidal fracture, and very much resembles pitch. It is hard, and if cut with a penknife presents a pitted surface due to its brittleness.

It generally occurs in those seams in which the charcoal is prominent, and is deceptive in appearance, as it looks rich and bituminous, whereas it cokes badly and contains much hygroscopic water.

Bright bituminous coal. This is intensely bright and brittle, often breaking up into little cubes. A single lamination rarely exceeds one-eighth of an inch in thickness, but they often occur together without any appreciable partings of other kinds of coal-forming material, and then the seam is very rich and pure, yielding a large quantity of gas of good illuminating power, splendid coke, containing very little mineral matter. The ash is derived from the inorganic matter evidently of vegetable substances and uncontaminated by mud or earthy impurities. There are some portions of the Silkstone and Hatton seams which yield this fine quality of coal in great excellence.

It is the proportion of the above kinds of coal added to laminations of cannel that gives a seam or portion of a seam its particular character. When the laminations of the charcoal and bright bituminous coal are thin and regular in arrangement, the two kinds have partially permeated each other and have formed a hard stony-like coal known as 'hard coal.' When the charcoal is in thicker laminations and more irregularly intercalated between the layers of bright coal, the whole becomes more easily cleaved and broken up.

A seam of coal which may be remarkably free from charcoal in a particular locality, and possessed of fine caking properties, may degenerate as it proceeds further and further in certain directions, the charcoal becoming more and more prominent and the coal dirtier in appearance and poorer and poorer in gas and coking properties, until at last it becomes useless for either one purpose or the other.

It sometimes happens that the pitch coal before described occurs deposited in considerable thickness without partings, and then the laminar structures are not very prominent. This coal is then mistaken for cannel coal, on account of its hardness and homogeneous appearance, and is sold under that title. It has some caking properties and melts slightly on heating.

Owing to the irregular manner in which these various kinds of coal are arranged in the seam, it becomes possible for a colliery to separate out a number of different qualities of coal suited to different uses.

All these coals, consisting however of numberless thin layers of more or less different kinds of coal, have been deposited by aqueous agency; and the sorting out power of flowing water of varying velocity, assisted by the different specific gravities and sizes of the various coal-forming materials, and perhaps the influence of prevailing winds and currents, has resulted in the collection of the woody matter that has been charred by the action of fire, preferably in certain directions and parts of the seam, whilst the vegetable matter that has escaped the action of fire is preferably collected in other parts.

The more highly comminuted organic matter, and possibly some liquid or semi-liquid products of the partial combustion of that portion of the woody matter which has suffered partial carbonisation, together with some earthy mud, has been deposited in places where the water has been more at rest or stagnant, and thus the cannels, which are found in every seam, have been formed.

This class of coal—the cannel coal—which includes a large series of coals differing less in appearance and structure than in internal properties, is tough, hard, and close in texture, has a homogeneous structureless appearance, and often occurs in very thick bands and very rarely presents any traces of lamination. The fractures are smooth, conchoidal, or rugose, clean and free from impurities, though occasionally specks of charcoal and clay are found embedded.

The thin vertical cracks, when these occur, are generally filled with a thin speck of 'simon' or calcareous scale, sometimes interspersed with pyrites.

The cannel coals, remarkably free as they are from any appearance of lamination, disclose this, however, in the coke, and ash resulting from the incineration of the coke.

There is a class of coal having all the external characteristics of the cannel class, but with generally a brighter lustre, which exhibits on distillation a tendency to melt and has slight coking properties—such as the Wigan coal of Lancashire. This class always goes by the name of cannel coal, but the members of it never reach the richness in gas of the best non-coking cannels, though there are non-coking cannels which are little superior to the common gas coal.

In this article the term gas coal is applied to the highly stratified and laminar caking coal, whilst the name cannel coal is given to the harder, more solid, compact, homogeneous, non-caking or semi-caking coals, such as the Wigan cannel, though it is questionable whether it would not be better to divide the cannel coal into two varieties according to the presence or absence of caking properties.

Gas coal. The best known and perhaps most representative seams producing this class of coal are the Hutton or Low Main of the northern coal field and the Silkstone seam of Yorkshire, which latter is of the finest quality about 12 miles north of Sheffield. The Newcastle gas coals have a very wide reputation and are extensively shipped to London and places on the English coast and Continent, and though perhaps the best are wrought from the Hutton or Low Main seams, yet there are excellent gas coals raised from the Maudlin seam. The general characteristic of this Newcastle coal is black, soft, and friable, laminated in structure, with shining, lustrous layers of the bright soft coal with charcoal partings. The lustrous layers have often a prominent fracture, but sometimes this is rugose. Deposits of iron pyrites and a calcareous scale are prominent in the vertical cracks. On the fire it fuses slightly, intumescing and agglutinating into a hard coke. Specific gravity ranges from about 1·26 to 1·33. On destructive distillation it yields from about 62 to 73 p.c. of coke, and at a fair carbonising temperature from about 10,000 to 11,000 cubic feet per ton of from 15 to 17 candle gas, as tested by the Sugg's London Argand burner.

The elementary composition of this coal may be seen from the table below:—

—	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Ash	Moisture
Nettlesworth .	83·0	5·1	—	—	—	3·2	1·5
Primrose . .	—	—	—	—	—	—	—
Boldon . .	80·2	5·0	—	—	8·47	5·62	1·74
Holmside . .	84·34	5·30	0·78	1·73	4·29	2·42	1·14
Haswell Hutton	81·16	4·66	1·34	·93	9·26	1·44	1·21

These Newcastle coals on distillation give off gas freely, and when producing over 10,500 cubic feet per ton of coals, have a tendency to stop up the ascension pipes and hydraulic mains with obstructions of an obstinate character. The amount of gas liquor yielded is low, as is the case with all good qualities of the caking coal; 13 gallons per ton of coals, or 5·9 p.c. by weight, may be taken as the average. The ammonia is about 6·5 per ton of coals, or 0·28 p.c. by weight. The tar is characteristic, being in normal works employing tolerably high distillation temperatures, thick, and of a specific gravity 1·2 to 1·22. These tars are known for the excellent quality of the anthracene they yield. The amount of tar per ton of coals is from 10 to 11 gallons or 182 lbs. per ton or 5·9 p.c. by weight. The crude coal gas after condensation contains 12 grains of carbonic acid and 9 grains of hydrogen sulphide per cubic foot, or 1·5 p.c. of CO_2, and 1·5 p.c. of SH_2 by volume, calculated on the finished, purified gas, or about 18 lbs. of CO_2 and 13·5 lbs. SH_2 per ton of coal, or 0·8 p.c. CO_2, and 0·6 p.c. SH_2 by weight of the coal.

The ammonia held by the unwashed gas varies with circumstances, but is about 1·80 grains per cubic foot, or 0·6 p.c. by volume, calculated on the finished gas, or 2·7 lbs. per ton of coal or 0·12 p.c. by weight of the coal.

The crude gas also contains 35 grains of sulphur as carbon bisulphide and about 8 grains of sulphur other than sulphuretted hydrogen and carbon bisulphide per 100 cubic feet. The 35 grains of sulphur or carbon bisulphide are amenable to special processes of purification, and are almost entirely removed in the Metropolitan gas works, but the 8 grains referred to are not removable by any known means of purification. The Newcastle coals give a gas subject to deposition of naphthalene in the street mains and service pipes, but which is fairly permanent in quality, though in very severe and sudden frosts it may lose a candle or so of its luminosity when stored in a gasholder. The gas coke is good—that from the New Pelton gas coals being specially fine.

The following may be taken as the composition of tar from Newcastle coal distilled at ordinary temperatures:—

	Percentage by weight
Ammoniacal liquor	4·0
Crude naphtha 45 p.c. at 120°C. .	1·5
Light oil	1·2
Creosote	15·0
Anthracene oil	14.0
Anthracene 30 p.c. . . .	1·8
Pitch	60·0
Loss	2·5
Total . .	100·0

The anthracene is free from paraffins, and the creosote is distinguished by low percentage of tar acids and large amount of naphthalene.

The following table gives the results obtained in good practice from some of the typical coals of this class:—

—	Gas per ton corrected to 30″B. & 60°F.	Coke p.c. by weight	Illuminating power Standard Sperm Candles London Argand	Candles per ton
Londonderry . .	10,525	65·5	16·46	36,648
West Leverson's .	10,983	68·5	16·06	35,277
New Pelton . .	10,662	70·0	16·08	34,289

The works employing this coal are mostly those accessible by sea, and it is extensively employed in the south of England, where it is commonly distilled alone or with unimportant quantities of cannel coal.

The most famous gas coal after the Newcastle coal is the South Yorkshire Silkstone, which is very similar in appearance to the Newcastle but on an average yields less coke.

The following are elementary analyses of some of the typical South Yorkshire Silkstone coals—sp.gr. 1·26:—

—	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Ash	Moisture
Barrow . .	80·33	5·04	1·94	7·26	1·24	3·24	0·95
Hoyland . .	80·46	5·09	1·67	6·79	1·66	3·30	1·03
Thorncliffe .	81·98	5·70	1·83	5·26	1·52	2·36	1·35

The gas-making qualities are excellent, as can be judged from the following table:—

Gas per ton corrected	Illuminating power candles	Coke p.c. by weight	Candles per ton
11,000	17·00	66·0	37·400

The coke is excellent, of bright steely colour and of great strength.

The Silkstone seam in Derbyshire produces valuable gas coals; but they are not so rich as the South Yorkshire, containing more charcoal, sulphur, moisture and ash.

Silkstone at Chesterfield.

—	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Ash	Moisture
Albert Coal .	76·84	5·22	1·59	5·60	2·34	4·45	3·96
„ Nuts .	75·71	5·83	1·72	7·50	2·33	2·99	3·92
Plumbley .	76·96	5·04	1·77	6·92	2·39	3·28	3·64

Gas per ton corrected	Coke p.c.	Illuminating power candles	Candles per ton
10,500	64	15·7	32·970

The coke is fairly good, but has not so fine an appearance as the South Yorkshire.

Some of the softer portions of the Barnsley Hard coal seam are used for gas-making, but the coke produced is not of very good quality. Otherwise they are good gas-making coals.

Elementary composition of Barnsley Gas Coals.

—	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	Ash	Moisture
Darfield . .	76·68	4·79	1·76	7·56	1·28	3·98	0·82
Monckton .	75·64	4·94	1·65	7·25	2·84	4·28	3·40
Treeton . .	75·61	5·08	1·59	6·90	2·61	4·65	3·56

The behaviour on distillation of the best of these Barnsley gas coals can be gathered from the following table:—

Gas per ton corrected	Coke p.c.	Illuminating power candles	Candles per ton
10,500	64	16	33,600

Some of the gas coals supplied from the Parkgate seam of South Yorkshire are excellent for gas-making though the coke is not so fine as the Silkstone at its best. The results obtained on distillation are given in the following table:—

Gas per ton corrected	Coke p.c.	Illuminating power candles	Candles per ton
11,600	67	16·3	37,816

The Arley coal of Lancashire and some of the North Staffordshire coals are esteemed for gas-making purposes, but none of them exceeds in value the Newcastle or Silkstone gas coals. The primary points to be held in view in the selection of gas coals, are of course the yield of gas and its luminosity. The total luminiferous content of the coal is expressed by the candles per ton. Since the luminosity of the gas is expressed per 5 cubic feet (corrected to 60°F. and 30″B.) it is obvious that the illuminating power of the gas multiplied by the volume of gas yielded per ton divided by 5 gives the candles per ton; thus:—

Illuminating Power × *cubic feet per ton of coals* = *Candles per ton of coals* 5.

Of very great importance is the yield, and more especially the quality, of the coke produced. Of secondary importance, the yield of ammonia and tar. Where the plant for the purification of the gas is not laid out on the best lines, of course the amount of sulphur impurities is a serious question.

The Yorkshire and other Midland coals are generally carbonised in works in company with large quantities of cannel coal, and it is difficult to arrive at the composition of tar from the gas coals. They appear, however, generally to be slightly richer in naphtha than the south country tars, and yield creosotes containing less naphthalene and more tar acids than these. They are generally thinner and lighter.

Cannel coal. It is the custom to call all hard, homogeneous, non-laminated coal cannel, and consequently this term applies to coals of very different gas-making properties; but as in practice the worst of the cannels yields gas of better illuminating power than the common caking coals, the application of the name to all materials of this distinctive appearance has some justification. It is almost impossible by outside appearance to gather any opinion of the gas-making value of these hard, homogeneous materials. The very finest, such as the Australian shale and the Boghead, are brown in colour, whilst the others are either dull black or bright black.

The following are some analyses of cannels as published by the purveyors, and are probably all the results of laboratory experiments, and are therefore slightly superior to the results to be obtained in practice:—

Name of cannel	Gas per ton	Illuminating power	Coke p.c.	Specific gravity of coal
Scotch cannels.				
Cleugh	12,350	31·02	53·9	1·287
Gorebridge.	12,560	35·46	40·4	1·226
Lesmahago Main	12,525	33·52	49·6	1·224
Cairntable	11,294	35·75	49·8	1·228
Lochore and Capeldrae . . .	13,165	35·16	43·6	1·225
Mainhill	11,125	29·07	56·2	1·304
Thorburn	13,120	36·12	45·3	1·189
Braehead	9,915	27·94	54·0	1·255
Orchard	12,525	33·52	49·5	1·224
Westwood	10,356	39·75	--	—
Old Wemyss.	11,720	34·92	50·1	1·250
Rigside.	11,732	35·31	50·5	1·269
Roslin	11,410	27·72	48·7	1·214
Lancashire cannels.				
Wigan Coal and Iron Co.'s cannel .	10,376	24·5	—	1·268
Bickershaw	14,800	29·2	48·6	—

It is usual to test the rich gas from cannels in a fish-tail burner or union jet. The usual size is a No. 5, and the gas pressure 0·5 of an inch.

The cannels yield more and thinner tar than the caking coals at the ordinary distillation temperatures. Information respecting the yield of ammonia, disposition of the sulphur on distillation, &c. &c., is not generally forthcoming.

The following results obtained by the writer for Nottinghamshire cannel indicate that the sulphur impurities are lower and the carbonic acid higher than is the case with caking coals:—

Sulphur other than sulphuretted hydrogen	Carbonic acid	Sulphuretted hydrogen
23·74 grains per 100 cubic feet	39·87 grains per cubic feet	3·69 grains per cubic feet
Or 0·328 lbs. per ton of coals	Or 55·13 lbs. per ton of coals	Or 5·1 lbs. per ton of coals
Or 0·015 p.c. by weight	Or 2·46 p.c. by weight	Or 0·23 p.c. by weight

The following elementary analysis of the celebrated Australian shale, the richest gas-making mineral known, will be interesting, for such analyses of cannels are rare. This cannel yields 14,500 cubic feet of 48 candles.

Moisture lost at 212°F.	0·23
Carbon	70·94
Hydrogen	9·21
Nitrogen	0·50
Sulphur	0·48
Oxygen by difference	3·80
Ash	14·84
	100·00

DESTRUCTIVE DISTILLATION.

The ultimate tendency of the action of high temperatures upon organic substances is to resolve them into their elements; but before this absolute degree of dissociation is reached new compound substances of a more or less complex kind are produced by a rearrangement of the atoms comprising the original molecule. Organic substances, consisting of carbon, hydrogen, and oxygen, generally produce hydrocarbons (compounds of hydrogen and carbon), water, and new oxygenated compounds containing the three original elements together with the two oxides of carbon, carbon dioxide and carbon monoxide, and some free hydrogen and free carbon. If the original substance was volatile, some generally passes over unchanged. The degree of temperature employed decides the quantity of the free hydrogen and free carbon produced, these increasing in amount with the temperature. Hydrogen generally makes its appearance in the free condition before the carbon. The great number of new bodies formed makes the process very complicated to follow theoretically, and there are at present no cases of the destructive distillation of an organic substance so perfectly studied as to enable us to give exact quantitative and qualitative expression to the changes occurring. The influence of the degree to which the destructive action of heat is carried is very subtle, each elevation of temperature bringing forth new compounds, and rendering the existence impossible of compounds formed at lower temperatures. The nature of the original substance, independently of its stoichiometrical composition, as well as the temperature, influences the character of the distillation products, and two substances having the same empirical composition, containing the same number of equivalents of the component bodies, do not undergo the same changes or produce the same rearrangements of their atoms. Thus dextrin and starch, both bodies containing carbon, hydrogen, and oxygen in the proportion $C_6H_{10}O_5$, will divide their content of oxygen differently between the carbon and hydrogen in the formation of the carbon oxides and the new compounds containing carbon, hydrogen, and oxygen. The action of high temperatures on hydrocarbons is also very complex, new hydrocarbons being formed by several processes:—

(1.) By the loss of hydrogen, as in the formation of chrysene from benzene, thus:

$$3C_6H_6 = C_{18}H_{12} + 3H_2.$$

(2.) By the loss of carbon and hydrogen.

(3.) By the union of two or more of the original molecules to form new hydrocarbons; thus the formation of benzene from three molecules of acetylene $3C_2H_2 = C_6H_6$.

(4.) By the union of two or more of the molecules of new hydrocarbons formed by the first three processes.

Thus the action of high temperatures in hydrocarbons is not only analytic and destructive, but also synthetic and constructive, new substances being formed out of the débris of the destroyed molecules. When the original substance contains nitrogen and sulphur as well as carbon, hydrogen, and oxygen, the reactions, resolutions, and compositions become much more complicated, the nitrogen and sulphur partly uniting with hydrogen to form such compounds as ammonia and sulphuretted hydrogen, with carbon to form cyanogen and carbon bisulphide respectively, and with carbon and hydrogen to form such compounds as aniline and pyridine, and, as was the case with the carbon and hydrogen, some nitrogen appears in the free state.

When we consider that there is a fresh equilibrium amongst the atoms at each temperature it is not difficult to imagine the immense complication of the distillation products of an organic substance.

Coal, which consists of carbon, hydrogen, oxygen, nitrogen, and sulphur, is the substance best known as regards its distillation products, but coal is evidently not a simple substance but a mixture of many compounds. The fossil character of coal, its insolubility in solvents, its powers of resistance to reagents, has prevented up to the present any investigation into the compounds of which it consists by their separation and isolation. However, the case of the destructive distillation of a complex substance like coal is very profound, as will at once be seen by an examination of any of the recent catalogues of its distillation products, to which almost every day new members are being added.

The following is a list of some of the most prominent of the substances occurring in the distillation products of coal:—

Hydrocarbons.

—	Formula	Boiling-point	Melting-point
Methane Series of Hydrocarbons C_nH_{2n+2}			
Methane	CH_4	—	—
Ethane	C_2H_6	—	—
Propane	C_3H_8	-20	—
Butane, Normal . .	C_4H_{10}	-1	—
Pentane „ . . .	C_5H_{12}	37–39	liquid
Isopentane	C_5H_{12}	30	„
Hexane, Normal . .	C_6H_{14}	69–71	„
Heptane, „ . .	C_7H_{16}	98–	„
Ethylisoamyl, „ . .	C_7H_{16}	90·3	„
Octane	C^8H_{18}	119–120	„
Nonane	C_9H_{20}	130	„
Decane	$C_{10}H_{22}$	158–161	„
Paraffins.		400°	solid
Ethylene Series C_nH_{2n}			
Ethylene	C_2H_4	-100°	—
Propylene	C_3H_6	-5°	—
Butylene	C_4H_8	-5°	—
Amylene	C_5H_{10}	35°	liquid
Hexylene	C_6H_{12}	65°	„
Heptylene	C_7H_{14}	96°	„
Acetylene Series C_nH_{2n-2}			
Acetylene	C_2H_2	—	—
Allylene	C_3H_4	—	—
Crotonylene . . .	C_4H_6	20°	liquid
Hexoylene	C_6H_{10}	85°	„
Terpene Series C_nH_{2n-4}			
Terpene	$C_{10}H_{16}$	171°	„
Benzene Series C_nH_{2n-6}			
Benzene	C_6H_6	81°	„
Toluene	C_7H_8	111°	„
Orthoxylene . . .	C_8H_{10}	141°	„
Metaxylene . . .	—	139°	„
Paraxylene	—	138°	„
Pseudocumene . .	—	169·5°	„
Mesitylene	C_9H_{12}	163°	„
Durene	$C_{10}H_{14}$	196°	„
Naphthalene series.			
Naphthalene . . .	$C_{10}H_8$	216°	79°
Naphthalene hydride	$C_{10}H_{10}$	205°	liquid
a Methylnaphthalene	$C_{11}H_{10}$	240°–243°	„
β „	$C_{11}H_{10}$	241°-242°	32·5
Dimethylnaphthalene	$C_{12}H_{12}$	262°–264°	liquid
Hydrocarbons of other Series.			
Acenaphthene . .	$C_{12}H_{10}$	280°	99°
Diphenyl	$C_{12}H_{10}$	254°	71°
Fluorene	$C_{13}H_{10}$	295°	113°
Anthracene . . .	$C_{14}H_{10}$	360°	213°
Methylanthracene .	$C_{15}H_{12}$	above 360°	200°
Phenanthrene . .	$C_{14}H_{10}$	340°	100°
Fluoranthene . . .	$C_{15}H_{10}$	above 360°	109°
Pyrene	$C_{16}H_{10}$	„ „	149°
Chrysene	$C_{18}H_{12}$	„ „	250°
Retene	$C_{18}H_{18}$	350°	98° to 99°
Picene	$C_{22}H_{14}$	520°	339°

Oxygenated Bodies.

Water.	H_2O	100°	0°
Acetone	C_3H_6O	56°	liquid
Acetic acid . . .	$C_2H_4O_2$	119°	16°
Benzoic „	$C_7H_6O_2$	250°	121°
Resolic „	$C_{19}H_{14}O_3$	—	—
Phenols.			
Phenol	C_6H_6O	184°	42°
Orthocresol . . .	C_7H_8O	188°	31°
Metacresol	C_7H_8O	201°	liquid
Paracresol	C_7H_8O	199°	36°
Cylenol	$C_8H_{10}O$	—	—
a Naphthol	$C_{10}H_8O$	280°	94°
β Naphthol	—	286°	123°

Nitrogen Compounds.

—	Formula	Boiling-point	Melting-point
Bases.			
Ammonia	NH_3	—	—
Pyridine	C_5H_5N	116·7°	liquid
a Picoline	C_6H_7N	135°	„
Lutidine	C_7H_9N	134°	„
Collidine	$C_8H_{11}N$	179°	„
Aniline	C_6H_7N	182°	„
Parvoline	$C_9H_{13}N$	188°	„
Coridine	$C_{10}H_{15}N$	211°	„
Rubidine	$C_{11}H_{17}N$	230°	„
Chinoline	C_9H_7N	239°	„
Chinaldine	$C_{10}H_9N$	243°	„
Viridine	$C_{12}H_{19}N$	257°	„
Lepidine	$C_{10}H_9N$	257°	„
Cryptidine	$C_{11}H_{11}N$	274°	„
Acridine	$C_{13}H_9N$	above 360°	111°
Non-Basic.			
Cyanogen	(CN_2)	-25°	—
Hydrocyanic acid .	CNH	—	—
Pyrrol	C_4H_5N	133°	liquid
Carbazol	$C_{12}H_9N$	355°	238°
Ammonium cyanide	$CN.NH_4$	—	—
Acetonitrile . . .	C_2H_3N	82°	liquid
Sulphur Compounds.			
Hydrogen sulphide	H_2S	—	—
Ammonium „ .	$(NH_4)_2S$	—	—
„ „ .	$(NH_4)HS$	—	—
„ sulphocyanide	$(NH_4)NCS$	—	—
Carbonbisulphide .	CS_2	47°	liquid
Carbonoxysulphide	COS	—	—
Thiophen	C_4H_4S	84°	liquid
Thiotolen	C_5H_6S	113°	„
Thiolen	C_6H_8S	137°	„
Other substances.			
Hydrogen	H_2	—	—
Nitrogen	N_2	—	—
Carbon (Soot) . .	C_x	—	solid

In practice, when coal gas is distilled, the first result is the separation of all that is volatile of the coal at the temperature employed from that which is fixed and must be left behind as a residue. The volatile matters are partly substances gaseous at ordinary temperatures, partly bodies liquid at ordinary temperatures, such as oils and water, and partly substances solid at ordinary temperatures, such as naphthalene, anthracene, &c., and free carbon, and on the cooling of the volatile products a natural separation is set up forming gas, tar (the oils and solid substances amalgamated into a more or less viscous fluid) and water containing certain substances, principally ammoniacal compounds, in solution.

If the operation of the distillation of the coal and the several collections of the volatile products could be conducted in absolutely closed vessels, the weight of the sum of these latter *plus* the weight of the residue would of course equal the weight of the original coal, and further, the weight of each of the elementary substances which entered into the composition of the original coal should be equalled by the sum of the various amounts of each of the elementary substances found in the various distillation products. In practice the distillation cannot be carried on without some loss, which is trifling in the best practice and more considerable where the operations are carelessly conducted.

The following table shows the amounts of the various elementary substances entering into the composition of a sample of Derbyshire Silkstone coal and the manner in which they became distributed amongst the products on the distillation of the coal at a high temperature of distillation.

Composition of the coal and distillation products per 100 parts by weight.

—	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Ash	Total
Coke	57·95	0·70	0·77	0·47	1·24	2·97	64·10
Tar	4·79	0·39	0·06	0·05	1·18	—	6·47
Liquid . . .	0·08	1·06	0·13	0·21	8·30	—	9·78
Gas purified .	8·53	3·42	trace	0·86	2·30	—	15·11
Purifiers . . .	0·38	0·04	0·74	0·02	0·93	—	2·11
	71·73	5·61	1·70	1·61	13·95	2·97	97·57
Coal	75·71	6·27	1·72	1·72	11·59	2·99	100·00
Error and loss.	−3·98	−0·66	−0·02	−0·11	+2·36	−0·02	−2·43

Volume of gas 11,189 cubic feet corrected to 30 in. barometer and 60°F.

Illuminating power 15·3 sperm candles.

Tar produce 12·01 gallons, 1207 specific gravity.

Liquor produce 21·6 gallons.

The percentage of the sum of each element (as found in the products) entering into the different products is shown in the following table:—

—	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Ash
Coke	80·8	12·5	45·3	29·2	8·9	100·0
Tar.	6·7	6·9	3·5	3·1	8·5	—
Liquid	0·1	18·9	7·7	13·0	59·5	—
Purified gas	11·9	60·0	trace	53·4	16·5	—
Impurities	0·5	0·7	43·5	1·2	6·6	—
	100·0	100·0	100·0	100·0	100·0	100·0

When the same coal was distilled at a very low temperature (below that employed in practice), the distribution of the components of the coal amongst the distillation products was slightly different, and is given in the following table:—

—	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Ash	Total
Coke	57·38	1·24	1·05	1·06	1·28	2·96	64·97
Tar	6·11	0·46	0·05	0·06	0·60	—	7·28
Liquid . . .	0·08	1·06	0·12	0·22	8·30	—	9·78
Gas purified .	7·56	2·85	—	0·36	1·46	—	12·23
Purifiers . . .	0·22	0·02	0·39	0·01	0·56	—	1·20
	71·35	5·63	1·61	1·71	12·20	2·96	95·46
Coal	75·71	6·27	1·72	1·72	11·59	2·99	100·00
Error and loss.	−4·36	−0·64	−0·11	−0·01	+0·61	−0·03	−4·54

From this table it will be found that the percentage amount of each element in the different products was as follows:—

—	Carbon	Hydrogen	Sulphur	Nitrogen	Oxygen	Ash
Coke	80·4	22·0	65·2	62·0	10·5	100·0
Tar.	8·6	8·2	3·1	3·5	4·9	—
Liquid	0·1	18·8	7·5	12·9	68·0	—
Purified gas	10·6	50·6	trace	21·0	12·0	—
Impurities	0·3	0·4	24·2	0·6	4·6	—
	100·0	100·0	100·0	100·0	100·0	100·0

It is difficult to obtain, even with great care in sampling, an analysis of coal that can be considered to exactly represent a large bulk such as 50 tons, the amount employed in each of the above experiments. There must also be some experimental errors in the analysis of the coals and the various products, and it is therefore difficult to say how much of the difference between the amounts found in the products and that found in the above coal analysis is due to error and how much to loss. The loss is most likely to be chiefly among the volatile products, as these find their way out through the pores of the clay retorts in which the coal is distilled, and is likely to be greater relatively to the coal the longer the operation of carbonisation is maintained, and therefore the lower the temperature.

An increase in the distillation temperature invariably results in an increase in the production of gas at the expense of the bodies which would otherwise go into the tar, and also because less quantities of hydrogen and nitrogen are left in the coke. At the same time the illuminating power of the gas is decreased, but not to the same extent as its volume is increased. Thus an increase in the volume of 20 p.c. is only attended by a decrease of about 6 p.c. in the illuminating power. This is when the coal is distilled in clay retorts, which after being in operation a short time become full of cracks, besides being porous. However, by a happy compensation, some of the free carbon produced by the destruction of the hydrocarbons &c., forms a coating on the inner surface of the retort, filling up the cracks as well as the pores, and thus rendering the retort less permeable by gas.

The change in the character of the tar with change of temperature of distillation is very marked. When coal is distilled at a temperature rising to about 800°F. the tar is thinner and lighter than water, and consists principally of paraffin and olefiant hydrocarbons, and contains but traces of free carbon; at a distillation temperature rising to about 1,700° to 2,000°, the tar becomes thick and contains but little of the paraffin and olefiant hydrocarbons, which become replaced to some extent by benzenoid hydrocarbons, and much free carbon is formed. There is, with increasing distillation temperature, a regular gradation in these particulars, the paraffin and hydrocarbons being destroyed, and benzenoid hydrocarbons, with free carbon and an increased production of illuminating gas, being formed out of their débris.

At the same distillation temperature cannel coals produce lighter and more paraffinoid tars than the common coals. This is to be partly accounted for by the greater ease with which the bulk of the volatile matters come off from the cannel coal, by which they escape the prolonged action of the heated retort.

There also seems to be a general tendency on the part of coals which yield much water on distillation to produce thinner tars than the drier coals of the same kind. The results in the table below indicate the manner in which volume and specific gravity of the tar vary with distillation temperature, and were obtained in ordinary practice with clay retorts:—

Class of coal	Temperature of distillation	Cubic feet of gas per ton	Gallons of tar per ton	Specific gravity of tar	Tar per ton. lbs.	Weight-percentage on coal
Derbyshire black-shale (No. 1) .	Very high	11·128	10·63	1210	128·62	5·74
	Normal	10·400	—	1185	—	—
	Very low	7·856	11·50	1145	131·67	5·88
Derbyshire black-shale (No. 2) .	Very high	11·190	12·01	1207	144·96	6·47
	Normal	10·400	—	1185	—	—
	Very low	7·562	14·38	1136	163·85	7·29
Notts top hard cannel . . .	Normal	9·852	21·32	1147	244·54	10·92
	Very low	7·125	23·81	1116	265·72	11·86

With increased temperature the phenolic compounds become less, and after a certain high temperature, the members of the benzene series of C_nH_{2n-6} hydrocarbons are considerably diminished in quantity.

The following results were obtained from a tar produced from a Yorkshire coal:—

Temperature of distillation	Cubic feet of gas per ton	Specific gravity of tar	Percentage of 50 p.c. benzol in tar	Tar acids in creosote p.c.
High	11·700	1206	0·6	21·0
Moderate	10·162	1154	1·2	27·0
Low	8·900	1140	1·6	28·5
Very low	7·200	1102	1·9	80·7
Very low indeed	6·600	1086	1·1	34·0

Though some coals under some circumstances of distillation yield thinner tars, containing less free carbon and more naphthas than other coals, yet all coals, even the cannels, can be made to produce thick tars by distilling them at high temperatures. Thus the rich cannels distilled at the highest temperatures obtainable with gaseous furnaces on the recuperative principle produce tars of specific gravity as high as those produced from Newcastle coals in the London works, but though the tars then are alike as regards viscosity and specific gravity, they exhibit material differences in the nature and amount of the various bodies, hydrocarbons, &c., which form their bulk.

Each variety of coal produces a generic tar, which, however it may be varied by distillation temperature, bears its characteristic qualities throughout.

The following experiments show the influence of temperature on the composition of the lime-purified gas, but having been made with an iron retort, are not affected by the loss which is inevitable with clay retorts. The coal from the Newcastle district was distilled at different temperatures, the degree of which is to be inferred from the volume of gas produced.

—	1	2	3
Cubic feet of gas per ton .	8,250	9,692	12.006
Illuminating power candles	20·5	17·8	15·6
Hydrogen (H) . . .	38·09	43·77	48·02
Carbonic oxide (CO) . .	8·72	12·50	13·96
Methane (CH_4) . . .	42·72	34·50	30·70
C_nH_{2n} Hydrocarbons .	7·55	5·83	4·51
Nitrogen (N) . . .	2·92	3·40	2·81
Density of carbon vapour in C_nH_{2n} hydrocarbons	2·73	2·91	2·62

The total volume of the various constituents produced per ton of coal at the three different temperatures is given in the following table:—

All evidence goes to show that the higher the temperature the more is the hydrogen and carbon gasified partly at the expense of the tar, and as regards the hydrogen partly by the lesser amount left in the coke residue.

The ammonia, which is an important product, appears to rise in amount with increasing temperature to a maximum somewhere about a yield of gas of 9,500 cubic feet per ton, and after that to fall.

From a large number of coals examined by the writer it was found in practice with clay retorts that from 11½ to 15¾ p.c. of the total nitrogen of the coals appeared as ammonia on their distillation.

Number of the experiment	Cubic feet of each constituent yielded by 1 ton of coal					Carbon as vapour per 100 vols. of gas
	H	CO	CH_4	C_nH_{2n}	N	
1	3142·4	719·4	3524·4	622·9	240·9	72·08
2	4242·6	1211·6	3344·1	565·1	329·6	63·93
3	5765·3	1676·0	3685·8	541·5	337·4	56·49

The impurities, carbonic acid, sulphuretted hydrogen, carbon bisulphide, and cyanogen, are considerably increased with increased distillation temperature.

In the case previously cited of the Derbyshire Silkstone coal distilled at two extremes of temperature, the amounts of the four impurities found at the two extremes of temperature were as follow.

High temperature, producing 11,187 *cubic feet per ton of coal.*

Carbonic acid (CO_2), 17·99 grains per cubic feet of gas, or 1·284 lbs. of CO_2 per 100 lbs. of coal.

Sulphuretted hydrogen (H_2S), 10·578 grains per cubic feet of gas, or equal to 0·71 lbs. of sulphur per 100 lbs. of coal.

Carbon bisulphide (CS_2), 0·4052 grains per cubic feet of gas, or equal to 0·029 lbs. of sulphur per 100 lbs. of coal.

Cyanogen, nitrogen as cyanogen equal to 0·3052 grain per cubic foot, or 0·022 lbs. per 100 lbs. of coal.

Low temperature, producing 7,562 *cubic feet of gas per ton of coals.*

Carbonic acid (CO), 15·94 grains per cubic foot of gas, or 0·769 lbs. per 100 lbs. of coal.

Sulphuretted hydrogen (H_2S), 8·40 grains per cubic feet of gas, or equal to 0·381 lbs. of sulphur per 100 lbs. of coal.

Carbon bisulphide (CS_2), 0·27 grains per cubic feet of gas, or equal to 0·013 lb. of sulphur per 100 lbs. of coal.

Cyanogen, nitrogen as cyanogen equal to 0·0734 grains per cubic foot, or 0·0035 lb. per 100 lbs. of coal.

Generally, the cannels yield less of the sulphur compounds and sulphuretted hydrogen, but much more carbonic acid than the common coals.

THE MANUFACTURE OF COAL GAS.

The manufacturing operations consist briefly of the distillation of the coal; the cooling and condensation of the volatile products; the washing of the gas for removal of ammonia; the purification of the gas from carbonic acid, sulphuretted hydrogen, carbon bisulphide, &c.; the measurements of the resulting gas and the storage of it in gasholders; and the plant consists, therefore, of retorts set in suitable furnaces, condensing and cooling apparatus, exhausting apparatus, washers and scrubbers, purifiers, meters, and gasholders, with suitable buildings and accessories.

The selection of site is a matter of great importance to the future of the works, as it is desirable to have free and direct access to as many means of transport as possible, water carriage included. Though many gasworks are situated in the centre of towns, it is always advisable that they should be as far as possible from populous districts, for though the neighbourhood of gas works is certainly not rendered unhealthy by the manufacturing operations, yet there are always people ready to harass the management with sentimental grievances. Certain modern instances, such as the Beckton Gasworks of the Gas Light and Coke Company of London, are practical evidences that proximity of the gasworks to the locality to be supplied with gas is not necessary. In the arrangement of the works it is most important that simplicity and economy in the modes of transporting the coal and coke should exist.

In this matter many large works fail to arrive at the greatest economy. In a first class works the coal should drop from the railway waggon which has borne it down on to the floor of the retort house, at the feet of the men who are to charge it into the retorts, and the waggons for removing the coke should enter the retort-house itself. It is to small economies that many works owe their great success. Canal carriage in this country is so badly developed and so crushed out by railway interests that it is hardly imperative in the design of the works to consider this system of transport. The finest site for a gasworks is on a navigable river, and there are no finer works in regard to site than the Beckton Gasworks, where large steamers can come alongside to discharge coal and other materials and to receive coke and other products. Beckton is a typical site for a gasworks, and has but one minor disadvantage, viz., the want of an immediately local outlet for the coke, which has to be transported, at a certain cost for freight, to its market. Gasworks situated in populous neighbourhoods often have the advantage of being able to dispose of coke at their doors at a comparatively high price.

A low level site is generally chosen on account of the increase in gas pressure obtained by the supply of elevated districts from points of lower level, and it often happens that the railway system adjacent is by embankment or viaduct at a higher level. Such a means of approach is most economical for delivery of the coal, which falls by gravitation into the retort house.

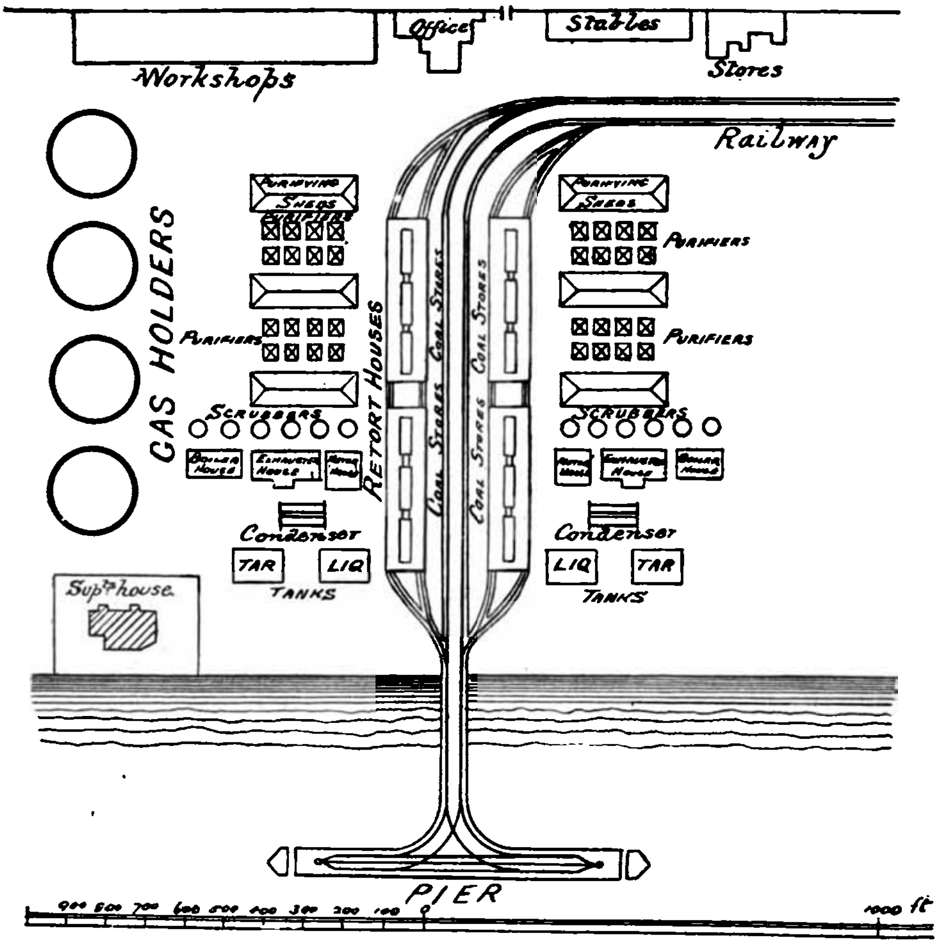


Fig. 1.

Fig. 1 is an ideal plan of a gasworks capable of manufacturing 10 to 12 millions of cubic feet of gas per diem.

The area of site required per 100 tons of coal carbonised per diem, is about 3 acres.

The variations in the daily requirements are very considerable, and it thus happens that in the summer months a large proportion of the manufacturing plant stands idle.

The day of greatest consumption varies in relation to the annual production from year to year with even the same undertaking. In Nottingham it has varied from 0·52 to 0·58 p.c. within 10 years, or in other words, the maximum gas consumption varied from the $\frac{1}{192}$ to the $\frac{1}{172}$ part of the annual production.

It is of course the period of maximum consumption that is provided for in the design of a gasworks.

The following German statistics for the year 1877, will show how the relation in question varies with locality:—

The maximum daily production was from	0·4 to 0·45 p.c. with 21 towns
Ditto	0·45 to 0·50 p.c. with 47 towns
Ditto	0·50 to 0·55 p.c. with 75 towns
Ditto	0·55 to 0·60 p.c. with 86 towns
Ditto	0·60 to 0·65 p.c. with 52 towns
Ditto	0·65 to 0·70 p.c. with 34 towns
Ditto	0·70 to 0·75 p.c. with 17 towns
Ditto	over 0·75 p.c. with 30 towns
Ditto	under 0·05 p.c. with 36 towns
Ditto	0·05 to 0·07 p.c. with 40 towns
Ditto	0·07 to 0·09 p.c. with 69 towns
Ditto	0·09 to 0·11 p.c. with 76 towns
Ditto	0·11 to 0·13 p.c. with 60 towns
Ditto	0·13 to 0·15 p.c. with 49 towns
Ditto	over 0·15 p.c. with 29 towns

The amount of gas consumed per inhabitant of a gas-lighted district depends very largely upon the character of the industries carried on or the nature of the population. In rural agricultural districts it may be as low as 500 cubic feet per annum per inhabitant, in the best parts of a large town it may be about 12,000 cubic feet per inhabitant. In the metropolis the average amount of gas consumed per consumer is about 74,000 cubic feet per annum.

In the provinces the amount is about one-half of this.

The public gas lamps consume about 20,000 cubic feet per annum.

The average capital employed per ton of coal carbonised per annum is 6*l.* 11*s.* 6*d.*, but varies very much with different undertakings, some having a capital as low as 2*l.* 3*s.* 3*d.* and others having over 16*l.*

It is quite possible to build works at the present time in the best and most efficient style at the rate of 3*l.* to 3*l.* 10*s.* per ton of coals carbonised per annum.

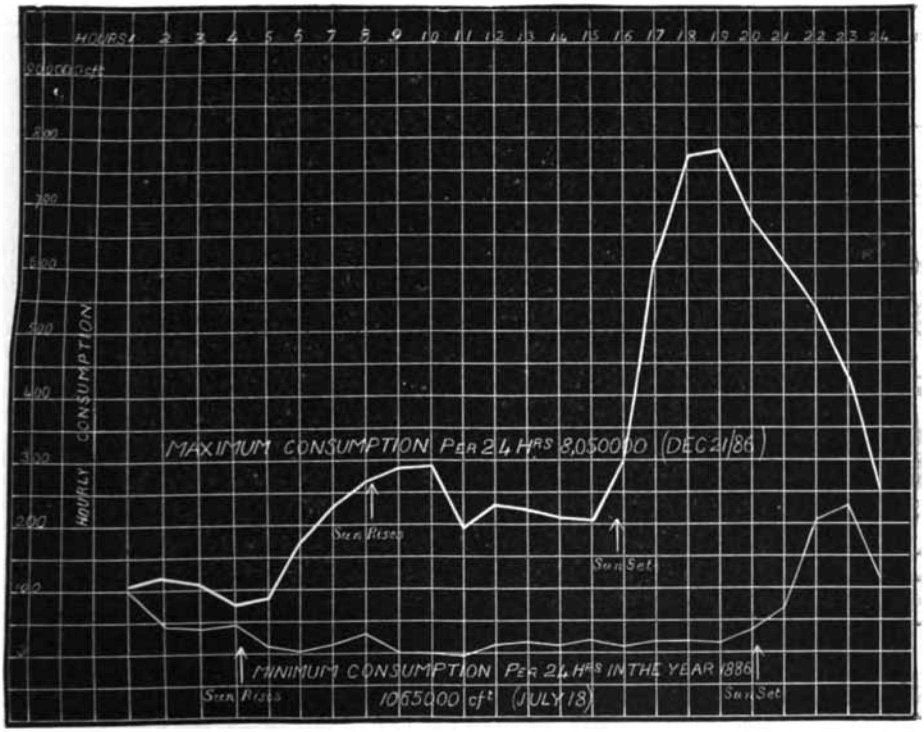


FIG. 2.

The diagram Fig. 2 gives the hourly consumption for days of largest and least consumption in Nottingham for year 1886.

The retorts and retort houses.—The vessels and retorts in use for the distillation of coal are nowadays made of fire-clay, and each retort is capable of holding from about 2 to 3 cwt. of coal, forming the 'charge,' which requires from 4 to 6 hours for the expulsion of its volatile matters. The dimensions of the retort are from about 16 to 22 inches in width, 13 to 16 inches in height, and 9 to 10 feet in length, and the thickness of the fire-clay 3 inches excepting at the mouth, where it is 4 inches thick. They are of various sections, oval, round, and ◠ shaped, and are set horizontally in groups. Seven is a very usual number to set in a group in ground floor retort houses, where the furnace is on the same level as the floor from which the retorts are charged. In stage floor houses provided with a coke cellar below the charging floor, it is usual to place the furnace in the coke cellar, and then there is room for 9 retorts.

Each group is called a setting and is heated by a furnace. These settings are placed in arches, which also carry the main flue, the hydraulic main, &c. Since the retorts are almost universally charged with coal by manual labour, the top tier of retorts must be within the reach of a man and the bottom tier must also be above the level of the floor. The dimensions of a gas retort admit of three tiers being placed in the group, and the arches are of such width as to admit of 3 retorts being placed in the tier, and thus 9 retorts is a convenient number where the furnace can be placed below the setting.

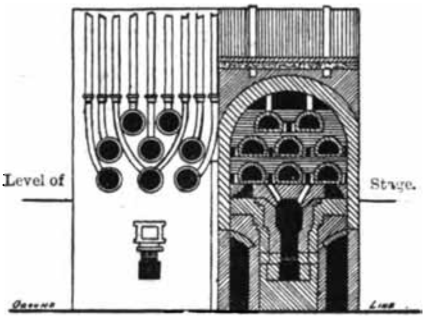


Fig. 3.

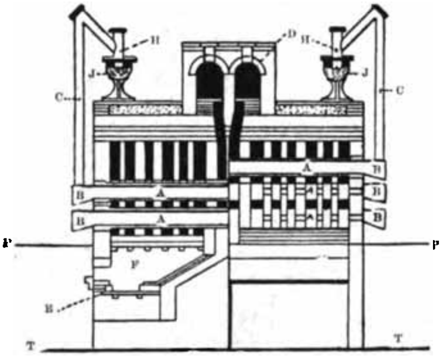


Fig. 4.

Figs. 3 and 4 are sections and elevation of an ordinary furnace and through retorts as arranged for a stage floor retort house.

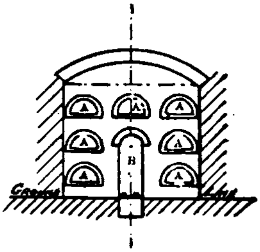


Fig. 5.

In cases where there is no floor below the charging floor the furnace occupies the space that would otherwise be utilised for the two middle retorts on the two lower tiers. Figs. 5 and 6 show the disposition in such cases. In all works but those of small size, it is usual to place the settings back to back and then to make the retorts continuous for a length of 18 to 20 feet, with two mouths. The retorts are then called 'doubles' in distinction to the 'singles,' which have only one opening and are closed off at the back ends. With the exception of this community of retorts the settings are distinct and have separate flues and furnaces. Considerable economy of space results from this system of placing the settings back to back; of course the two retorts which thus communicate are drawn and charged simultaneously. At the mouth of each retort is bolted on by a flange an iron mouthpiece similar to the one shown in fig. 7 and for this purpose suitable holes are prepared in the fire-clay, which is thickened to 4 inches for the purpose of recovering the strength lost by the holes. This iron mouthpiece generally projects out beyond the setting about 16 inches and serves to carry the lid which shuts off the retort from the atmosphere when it is charged, and also to carry an opening and socket in which is placed an upright pipe called the ascension pipe to lead the gas away upwards into the hydraulic main. The usual diameter of these ascension or stand pipes, is 6 or 7 inches. The lid which forms the door of the retort is made to fit tightly against a face on the mouthpiece and is ingeniously carried by an arrangement which besides serving as a hinge on which it turns is also a lever for pressing the lid against the face. The drawing, fig. 8, shows the apparatus. The charge of coal is spread as evenly as possible on the floor of the retort by means of

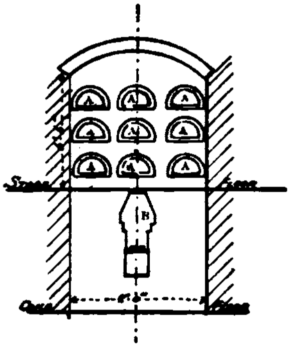


Fig. 6.

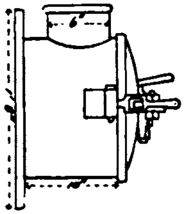


Fig. 7.

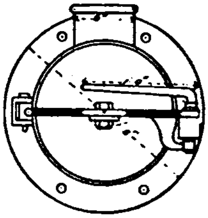


Fig. 8.

a long, thin scoop or sometimes by an ordinary shovel. When a scoop is employed, the time occupied in charging the retort and closing the door is about 40 seconds. When the coal is completely carbonised, in about 4 to 6 hours, the retort is opened and the coke is raked out by means of a long iron rake, either into iron barrows to be wheeled outside the retort house, or in the case of stage floor retort houses it falls through a space there is between the front of the settings and the stage into the coke cellar below. Attempts to introduce power machinery for the charging and drawing of gas retorts, though mechanically successful, have not resulted in the displacement of manual labour for charging and drawing the retorts. The retorts are heated to such an extent that at the end of the charge the temperature is 1,800° to 2,000°F. Of course, when the coal is first put in, the temperature inside the retort is considerably lowered. The following table gives the range of temperature during a 5 hours' charge:—

Temperature on floor of retort about 3 *feet from mouthpiece. Coal producing* 10,900 *cubic feet to the ton on five-hour charges.*

—	Time	Temperature degrees Fahrenheit
Retort charged at 11 A.M.	11.15 A.M.	1,160
	11.30 „	1,290
	11.45 „	1,350
	12 „	1,350
	12.15 „	1,400
	12.30 „	1,410
	12.45 „	1,420
	1 P.M.	1,430
	1.15 „	1,440
	1.30 „	1,450
	1.45 „	1,470
	2 „	1,480
	2.15 „	1,500
	2.30 „	1,590
	2.45 „	1,670
	3 „	1,714
	3.15 „	1,742
	3.30 „	1,762
	3.45 „	1,784
Retort drawn	4 „	1,795

The amount of gas produced by these retorts varies of course with their size and temperature. About 130 to 150 cubic feet of gas per twenty-four hours per superficial foot of retort is an average production, which amounts to from 5,000 to 10,000 cubic feet per day, per mouthpiece or per retort according to circumstances. These fire-clay retorts have an average durability of thirty working months. Since the introduction of regenerative or the recuperative systems of gaseous firings the temperatures have in some works become very high, whilst the economy in the use of fuel required for feeding the furnaces is very marked. With the ordinary furnace about 25 tons of coke are required to distil 100 tons of coal, but with the regenerative furnaces about 15 tons are sufficient. The gaseous system of firing, with heating of the air by means of the waste heat in the products of combustion, is the scientific system of heating gas retorts, both as regards the temperature attained and the economy in the use of fuel. The best system is that invented by Drs. Schilling and Bunte, and called the Munich regenerative system. The illustrations (figs. 9 and 10) represent transverse vertical section through generator, and transverse vertical section through retorts and generator respectively. The fuel is gasified in the generator B′ into carbonic oxide by means of half the air supplied, called the primary air, which enters at the side of the generator by means of the small channel A (as shown in fig. 9) directly over the water in pan B, where it becomes charged with steam.

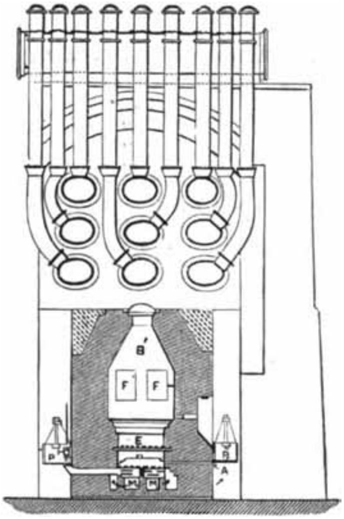


FIG. 9.

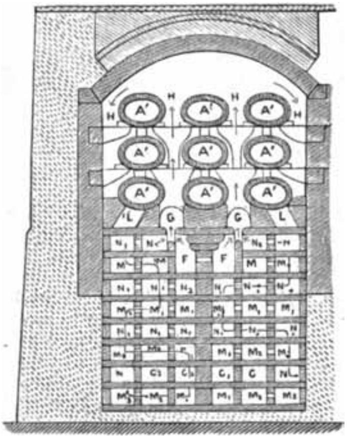


FIG. 10.

The primary air then passes through the channels C C C and C, and is warmed by contact with the walls of adjoining flues that are carrying away the spent gases. It then returns to the grate D and enters the generator. The carbonic oxide or generator gases pass up the channels F, where they meet the second half of the air supply called the secondary air, which enters at P (fig. 9), and passes upwards through the channels N N N, meeting the generator gases in G, where combustion takes place. The combustion gases, after passing round the gas retorts A' A' in the usual manner, descend through the channels M M M, heating the primary and secondary air, and finally escape by the main flues into the chimney. The composition of the generator gases averages

CO_2	8·6 p.c.
CO	20·6 „
H_2	15·0 „
N_2	55·8 „

The temperature of the generator gases is about 1,150°C., and the combustion gases enter the regenerator M M M at about 1,400°C. The secondary air is heated to about 1,000°C. by the combustion gases which leave the setting after further heating the primary air and steam at about 500°C. The consumption of fuel is about 10 of coke per 100 of coal distilled, and the retorts produce 10,000 cubic feet of gas per diem. The retorts are singles.

Fig. 11 is an illustration of a stage retort house filled with the Munich furnaces.

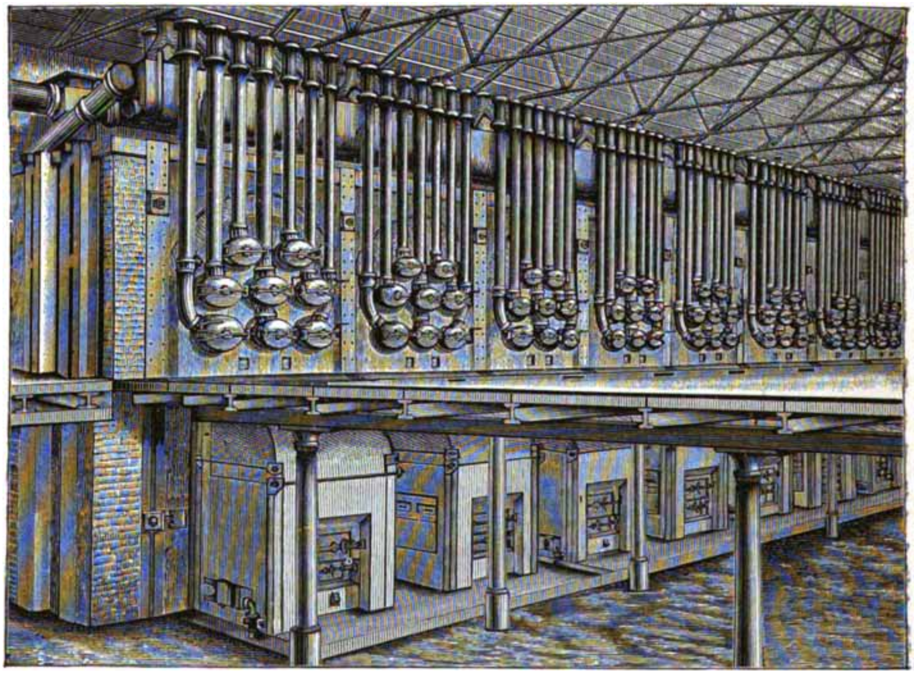


Fig. 11.

The ascension pipe, which is connected with each retort mouthpiece, rises and then bends over and dips into a long iron box called the hydraulic main, half filled with tar and liquor. This box is sometimes independent for each setting, receiving a pipe from each retort, and sometimes continuous over a great many settings, and is provided with an outlet pipe that carries away the gas and liquid products to be further dealt with, and the height of this outlet in relation to the hydraulic main determines the extent to which the dip pipe is sealed by the liquid products therein. This hydraulic main is a most important piece of apparatus. It serves to collect the volatile products from a large number of retorts into a common stream, and is therefore a collecting box; it serves as a cooler to liquefy some of the volatile products, and it also serves as an hydraulic valve for the purpose of preventing any gas passing backwards through the ascension pipe to escape into the open air when the retort lid is open. In the place of this hydraulic valve other contrivances have been designed to dispense with the hydraulic seal, such as valves on the dip pipes, which are opened on the closing of the retort lid and closed when the retort is open, but they offer no advantages over the time-honoured hydraulic seal, which is an automatic valve. Fig. 12 is an illustration of an hydraulic main in section. The usual dip is from 1 to 1½ inch, and the pressure of gas required to force the gas through this seal is supplied by a mechanical gas pump, or 'exhauster,' as it is technically called, which reduces the pressure in the hydraulic main nearly to the extent of the seal, and therefore the pressure in the retort is reduced to the lowest extent consistent with safety, and the tendency of the gas to escape through the cracks and pores of the retort is counteracted. To charge the 'through' retorts or 'doubles' with scoops three men are required on each side, or six in all. When charged with a shovel one man at each mouth is sufficient. The amount of work allotted to each man varies with the establishment. The retort houses, which are necessary to protect the men from exposure and also to reduce as much as possible loss of heat from the settings by radiation, are sometimes of large size. Ample room from the face of the setting to the retort house wall is provided to enable the men to freely conduct the operations of charging and drawing the retorts, and in cases where the coal is brought directly by rail into the retort house and a coke cellar is provided with railway access for removal of coke the area occupied is considerable. Fig. 13 shows a section through such a retort house, and sufficiently explains itself.

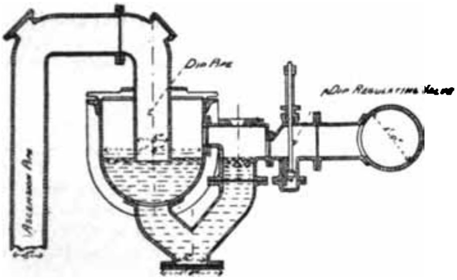


Fig. 12.

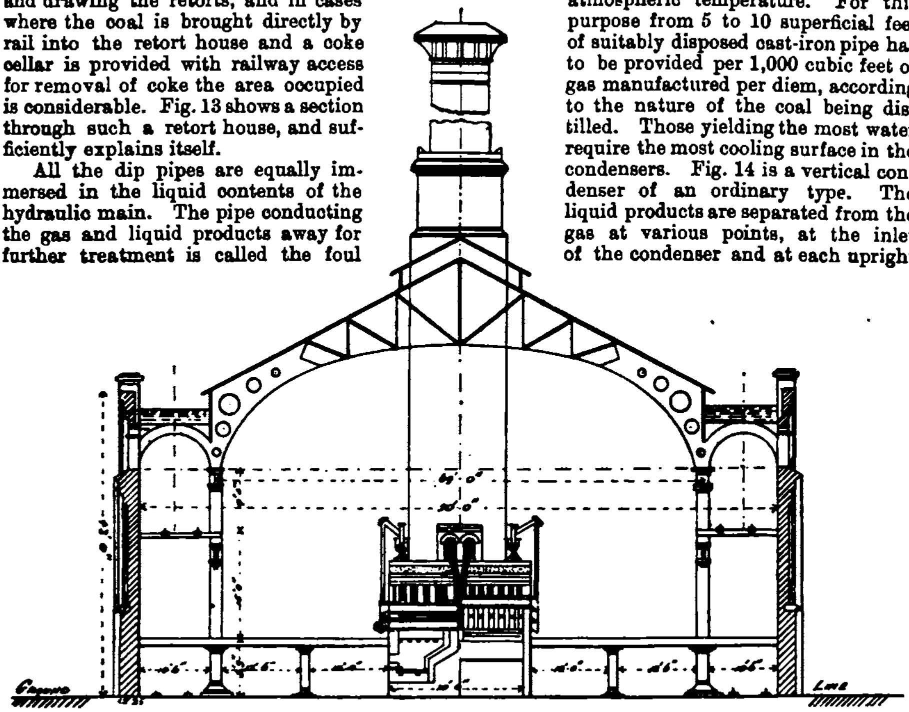


Fig. 13.

All the dip pipes are equally immersed in the liquid contents of the hydraulic main. The pipe conducting the gas and liquid products away for further treatment is called the foul main, and sometimes takes the shortest route to the condensers, or sometimes it is made to extend as far as possible round the retort house.

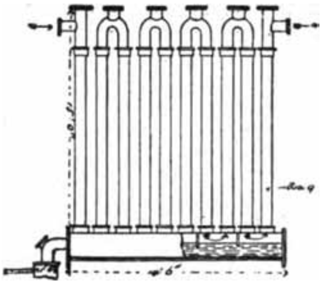


Fig. 14.

The condenser generally consists of rows of cast-iron pipes placed vertically or horizontally, and exposing a sufficient surface to the atmosphere to admit of the cooling of the gas to atmospheric temperature. For this purpose from 5 to 10 superficial feet of suitably disposed cast-iron pipe has to be provided per 1,000 cubic feet of gas manufactured per diem, according to the nature of the coal being distilled. Those yielding the most water require the most cooling surface in the condensers. Fig. 14 is a vertical condenser of an ordinary type. The liquid products are separated from the gas at various points, at the inlet of the condenser and at each upright pipe, the tar and liquor being conducted by pipes to the tar and liquor wells where the two liquids become separated by virtue of their different gravities. Sometimes the liquid products are all collected into a 'separator' which divides the tar from the liquor and sends each forward to separate receptacles. It is usual to provide storage for considerable quantities of these liquid products. The operation of cooling the gas, technically termed 'condensation,' does not generally effect the complete separation of the liquid products from the gas, some of the former still remaining suspended in the gas in a state of fog, and it thus happens that in points of the manufacturing plant beyond the condensers deposition of tar and liquor takes place. Immediately after the condensers it is usual to place the 'exhausters' or pumps for pulling the gas away from the retorts and forcing it through the purifiers into the gas-holder. These exhausters are of various kinds, but the most popular is the Beal's rotary exhausters, illustrations of which are given in figs. 15 and 16. These are generally driven by steam engines provided with apparatus for regulating their speed so as to maintain the necessary 'vacuum' on the hydraulic main. It is very important that the vacuum there should not exceed the extent of the seal given to the dip pipes, generally from 1 to 1½ inches, or air would be drawn into the retorts and up the ascension pipes when the retorts were open. It is also important that the exhauster should be driven at sufficient speed to maintain a vacuum nearly equal to the seal, or the gas in the retort will be under excessive pressure, and some be lost. Therefore considerable attention is paid to the regulation of the exhausters, which by carefully adjusted governors becomes almost automatic. The operation of exhausting is one purely mechanical, and is followed by the chemical and other methods of purification necessary to free the gas from objectionable constituents.

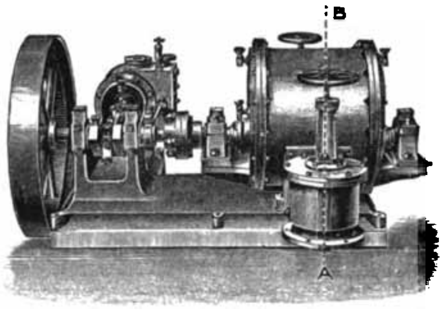


FIG. 15.

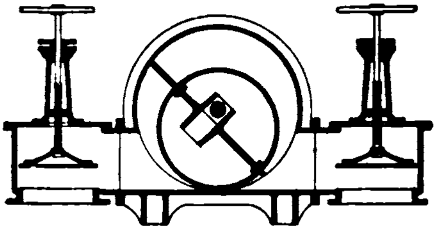


FIG. 16.

The Gas Works Clauses Act of 1847 orders that a testing place shall be provided for testing the purity of the gas as regards sulphuretted hydrogen with the following apparatus:—

A glass vessel containing a strip of bibulous paper, moistened with a solution of acetate of lead, containing 60 grains of crystallised acetate of lead dissolved in 1 fluid ounce of water, and that the mode of testing shall be:—

The gas shall be passed through the glass vessel containing the strip of bibulous paper moistened with the solution of the acetate of lead for a period of three minutes or such longer period as may be prescribed; and if any discolouration of the test paper is found to have taken place, this is to be held conclusive as to the presence of sulphuretted hydrogen.

This Act of Parliament is not sufficiently comprehensive as regards the substances to be regarded as impurities of coal gas. The penalty for presence of sulphuretted hydrogen is 20*l.* for every such case.

Since 1871, public opinion has been educated as regards the quality of coal gas, and the regulations imposed upon certain gas undertakings having special Acts of Parliament have been made very severe. As a type of the demand upon gas companies, the Commercial Gas Company's Act of 1875 may be quoted. This Act enacts that the Board of Trade shall appoint three competent and impartial persons as 'gas referees.' These 'gas referees' have power to inspect the works of the company, to ascertain the means there adopted for the purification of gas. They shall have power to ascertain what reasonable degree of purity the company can arrive at as regards sulphur and ammonia, and of compounds thereof, *or other impurity with which* the gas supplied *by them* is charged, without occasioning a nuisance to the neighbourhood in which the works are situate, and shall prescribe and certify the maximum amount of impurity in each form with which the gas should be allowed to be charged. The gas, however, shall be wholly free from sulphuretted hydrogen. The gas referees are to certify the places, mode and times of testing. The average of three successive days shall be deemed to represent the purity in each of such days. The gas examiners appointed by the Metropolitan Board are to make a report each day to the Metropolitan Board, to the Gas Company, and to the Chief Gas Examiner. The gas company can appeal against the report of a Gas Examiner to the Chief Gas Examiner within seven days. The opinion, however, of the Chief Gas Examiner is to be final. In case the company do not appeal, then the report of the Gas Examiner shall be final. The penalty for supplying gas of less than the prescribed purity shall be 50*l.* for each station in respect of which the company is at fault. The report of the Chief Gas Examiner on appeal, or the report of the Gas Examiner after the time for appeal has elapsed and no appeal has been brought, shall be conclusive evidence of the liability of the company.

By virtue of the powers conferred upon them, the gas referees issue instructions to the Gas Examiners, and have prescribed that the maximum amounts of sulphur, other than sulphuretted hydrogen and ammonia, allowed per 100 cubic feet of coal gas supplied to the metropolis shall be as follows:

Sulphur other than—

Sulphuretted hydrogen .	17·5 grains
Ammonia . . .	4·5 „

GAS PURIFICATION.

The subject of gas purification is one of great interest, both to the maker and consumer of coal gas. Legislature demands a certain degree of purity represented by the complete absence of sulphuretted hydrogen, and in some cases the reduction of ammonia and carbon bisulphide to certain limits. In many cases, notably those of the metropolitan gas companies, the gas is supplied in a high state of purity compared with what was customary years ago. There is a great practical difference between coal gas containing 40 to 50 grains of sulphur per 100 cubic feet, and coal gas otherwise the same, but containing only 10 grains of sulphur per 100 cubic feet. There can be no doubt that when gas contains as much as 30 grains of sulphur it is disagreeable when burnt in close and badly ventilated rooms, but it is questionable whether the most refined taste or smell can detect the sulphur on the combustion of gas containing 10 or less per 100 cubic feet. It is unfortunate that with all the recent advances in the conveniences of modern household life, there has been so small an amount of attention and study given to the ventilation of ordinary dwelling rooms, and that too by the aid of coal gas which can so readily be burned as not only to provide for the discharge of its own products of combustion, but also to induce currents of air and provide for the introduction and circulation of fresh air.

The objections that have been constantly held to the use of coal gas containing much sulphur are certainly not sentimental ones, and it happens that in very rare cases only is gas so consumed as not to discharge its products of combustion into the air of the apartment, and it therefore is important to reduce the sulphur to as low a degree as is possible, for gas makers must, to a large extent, take things as they find them, and while gas consumers are willing to use open gas flames in their apartments they must endeavour to minimise any objections that may arise from this custom.

The sulphur which has caused the greatest amount of solicitude is that which, occurring principally in the form of carbon bisulphide, is known technically as 'sulphur other than sulphuretted hydrogen.' Of this sulphur the greater part is in the form of carbon bisulphide, but there are about eight grains per 100 cubic feet in the form of compounds not yet identified.

As a type of well-purified gas may be taken—

Gas containing only 7 to 10 grains of sulphur per 100 cubic feet.

Sulphuretted hydrogen totally absent.

Ammonia present only in traces, say less than 1 grain per 100 cubic feet.

There are three impurities in coal gas the subject of legislation:—

1. Sulphuretted hydrogen to be entirely absent.
2. Ammonia which must not be present beyond 4 to 5 grains per 100 cubic feet.
3. Sulphur other than sulphuretted hydrogen, which must in some cases be reduced to an amount not exceeding 15 grains per 100 cubic feet.

In the case of towns not the subject of special legislation in this respect it is not a legal impurity, and then it is not common to make serious attempts towards its reduction, and the gas may contain from 30 to 50 grains. But since there are definite and perfectly understood methods of dealing with carbon bisulphide, there can be no hardship in imposing regulations for its removal from coal-gas.

There is another impurity, only of direct importance to the gas manufacturer—viz., the carbonic acid.

This body affords nothing to the heat or luminosity of the flame, but on the contrary is an objectionable diluent, as on account of its high specific heat, its cooling action considerably reduces the luminosity of the flame. Its removal is attended with an increase in the illuminating power of the gas, and on the grounds of economy it is the duty of every gas undertaking to purify the gas from carbonic acid when the gain in illuminating power exceeds the cost incurred in its removal. It happens also that in cases where the gas undertaking is under restrictions to remove the sulphur compounds other than sulphuretted hydrogen its removal is a *sine quâ non*, for, as will be shortly explained, the sulphur purification process is disturbed by carbonic acid. The influence of the distillation temperature upon the amount of these impurities has been before referred to, and it was stated that all these increase with the distillation temperature, but the economical exigencies of modern gas manufacture make the comparatively trifling expenses due to purification a matter of no moment beside the important necessity of utilising the light-giving constituents of coal, which is best effected at high temperatures.

The first step in the purification of the cooled crude coal gas is the extraction of ammonia. This step cannot be delayed to later stages in the treatment of the gas, for if gas containing ammonia were passed through solid materials such as lime or oxide for removal of other impurities, large quantities of ammonia would be retained by these materials and lost. Though various methods for the extraction of ammonia from coal gas have been employed, such as the use of the sulphate of lime, acid phosphatic manures, sulphuric acid absorbed in sawdust, the method of washing it out of the gas by water is the only method in vogue. The operation of 'scrubbing' or 'washing' crude coal gas for extraction of ammonia is carried out with the forms of apparatus designed to bring the gas into contact with water, which consist of vessels of two types. The first and oldest are the scrubbers, which are tall towers packed with coke, wooden boards, or flints, down which water percolates whilst the gas rises upwards; fig. 17 is an illustration of the usual scrubber, which is provided with devices for the distribution of the water as evenly as possible over the surface of the interior.

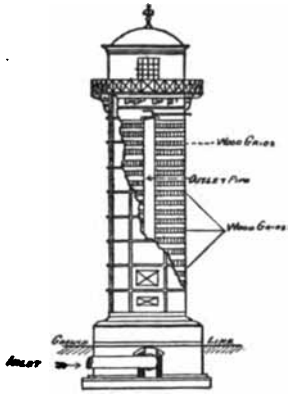


FIG. 17.

Washers are either vessels wherein the gas is broken up into fine streams and caused to bubble through water, or are tanks half filled with water and fitted with a central shaft carrying a large number of metal discs which by the rotation of the shaft are continually rising from the water, presenting newly wetted surfaces to the gas, fig. 18. The rotation of the shaft is effected by a steam-engine.

When scrubbers are employed it is usual to have two or more in series, the first being fed with the natural gas liquor whilst the last in the series is kept supplied with clean water. The success of these appliances depends upon the efficiency of the apparatus used for the distribution of water or gas liquor and the degree of freedom from contamination by tar they enjoy. Scrubbers charged with coke are especially liable to become clogged with tar, and their performance then is unsatisfactory. A freshly charged coke scrubber will perhaps be able to produce gas liquor of 10° to 12° Twaddell, but when the coke is clogged with tar, all other conditions being the same, would only yield liquor at 4°Tw. The water washes 'rat-holes' through the coke, and instead of coming down uniformly runs in one or two main channels whilst the gas is passing up through other parts of the scrubber, insufficiently brought into contact with the descending water.

With coke scrubbers alone a gross cubical capacity of about 15,000 cubic feet per million cubic feet of gas washed per diem is required, and then it is difficult, if the gas must be so free from ammonia as not to contain more than two grains per 100 cubic feet, to produce liquor much stronger than 4°Tw.

Washing with gas liquor alone will not of course secure the removal of all the ammonia, and that is why clean water must be employed. The natural gas liquor running from the hydraulic main and condenser is perhaps 3°Tw. and capable of absorbing much more ammonia. The best way of purifying the gas from ammonia is to treat the gas in scrubbers with copious washings of the gas liquor, and then, having removed all but a very small quantity of ammonia, to wash it with clean water with some form of rotary washer. Whilst under ordinary circumstances it is comparatively easy to remove the great bulk of the ammonia from the gas, it is only by well-arranged apparatus that the last traces can be abstracted. If the gas is to be free from ammonia, the last water it leaves contact with must be ammonia free.

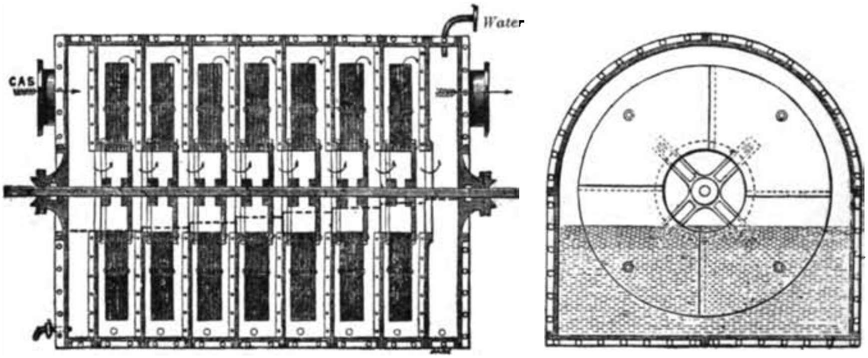


FIG. 18.

Crude coal gas has a strongly alkaline reaction, which does not disappear till about only 2 grains per 100 cubic feet of ammonia are present, and then the reaction of the gas becomes neutral or even acid. An acid reaction to delicate litmus paper does not indicate entire absence of ammonia, for 1 grain may still be present, but masked by the acid reaction of the carbonic acid. The strength of the gas liquor or its degree of concentration is limited by the temperature of the scrubbers and washers, and it often happens in very warm summer weather that the strength cannot be made to extend beyond 6·5°Tw. or about 13 oz. strength, whilst with the same plant and a much larger volume of gas to be treated, it could easily be made much stronger in colder weather.[1]

THE COMPOSITION OF GAS LIQUOR.

The principal constituents of gas liquor are ammonia combined with carbonic acid and sulphuretted hydrogen, technically known as 'free' ammonia, and ammonia called 'fixed,' combined with chlorine, sulphocyanogen, and thiosulphuric acid, and traces of other sulphur acids and cyanogen compounds, together with some tarry matters (phenols &c.).

The following is an analysis of Leeds gas liquor by Dyson:

	Grams per litre
Ammonium sulphide . . .	3·03
„ monocarbonate	39·16
„ chloride . .	14·23
„ thiocyanate . .	1·80
„ sulphate . . .	0·19
„ thiosulphate . .	2·80
„ ferrocyanide . .	0·41

The volume of gas liquor made in a gasworks is obviously the natural liquor made by the coal, *plus* the clean water employed to wash the gas clean. As the carriage and disposal of large quantities of gas liquor is sometimes a considerable item of expenditure, it is most important that the bulk of added water for washing the gas free from ammonia should be strictly limited. It will of course be evident that the maximum strength of the gas liquor consistent with clean gas is determined by the total amount of ammonia

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[1] The operation of washing removes about two or three grains of sulphur as carbon bisulphide per 100 cubic feet from the crude gas, and affects the luminosity of the gas to a very trifling extent.

and natural liquor yielded by the coal and the quantity of clean water introduced into the process. In the London districts the coals generally employed yield but a small amount of natural liquor less than is the case with the coals employed in the midland counties. However, weak liquor is the rule in London because of the large quantities of clean water introduced into the process.

The strength of liquor is often expressed in terms of gravity by Twaddell's hydrometer. This is the usual method in the midland counties; 5° to 6°Tw. or 1025 to 1030 sp.gr. may be taken as the average strength. In the south the strength is expressed in terms of ounces of sulphuric acid, neutralised by a gallon of the gas liquor. In other cases the ammonia is expressed as a percentage.

As before explained, the ammonia of gas liquor is partly combined with feeble acids and is then capable of being expelled from solution by simple boiling, and is therefore called 'free' ammonia. The remainder, being combined with stronger acids, requires to be replaced by a stronger alkali before it can be expelled from the solution by boiling, and is therefore called 'fixed' ammonia.

The gravity is a rough guide to the strength of gas liquor in ammonia, but the glass hydrometers employed under the dissolving action of the strong gas liquor soon get light, and giving false results lead to disputes. The following table of natural liquors from various coals will give the relation between gravity and percentage of total ammonia.

The 'factor' in the table is that number which, multiplied into the degrees by Twaddell's hydrometer of the liquor in question, will give the percentage of ammonia as found by analysis. Thus in the case of the first coal on the list the natural liquor showed 4°Tw.; this number multiplied by ·56 (the factor) gives the strength of ammonia in percentage: 4 × ·56 = 2·24 p.c.

Description of coal	Ammonia			Degrees Twaddell	Factor
	Fixed per cent.	Free per cent.	Total per cent.		
Silkstone 1 . . .	1·891	0·354	2·245	4·0	·56
,, 2 . . .	2·211	0·276	2·487	4·5	·55
,, 3 . . .	2·254	0·392	2·646	4·9	·54
,, 4 . . .	2·277	0·469	2·746	5·14	·53
,, 5 . . .	2·071	0·696	2·767	5·03	·55
,, 6 . . .	2·240	0·482	2·722	5·77	·53
,, 7 . . .	2·405	0·482	3·110	5·74	·54
Parkgate. . . .	2·404	0·705	3·245	6·16	·53
Cannel 1. . . .	1·415	0·841	1·872	3·88	·48
,, 2. . . .	1·598	0·457	2·196	4·70	·47

The relation between the gravity and actual strength in ammonia is, however, not the same in the case of the liquors which are the result of washing with the addition of clean water, the factor then required to bring the degrees Twaddell into percentage of ammonia being about ·42, but varying, of course, with the circumstances of production.

The original sulphuric acid test which is expressed in 'ounces,' and still very largely employed, only gives the free ammonia, and then too only in terms of ounces by weight of pure sulphuric acid by weight the free ammonia present per gallon of gas liquor is capable of neutralising. Thus each 1 oz. strength is equal to 0·34694 oz. or 0·02168 lb. of ammonia per gallon. As it is very convenient, since gas liquor is measured and not weighed, to consider the gallon as equal in weight to a gallon of pure water, viz. 10 lbs., and then the actual amount of ammonia in weight can readily be obtained by multiplying the strength in ounces by the factor 0·2168, which gives the percentage in weight.

Thus '10 ounce' liquor contains 2·168 p.c. by weight of ammonia.

The old sulphuric acid test only gave the 'free' ammonia and not the 'fixed,' and as soon as attention became drawn to this fact the whole of the ammonia, before being determined, was distilled out of the gas liquor with the help of a stronger alkali, and then a distinction was set up between 'ounces saturation test' and 'ounces distillation test.'

The special standard solution of sulphuric acid employed is so arranged as to contain 16 ounces of concentrated sulphuric acid, or H_2SO_4, per gallon, which solution has a sp.gr. at 60°F. compared with water of same temperature of 1064·3.

The liquor is then tested with the following apparatus (fig. 19).

A Binks' alkalimeter holding rather more than 2 fluid ounces, graduated downwards from 0 to 16 principal divisions, each of which is further divided into tenths. These 16 divisions measure 2 fluid ounces.

A white porcelain dish.

A glass rod.

And some pink litmus papers.

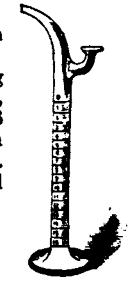


Fig. 19.

Two fluid ounces of the gas liquor to be tested are measured out and poured into the clean porcelain dish. The Binks' alkalimeter is charged with the sulphuric acid solution before described, and known as '10 p.c. acid' up to the zero mark, and from this alkalimeter the standard solution is delivered out in the dish until the contents are neutralised. This point is ascertained by stirring with the glass rod and applying it to the pink litmus paper, which is cut up into small slips.

The quantity of acid solution required is read off in ounces and tenths, each big division being numbered, and equal to an ounce of strength. As thus applied the test is only one of saturation, and ignores the fixed ammonia which may amount to several ounces. In the distillation test the liquor is distilled with caustic potash into a measured quantity in excess of the '10 p.c. acid,' and the excess of acid determined by an alkaline solution of equivalent strength delivered out of a burette. The test is then 'distillation.' Most of the results or statements of strength are in 'saturation' and not 'distillation' test.

The amounts of carbonic acid and sulphuretted hydrogen, and the proportions of these relative to each other, vary principally with the strength, but partly with the circumstances of the production of the liquor. In a general way, every 100 equivalents of ammonia (17) are combined with 65 equivalents of carbonic acid and sulphuretted hydrogen (44 and 34 respectively); of these 65 equivalents of the acids, 13 equivalents, or about 20 p.c., are sulphuretted hydrogen.

Strong liquors contain less sulphuretted hydrogen in proportion to the ammonia than the weak ones.

The gas liquor produced is almost always employed in the manufacture of sulphate of ammonia by a process of great simplicity.

The free ammonia is first expelled by means of steam, and when this operation is effected the liquor is treated with lime and further steam to expel the fixed ammonia. The steam. ammonia and other gases, are passed through strong sulphuric acid in lead tanks, and the crystals of sulphate of ammonia then forming are 'fished' out from time to time by means of perforated copper ladles. The process is a continuous one—a stream of gas-liquor passing through the apparatus in one direction, whilst steam passes in the contrary direction.

The total quantity of sulphate of ammonia produced in the United Kingdom in 1886 was about 100,000 tons, of which 70,000 tons were exported (*v.* AMMONIA).

When the gas has been washed free from alkalinity, it contains, besides a slight trace of ammonia, carbonic acid, sulphuretted hydrogen, carbon bisulphide, and some 7 or 8 grains of sulphur in unknown forms of combination per 100 cubic feet. For the removal of the carbonic acid, sulphuretted hydrogen, and carbon bisulphide lime alone can be employed, but since the sulphuretted hydrogen is more economically dealt with by means of ferric hydrate purifying materials, it happens that Irish bog ore and some forms of precipitated oxide are commonly employed in gas purification. This form of iron is quite inactive as regards the sulphur compounds other than the sulphuretted hydrogen, such as the carbon bisulphide.

The reaction between the sulphuretted hydrogen and the hydrated ferric oxide takes place according to the two following equations:

1. $Fe_2O_3,H_2O + 3H_2S = Fe_2S_3 + 4H_2O$;
2. $Fe_2O_3,H_2O + 3H_2S = 2FeS + S + 4H_2O$.

The first is the predominating reaction. The iron sulphides formed are easily oxidised on exposure to the atmosphere, and this property is made use of in gasworks to reproduce from them hydrated oxide of iron for the further removal of sulphuretted hydrogen from the impure coal gas.

In oxidation the sulphides deposit all their sulphur in the free state, so that finally the sulphur in the sulphuretted hydrogen appears as free sulphur in the 'oxide.'

Thus (1) $FeS + O = FeO + S$;
and (2) $Fe_2S_3 + O_3 = Fe_2O_3 + S_3$;

the FeO rapidly passes into Fe_2O_3 by further oxidation.

The process of oxidation is called 'revivification,' and is effected by spreading the 'fouled' oxide or sulphide of iron on a floor, when the mass becomes warm and changed from black to a reddish-brown colour. Sometimes the oxidation takes place so rapidly that the 'oxide' takes fire, and in some rare cases the 'fouled' material is so intensely pyrophoric as to fire in the purifiers immediately the lid is lifted and air admitted.

Lime, when slaked and in a moist condition, rapidly absorbs carbonic acid, thus:

$$CaH_2O_2 + CO_2 = CaCO_3 \text{ and } H_2O,$$

and sulphuretted hydrogen thus: $CaH_2O_2 + 2H_2S = CaH_2S_2 + 2H_2O$, and

$$CaH_2O_2 + H_2S = CaHS,HO + H_2O.$$

The calcium hydrosulphide, which is very soluble, has a valuable property of absorbing carbon bisulphide, with liberation of sulphuretted hydrogen, and forms calcium sulphocarbonate, thus: $CaH_2S_2 + CS_2 = CaCS_3 + H_2S$.

This sulphocarbonate is rather a feeble compound, being readily destroyed by carbonic acid and the action of atmospheric oxygen.

The methods employed at different works for the purification of the gas are various.

In many only sulphuretted hydrogen is taken out by means of the oxide of iron process, the carbonic acid and carbon bisulphide being left in the gas.

In some works the sulphuretted hydrogen is first completely removed by oxide of iron, and then the carbonic acid by means of lime. This process leaves the carbon bisulphide untouched. In cases where the removal of a great proportion of the carbon bisulphide—as in the case of the London gas companies—is compulsory, to enable the gas to comply with special regulations limiting the amount of sulphur in forms other than sulphuretted hydrogen, a certain amount of the compound CaH_2S_2, or other calcium sulphides capable of combining with carbon bisulphide, must be present in the purifiers, and this can be arranged for either by reserving special purifying vessels containing calcium sulphides protected from the action of carbonic acid, or by first passing the crude gas into lime and removing by this material the greater portion of the sulphuretted hydrogen.

This latter system practically amounts to purification by lime alone, and then the process of the removal of the impurities may be thus traced. The fresh lime absorbs sulphuretted hydrogen and carbonic acid; but this latter impurity attacks the calcium sulphides as well as the free lime, so that the sulphuretted hydrogen is always pushed on in front of the carbonic acid. The calcium sulphides absorb some of the carbon bisulphide.

In a series of four vessels the sulphuretted hydrogen will reach the outlet of the fourth or last vessel in the series quite as soon as the carbonic acid makes itself evident in the gas leaving the first, so that there will be three vessels filled with calcium sulphides and some sulphocarbonate unattacked by carbonic acid. If only four vessels are used, then, before the sulphuretted hydrogen appears on the outlet of the fourth vessel, it will have to be made third in the series by placing one containing clean lime in the fourth position. This is done by emptying the first vessel, which has not commenced to pass carbonic acid, and charging it with clean lime and placing it fourth in the series. The original second vessel is now first, and becomes the recipient of the carbonic acid, which partially drives out from it the sulphuretted hydrogen and carbon bisulphide previously absorbed. The other vessels have now, in addition to the sulphuretted hydrogen present in the gas, an additional quantity of sulphuretted hydrogen to remove, and therefore the last vessel would be on the point of passing sulphuretted hydrogen considerably before the first is likely to pass carbonic acid, and then the emptying and charging of the first vessel must be effected, so that in this case the first vessel is thrown out of action considerably before it is charged with carbonic acid, and whilst containing considerable quantities of the sulphur impurities. This process, though simple, is not economical, nor is it very efficient and certain in its action as regards the carbon bisulphide.

The extent to which the carbonic acid can act upon the lime sulphur compounds is limited, and it is impossible therefore to completely destroy these by even prolonged treatment with carbonic acid. In dilute solutions carbonate of lime is attacked by sulphuretted hydrogen. Thus there is a reverse reaction:

$$CaCO_3 + 2H_2S = CaH_2S_2 + CO_2 + H_2O,$$

limiting the main reaction:

$$CaH_2S_2 + CO_2 \text{ and } H_2O = CaCO_3 + H_2S.$$

This reverse action is not of a very great practical importance, but helps to explain why the prolonged action of carbonic acid does not completely drive out the sulphur from the fouled lime.

In the case of a system of purification dependent upon the removal of carbonic acid by lime, and then the after-removal of the sulphuretted hydrogen by means of oxide of iron, it will happen that, in practice, though the lime be as fully saturated with carbonic acid as is possible, 8 to 10 grains of sulphur—as carbon bisulphide—are removed from the gas.

In addition to the impurities mentioned, there is present in the gas some cyanogen equal to about 35 grains of nitrogen per 100 cubic feet, and is partly found as sulphocyanogen in the gas liquor and foul lime, and also in the spent oxide of iron material as ferrocyanogen.

For removing the bulk of the sulphuretted hydrogen certain materials containing some hydrated form of ferric oxide are employed, and, preferably, Irish bog ore, which contains—

Moisture lost at 212°, up to 50 p.c.
Fe_2O_3,H_2O . . . . 32 „
Vegetable fibre, &c. . . 18 „

but of the 32 p.c. of Fe_2O_3,H_2O only a quantity (about two-thirds) is in a form active with sulphuretted hydrogen.

This oxide is not very sensitive to the action of sulphuretted hydrogen when wet; in fact, one of the greatest mistakes that can be made with this material is to work it in too wet a condition. At 25 p.c. of moisture it works well, but if too dry it gets dusty and very finely divided, and runs through the grids in which it is placed in the purifiers, and further resists the passage of the gas to a serious extent. The rule with regard to moisture must be that it is just damp enough not to run through the grids or to cause the purifiers to offer too much resistance to the passage of the gas.

After the saturation of the oxide purifying material with sulphuretted hydrogen it turns quite black owing to the formation of iron sulphides and then it is exposed to the air for a few days when it recovers its original colour by the oxidation of the sulphides.

This material can be economically sulphided and oxidised about 16 times, thus gradually accumulating free sulphur until it contains about 55 p.c. of free sulphur, when it is sold to makers of sulphuric acid.

If the gas admitted to the purifiers filled with 'oxide' contains ammonia and cyanogen, there is in course of time an inconvenient formation of ferric ferrocyanide, and the active iron being thus locked up the material becomes spent at perhaps 35 p.c. of free sulphur. As these cyanogen compounds increase in quantity the material becomes bluer in colour. Oxide of iron used for the purification of gas that has already been passed through lime for carbonic acid purification does not nearly so soon become charged with these cyanogen compounds and can be economically employed for purification till 60 p.c. of free sulphur is present.

In the two following cases the same Irish oxide was employed. In the case A the gas had previously been treated with slaked lime and was free from ammonia and cyanogen. In the other case, B, the gas was unwashed and thus contained large quantities of ammonia and cyanogen. These cases serve to show the influence of two extremes on the percentage of sulphur present after sundry revivifications.

Number of times 'fouled' and revivified	Series A Percentage of free Sulphur	Series B Percentage of free Sulphur
2	15·8	15·1
3	—	24·3
4	24·6	28·8
5	—	31·7
6	31·2	—
7	—	31·8
8	35·4	—
10	39·5	32·0
12	42·4	32·1
14	45·6	—

The oxide in Series B was practically spent in the 5th revivification, when containing only 32 p.c. of sulphur. Oxide of iron in this condition can be partly rendered active by treatment with lime which liberates a great part of the locked up iron oxide. Spent oxide often contains large quantities of ammonium salts and tarry matter. These are very objectionable constituents, and interfere with its use in the manufacture of sulphuric acid. To successfully and economically use oxide of iron for gas purifications the following rules should be observed:

1. It should contain not more moisture than 20 p.c. nor less than 10 p.c.
2. It should be only used to purify gas already free from ammonia and cyanogen.

On the Continent spent oxide is valued for the Prussian blue it contains, though in this country it is only prized for its free sulphur.

With a combined system, using both oxide and lime and a proper arrangement of purifiers, the whole of the carbonic acid, sulphuretted hydrogen, and carbon bisulphide can be easily and economically removed.

To effect this an arrangement of eight purifying vessels is essential, arranged to work in four couples.

The first couple for removing the carbonic acid by means of moist slaked lime.

The second couple for removing the *bulk* of the sulphuretted hydrogen by means of oxide of iron purifying material.

The third couple for removing the *bulk* of the carbon bisulphide with calcium hydrosulphide, and the fourth couple for completely removing the last traces of sulphuretted hydrogen by means of moist slaked lime.

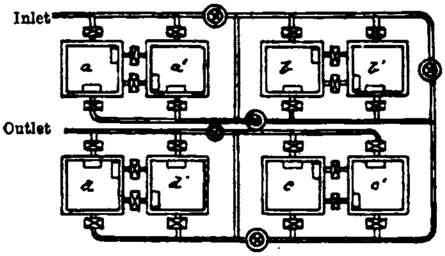


Fig. 20.

Fig. 20 gives the arrangement of eight purifiers for this system of gas purification.

Each pair of vessels is connected in such a manner that the purifiers can be worked in five different ways. Let *a* and *a′* be two vessels of a pair, then the following are the possible arrangements.

1. Gas first through *a* and then through *a′*.
2. „ „ „ *a′* „ „ „ *a*.
3. „ „ „ *a* alone, *a′* being shut off.
4. „ „ „ *a′* „ *a* „ „ „
5. „ partly through *a* partly through *a′*.

The diagram fig. 20 shows the pair of oxide purifiers for removal of sulphuretted hydrogen in the second position, but it is possible to place the oxide of iron also in the first or third pair without affecting the efficiency of the method. When the oxide is in the first pair it sooner becomes charged with Prussian blue, but the lime in the carbonic acid purifiers being free from contact with sulphuretted hydrogen is discharged in a less offensive condition.

The size of the purifying vessels relatively to the quantity of gas to be purified is largely dependent upon the amount of impurity in the raw gas, and therefore will vary with the locality, since upon the position of the gasworks depends the class of coal employed. Gas made from Newcastle is not largely charged with carbonic acid and sulphuretted hydrogen, about 12 grains of the former or 0·765 p.c. by weight of the coal, and 10 grains of sulphuretted hydrogen per cubic foot, equal to 0·6 p.c. of sulphur by weight of the coal. Some of the Derbyshire Silkstone coals give as much as 18 grains of carbonic acid and 15 grains of sulphuretted hydrogen per cubic foot.

The cannels yield more carbonic acid than the common gas coals.

Another point of importance in the consideration of the necessary size to give to the purifiers is the period it is desired that the purifying material shall remain in action before being saturated and therefore requiring removal. In the case of very large purifiers, 30 to 40 feet square, which take up the best part of a day for the discharging of the spent material and recharging with fresh, it is not economical to make the changes too frequently, since the exigencies of gas purification render it necessary that no trace of the impurity should pass the purifier; and it is evident that the clean purifier must always be in action ready to receive the first traces of impurity leaving the vessel that was last and is now last but one of the series, and the clean vessel has therefore to be ready in action in anticipation.

If the first vessel, say in a series of two, is likely to pass impure gas in 48 hours after being put to action there will be a period of less than 48 hours for the preparation of a second vessel with clean material; and, as it is not convenient to do this but in daylight, the second clean vessel will have to be prepared the day after the first vessel is put into action. The first vessel will then immediately have to be cleaned in order to be placed second. Since purifying vessels, even when most carefully charged, commence passing impurity some considerable time before being saturated, it is most uneconomical to shut them off for cleaning directly they pass impure gas. If the size of a purifier be such that it can normally purify seven days' make of gas, it can easily be left in action twelve days, and thus become saturated and fully spent.

Another important consideration is the pressure required to force the gas through them, and since all works have a limiting pressure determined by the depth of the numerous water seals in connection with the various apparatus, generally in large works about 30 inches, the two considerations determining the capacity of purifying vessels are (1) the time it is desirable they shall last before being recharged, and (2) the maximum resistance that can be permitted.

The following rules are given for a gasworks with a *maximum production* of 2½ millions of cubic feet per diem, made from Newcastle coal, or coal yielding an equivalent amount of impurity to be removed, and with a limiting seal of 30 inches. For other classes of coal the capacities and dimensions of the purifiers will have to be correspondingly altered. Four pairs of vessels, or eight vessels in all, each 30 feet square, with six tiers, each charged with 5 inches in depth of purifying material. Such vessels will hold about 83 cubic yards of material. The practice which obtains in some establishments of filling up the vessel with material on one tier only, in a thickness of two or three or more feet, is crude and wasteful.

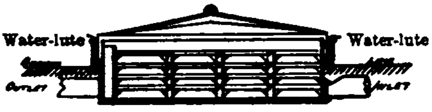


FIG. 21.

Fig. 21 is a section through a purifier provided with four tiers.

Carbonic acid. The first pair is charged with lime for removing the whole of the carbonic acid, and the gas must always be free from this impurity at the completion of this stage of purification. The purifiers having a capacity of about 83 cubic yards of lime per million cubic feet of gas to be purified per diem, it has to be considered how often they must be cleaned. In practice about 5·7 cubic yards of slaked lime per million cubic feet of gas purified is required for carbonic acid purification. This will give a period of about six days between the cleaning of each vessel, but the clean vessel of the pair should be in action about two days before the passing of carbonic acid by the first vessel of the pair to provide for contingencies, and the first or foul vessel should not be put out of action for cleaning until about four days after it has *commenced* to pass carbonic acid. The greatest care must be taken that all valves are in first-rate working order and competent to completely prevent the passage of the gas when they are shut. The efficiency of lime in this process is about 70 p.c. of the theoretical power, supposing all calcium hydrate present to be saturated with carbonic acid only. One yard of raw lime made from chalk weighs 10 cwt., and, in the operation of slaking, slightly more than doubles its volume.

The 5·7 cubic yards of slaked lime required to purify 1,000,000 cubic feet of gas from carbonic acid is about equal to 2·8 cubic yards of raw lime, or 3,136 lbs. in weight. Theoretically this quantity should be equal to the absorption of 2,462 lbs. of carbonic acid, but as the efficiency is only 70 p.c. it is in practice only equal to the removal of 1,714 lbs. of carbonic acid from the foul gas, since some of the lime in the interior of the nodules remains untouched, and other portions are left in combination with sulphur compounds.

100 parts of spent lime from these carbonic acid purifiers are thus disposed:

70 parts combined with carbonic acid.
15 „ „ „ sulphur compounds.
15 parts not acted upon, or original impurities in the lime, such as cinder from the fuel used in its preparation, or unburnt chalk.

If the purifiers are not properly managed the loss will be greater, and care must be bestowed upon the proper spreading of the material on the tiers, so that the gas may pass as evenly and regularly as possible through all parts of the vessel alike, for there is a great tendency for the gas to creep up the sides of the vessels, and the lime has to be pressed down so as to come well in contact with the sides of the purifiers or with the standards employed to support the iron bars on which the purifying grids rest.

When the carbonic acid is attacking the upper tiers a rise of temperature, sometimes considerable, takes place. This is due to the reaction between the carbonic acid and the lime sulphides. Thus,

$$CaH_2S_2 + CO_2 + H_2O = CaCO_3 + 2H_2S,$$

which is an exothermic reaction. The gas, therefore, carries off from these vessels a large quantity of water vapour, which condenses out again in the succeeding purifying vessels.

In addition to the removal of the whole of the carbonic acid, these purifiers also take out from the gas about 8 to 10 grains of sulphur per 100 cubic feet in the condition of carbon bisulphide and some sulphuretted hydrogen and cyanogen, which latter is always found in the spent lime as calcium sulphocyanide.

Sulphuretted hydrogen. The next pair of vessels serves to take out the bulk of the sulphuretted hydrogen by means of some active form of hydrated oxide of iron. For this the natural Irish bog ore is much used.

The quantity of Irish oxide fouled per 1,000,000 cubic feet of gas varies, of course, with its condition, but averages from 4 to 6 cubic yards. On an average, 6 yards will have to be put in action per 1,000,000 cubic feet of gas to be purified.

The pair of oxide vessels is manipulated in the same manner as the carbonic acid pair. Under the circumstances previously mentioned the foul oxide on being turned out of the purifier will be found quite black. It is spread out on concrete floors to the depth of about 10 inches, and turned over with a shovel once a day for two or three days when it is reoxidised and ready for work again. If, instead of spreading the foul oxide on concrete floors, it be placed on a floor made up of purifying grids raised 18 inches off the ground, and through which air can circulate, the revivification is more rapid, and one turning over with shovels will be sufficient. This oxide is only useful for removal of sulphuretted hydrogen, and is absolutely inert as regards carbon bisulphide. When the oxide, after about fourteen successive revivifications, contains from 45 to 60 p.c. of free sulphur, it is considered to be spent, and is replaced by new material. The many attempts made to produce continuous revivification of the foul oxide *in situ* and whilst in action, by the introduction and admixture with the gas of a small percentage of air, have not been successful. The practice of admitting a small percentage of air to the gas is to be deprecated, as it leads to many abuses.

Carbon bisulphide. This impurity is removed by means of lime that has been saturated with sulphuretted hydrogen. The active sulphide is probably the soluble hydrosulphide CaH_2S_2, which saturates the mass when moist slaked lime is treated with sulphuretted hydrogen. If the mass is dry or becomes crystalline it is no longer efficient. There is a considerable quantity of water liberated by the reaction between the lime and sulphuretted hydrogen, thus:

$CaH_2O_2 + 2H_2S = CaH_2S_2 + 2H_2O$; this water, with the excess of water employed in the slaking and preparation of the lime, causes large quantities of the soluble CaH_2S_2 compound to be continually percolating through the mass of sulphides. The calcium sulphocarbonate formed is easily dissociated by carbonic acid. It sometimes happens that the CaH_2S_2 crystallises and the mass of sulphides becomes very dry. On exposure to the air the heating that takes place by the oxidation of some portion of the sulphides destroys the crystalline character, and the water liberated, with the addition of some water sprinkled over the mass, enables it to become very active again as regards carbon bisulphide. Material that is working badly can generally be brought back into a highly efficient condition by being exposed for a short time until deliquescence sets in, and then being beaten up with a shovel and sprinkled with water.

The third pair of purifiers is retained for this process of carbon bisulphide removal. These vessels will last, if kept in good working order, for a very long period without attention, and will remove most of the carbon bisulphide from the gas. Gas purified by this system commonly contains as little as 7 to 10 grains of sulphur per 100 cubic feet in forms other than sulphuretted hydrogen, of which 5 to 8 grains are in forms other than carbon bisulphide, and not amenable to any known process. The fouled material from these vessels is very offensive when exposed to the air, the oxidation that then takes place resulting in a great rise of temperature, with the expulsion of large quantities of sulphuretted hydrogen and carbon bisulphide. In extreme cases the oxidation is so rapid that the mass fires. It is unfortunate that no other process for removal of carbon bisulphide is yet available, but the whole of the nuisance attending the emptying of these 'sulphur' vessels and the disposal of the offensive spent material can be obviated by a process of ventilation in which air is driven through the spent lime and purified by oxide of iron and other means before being discharged into the atmosphere. Submitted to such a process the contents of these sulphur vessels become quite inodorous and inoffensive. When one of these vessels is charged with fresh lime, the second pair of vessels containing the oxide of iron is 'slipped,' or allowed to pass gas containing sulphuretted hydrogen until such time as the lime becomes saturated with sulphuretted hydrogen, and it is also customary, from time to time, to allow the oxide vessels to pass a little sulphuretted hydrogen to keep the 'sulphur' vessels or third pair saturated. In addition to this small quantity of sulphuretted hydrogen there is some liberated from the calcium sulphides by their reaction with the carbon bisulphide in the formation of sulphocarbonate—$CaH_2S_2 + CS_2 = CaCS_3 + H_2S$. The gas leaving this third pair of vessels is more or less contaminated with sulphuretted hydrogen, and it is the office of the fourth pair to effect the complete removal of this impurity from the coal gas. In London the test employed for detecting the presence of sulphuretted hydrogen in the finished gas is so severe that oxide of iron is not found sufficiently sensitive to produce gas of the requisite degree of purity. Lime has, therefore, to be used, but as the calcium hydrosulphide formed is not a very stable compound, and evolves sulphuretted hydrogen, especially in hot weather, the two last lime vessels, which are usually called 'check' purifiers, are not allowed to receive any notable quantity of sulphuretted hydrogen, and are cleaned and charged with clean lime when only very partially saturated with sulphuretted hydrogen. The lime emptied from them is not, however, wasted, but is placed in the first pair of vessels, or carbonic acid vessels.

The difficulties attending the complete and economical purification of gas are very great and require efficient control.

Out of London complete sulphur purification is not a common practice, and simple removal of sulphuretted hydrogen is often only aimed at, and the carbonic acid and carbon bisulphide are left in the gas. This practice is to be deprecated, as a large amount of the unpopularity of coal gas which exists in some quarters is due to the sulphur it contains. In places where lime only is employed for gas purification the sulphur can be reduced to about 18 grains per 100 cubic feet, but the use of all lime is not so economical, nor is it so efficient as the process described, which reduces the sulphur to about 8 to 10 grains per 100 cubic feet with a very moderate expenditure. The disposal of waste lime is generally a difficulty, and that containing much sulphur is always objectionable; there is therefore an advantage in not only reducing the amount produced, but by absorbing sulphuretted hydrogen in oxide of iron purifying materials avoiding the nuisance that would arise if it had been removed by lime.

A systematic process, wherein the removal of the various impurities is allocated to distinct purifying vessels is the only one that is really efficient and economical.

The pressure required to force the gas through the purifiers is in all works a consideration of some importance. Purifiers having the area and capacity mentioned will require on an average about 2 inches each—with maximum gas reproduction. Very often the material in the purifiers will offer considerable resistance. In a large works, with limiting seals of 30 inches of water pressure, the pressure will be about 26 inches to leave a safe margin thus originating.

Scrubbers and washers .	2 inches
Purifiers	16 "
Gas meter	1 "
Gasholder	7 "
	26 inches

This pressure is given to the gas by the gas exhauster before mentioned. The functions of a gas exhauster are, therefore, not only to draw the gas away from the retorts precisely as it is made, so as to avoid any accumulation of pressure in them, but also to force the gas through the apparatus into the gasholder, the weight of which is in most cases sufficient to force the gas through the mains and pipes of the distributing system.

The purification of the gas being completed, it is measured in large station meters, which are in principle identical with the consumer's wet meter, but without the compensating arrangement of these for maintaining the correct water level. These meters are of very great size in the large gasworks.

The correct measurement of the gas is a matter of great interest and value to the management, as any defect in the working of the retorts can be quickly detected. In order to make the comparison of the gas make per ton of coals it is necessary to know the average temperature and pressure under which the gas was measured, so that the observed bulk can be corrected to the standard temperature and pressure for gases, viz. 60°F. and 30″ Barometer.

The gas having been accurately measured is passed into the gasholders, where it is stored until required. It is requisite to provide for a storage of at least a day's maximum make of gas, to provide for the variations in the consumption of gas consequent upon weather and day of the week. Saturday, if a day of half holiday, and of course Sunday, are days of short consumption.

The gasholders, an illustration of which is shown in fig. 22, and also in section in fig. 23, are of very great size, and made to hold as much as 7,000,000 cubic feet of gas.

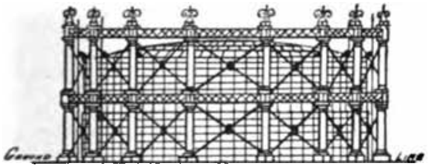


FIG. 22.

The water tanks in which the holder works are made of brick, concrete, or masonry, and sometimes of iron.

They are mostly telescopic, and have from 2 to 4 lifts, and are generally designed to give sufficient pressure to their gaseous contents to force the gas into the districts to be supplied. In some isolated cases of works far distant from points of consumption to which the gas is led by large trunk mains, pumps of similar construction to those used for exhausting the gas from the retorts are employed to obtain a higher initial pressure than is naturally afforded by the gasholder.

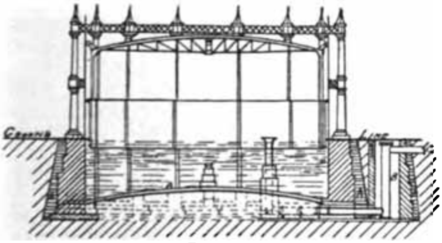


FIG. 23.

DISTRIBUTION OF GAS.

This is effected by cast-iron main pipes, which are laid under ground at a convenient depth dictated by circumstances, and of size varying from 48 inches to 2 inches in diameter, and from 12 feet to 9 feet in length, joined together by a spigot and socket joint made with hempen yarn and lead as shown in fig. 24. Occasionally the socket end of the pipe is accurately bored out with a slight taper, and the spigot end is turned to be an accurate fit to the socket. When this joint is painted with red lead and the spigot driven into the socket a tight joint is made. The advantages of this joint are doubtful. It is not flexible. The same objection applies to the ordinary form of lead joints, and where the ground in which the pipes are laid is uncertain and settles, the pipes are fractured. This difficulty is found to be very serious, both in mining districts, and in towns; where new roads are formed of made ground, the construction of sewers very often takes away the support from gas mains, and many accidents have resulted from the fracture of mains by heavy steam rollers. A flexible joint of caoutchouc has been lately employed with great success in some colliery districts adjacent to Nottingham, where settlements and consequent fractures of gas mains were very frequent. It is shown in fig. 25, and is of extreme simplicity. A slight groove is cast on the spigot end of the pipe, on which is placed a caoutchouc ring. The space between the spigot and socket is about one-eighth of an inch. When the spigot and its caoutchouc ring is forced into a socket, the ring rolls over as the pipe advances and flattens out very considerably, forming a tight but flexible joint.

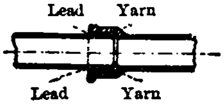


FIG. 24.

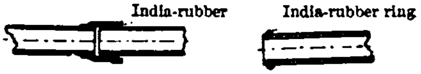


FIG. 25.

The advantage of this joint is that it allows the line of pipes to be compressed or extended or undulated without any strain being put upon the metal.

The amount of gas capable of being delivered by a particular main at a given loss of pressure is given in the following formula, from which tables have been constructed for most of the usual sizes of gas mains.

$$Q = 1{,}350\, d^2 \sqrt{\frac{pd}{sl}}$$

where Q = quantity of gas in cubic feet per hour
l = length of pipe in yards
d = diameter of pipe in inches
p = pressure in inches of water
s = sp.gr. of the gas;
atmospheric air being 1.

It will be seen by examining the above formula, that the discharge of gas will be doubled by the application of four times the pressure.

The pressure required to force the gas through the distributing mains varies of course with the quantity of gas being consumed, and this varies with time of day and season of year. To regulate the pressure governors are employed at the gasworks, and in large towns also at certain distributing stations in the district itself. Such a governor is shown in fig. 26, and is only automatic in so far as it serves to maintain a certain definite pressure in the gas main at the point where it is attached. It only partially changes the pressure to suit the varying requirements of the town, and its natural operations have to be supplemented by alterations in its adjustment by means of weights, which are placed on or removed from the small gasholder by an attendant according to the necessities of the time being. The action of the instrument can be shortly explained. The small gas holder by means of a rod actuates the throttle valve A placed in the gas main. The movement of the gasholder is controlled by the pressure of the gas in the main in the outlet side of the throttle valve, with which it is in communication by the pipe *c*. When the pressure at this point rises, the gasholder also rises, and partially shuts off the throttle valve until the original equilibrium is arrived at. Thus, if the bell or small gasholder is in equilibrium at say thirty-tenths of an inch of water pressure, any variation in the pressure of the gas in the main at the point where the pipe c enters will actuate the gasholder, which in its turn will either open or shut the throttle valve A, until the thirty-tenths pressure is again arrived at.

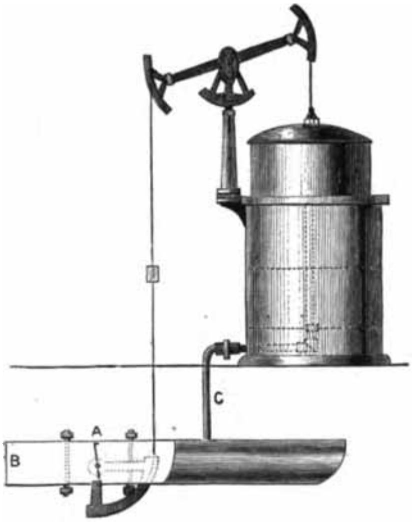


FIG. 26.

The object of the governor is therefore to maintain a constant pressure on the main to which it is connected. If any additional consumption of gas takes place in the town, the pressure on the outlet of the throttle valve will be reduced, and conversely when a reduction in the quantity of gas being used takes place it will be increased. The governor will by opening or shutting the throttle valve bring the pressure back to what it was before the alteration in the consumption of gas took place.

But since the pressure required at the works to maintain a certain pressure in the town varies with the consumption, and the governor only of itself serves to maintain a constant pressure depending upon the weight of the small gasholder, the necessary alterations of pressure at the works with increasing or diminishing consumption in the district are effected by an attendant who works upon a preconceived plan of what the requirements of the town are likely to be. The telegraph and telephone in some places are used to assist the attendant at the works by warning him of any excess or deficiency of gas pressure in the district.

The diagram, fig. 27, shows the pressure required at the gasworks end of the main to maintain the requisite pressure at a distant point of the district. The differences in the pressure at the hours of small or no gas consumption are due to difference in level of the observing stations, which in this case illustrates a gain in pressure as the works are at the lower level.

With any fall of temperature the moisture-saturated gas deposits water in the mains, which are so laid as to drain towards certain points where small reservoirs called 'syphons' are placed to collect the water. A pipe reaching from the level of the road passes down into the bottom of the syphon, and by periodically attaching a small portable hand-pump to this pipe the water collecting in the mains is removed.

The service pipes used to conduct the gas from the street mains into the houses of the consumers are of wrought iron, from $\frac{1}{2}''$ to $2''$ internal diameter. To prevent these pipes suffering from the corroding influences of the soil in which they are placed it is usual to bury them in asphalt or in wooden troughs filled with pitch. These pipes are connected to the gas meters and are fitted with a cock and key so that the gas can be shut off at will. The frequent stoppages of these pipes by crystalline deposits of naphthalene are often very largely due to their being placed at insufficient depth in the ground and consequently exposed to frosts and low temperature.

Gas meters.—There are two kinds of gas meters used. The one called the 'wet' is a most accurate instrument of measurement within certain ranges of water line determined by special devices, but suffers from the disadvantage of occasionally being frozen in very severe weather if placed in unprotected situations, and also requires a certain amount of attendance, as, though it is provided with a reservoir of water in connection with compensating apparatus to maintain a constant water line, the water evaporates and requires replenishing from time to time. These water meters are provided with a float which shuts off the gas supply when the water level is too low for correct registration. As far as concerns general accuracy of registration, it is hardly likely that a more perfect instrument will be invented, but it is not entirely popular with gas consumers on account of its ceasing to pass gas when the water line is low, and the registration is commencing to operate in disfavour of the gas undertaking.

A wet meter (shown in fig. 28) consists essentially of three parts. First a hollow drum or wheel, working partly in water, through which the gas passes, producing a rotation the registration of which on a dial indicates the quantity of gas

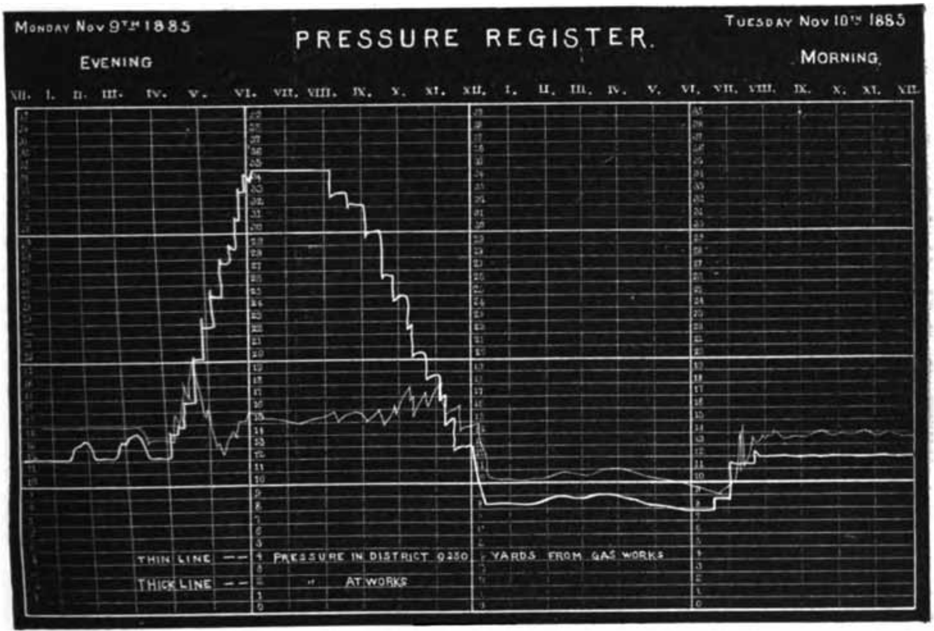


FIG. 27.

being consumed; secondly, a compensating arrangement for keeping the chamber in which the measuring wheel revolves at a constant level; and, thirdly, the index which shows the quantity of gas passed in cubic feet. The illustration shows compensating arrangement, which is a long spoon actuated by the rotation of the measuring wheel, and lifts water over from the reservoir into the measuring chamber.

The dry meter is liable to great errors of registration. Its action can be understood by reference to the illustration, fig. 29, which shows the internal parts of a dry meter, the outer tin case being removed. The case is horizontally divided into two parts by the partition F, on which are seen two valves V V which open and close ports communicating with the four chambers below; the four chambers below are formed by a vertical division and by the movable diaphragms C C.

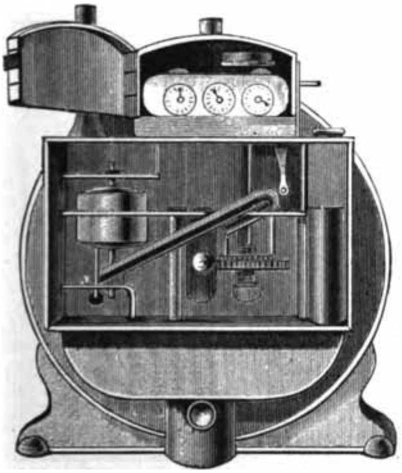


FIG. 28.

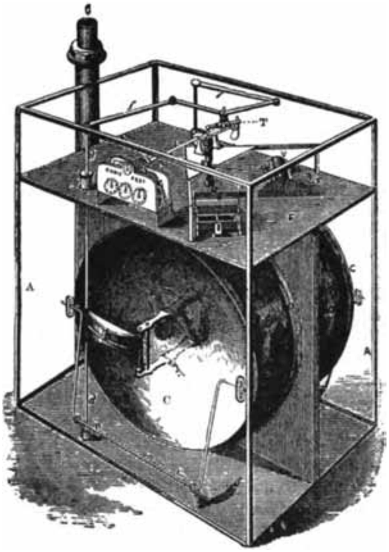


FIG. 29.

The movable chambers are made up of the fixed vertical division plate, the flexible leather band D, and the plate or movable diaphragm C. The movable diaphragm C is maintained in a vertical position by the arms *b* and the guides *c*. The reciprocating motion of the movable chambers works the levers *ff* by means of the spindle *d*, and these actuate the valves v v and the index.

Each of the valves has three ports, the centre one being the outlet and the others for the gas to the one or other side of the movable diaphragm.

On the Composition of Coal Gas.

Whilst purified coal gas contains probably a large number of compounds whose presence is not yet definitely recognised, it may be said broadly to consist of marsh gas and other members of the paraffin series of hydrocarbons, hydrogen, carbonic oxide, and hydrocarbons of other series than the paraffin, such as acetylene, crotonylene, ethylene, and the benzenoid hydrocarbons, benzene, toluene, xylene, traces of naphthalene &c., some nitrogen, and occasionally traces of oxygen which last is evidence of atmospheric contamination. Modern gas analysis recognises marsh gas, hydrogen, hydrocarbons other than paraffin absorbable by fuming sulphuric acid or bromine acid termed C_nH_m, hydrocarbons, carbonic oxide, carbonic acid, which should not be present in properly purified coal gas, nitrogen, some traces of sulphur compounds, and oxygen. The following analyses will serve to give a general idea of the composition of coal gas.

The constituents of coal gas may be divided into three groups:—

1. Luminiferous bodies which on combustion deposit free carbon in the flame and give a luminous effect. This group includes all the hydrocarbons.

2. Non-luminiferous gases which on combustion afford a considerable heat effect but give no light, such as hydrogen and carbonic oxide.

3. Diluents; nitrogen and carbonic acid, which diminish the luminous effect by dilution and cooling, and oxygen which acts by dilution.

The luminous effect was generally attributed to ethylene, a body certainly not an important constituent in value as a light-producing agent. Ordinary 16-candle coal gas deprived of all hydrocarbons capable of absorption by fuming sulphuric acid, termed C_nH_m hydrocarbons, has still a luminosity of about 6 to 8 candles of which very little can be due to marsh gas, since this gas has only when pure a luminosity of two candles. Nearly the whole of these 6 to 8 candles is due to paraffin hydrocarbons other than marsh gas which cannot be recognised by the ordinary eudiometric analysis. The remaining 10 to 8 candles are given by the 4 p.c. or less of the C_nH_m hydrocarbons. The numerous attempts made to arrive at the lighting power of coal gas indirectly by the determination of the amount of these C_nH_m hydrocarbons have always been unsuccessful. Some coals yield gas of 25-candle power containing 17 p.c. of these C_nH_m hydrocarbons, whilst many samples of 16 candle gas contain less than 4 p.c. The simple volume of these hydrocarbons is absolutely no measure of the luminosity of the gas. The carbon density of the C_nH_m hydrocarbons varies. For the sake of illustration it may be said that the average composition of the absorbable hydrocarbons contained in 16-candle coal gas made from Newcastle coal is about C_3H_3. Benzene and some toluene are certainly important constituents, and these benzenoid hydrocarbons probably amount to about 10 p.c. ordinary 16-candle coal gas.

The analyses published by Dr. Percy Frankland (S.C.I.) give carbon densities for the C_nH_m constituents of 16-candle coal gas from 2·45 to 3·39, a range more closely agreeing with the writer's experience than that found by Dr. Edward Frankland for London coal gas in 1851—viz. from 3·35 to 4·57, or by Mr. Humpidge in 1876 who found carbon densities ranging from 3·16 to 3·94. The older analyses show the highest carbon densities for the C_nH_m hydrocarbons, and it might be thought that the composition of these had altered in the course of years with differences in the process of manufacture, but it is more probable that the differences between the older and the newer analyses are due to analytical methods.

The great interest that has always been displayed towards these absorbable hydrocarbons arises from an erroneous belief that the whole luminosity of coal gas was produced by them, and it was not until recently known that paraffins higher in the series than marsh gas were present.

Davis, in his experiments in the extraction of liquid hydrocarbons from coal gas, isolated pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}), octane (C_8H_{18}), and nonane (C_9H_{20}).

The carbonic acid occurring in the gas of many towns is objectionable on account of the loss of illuminating power resulting from its presence. The following experiments made by the late Mr. Alexander Wright in 1853 show the extent and scope of the injury.

The gas employed in the experiments was of 26-candle power per 5 cubic feet per hour when consumed in a No. 2 union jet at the rate of 2½ cubic feet per hour, and it was found that the influence of 1 p.c. of carbonic acid contained in the gas, when compared with the same gas but free from carbonic acid burning at the same rates in the same burners, varied from about 7 p.c. with the Argand burner to 11 p.c. with a No. 1 union jet burner. It was also found that the Argand burner requires 3 p.c. and the No. 1 union jet 7 p.c. more of the gas containing 1 p.c. of carbonic acid to produce equal amounts of light to the gas free from carbonic acid.

The presence of carbonic acid in coal gas is the more to be condemned since it is evidence that the sulphur compounds other than the sulphuretted hydrogen remain in the gas. At the same time its absence is no evidence that these objectionable sulphur compounds have been removed.

The specific gravity of coal gas as compared with air varies with the composition of the gas. Generally the richer gases have a higher specific gravity than the poorer.

16-candle gas is about 0·36 to 0·38 sp.gr.
19 „ „ „ 0·42 to 0·43 „
20 „ „ „ 0·45 to 0·46 „
36 „ „ from Boghead Cannel 0·75

PHOTOMETRY.

The determination of illuminating power of coal gas is a matter of great moment, for the Gas Works Clauses Act of 1871 enacts that every undertaking shall provide a testing place, with apparatus for testing the illuminating power of the gas, and gives authority to the local authority of the district supplied to appoint a gas examiner to test the gas at the testing place. Whilst no doubt the control exerted by some local and other authorities over the quality of the gas supplied by some of the less important undertakings is of a nominal and perfunctory character, yet generally the question of the illuminating power of coal gas is treated as one of high importance, and in many places rigid and effective means are taken by constant testing of the gas to compel the supply of gas of the prescribed quality. The gas supplied by the London gas companies is tested at numerous points under the supervision of a body styled the 'Gas Referees,' who order the mode of testing within the limits of the Acts of Parliament relating to the Metropolitan Gas Companies.

The Acts prescribe that the gas shall be equal in intensity to the light produced by sixteen sperm candles of six to the pound, each burning 120 grains per hour; and the discretionary power of the 'Gas Referees,' as regards illuminating power, is more confined to details of operation and forms of apparatus. The printed instructions issued by them are generally regarded as a model.

The photometer employed is some approved form of the Bunsen photometer, and consists of a device whereby the light from the coal gas flame to be tested can be brought upon one side of a paper disc, whilst the light from the standard candles can be brought on the other side. This paper disc, which is greased, with the exception of a circular spot about 1½ inch in diameter, is placed in a box or holder, called the disc box, in such a manner that its plane is at right angles to the axis of the photometer, or to the line joining the two lights to be compared. The disc box slides along a graduated bar. The two lights are fixed at the ends of this bar, the length of which varies from 50 to 60 or 100 inches in different instruments, and the graduations on the scale of the bar are so arranged as to show at a glance, without calculation, the relation in the intensities of the two lights on the principle of the intensity of light being inversely as the square of the distance from the source of illumination. The coal gas is burned in a standard burner.

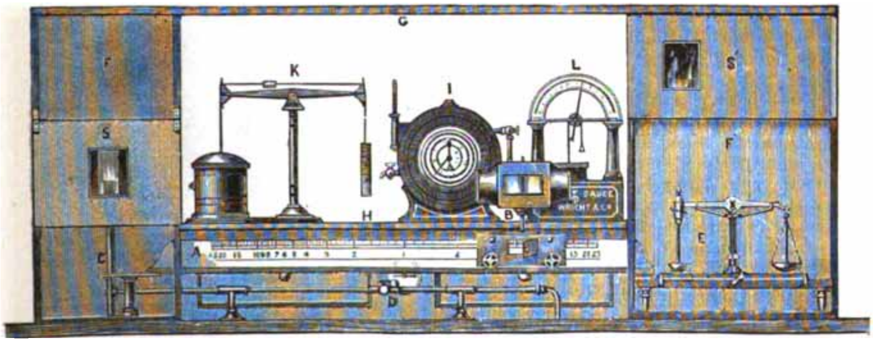


FIG. 30.

For testing ordinary coal gas the burner employed is known as 'Sugg's London Argand,' No. 1. It has twenty-four holes each of 0·045 inch in diameter, and is used with a glass chimney 1¾″ diameter and 6 inches height.

The standard burner for testing the so-called London cannel gas is a steatite batswing burner consisting of a cylindrical stem, the top of which is divided by a slit of uniform width. The width is 0·02 of an inch.

In Scotland, a union jet or fishtail burner is commonly employed for testing rich cannel gases.

The standard rate of gas consumption is 5 cubic feet per hour. It is not practicable to consume precisely 5 cubic feet per hour, but the consumption is adjusted as nearly as is convenient to that rate, and the results are afterwards corrected by proportion to the standard rate.

The apparatus required to measure the gas being consumed is an accurate wet meter of special construction fitted with a thermometer for showing the temperature of the gas. A gas governor is employed to maintain a constant rate during the experiment, and a micrometer cock to assist in the regulation of the quantity being burned.

As the sperm candles (six to the pound) used as a standard in this country do not burn a constant amount of sperm (120 grains per hour is the standard consumption of sperm), a delicate balance is employed for weighing the candles before and after the experiment, to ascertain the precise quantity used.

It is usual to employ two candles, though the scale is graduated on the basis of one candle. All the scale readings are to be doubled when two candles are employed.

As it is necessary that the only light falling on each side of the paper disc shall be light from the two lights to be compared, viz. the gas flame and the candle flame, each to its own side, the photometer is either placed in a dark room painted with a dead black, or it is surrounded by suitable screens properly blackened.

The photometer used in the London gas testing stations is slightly different to the one first described, and is called an 'Evans' photometer. In this the gas flame and disc are stationary whilst the candles are moved. The whole is inclosed in a long box lined with black velvet. This photometer is not so accurate as the other, and is too favourable to the gas. The movement of the candles and the hot, badly ventilated atmosphere in which they are caused to burn, is unfavourable to their action.

The object of the disc of partially greased paper is to discover the point of equal illumination between the two lights, which is done by moving it until the ungreased central spot is no longer distinguishable from the surrounding greased paper. The disc box carries a pointer indicating the relation between the two lights in the scale. It is usual to make ten observations during a period of ten minutes. These are then averaged and corrected for variations in the consumption of both candles and the gas flame. Fig. 30 is an illustration of a closed photometer not requiring a darkened room, but free from the defects of the Evans photometer.

In order to reduce the observed volume of gas to the standard condition a table is employed calculated from the formula

$$n = \frac{17{\cdot}64\,(h-a)}{460}$$

Where

h = height of barometer in inches.

t = temperature in Fahrenheit degrees.

a = tension of aqueous vapour.

n = the number which, used as a multiplier, reduces observed volume to standard conditions.

The amount of light yielded by the standard candle burning 120 grains per hour, or corrected to that consumption, is not invariable, and for a long time photometrists have been seeking for some invariable standard. In a report presented by a committee on photometric standards to the Board of Trade, in 1881, it was stated that candles from the same packet varied 11·6 p.c., and that candles examined from different packets showed variations as great as 22·7 p.c. Thus the illuminating power of a sample of coal gas was given by one candle as 17·8, and 14·5 by another, even though the method of examination was conducted by the same operator in the most careful manner. It must be admitted that such extreme differences are exceptional in the best practice, as a skilled operator would reject a candle that was burning improperly, say, owing to a knot or other defect in the wick. In practice it is considered always possible for two operators who are constantly engaged in testing gas with the same apparatus to agree within half a candle. Though an absolutely invariable standard will never be discovered, yet there is not only every hope of finding some source of light less subject to vagaries than the sperm candle, but it is possible that even now we are acquainted with several which are more perfect than the candle. The two most prominent competitors of the candle are the Methven Screen and the Harcourt Pentane lamp.

Fig. 31 shows the Methven Standard consisting of an Argand burner similar to that prescribed by the Board of Trade, in front of which is a brass screen provided with a rectangular slot of such size and position as to pass a light equal to two candles when the gas flame in the Argand burner is adjusted to a height of 3 inches. The assumption upon which this instrument is based, viz. the equality in the amount of light emitted, equal areas taken from a particular zone of flames from different gases consumed in an Argand burner at a constant flame length, is neither suggested by theory nor supported by practice. However, the Board of Trade report referred to states that when gas ranging in quality is used in the Methven Standard from 15½ candles to 19 candles, there is not a serious error in the result (0·7 of a candle), and that with ordinary coal gas ranging from 16 to 18 candles the result given may be taken as constant.

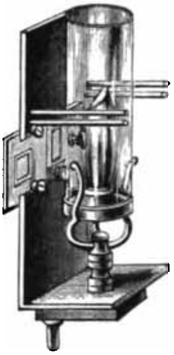


FIG. 31.

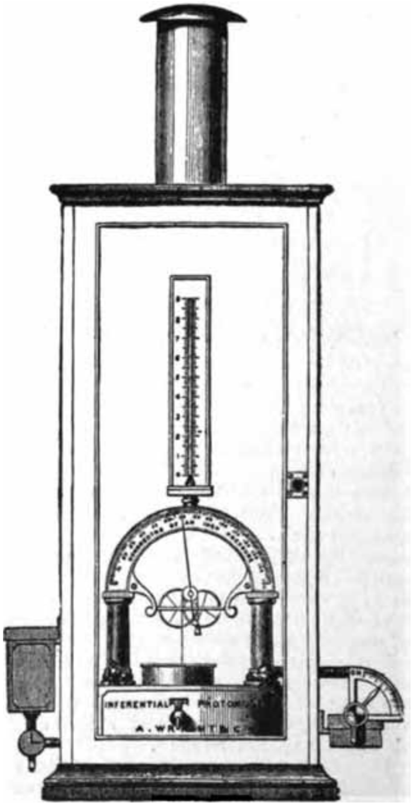


FIG. 32.

Harcourt's Pentane Standard has not been yet extensively employed in practice, owing to its want of simplicity. The principle upon which it is based is the uniformity of the light yielded by a definite mixture of pentane and air consumed in a brass burner consisting of a brass tube 1 inch in diameter and 4 inches long, furnished at the top with a soundly fitting brass plug half an inch in thickness, having a central hole exactly a quarter of an inch in diameter, so as to produce a flame 2½ inches high.

The standard pentane gas is prepared in a gas-holder by diffusing the vapour of 3 cubic inches of liquid pentane in one cubic foot of air.

This gas, burned under the conditions laid down by Mr. Harcourt, yields a light equal to 1 sperm candle.

A sensitive governor and meter are employed to maintain the uniformity of rate of combustion, which is half a cubic foot per hour to produce the standard flame length of 2½ inches.

Of the inferential photometers employed, the one most generally in use and to be found in almost every gasworks is the jet photometer, an instrument extremely simple both in construction and use. Fig. 32 is an illustration of one. The basis of its action is to find the pressure required to yield a flame 7″ in height, burning from a steatite jet with stand and orifice. This instrument is quite empirical. The amount of gas issuing through an orifice of constant diameter at constant pressure is dependent on its specific gravity. The flame length yielded by equal volumes of different gases varies mainly with the amount of oxygen required for their respective combustion. There is no precise connection between specific gravity and luminosity of different coal gases, or even between either of these qualities and that of flame length. Sometimes Lowe's jet photometer is provided in addition to the scales for measuring flame length and gas pressure with a scale of candles. This scale of candles is generally unreliable. The orifices in the steatite jets of these instruments gradually become less owing to the deposit of some carbon, and then more pressure is required to pass the quantity of gas requisite to produce the 7″ flame.

Whilst these jet photometers are unscientific instruments, yet in the hands of practical men they yield practical results, and warn the foremen and managers of the gasworks of change in the quality for better or worse of the gas.

It is unfortunate that these jets have not been employed with comparison of the flame lengths of different gases in the basis of equal volumes, which could be effected by burning the gas in a jet at a standard rate of consumption and measuring the flame length.

The relation between the flame length and luminosity as determined directly in the Letheby Bunsen photometer of a large number of different samples of gas produced on a large scale of practice, is given in the annexed table. Each result is not a single estimation, but the average of several hundred.

These tables show that every inch of flame given by a quantity of coal gas equal to 2½ cubic feet per hour burning in a jet (the precise diameter is not a matter of great moment in this system) represents about two candles illuminating power, as determined in the ordinary photometrical manner.

Various but unsuccessful attempts have been made to arrive at other indirect or inferential methods of photometry, such as specific gravity or percentage volume of hydrocarbons absorbable by sulphuric acid or bromine.

Class of coal	Candle power per 5-c. per hour in sperm candles tested in London Argand	Sperm candles per inch of flame length per 2½ cubic ft. per hour consumed in jet 1 mm. dia.
Nottinghamshire top hard cannel . .	24·61	2·109
" " . .	23·51	1·985
" " . .	22·97	1·839
" " . .	22·72	2·112
Nottinghamshire deep soft cannel .	22·57	2·080
Newcastle coal .	18·83	2·039
" " . .	18·33	2·023
" " . .	17·77	2·077
Derbyshire Silkstone	17·49	2·016
Yorkshire " .	17·04	1·950
" " .	16·94	1·894
" " .	16·55	1·998
" Parkgate .	16·31	1·960
" Barnsley .	16·04	1·992
" Bowling Black	15·76	1·921

Testing for sulphuretted hydrogen.—This is effected by exposing slips of bibulous paper soaked in a solution of sugar of lead to a current of 10 cubic feet of the gas. The test papers are prepared by moistening sheets of the paper with a solution of 1 part of sugar of lead in 8 or 9 parts of water, and exposing such sheets whilst damp to an atmosphere containing ammonia vapours. On drying the free ammonia escapes. Any discolouration of the paper is considered as evidence of the presence of sulphuretted hydrogen.

Testing for ammonia.—The gas tested for sulphuretted hydrogen is next passed through a small glass cylinder filled with glass beads holding 50 septems of a standard solution of sulphuric acid of such strength that 25 septems will exactly neutralise 1 grain of ammonia. By means of another test solution of ammonia containing 1 grain per 100 septems, the free sulphuric acid remaining after the passage of the 10 cubic feet of gas is estimated, and from the loss of acidity the amount of ammonia in the gas is calculated into grains per 100 cubic feet.

Testing for sulphur compounds other than sulphuretted hydrogen.—The gas after passing through the apparatus for testing the sulphuretted hydrogen and ammonia is now caused to pass through an experimental test meter fitted with a self-acting apparatus for shutting off the current of gas when 10 cubic feet of gas have passed. The gas passing through the meter is burned in a small Bunsen burner surrounded by lumps of sesquicarbonate of ammonia. The products of combustion charged with vapours of ammonia are led by means of a bent trumpet tube into a tall glass cylinder having a side tubulure at the lower part. The upper part of the cylinder is fitted up with glass marbles, and on the top of the cylinder is connected a long glass pipe falling into the cylinder. This pipe, called the eduction pipe, acts as a condenser, and the drops of water condensing within it fall back into the cylinder, and moistening the marbles causes these to act as a 'scrubber' to the ascending products of combustion. In the bottom of the cylinder a small hole is bored, and a small piece of glass tubing conveys the condensed liquid into a beaker.

The whole of the sulphur of the gas first forms sulphurous acid, and this, with the ammonia, yields ammonium sulphite, which rapidly oxidises to ammonium sulphate, in which condition the sulphur is found in the condensed liquor.

The sulphur present in the condensed liquor and the washings of the condenser and trumpet tube is estimated by precipitation of the sulphuric acid as barium sulphate in the usual manner and the amount calculated into grains per 100 cubic feet of gas.

If the atmosphere in which the small test flame is burning is impure the oxidation and arrest of the sulphur is incomplete.

The whole apparatus is shown in fig. 33.

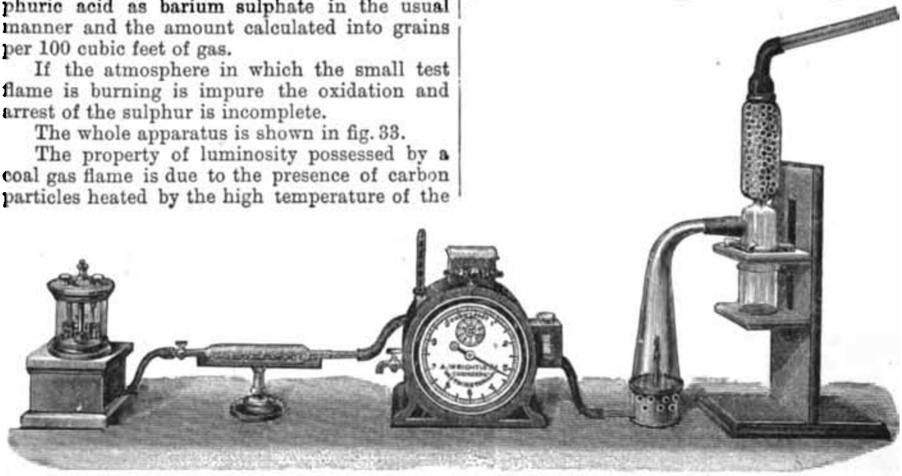


FIG. 33.

The property of luminosity possessed by a coal gas flame is due to the presence of carbon particles heated by the high temperature of the flame to incandescence. The carbon particles arise from the gradual combustion of the hydrocarbons present in the coal gas, which first part with their hydrogen when presented at a high temperature to insufficient air for their complete combustion. When the coal gas is previously mixed with sufficient air to provide for its complete or nearly complete combustion a non-luminous flame is produced, as in the Bunsen laboratory burner. The degree of temperature to which the free carbon precipitated in the flame by the fractional combustion of the hydrocarbon gases is raised is one of the most important factors in the production of light from hydrocarbon flames, and it may be said that the object to be attained is (1) the precipitation of the largest possible amount of free solid carbon in the flame, and (2) the raising of this free carbon to the highest possible state of incandescence. It may often happen that attempts to attain the first of these objects neutralise or militate against the attainment of the second, and that the best result may be attained by a *juste milieu*. If the air necessary to the proper combustion of the flame be introduced or approached to the flame too gradually, some of the precipitated carbon will be cooled below its point of ignition and leave the flame amongst the products of combustion unconsumed. With the ordinary flat flame so commonly employed for gas lighting, the thickness of the flame is the great factor in the utility of the burner. With too thin a flame produced by orifices too small in diameter in the case of fishtail or union jet burners or too narrow in slot in the case of batswing burners, the air will obtain too ready access to the interior of the flame, and the hydrocarbons will be consumed without the precipitation of sufficient carbon. On the other hand, with too thick a flame produced by orifices too great in diameter or slots of too great width, the precipitation of carbon will be too great and too prolonged for the circumstances of the flame, and a smoky flame will result.

The amount of hydrocarbon vapour varies with the quality of the gas. The richer gases containing the most hydrocarbon vapours will require thinner flames than the poorer gases to produce the best effect, and burners quite adapted to high power gases will be too severe with poor gases and produce thin weak flames from these. Thus the burners must be adapted to the quality of gas intended to be consumed in them.

The same remark applies, but not perhaps with equal force, to the flames of burners provided with chimneys for producing artificial air supply, such as the Argand burner.

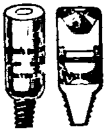


FIG. 34.

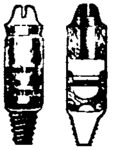


FIG. 35.

The best light effect from any burner appears to be produced at the smoking point, or point when the air supply is just beginning to be deficient. It is not convenient, however, to burn the gas too close to this limit, as a margin of safety is required to avoid occasional smoking.

The burner most commonly employed is the fishtail or union jet, fig. 34, having at its top two holes inclined at an angle towards each other. The gas issues out in two streams which coalesce into one flat flame at right angles to a plane passing through the two orifices. The diameter of these orifices varies in different burners so as to produce flames of thickness suited to the quality of the gas they are intended to consume.

The other class of flat flame burners is the batswing or slot burner, fig. 35, which has a dome-shaped top across it with a narrow slit cut down through the top. The slit varies in width to suit various qualities of gas. Great improvements have been made in the manufacture of these burners to produce flames of proper shape and regular thickness. The batswing burner requires less pressure than the fishtail or union jet, and consequently the gas issues with less directive energy and the flame is not so stiff as with the fishtail, and it therefore becomes necessary to protect it from draughts or movements of air by a globe, or there is danger of flaring or smoking.

The accompanying table gives the results yielded by some of the best-known flat flame burners corrected to 18-candle gas:—

Burners.

Date of test	Description	Illuminating power		Rate of gas			Candles per foot	
		London Argand	Candles	—	Corrected	Pressure in inches	—	Corrected to 18-c. gas
1884				ft.	ft.			
Dec.	Bray's No. 2 Fishtail . .		5·00	3·10	3·08	·65	1·62	1·62
		18·00	5·40	3·79	3·77	·89	1·43	1·43
			6·00	4·75	4·73	1·28	1·27	1·27
„	„ No. 3 „ . .		7·60	3·93	3·88	·69	1·96	1·92
		18·40	8·40	5·00	4·95	1·03	1·70	1·66
			8·40	5·49	5·44	1·24	1·54	1·51
„	„ No. 5 „ . .		10·00	3·90	3·82	·38	2·62	2·56
			12·40	5·00	4·90	·60	2·53	2·47
		18·40	13·20	6·10	5·97	·80	2·21	2·16
			15·40	7·71	7·55	1·18	2·04	2·00
„	„ No. 2 „ . .		6·80	3·16	3·10	·70	2·19	2·17
„	„ „ „ 'Special'	18·20	8·00	3·84	3·77	1·00	2·12	2·10
			9·00	4·46	4·41	1·30	2·04	2·02
„	„ No. 3 „ . .	18·00	8·20	3·12	3·10	·36	2·65	2·65
			9·40	3·73	3·71	·75	2·53	2·53
			12·40	5·05	5·03	1·25	2·47	2·47
„	„ No. 5 „ . .	18·20	12·00	4·16	4·08	·46	2·94	2·91
			14·40	5·00	4·91	1·64	2·93	2·90
			17·00	6·02	5·90	·88	2·88	2·85
			19·60	7·35	7·21	1·20	2·72	2·69
„	„ No. 8 „ . .	18·00	12·80	4·00	3·97	·49	3·22	3·22
			17·40	5·10	5·08	·76	3·43	3·43
			21·00	6·09	6·06	1·05	3·47	3·47
			23·00	6·66	6·61	1·22	3·48	3·48
„	Sugg's No. 1 Batswing . .	17·77	9·00	2·95	2·85	·47	3·16	3·20
			12·80	4·00	3·87	·77	3·31	3·35
			16·80	5·00	4·84	1·12	3·47	3·51
			17·20	5·20	5·03	1·20	3·42	3·46
„	„ No. 2 „ . .	17·77	9·40	3·24	3·13	·40	3·00	3·04
			11·60	4·00	3·87	·55	3·00	3·04
			14·00	5·00	4·84	·72	2·89	2·93
			15·60	5·95	5·75	·90	2·71	2·75
			17·60	6·94	6·69	1·15	2·63	2·66
„	Table Top Burner (4) Batswing	18·29	10·80	3·43	3·38	·18	3·19	3·14
			13·00	4·11	4·06	·22	3·20	3·15
			16·20	5·00	4·94	·30	3·28	3·23
			20·00	6·00	5·92	·40	3·38	3·33
			22·60	7·03	6·94	·54	3·26	3·21
„	Bray's No. 4 Reg. Batswing .	18·40	9·80	4·03	4·03	·54	2·43	2·38
			11·80	5·00	5·00	·54	2·36	2·31
			13·40	6·02	6·02	1·01	2.23	2·18
			14·80	6·75	6·75	1·21	2·19	2·14
„	„ No. 5	18·20	11·80	4·00	3·94	·37	2·99	2·96
			15·00	5·00	4·91	·54	3·05	3·02
			17·80	5·95	5·81	·69	3·06	3·03
			20·40	6·94	6·82	·88	2·99	2·96

It has become a practice with some makers to place a 'check' in the barrel of the burner to reduce the consumption of the gas by checking the pressure at point of ignition. These check burners in districts supplied with gas at good pressure certainly diminish the tendency to flare and to some extent save the gas consumer the trouble of checking the tap when the gas pressure rises from any cause. They have been prejudicial to the gas undertakings in many cases, as their use often causes complaints about insufficient supply, and if to meet these complaints a higher pressure be employed, other consumers not provided with check burners complain of overpressure. It is a curious feature of gas lighting, that concurrently with these check burners other manufacturers are pushing the sale and use of gas service regulators having for object the restriction of the pressure necessitated by the use of these 'checks.'

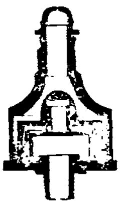


FIG. 36.

The proper system is to employ a regulator similar to that shown in fig. 36, which controls the maximum quantity to be consumed at the burner, generally 5 cubic feet per hour, by means of a float rising or falling with variations of gas pressure. These quantity regulators are cheap and efficient, and whilst allowing the proper quantity of gas to pass into the burner at a low pressure, immediately reduce any excess of pressure, so that no more gas than the quantity they are designed to pass (about 5 cubic feet per hour) can be consumed. They also give satisfaction where used, whereas the service regulators commonly cause complaints of shortness of gas supply.

The Argand type of burners differs from the preceding principally in respect to air supply, created by a glass chimney, and directed by special arrangements against the flame.

The best-known Argand burner is 'Sugg's London Argand,' also employed for testing coal gas of about 16 to 18 candle quality.

These burners are designed to produce a good result at a certain rate of gas consumption, which is for the 'London' about 5 cubic feet per hour for 17¾ candle gas. These burners are only economical at a certain rate of consumption, when the air supply is in correct adjustment. When the gas is in excess, the burners produce much smoke, and when the air supply is in excess the duty is very low, as will be seen by the following table:—

Results yielded by the London Argand Burner at various rates of consumption.

Illuminating power candles observed	Rate of Gas consumed corrected cubic feet per hour	Candles per cubic foot per hour	Corrected to 18 candles
2·40	2·28	1·05	1·07
4·00	2·73	1·46	1·49
5·40	2·89	1·87	1·91
7·00	3·18	2·20	2·25
8·20	3·39	2·42	2·475
9·60	3·64	2·64	2·70
11·40	3·92	2·91	2·98
13·20	4 12	3·20	3·27
15·80	4·59	3·44	3·52
16·60	4·83	3·44	3·52
17·60	5·03	3·50	3·58

It is usual to use globes with flat flame burners, but these are often prejudicial to the lighting effect, partly because they originate ill-regulated air currents which distort the flame and impinge upon it an excess of cold air, and partly because they obstruct a large percentage of the light. The following table will show the serious loss that results from these causes:—

Illuminating power of Bray's No. 5 Batswing Burner, with and without a globe.

Illuminating power observed	Rate of gas corrected	Per cent. of light lost by globes	Candles per foot	No. of globe tested
14·19	4·93	—	2·88	Without globe
7·40	4·93	47·84	1·50	Red globe on burner
5·20	4·93	63·35	1·05	No. 2 globe, opal glass
6·40	4·93	54·89	1·30	No. 3 " " "
7·60	4·93	46·44	1·54	No. 1 " " "
7·00	4·93	50·66	1·42	No. 4 " " "
11·60	4·93	18·25	2·35	No. 5 " " "

There is another type of burner now being much used and becoming better known, viz. those wherein the air supply is previously heated by the hot waste products of combustion, and called regenerative or recuperative burners. These burners produce a high duty from the gas. The best known are the 'Wenham,' 'Bower,' 'Schulke,' 'Siemens,' and 'Fourness.' It is not only the increase in the duty of these lamps that renders them valuable, but the quality of the light, which, being emitted by incandescent carbon at a higher temperature than with the open-flame burners, is white and more brilliant. The best yield obtained with these lamps is about 11 candles per cubic foot per hour with the 'Schulke,' consuming 19-candle gas. The following table gives results obtained by the writer with various regenerative burners consuming 19-candle gas:—

Results of Experiments on various Regenerative Lamps.

Actual angle of light to disc	Power of lamp. Candles	Power of lamp per cubic foot of gas. Candles	Gas consumed per hour. Cubic feet
Schulke Lamp.			
12°	171·0	10·2	16·8
13°	220·4	10·6	20·8
23°	226·4	10·9	20·8
Fourness Lamp.			
16°	99·0	6·14	16·1
13°	105·8	6·4	16·3
12°	99·6	6·1	16·25
11°	110·4	6·31	17·5
20°	106·	6·06	17·5

Results of Experiments on various Regenerative Lamps (continued).

Actual angle of light to disc	Power of lamp. Candles	Power of lamp per cubic foot of gas. Candles	Gas consumed per hour. Cubic feet
Wenham Lamp (*No.* 1).			
34°	32·14	4·23	7·6
36°	28·36	5·06	5·6
40°	32·88	5·39	6·1
Wenham Lamp (*large*).			
25°	89·0	5·39	16·5
26°	101·4	5·51	18·4
29°	111·8	6·10	18·3
33°	144·6	7·99	18·2
36°	177·0	9·50	18·4
24°	94·2	5·77	16·3
23°	91·4	5·59	15·5
26°	99·0	6·51	15·2
28°	100·0	6·42	15·4
32°	96·8	6·33	15·3
26°	87·6	5·89	15·2
Siemens.			
15°	52·9	2·61	20·2
19°	58·6	2·72	21·5

The regenerative burners being provided with a flue, are easily adapted to ventilation purposes. The drawing (fig. 37) shows how the Wenham Lamp Company adapt their burner to ventilation. The writer uses cast-iron water pipes of rectangular section for the flues, and these, if laid between the joists of the floor, are surrounded by non-conducting, non-combustible material, such as asbestos or slag wool. The cast-iron pipes lead the products of combustion into an ordinary chimney-flue, and are protected against occasional back draughts, which would cause a downpour of coal-smoke into the apartment, by a talc valve opening into the chimney. L. T. W.

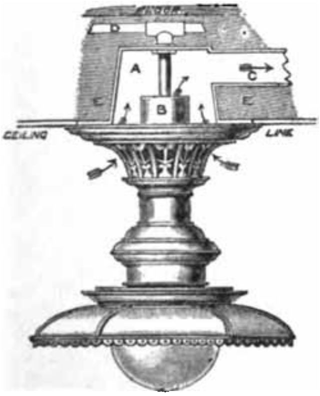


FIG. 37.

GAS, DOWSON, *v.* GAS, WATER.

GAS, GENERATOR, *v.* GAS, WATER.

GAS, NATURAL, *v.* FUEL.

GAS, OIL. Although almost the forerunner of coal gas, oil gas has only within recent years come largely into use, at first for the illumination of railway trains, and latterly also for the illumination of buoys and lighthouses and on board the mail steamers of the Dublin Steam Packet Co. Its superiority to coal gas for such purposes arises not only from its higher illuminating power, but also from the circumstance that it is much more compressible, and therefore more portable, than coal gas. Its value is well illustrated by the fact that the two reservoirs, having a collective capacity of 27½ cubic feet, placed underneath one of the London and North-Western six-wheeled first class carriages, contain sufficient gas when charged to a pressure of about 120 lbs. per square inch to supply the seven lamps of the carriage during the entire run from Euston to Aberdeen and back, a distance of 1,080 miles, the lamps burning continuously for thirty-three hours.

Literature.—In writing this article much information has been derived from an account of compressed oil gas and its uses, together with an interesting discussion thereon, given in a paper by Mr. A. Ayres, M.Inst. C.E., printed in the Proceedings of the Institute of Civil Engineers, session 1887–88, vol. 93, part 3. The figs. 1, 5, 6, illustrating the arrangement of the Pintsch Patent Lighting Company's plant used by the Honourable Corporation of Trinity House at Blackwall for the service of their gas-buoys and beacons, have been reprinted from this paper with the permission of the Council of the Institute of Civil Engineers.

Details of the plant used in the manufacture of oil gas at various times are to be found in F. N. Küchler's Handbuch der Mineralöl-Gasbeleuchtung und der Gasbereitungs-Oele: Anleitung für den Bau und Betrieb der Mineralöl-Gasanstalten (München, R. Oldenbourg, 1878).

A paper by the present writer, 'On the manufacture of gas from oil' is to be found in the Journal of the Society of Chemical Industry for September 1884, pp. 462–468; and an investigation of the liquid by-products of the oil gas manufacture has been published by the writer in conjunction with Dr. A. K. Miller in the Transactions of the Chemical Society for 1886, pp. 74–93.

History.—It appears that Murdoch as early as 1792 compressed coal gas and used it as a substitute for lamps and candles. In 1815 Mr. John Taylor, of Stratford, Essex, took out a patent, in which an apparatus is described for producing gas by the decomposition of oils, which in principle resembles that at present employed. The compression of such gas was patented in 1819 by Messrs. David Gordon and Edward Heard, and that chemical technology owes much to Mr. Gordon will be apparent from the following extract from Faraday's celebrated memoir of 1825 in the Philosophical Transactions of the Royal Society, 'On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat,' read June 16, 1825. 'My attention was first called to the substances formed in oil at moderate and at high temperatures in the year 1820; and since then I have endeavoured to lay hold of every opportunity for obtaining information on the subject. A particularly favourable one has been afforded me lately through the kindness of Mr. Gordon, who has furnished me with considerable quantities of a fluid obtained during the compression of oil gas, of which I had some years since possessed small portions, sufficient to excite great interest but not to satisfy it. It is now generally known that in the operations of the Portable Gas Company, when the oil gas used is compressed in the vessels, a fluid is deposited which may be drawn off and preserved in the liquid state. The pressure applied amounts to thirty atmospheres; and in the operation, the gas previously contained in a gasometer over water, first passes into a large strong receiver, and from it by pipes into the portable vessels. It is in the receiver that the condensation principally takes place; and it is from that vessel that the liquid I have worked with has been taken.' One of the *new compounds* of carbon and hydrogen discovered by Faraday in the liquid was the hydrocarbon now known as *benzene*, and this circumstance invests the products of the oil gas manufacture with peculiar interest; no other substance having played so important a part in contributing to the advancement of modern chemical theory or of modern chemical industry.

Compressed oil gas, however, soon succumbed to its rival coal gas, and for more than forty years was in almost complete abeyance, until in 1871 it was used with satisfactory results in illuminating railway carriages in Germany. Its adoption by the Metropolitan Railway in 1876 in place of coal gas served to reintroduce it into this country, and it is now very largely used throughout Europe and in America.

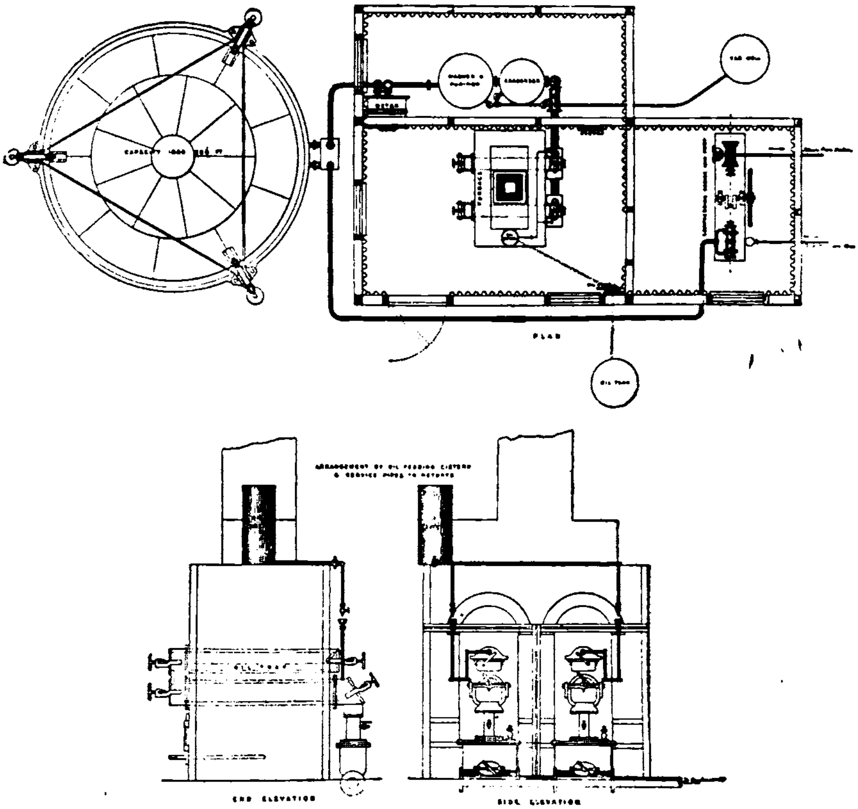


Fig. 1.

Manufacture.—In most cases the plant employed in the manufacture of compressed oil gas is that devised by the Pintsch Company; the London and North-Western Railway Company, however, adopt that of Messrs. Pope and Son.

The arrangement of a Pintsch plant is shown in fig. 1.

The oil is run from a cistern, preferably placed in a less dangerous position than that shown, into the uppermost retort, being delivered at the end furthest from the furnace, the oil being received on a sheet-iron tray, on which non-volatile matters are retained. The vapours and gaseous products of decomposition pass down into the lower hotter retort, and thence into the hydraulic main, where a large portion of the tar is deposited; the gas is next cooled by passage through a condenser, and, after passing through water and over a mixture of lime and sawdust, is collected in the holder.

The retorts are of cast-iron and D-shaped, the largest size in use being 6 feet 2 inches to 6 feet 4 inches long, 10 inches wide and 9¾ deep. The temperature at which the retorts are worked is very high, a bright cherry-red. The pressure in the retorts should be about that of a water pressure of 3–4 inches. The oil may be run in at the rate of about twelve gallons per hour; about 80 feet of gas per gallon of oil may be regarded as a good average yield. It is usual to ascertain whether decomposition of the oil has been properly effected by receiving a small portion of the tar, as it overflows from a trap placed between the hydraulic main and the condenser, on a piece of white paper; if a strongly marked greasy border be observed, either the supply of oil must be reduced or the temperature of the retorts must be raised. No greasy mark is noticeable when the supply of oil and temperature are properly adjusted.

Messrs. Pope are said to use cylindrical retorts, 6 inches in diameter, and introduce the oil into the lower retort. No data are known to the writer which admit of any comparison of the two systems being made, but it appears to be the opinion that the practice of those who follow the Pintsch system is preferable.

The condenser and purifier are of very simple construction. At the Trinity House works the former is simply a cylindrical vessel of cast-iron 8 feet high by 2 feet 4 inches in diameter. The purifier is a cylindrical vessel 3 feet in diameter by 2 feet 6 inches high; the lower portion contains water, maintained at a proper level by an overflow pipe, and there are two perforated trays above on which the lime and sawdust mixture is placed. The purification by lime is an undoubted advantage on account of the production of carbon dioxide and the constant presence of sulphur compounds in the oils used. Messrs. Pope, however, are said not to purify the gas.

Mr. James Keith has a patent plant for the manufacture of oil gas, which has been used in a number of places where coal gas is not available. A notable case of its adoption is at Ailsa Craig, Firth of Clyde, where the oil gas is used both in the lighthouse and in driving the engines for the fog horns. Mr. Keith employs only a single retort, but this is of peculiar form. At the Ailsa Craig works the retort is 6 feet 5 inches long, 5 inches broad, and 10 inches deep at the end; although shallower in the middle, it is proportionately broader, so that the sectional area is the same as at the end. The oil is delivered into an inclined trough so that it strikes the retort near the constriction where the temperature is highest. Figs. 2, 3, and 4, representing the Keith plant, are taken from the writer's paper in the Journal of the Society of Chemical Industry; it will be seen that no purifier is used. The Keith plant does not appear to have been used in manufacturing oil gas for compression.

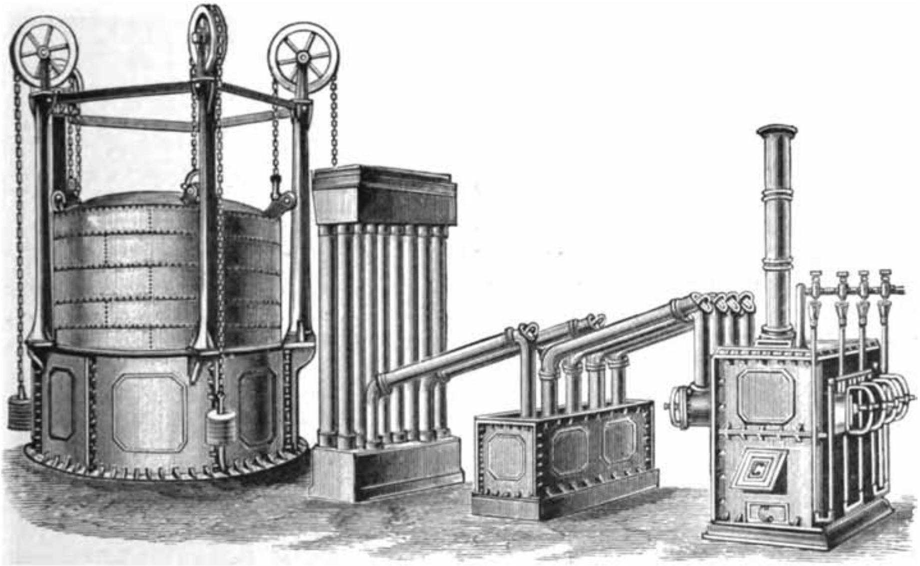


FIG. 2.

The oil which is most commonly employed is that portion of shale oil of about ·840 relative density which is too heavy for use as a burning oil and too light for use as a lubricating oil; the main reason for taking this oil being its cheapness. Lighter as well as heavier oils may be used, however, and it is within the writer's knowledge that both American burning oil and Russian oil have been decomposed with advantage. The lighter oils no doubt require a higher temperature and more care in working in order to effect their complete decomposition, but they can be used with greater advantage, as they cause less furring in the retorts, and with less risk of stoppage of the pipes. Certain oils rich in unsaturated hydrocarbons undoubtedly yield a high percentage of non-volatile and very difficultly volatile products and are therefore less suitable, but our knowledge of these matters is of a very fragmentary and empirical character.

Oil gas is usually compressed to about 10 atmospheres, and stored in large cylindrical boiler-like iron or steel vessels, from which the smaller reservoirs attached to railway carriages, gas buoys, &c., are charged to a pressure of 6–8 atmospheres. During compression the gas loses considerably—as much as 20 p.c. it is said—in illuminating power, to an extent which, however, is very variously estimated, depositing a considerable quantity of liquid; this last varies in quantity, and depends both on the pressure and temperature, but may be estimated at one gallon per 1,000 cubic feet of gas compressed.

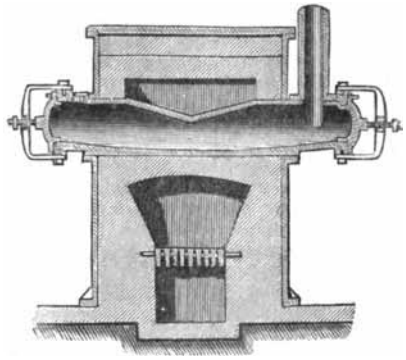


Fig. 3.

The illuminating power after compression may be taken at from 40 to 50 candles when burned from a London standard argand consuming 5 feet per hour at a water pressure of ·5 inch, but such a burner is not well suited for burning so rich a gas, and the estimate is but an approximation.

The successful use of compressed oil gas in all cases depends on the provision of a satisfactory regulator by means of which the gas is supplied to the burner at a sufficiently reduced and regular pressure. Figs. 5 and 6, which represent the arrangement of a gas buoy, serve to illustrate the mode of storing the gas and the construction of the regulator.

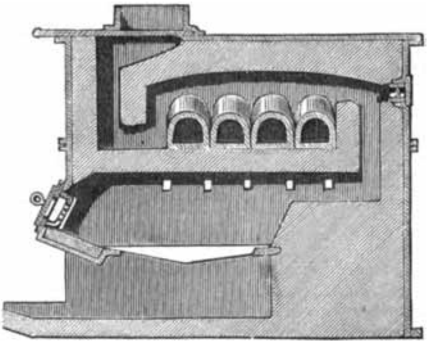


Fig. 4.

The cost of compressed oil gas varies greatly according to circumstances, and especially with the quantity of gas produced. Mr. Ayres estimates it at from 5*s*. 6*d*. to 16*s*. per 1,000 cubic feet. According to Mr. Tomlinson, on the Metropolitan Railway the consumption is ·7 cubic foot per burner, and the cost is not much more than half that of coal gas; in the three years 1882–1884, during which over 1,500,000 train miles were run in each year, the cost per train mile, with trains consisting of 50 lights, was ·263*d*. per light per hour, after adding capital and interest, as against ·396*d*. for coal gas during the years 1873–1875, when under 900,000 train miles were run in each year.

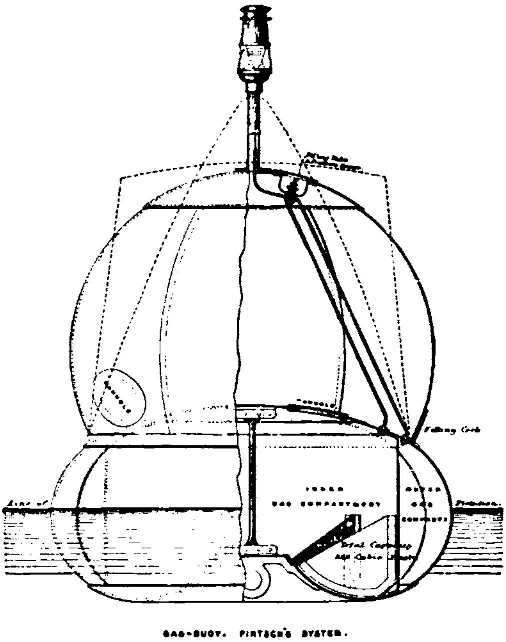


Fig. 5.

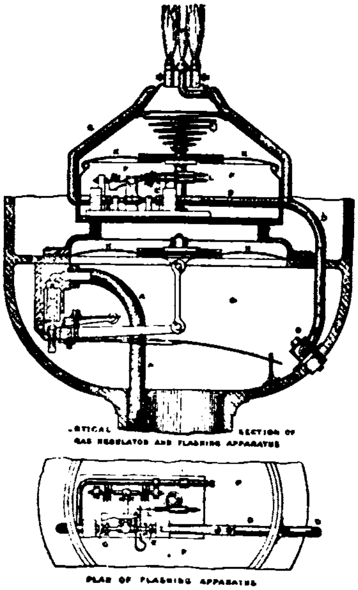


Fig. 6.

Nature of the products of the oil gas manufacture.—Comparatively little is known of the gas itself. Dr. Martius, in a paper read before the German Chemical Society in 1868 (B. 1, 88), describing Hirzel's apparatus for the production of gas from petroleum, states that the gas is rich in acetylene; but Dr. Miller and the writer were unable to detect acetylene in the gas manufactured at either the Great Eastern Works at Stratford or the District Railway Works at the Mansion House. The gas was very rich, however, in ethylene and crotonylene, which are undoubtedly its chief illuminating constituents.

The liquid deposited during the compression of the gas is a very complex mixture. It is saturated with ethylene and crotonylene gases. According to Mr. Greville Williams, it contains from 24 to 65 p.c. of benzene and toluene (C. N., May 2, 1884). It is all but free from hydrocarbons of the paraffin series, so completely are these decomposed during the manufacture of the gas: but it is rich in olefines or hydrocarbons of the C_nH_{2n} series. It is remarkable, however, that the olefines are all of a particular type—viz. normal olefines—and that the highest olefine present is normal heptylene. Hydrocarbons either identical with or closely related to those discovered by Schorlemmer in cannel oil are also important constituents of the liquid. Hitherto it has been the practice to sell the liquid in question, and it appears to have been almost all sent to Belgium, where it is used—so it is said—as a solvent and for enriching gas. The writer has always been of opinion that, owing to its extreme richness in very volatile constituents, the sale of the liquid in the form in which it is at present disposed of is a very uneconomical practice. If it were but stored in the reservoirs into which the gas is compressed, much of it would volatilise during warm weather; and if it were submitted to distillation and the more volatile portion were returned into the gas, the residue would be valuable as a source of benzene and toluene of a high degree of purity, and the volatile portion would increase the illuminating power of the gas. No doubt great care would be requisite in dealing with such a liquid; but the problem of arranging a suitable apparatus does not appear to be one of very special difficulty. Besides benzene and toluene, the three xylenes, mesitylene and pseudocumene, naphthalene and minute quantities of other benzenoid hydrocarbons are present; these are all separated with comparative readiness by steam distilling after treating the portion boiling above about 70° with somewhat diluted sulphuric acid, which polymerises and dissolves the greater part of the non-benzenoid hydrocarbons.

Oil gas tar is an altogether peculiar product, and has but very little value; in fact, the only use which apparently can be made of it with advantage is to burn it underneath the retorts. The amount produced may be estimated roughly at 5 gallons per 1,000 feet of gas. It is free from phenols and basic constituents, and contains but little benzenoid hydrocarbon—chiefly naphthalene; apparently, however, it is subject to considerable variation in composition. If the tar be again passed through the retorts, it yields but very little gas, being for the most part carbonised or distilling over apparently unaltered.

H. E. A.

GAS, PRODUCER, *v.* GAS, WATER.

GAS, WATER. This term is confined to the gas produced by the action of steam upon carbon. True water gas consists of about equal volumes of hydrogen and carbon monoxide, with small quantities of carbon dioxide, nitrogen, &c., but many other gaseous mixtures containing air or illuminating gases are usually included under the title.

The action of steam upon carbon at a temperature below 500°C. produces a mixture of carbon dioxide and hydrogen, according to the equation $2H_2O + C = 2H_2 + CO_2$. At more elevated temperatures, however, a portion of the carbon dioxide is converted into the monoxide by combination with a further proportion of carbon $CO_2 + C = 2CO$, this action being almost complete above 1,000°C. At temperatures above 600°C., however, steam itself acts upon the monoxide with production of a small proportion of carbon dioxide.

Although this gas has only recently been employed on the large scale, its manufacture is by no means new. F. Fontana appears to have first proposed the production of this gas by the passage of steam over heated carbon. In 1823 Vere and Crane patented a process for procuring inflammable gases by passing water or steam into a retort containing strongly-heated coal tar or similar materials. In 1824 Ibbetson proposed to pass steam, with or without tar or oil, through the coke remaining in the gas retorts after distillation for coal gas, and in 1830 Donovan proposed to bring water gas into contact with tar, naphthalene, or like materials in the liquid or vaporous condition. In 1845 Pollard passed a mixture of steam and air through ignited coke, and in 1849 Gillard erected a cupola furnace at Narbonne in which coke was alternately heated to incandescence by an air blast, and treated with steam for the production of water gas.

The many processes proposed and the few in use will be found to depend on one or other of the four last methods, particularly upon that of Gillard.

On account of the highly poisonous nature of the carbon monoxide in the water gas, attempts were formerly made, notwithstanding its high heating power, to eliminate it by conversion into carbon dioxide and removal of that gas by absorbents. It is, however, quite easy to impart an odour to water gas sufficient to indicate leakage, and even that precaution is unnecessary where the gas is conveyed direct from the holder to the furnace.

Water gas has been largely made and supplied to householders in parts of America where coal gas is extremely dear. The apparatus used in America and elsewhere usually consists of two firebrick-lined cupolas. The first is known as the 'generator,' and contains a column varying in height from 3-12 feet of fuel, which is preferably coke, although anthracite, wood charcoal, and other materials are sometimes used. The second cupola is charged with broken firebrick, with the exception of a gas-chamber 3 or 4 feet square at the base, and is known as the 'superheater.' The fuel in the generator is fired and is blown by an air-blast until incandescent, the product of combustion, which is known as *pro-*

ducer or *generator gas*, being passed from a pipe at the generator top through the superheater, where it heats the firebricks to whiteness. Steam is then passed through the superheater and through the fuel, preferably entering above and passing *downwards*, and the gas produced is passed through washers &c., as in the ordinary processes for purifying coal gas.

In some cases the superheater is arranged above the generator in the same cupola.

When the heat absorbed by the decomposition of the steam has reduced the temperature of the fuel, the steam is turned off and the air-blast is applied to again raise the heat to incandescence. The manufacture is thus intermittent, the production of the water gas occupying from three to five minutes, and the reheating of the fuel requiring about ten minutes.

Only about one-fifth of the fuel is converted into water gas, the remaining four-fifths being consumed in the heating by the air-blast, although a large proportion of this is available in the generator gas, which contains a large proportion of combustible gases (*v.* Table of Analyses), and whose heating power is equal to over 40 p.c. of that of the original fuel. While one ton of coke produces from 30,000 to over 40,000 cubic feet of water gas, the amount of generator gas obtained is from 100,000 to 140,000 cubic feet, possessing, volume for volume, about one-fourth the calorific power of water gas.

Where water gas is prepared for immediate use, as in metallurgical works &c., the generator gas is made full use of, but where supplied for domestic purposes, as in many towns in America, the use for generator gas is so limited that the greater proportion is wasted, or is met by an air-blast immediately after leaving the fuel, and is ignited to increase the temperature of the superheater.

The yield of water gas is said to be increased (as in Strong's process) by passing a shower of finely divided fuel through the steam before it reaches the coke.

Processes in which the fuel is heated in retorts by external means, although rendering the process continuous, are not so satisfactory as those in which the fuel is heated by its own combustion.

The first plant successfully worked in Europe was that of Messrs. Schulz, Knaudt & Co., of Essen. It consists of an iron cupola lined with firebrick, 18 feet high and 5 feet 6 inches in diameter at the widest part, from which it tapers to 3 feet 3 inches at the bottom. No grate is used, but the charge rests on a hearth with an elevated bench in the centre, and the cupola is encircled, where the grate is usually placed by a water jacket. The cupola is charged with coke, cinders, &c., obtained from gas works, and containing from 15 to 20 p.c. of ash. The charge is fired and is blown to incandescence by an air-blast, the generator gas being at once conveyed and burned, while still hot, beneath the boilers. Steam is then turned on and is passed *downwards* through the incandescent fuel, and the water gas is passed through two vertical cylindrical washing and straining vessels to the reservoirs. Two cupolas are used to render the supply of gas nearly continuous.

One ton of coke produces about 39,000 feet of water gas, whose heat value is about 42 p.c. of that of the coke, and 110,000 feet of generator gas, corresponding in heating power to about another 42 p.c. of that of the coke. Analyses of these gases are given in the table.

When manufactured for domestic use in America, water gas is usually 'carburetted.' The apparatus used for making such gas is identical with that described above, but the steam is passed upwards through the fuel, and naphtha or (where working on the large scale) 'crude oil' is poured upon the fuel, slowly at first, and more rapidly towards the middle of the reaction, the supply being stopped shortly before the steam is shut off. About four gallons of naphtha of 0·694 sp.gr. thus permanently gasified are said to be required for the production of 1,000 cubic feet of 20-candle water gas.

Tessié du Mothay passes the purified water gas over shelves upon which naphtha is caused to flow, and the carburetted gas is passed through a series of empty, intensely-heated retorts to decompose the naphtha into permanent gas.

The carburation may also be performed by passing the gas through naphtha or over liquefied naphthalene before burning, or the gas may be used in its original non-luminous condition by the use of an incandescent burner such as the Fahnejelm magnesia comb.

Other gases are manufactured which may be described as mixtures of generator gas and water gas. A gas of this description, largely used for gas-engines, is known as the *Dowson gas*, and is prepared by passing a small jet of sulphuretted steam mixed with air through red-hot anthracite or coke. As the air maintains the temperature of the fuel, the process is not intermittent. One ton of anthracite produces about 149,000 cubic feet of Dowson gas, 4 volumes of which possess the same calorific power as 1 volume of coal gas.

A somewhat similar gas is produced by Wilson's process.

The calorific power of coal gas is *two and a half times* that of water gas. The price of coal gas to householders is principally made up of the cost of distribution, &c., which amounts to more than the total cost of manufacture. It is, therefore, evident that water gas, whose maximum heating power is to that of coal gas as two is to five, could not compete with coal gas, at its present price in London or other large towns, for domestic heating purposes, even if it could be produced at the works for nothing.

Water gas, when prepared and used on the spot, especially when the generator gas can be usefully employed, is, however, of the utmost value. Its extremely low price, the absolute freedom of its flame from smoke, its comparative freedom from sulphur gases, and the small quantity of air required for its complete combustion (less than one-third that required by coal-gas), render it most valuable for the production of high temperatures, as in the melting, refining, and welding, &c., of metals, and where a 'clear' heat is required, as in porcelain burning, glass melting, &c.

The following analyses show the composition of some varieties of water gas &c.:—

	Water gas						Generator gas		Dowson gas
—	Essen. From coke (F. Fischer)	'Lowe' Gas. From anthracite (Green)	New Haven Gas. (Silliman and H. Würtz)	'Kirkman-Rowland' Gas. Supplied by the Municipal Gas Company, New York (H. Würtz)		'Du Mothay' Gas. Carburetted (Morton)	Essen. From coke	Pennsylvania Steel Works. From anthracite	From anthracite
				Ordinary	Carburetted				
Hydrogen	49·17	44·5	56·5	49·32	38·20	23·487	6·5	6·0	18·73
Marsh gas	0·31	—	3·5	7·65	15·82	24·622	1·9	3·0	0·31
Carbon monoxide	43·75	42·1	36·0	37·97	27·14	27·893	23·7	23·5	25·07
Olefiant gas	—	—	—	—	—	—	—	—	0·31
Carbonic anhydride	2·71	3·6	—	0·14	0·10	0·371	5·3	1·5	6·57
Nitrogen	4·06	9·8	4·0	4·79	3·35	5·235	62·6	65·0	48·98
Oxygen	—	—	—	0·13	0·10	1·021	—	—	0·03
Water	—	—	—	—	—	—	—	1·0	—
'Olefines'	—	—	—	—	9·29	17·363	—	—	—
Paraffins	—	—	—	—	6·00	—	—	—	—

For further information and technical details regarding the various processes, *v.* A. Naumann (Die Heizungsfrage); Quaglio (Wassergas als der Brenstoff der Zukunst); Naumann and Pistor (B. 18, 1647); Dowson (J. Soc. Arts, 1882 [30], 388); Wilson (S. C. I. [1] 53); Strong's process (C. N. 42, 27, and Eng. and Mining J. 29, 369), and a large collection of papers from various sources in the Journal of Gas Lighting, &c. (London), during the last fifteen years (*v.* also article Fuel).

GAS, WOOD. The gases evolved during the distillation of wood in retorts amount usually to from 20–37 p.c. of the total weight, and contain about 40 p.c. carbon monoxide, 26 p.c. carbon dioxide, and 11 p.c. marsh gas. The removal of the carbon dioxide by lime is difficult and expensive, and is never complete.

On account of the large proportion of water even in thoroughly dried wood, the full red heat required for the distillation is difficult to maintain, especially at the commencement of the operation. The greater yield is obtained by a rapid distillation.

When wood is distilled mainly for the production of gas, the distillate is passed directly from the retort through a heated chamber in which it is further decomposed into a larger quantity of gas of lower illuminating power.

Purified wood gas contains about 30 p.c. hydrogen, 25 p.c. marsh gas, 30 p.c. carbon monoxide, 8 p.c. hydrocarbons, and 7 p.c. carbon dioxide and air. Its illuminating power is much higher than that of coal gas, and its density is 1·2, taking coal gas as unity.

By the distillation of pitch pine in ordinary retorts, Mr. McCrae obtained 67–75 p.c. of gas (12,500 cubic feet per ton) of which the illuminating power was 16 candles.

When sawdust is distilled, an endless screw is used for carrying it through the retort.

Pettenkofer's process for the distillation of peat has been employed in America by Wilkinson for the distilling wood. After the first charge of wood has been carbonised, the charcoal produced is pushed to the back of the retort so that the gas from the next charge of wood, which is heated as highly as possible, passes through the incandescent charcoal. In this way the water in the wood introduces a large amount of water gas into the product, while the whole of the tar is gasified. One ton (2,240 lbs.) of Virginia pine is said to produce 36,500 cubic feet of gas of the following composition:—hydrogen 44·1, marsh gas 5·4, carbon monoxide 33·7, carbonic anhydride 10·5, nitrogen 6·0, oxygen 0·25 (Doremus, Journal of Gas Lighting &c. 38, 225).

Wood gas is sometimes carburetted with rosin oil, oil gas, or petroleum spirit.

The distillation of *peat* produces gas similar to wood gas, but of much lower illuminating power. In experiments by Somerville at Dublin one ton of black or 'bottom' peat gave 18,400 cubic feet of 7 candle gas, the yield from light brown or surface peat being 13,200 cubic feet of 5 candle gas. The evolution of gas is very rapid at the commencement of the distillation. Pettenkofer's method consists in passing the gas from one charge of peat or wood through the charcoal produced by the previous charge. As already stated, a considerable amount of water gas is thus introduced into the gas. One ton of average peat is said to produce 33,600 cubic feet of gas containing carbon monoxide 28·0, marsh gas and hydrogen 58·0, carbon dioxide 13·5, hydrocarbons 0·5.

In Martin's process for making peat gas, which has not been successfully worked, the peat before distillation is soaked in a liquid containing 80 p.c. of naphthalene and 20 p.c. heavy petroleum oil.

Illuminating gas is also produced by the distillation of *cork*.

GASEOUS FUEL *v.* Fuel.

GASES, BLAST FURNACE, *v.* Fuel.

GASES, PRODUCER, *v.* Fuel.

GAULTHERIA OIL *v.* Oils.

GEISSOSPERMINE *v.* Vegeto-alkaloids.

GELATIN, *Glutin,* and **ISINGLASS.** Gelatin, the purest form of glue (*q. v.*), may be obtained by the action of hot water or of water in presence of dilute acids, on intercellular connective tissue such as the skin, tendons, muscles,

&c. Hoofs, bones, intestines, bladders, fish-bones, &c., are also made use of for preparing crude gelatin.

According to the process employed by Nelson, the parings &c. of skins are scored on their surface, and are digested in a dilute soda lye for ten days. They are then digested at 70°F. in an air-tight, cement-lined vat, and are washed with cold water in a revolving cylinder, and are bleached by means of sulphurous acid gas. After being freed from moisture by pressure, they are digested with water in earthen vessels inclosed in steam chests, and the resultant solution is strained at 100 to 120°F. It is then solidified in a thin layer on a marble slab, and is washed free from acid, redissolved at the lowest possible temperature, and dried in thin sheets on nets. According to the process employed by Cox at Gorgie, near Edinburgh, the hides, of which the shoulders and cheeks are preferred, are washed, and are cut up and pulped by special machinery. The pulp is pressed between rollers, and is mixed with water and heated from 150° to 212°F. A little cow's blood is added to the gelatin solution thus produced, at a temperature not exceeding 170°F., and the solution is further heated, the scum produced by coagulation of the blood albumen being skimmed off. The pure solution remaining is run off and solidified. As prolonged heating impairs the gelatinising power of gelatin, it is preferably dried *in vacuo*.

Several other processes, not differing widely from the above, are also employed. A mixture of vegetable and animal charcoal is sometimes used for purifying dark solutions. Gelatin may also be extracted from bones (which yield one third of their weight) by causing water to trickle over crushed bones, through which steam is constantly passing.

Isinglass, the dried swimming bladder of fish, usually contains from 86 to 93 p.c. of gelatin. Russian isinglass is prepared by cutting open and washing the bladder and exposing it to the air with the delicate silvery inner membrane turned upwards. This membrane is stripped off, kneaded in damp cloths and dried. According to Martin, the bladders are first cleansed from blood in hot water, and are cut open and exposed as above, the inner membrane being finally removed by beating and rubbing.

The varieties of isinglass are known by special names dependent on the place of production and their appearance. The Russian varieties are obtained from the sturgeon, Brazilian (sometimes known as Cayenne) from the *Silurus Parkerii*, Manilla and East Indian from an uncertain source. The bladders of cod, hake, and other fish are also employed. *Lump*, *pipe*, and *purse* isinglass are obtained from the unopened bladder, and *leaf* and *honeycomb* from the cut and opened bladder. Long or short *staple* and *book* and *ribbon* isinglass are respectively twisted, folded in packages, and rolled out.

Pure gelatin is an amorphous, brittle, transparent, tasteless, inodorous body, neutral to test paper, and absolutely permanent in dry air. It is heavier than water, and is insoluble in alcohol or ether.

It contains about 50·0 p.c. of carbon, 6·6 p.c. of hydrogen, 18·3 p.c. of nitrogen, and 25·1 p.c. of oxygen. According to Mulder, phosphate of lime is always present. Schlieper finds sulphur in bone and ivory gelatin to the extent of 0·12 to 0·14 p.c. Von Bibra has also found it in bone gelatin, and Hammersten (J. Ph. 9, 273) has found about 0·7 p.c. of sulphur in fine commercial gelatin.

When moist or in solution, gelatin rapidly putrefies, and possesses the characteristic property of becoming acid at the commencement of the change, although ammonia is finally evolved.

When steeped in water, gelatin takes up from 5 to 10 times its weight of water, a sufficient quantity to dissolve it when warmed to 30°C.

A solution containing only 1 p.c. of gelatin becomes a jelly on cooling. Prolonged or repeated heating reduces and finally destroys this property on which the value of gelatin principally depends, so that the preparation is usually conducted at as low a temperature and as rapidly as possible.

Gelatin is soluble in concentrated acetic acid and in mineral acids, and loses its gelatinising power, but the solution forms a powerful cement for glass, &c. Dumoulin's liquid glue consists of a solution of 2 lbs. glue or gelatin in 1 quart of water and 7 oz. of nitric acid (1·355 sp.gr.). It is also soluble in alkalis, and the solution, as well as the acid solution, is lævorotatory.

Gelatin is precipitated from solution by tannic acid forming tannate of gelatin, similar in composition to leather, but not capable of employment as a substitute for that material on account of its want of structure. Corrosive sublimate also precipitates gelatin, but the acetates of lead and potassium ferrocyanide have not that power.

By prolonged boiling with hydrolytic agents such as sulphuric acid, gelatin yields leucin and glycocol, but no tyrosin, in which it differs from most other proteids.

The value of gelatin as a food is somewhat doubtful. Gelatin prepared from bones was largely used for the soldiers and poor of France during the first Revolution, but the idea that its large proportion of nitrogen renders it valuable as a flesh-former appears erroneous. It is, however, of limited value as a heat-producer instead of fat and carbohydrates.

A useful article on the origin and treatment of isinglass is given in the Journal of the Soc. of Chem. Ind. 1887, 764. The following table from Abney's Photography with Emulsions shows the composition of gelatin used for photography:—

	Ash p.c.	Water absorbed by 50 grains
Coignet's gold-label gelatin	nearly 1	7 dr.
„ special „ .	„ 1	7 „
Nelson's No. 1 Photographic gelatin . . .	„ 2	5·5 „
Nelson's Opaque . .	„ 2	8 „
„ Amber . .	„ 1	4 „
Ordinary French (not branded) . . .	„ 2	6 „
Swinburne's No. 2 patent isinglass . . .	„ 1	5·75 „
Cox's gelatin in packets .	„ 1	4·75 „
Gelatin supplied through Mr. Henderson . .	„ 2	8 „
'Swiss' gelatin supplied through Houton . .	„ 2	5 „

Prollius (D. P. J. 249, 425) gives the following table showing the composition, as far as requires to be known for commercial purposes, of several varieties of *isinglass*:—

—	Ash p.c.	Water p.c.	Insoluble in water p.c.	Time required for a solution of 1 part in 90 of water to 'run out' (*i.e.* Viscosity of solution)
Astrachan from Schmidt and Dillmann, of Stuttgart	0·2	16·0	2·8	507
Ditto, from a collection	0·37	18·0	0·7	485
Ditto, fine iridescent Russian from the Tübingen collection	1·20	17·0	1·0	500
Ditto, Russian from Gehe of Dresden	0·8	19·0	3·0	491
Ditto, in laminæ " "	0·5	19·0	0·4	480
Ditto, 'Hamburg threads'	0·4	17·0	1·3	477
Hamburg isinglass	1·3	19·0	2·3	470
Another quality	0·13	19·0	5·2	—
Rolled Northern fish bladder	3·20	15·0	10·8	467
Icelandic bladder	0·60	17·0	21·6	463
Indian isinglass	0 78	18·0	8·6	437

Gelatin differs but little in appearance from *chondrin*, which is obtained from cartilaginous tissue, but has a much higher gelatinising power than that substance. Gelatin almost invariably contains chondrin, and is of considerably less value, especially for the preparation of photographic emulsions which require a maximum of tenacity when the proportion of that substance is high.

Chondrin is precipitated from aqueous solution by acetic acid, and is not soluble in excess. Lead acetates, alum, and the sulphates of iron, aluminium, and copper also precipitate chondrin. A rough test for the presence of chondrin in gelatin, useful for photographic work, consists in adding a concentrated solution of chrome alum to a 10 p.c. solution of the gelatin in hot water. If an injurious amount of chondrin be present, the gelatin will set while hot. Most photographic gelatins, however, contain but little chondrin.

Abney (Photography with Emulsions) and Elsden (Photographic Year Book, 1881, 51) have described the properties of photographic gelatins.

In judging the value of gelatin, especially for photography, the following properties and tests will be useful. (1) The ash, according to Eder, varies from ½ p.c. in good, to 5 p.c. in inferior, and 10 p.c. in adulterated varieties. According to Abney, however, excellent photographic gelatins sometimes contain as much as 2·5 p.c. (2) A good gelatin will take up from 5–10 times its weight of cold water when soaked, *i.e.* sufficient to dissolve it on warming to 30°C. (3) The solubilities of gelatins vary considerably. Nelson's No. 1 will dissolve in the ordinary 'cold' water in warm weather, and scarcely sets at 75°F., whereas Coignet's gold label only melts at about 110°F., and sets rapidly. For ordinary photographic emulsions, Abney recommends a mixture of 'hard' and 'soft' gelatins in proportions dependent on the weather, a good mixture containing 1 part of the former to 3 of the latter. (4) The amount of fat in the gelatin should be estimated by precipitating the gelatin by addition of alcohol to the solution. Fatty matters are best removed by skimming the solution or by making a jelly and removing the top. (5) The colour of the solution, the tenacity of a jelly of known strength, and the presence or absence of acid. which is frequently present in sufficient quantity to be distinguished by taste, should also be noted.

Isinglass, although free from chondrin, is not available for photographic purposes on account of its great solubility and inferior tenacity.

Gelatin is largely used for culinary purposes as a vehicle for other materials, and is similarly employed in *bacteriology*. It is valuable for taking casts and impressions for electrotypy, &c. In photography it is employed, in addition to its use for gelatin dry plates, in the carbon process of photographic printing, which depends on the power of potassium bichromate to render gelatin insoluble when exposed to the action of light. This property is also employed in making an insoluble glue or a waterproofing material, by adding bichromate to glue or gelatin just before use.

It is also used in dyeing and for making inking rollers for printing, and as a size for paper making and painting.

For clearing beer, wine, &c., isinglass is infinitely superior to gelatin. This property is said by some to be due to the fine, net-like structure of the former. Coarse Brazilian isinglass is usually employed. It is 'cut' or dissolved in sulphurous or other acid before use.

GELATIN-DYNAMITE *v.* Explosives.

GELIGNITE *v.* Explosives.

GELOSE *v.* Gums.

GELSEMINE *v.* Vegeto-alkaloids.

GEMS, ARTIFICIAL. The manufacture of artificial gems has been practised from very early times. *Opals* and *emeralds*, amongst others, were imitated in the time of Pliny, and, according to St. Thomas Aquinas, *hyacinth*, *sapphire*, *emerald*, *topaz*, and *ruby* were manufactured in the twelfth century. The *emerald* was the gem most successfully imitated by the ancients; the 'sacro catino' of the Cathedral of Genoa and the celebrated 'Table of Solomon' seized by Vespasian from the Temple of Jerusalem have been found to be glass. Ancient emerald glass is so superior to that now made that it is frequently recut and sold as modern work.

Artificial gems may be divided into two classes—(1) mineral substitutes and 'doublets'; (2) gems made by chemical processes, pastes &c., and minerals treated by chemical means or by heat.

Of minerals sold as diamonds may be mentioned *quartz*, *white Brazilian topaz* (*novas minas*), and colourless varieties of *emerald*, *sapphire*, *beryl*, and *zircon*. The extensive use of topaz for this purpose may be inferred from the fact that the colourless gem which can have no value as topaz secures the highest price. Coloured varieties of quartz are largely substituted for other gems; *cairngorms* are sold as topaz, and spinels and garnets replace rubies.

Doublets consist of a thin plate of a genuine gem secured by gum mastic upon a valueless backing.

Topaz, *sapphire*, and other stones possessing a faint colour are frequently rendered colourless and acquire increased brilliancy, on exposure to a carefully regulated heat for some hours. Dark spots or inequalities may be similarly removed. Cardan tells us that 'a limpid sapphire of faint colour may be converted into a true diamond if heated in melted gold.'

The basis of most artificial gems is a heavy lead glass of great brilliancy, known as *paste* or *strass*. Its composition varies considerably, but a common mixture, according to Dumas, is the following:

Pure powdered rock crystal . .	38·2
Red lead	53·3
Dry potassium carbonate . .	7·8

According to other recipes, these proportions admit of wide variation. Borax, arsenious oxide, potassium nitrate, alumina, and calcium carbonate are also frequently added.

The ingredients are powdered separately, carefully mixed, and heated in a Hessian crucible by charcoal. The heat is gradually raised to fusion, and is maintained and carefully regulated at that temperature for about thirty hours, after which it is very slowly cooled. The value of the product depends entirely on the regularity of the temperature, the intimacy of the previous admixture, and the slowness of cooling, and is much increased by prolonging the fusion. The manufacture of pastes forms an important industry in many districts of France and Germany. The Crystal Works of the Jura is said to employ twelve hundred workmen.

Artificial *diamonds* are cut directly from the paste, but for imitating coloured stones the required tint is imparted by the solution in the paste of certain metallic oxides and other substances, the mixtures most frequently used being shown in the following table:—

—		Paste	Glass of Antimony	Purple of Cassius	Gold	Cobalt oxide	Copper oxide	Chromium oxide	Manganese dioxide	Iron oxide	Uranium trioxide
Ruby . .	1.	1,000	40	1	1	—	—	—	—	—	—
	2.	1,000	–	trace	—	—	—	—	5	—	—
	3.	1,000	—	—	—	—	—	—	25	—	—
Sapphire . .		1,000	—	—	—	14-25	—	—	—	—	—
Topaz . .	1.	1,000	40	1	—	—	—	—	—	—	—
	2.	1,000	—	—	—	—	—	—	—	—	16
Emerald .	1.	1,000	—	—	—	—	8	0·2	—	—	—
	2.	1,000	—	—	—	—	8	0·53	—	—	—
Amethyst .	1.	1,000	—	—	—	25	—	—	—	—	—
	2.	1,000	8	0·2	—	5	—	—	—	—	—
	3.	1,000	—	2	—	5	—	—	8	—	—
Garnet . .		1,000	—	variable	—	—	—	—	—	—	—
Syrian Garnet or Carbuncle		1,000	500	4	—	—	—	—	4	—	—
Beryl . . .		1,000	7	—	—	0·4	—	—	—	—	—

The temperature at which the mixture is fused and the time occupied considerably affect the product. The proportion of the colouring ingredients also admits of considerable variation. Thus, the composition used for making ruby glass is colourless after fusion, and only acquires the ruby colour after being cooled and re-fused. The addition of compounds of tin and silver varies the colour between rose red and purple red. If the first mixture given above for *topaz* be mixed, after one fusion, with eight parts of paste, and fused for thirty hours, ruby glass is obtained. Silver chloride and borate have been added to paste to produce the *topaz* yellow.

According to Bryce Wright, *emeralds* are sold having the following composition: silica 35·70, lime 41·66, potash and soda 13·00, beryllia 9·54, iron, chromium, and lead, traces.

Opals may be imitated, according to Bastenaire Daudenart, by fusion of the following mixture in which the tin oxide produces the opalescence: Silica 25, red lead 20, calcined potassium carbonate 10, potassium nitrate 2, tin dioxide 16. A green opaline glass is produced by the addition to paste of bone ash with nickel oxide or uranium trioxide.

Artificial *avanturine*, as made in Venice, consists of a soda lime glass containing excess of alkali, coloured yellow by iron oxide, and holding in suspension minute particles of metallic copper. According to Hautefeuille, a green copper glass is first made, and iron filings are added to reduce the copper, partly to the cuprous and partly to the metallic condition, the glass, when it becomes reddish-yellow and opaque, being covered and cooled gradually. According to Pelouze, it may be obtained without the use of copper, and of great hardness, by fusing a mixture of silica 25, sodium carbonate 10, calcium carbonate 5, and potassium bichromate 4.

Agate, *onyx*, *chalcedony*, and *carnelian*, for making jewellery and for engraving, are artificially stained to a very large extent at Oberstein, Idar, and other towns in Germany. The stones are soaked in oil or sugar syrup, and, after cleaning, are heated in strong sulphuric acid until the acid commences to vaporise. The organic matter absorbed by the stone is thus carbonised, and a black colour is produced. For the production of a red colour, the stone is soaked in a solution of ferrous sulphate, and by afterwards soaking in a solution of potassium ferricyanide, a deep blue colour is obtained. As only the most porous parts of the stone absorb the solution, the colour is irregular and enhances the value of the stone. A number of the staining processes are jealously kept secret (*v.* Agate).

A few artificial gems have been prepared, identical in composition and properties with the natural gems; rubies, sapphires, and spinels being the most important. The methods of preparation of these have been described under *aluminium oxide*, including the most recent process of Fremy and Verneuil for the production of rubies. Diamonds do not appear to have been prepared artificially.

Bibliography.—Feuchtivanger, Treatise on Gems (1838); Fontenelle and Malepeyre, Glass, Artificial Stones, &c., 2, 173–205 (1854); Emanuel, Precious Stones (1867); Streeter, Precious Stones and Gems; Dieulafait, Diamonds and Precious Stones (1874); Burnham, Precious Stones (1886).

GENISTA *v.* Broom tips.

GENTIAN. *Gentianæ Radix; Racine de Gentiane* (Fr.); *Enzianwurzel* (Ger.). The dried root of the *Gentiana lutea* (Linn.; Bentl. a. T. 182) is used in medicine as a bitter tonic. Its physiological activity appears to depend upon the presence of a small proportion of a bitter crystalline glucoside *gentiopicrin*, *gentian-bitter*, or *gentianin* $C_{20}H_{30}O_{12}$ (?), which was first obtained in a definite form by Kromayer (Die Bitterstoffe, Erlangen, 1861, 105; Gm. 16, 193). An aqueous solution of an alcoholic extract of the fresh roots is treated with animal charcoal, which removes the gentiopicrin and yields it again in a crude condition, when the washed and dried charcoal is treated with boiling 80 p.c. alcohol. After removal of the alcohol from the solution by distillation, the residue is freed from resin by the addition of water, and from colouring matter by treatment with hydrated oxide of lead, and finally on mixing the residue with ether and allowing it to stand, the gentiopicrin slowly crystallises out. Purified by recrystallisation from water, gentiopicrin consists of efflorescent needles, intensely bitter and melting at 120°–125°. It is readily soluble in water, sparingly in alcohol, and quite insoluble in ether. It dissolves in sulphuric acid, forming a colourless solution which, on warming, becomes carmine-red. By the action of dilute acids gentiopicrin breaks up into *glucose*, and flakes of a yellow amorphous compound *gentiogenin* $C_{14}H_{16}O_5$ (?), which is soluble in alcohol, but almost insoluble in water.

Gentian also contains in very small proportion another compound which, though physiologically inactive, is much better known. It is a yellow crystalline acid, *gentianic acid*, *gentisin*, or *gentianin* $C_{14}H_{10}O_5$, and by the earlier investigators (Gm. 16, 178) was confused with gentian-bitter or gentiopicrin, and to both these compounds the name 'gentianin' has been applied. To obtain gentianic acid the powdered root, after removal of pectin and saccharine constituents by prolonged maceration in cold water, is extracted with boiling alcohol. Most of the alcohol is removed from the solution by distillation, when on the addition of water a precipitate forms consisting of impure gentianic acid. This, after washing with ether, may be purified further by recrystallisation from alcohol or by conversion into a potassium salt, and regeneration with acetic acid (Henry a. Caventou, J. Ph. 7, 173; Trommsdorff, A. 21, 134; Leconte, A. 25, 202; Baumert, A. 62, 106; Hlasiwetz a. Habermann, A. 175, 63; 180, 348).

Gentianic acid crystallises in large pale-yellow silky needles. Heated to 200° it darkens in colour, and sublimes with decomposition at 300–400°. It is nearly insoluble in water, at 16° 1 part requiring 3630 parts of water for solution, but in alkaline solutions and in hot alcohol it dissolves readily. Melted with potash compounds of *acetic acid*, *phloroglucin*, and *di-hydroxybenzoic* or *gentisic acid*, $C_6H_3.COOH.OH.OH$ (1 : 2 : 5) are formed (H. a. H.). In a current of hydrochloric acid it yields *methyl chloride* (H. a. H.). The more important *metallic derivatives* are the following: $C_{14}H_9NaO_5,2H_2O$, obtained in silky needles by precipitating a solution of gentianic acid in alcoholic soda by the addition of ether (H. a. H.); $C_{14}H_9KO_5,H_2O$ (H. a. H.); $C_{14}H_8BaO_5,H_2O$ (B.); $C_{14}H_8PbO_5,Pb2OH$ (B.). A *diacetyl derivative*, $C_{14}H_8Ac_2O_5$, in crystals melting at 196°, has been prepared (H. a. H.), and also two *nitro- derivatives*: $C_{14}H_8(NO_2)_2O_5$ and $C_{14}H_7(NO_2)_3O_5$ (B.).

Pectin is present in gentian root in large proportion, together with 12–15 p.c. of a fermentable *uncrystallisable sugar* (Ludwig, Ar. Ph. [2] 107, 132) and small quantities of a crystallisable sugar *gentianose* $C_{36}H_{66}O_{31}$ (?), which melts at 210°, is fermentable, but does not reduce Fehling's solution (A. Meyer, H. 6, 135). The presence of so much fermentable sugar has led to the root being employed in Switzerland and Bavaria in the manufacture of spirit. Whether gentian root contains traces of *tannin* or not has been much disputed (Ville, Y.-Book Ph. 1877, 217; Davies, Ph. [3] 10, 230; Thompson, Ph. [3] 18, 500; Maisch, Ph. [3] 6, 775; 10, 602). For the detection of gentian-bitter in beer *v.* Dragendorff (C. C. 1881, 285 a. 299); Allen (An. 12, 107; 13, 43). A. S.

GENTIAN-BITTER *v.* Gentian.

GENTIAN BLUE 6 B. Synonym for *Spirit Soluble Blue, Spirit Blue O, Opal Blue* *v.* Aniline blue.

GENTIANIC ACID *v.* Gentian.

GENTIANIN *v.* Gentian.

GENTIANOSE *v.* Gentian.

GENTIOGENIN *v.* Gentian.

GENTIOPICRIN *v.* Gentian.

GENTISIC ACID *v.* Gentian.

GENTISIN *v.* Gentian.

GERANIUM OIL *v.* Oils, essential.

GERMANIUM. Ge. At. wt. 72·32 (Winkler). This element occurs to the extent of 6–7 p.c., with 73–75 p.c. of silver, 17–18 p.c. of sulphur, and 0·2 p.c. of mercury in the very rare mineral *argyrodite* from the Himmelsfürst mine near Freiberg, in which mineral it was discovered by

Winkler in 1886. Argyrodite occurs elsewhere as a thin coating over other silver ores, the richest of which contain only 0·03 p.c. of germanium. Germanium has also been found to the extent of 0·1 p.c. in *euxenite* (Krüss).

It is brittle and easily powdered, of metallic lustre, and sp.gr. 5·469 at 20·4°. It melts at about 900°, and volatilises at a slightly higher temperature, crystallising in octahedra on cooling. It oxidises when heated in air, and combines directly with chlorine, forming the tetrachloride. When gently heated in a current of hydrochloric acid gas, the metal becomes red hot, evolving hydrogen, and forming a colourless liquid which separates into two layers, the heavier being *germanium chloroform* $GeHCl_3$, and the lighter *germanium oxychloride* $GeOCl_2$. Germanium is soluble in sulphuric but not in hydrochloric acid. Germanium is identical with the element ekasilicon predicted by Mendeléef, being placed between arsenic and gallium in the periodic arrangement of the elements. It appears to be capable of replacing silicon in ultramarine. It forms two oxides GeO and GeO_2, and two sulphides GeS and GeS_2, the latter white and soluble in alkaline sulphides. The tetrachloride $GeCl_4$, bromide $GeBr_4$, iodide GeI_4, fluoride GeF_4, and ethide $GeEt_4$, are also known.

GETAH WAX *v.* Wax.

GHATTI *v.* Gums.

GHEE. A clarified butter used in the East mainly for cooking.

GIALLOLINO or **NAPLES YELLOW** *v.* Pigments.

GIANT POWDER *v.* Explosives.

GIN or **GENEVA**, a corruption of the French *genièvre* (juniper). A flavoured spirit prepared from grain spirit (*v.* Alcohol). The distiller manufactures the raw spirit. The rectifier redistils and flavours it. In the process of redistillation he puts into the still along with the spirit either common salt or a mixture of salts of sodium and potassium. The purified spirit is then mixed with the necessary flavouring ingredients and redistilled. The essential oils of these ingredients being more or less volatile pass over in small proportions with the spirit and impart to it the characteristic flavour. Each rectifier has his own receipt for flavouring ingredients.

The following are the principal flavouring substances used in making gin: Angelica root, almond cake, calamus root, cardamoms, cassia, cinnamon, coriander, juniper, liquorice powder, orris root, and sweet fennel.

Gin of good quality should be free from any tinge of blue colour or cloudiness.

Sweetened gin may be prepared from plain gin by dissolving refined sugar in its own weight of pure water so as to produce a clear solution, and adding the syrup thus produced (capillaire) to the gin, in the proportion of six gallons syrup to 100 gallons of gin.

Plymouth gin. Used extensively in the West of England. The chief feature in its manufacture is, that a little sulphuric acid is mixed with the spirit to be rectified, which—probably owing to the formation of ether—produces a characteristic flavour.

Hollands gin. Under the name of Hollands a flavoured spirit is manufactured by the Dutch which is imported extensively into this country. The principal seat of this manufacture is at Schiedam, where there are not fewer than 200 distilleries. The best Hollands is said to be prepared as follows:—

A mixture of two measures of ground rye with one measure of ground barley malt is mashed with about 24 gallons of water for each cwt. of the mixed meal. The mashing being completed, the sp.gr. of the wort is brought down by cold water to between 1033 and 1038. It is then fermented, after which the whole is thrown into the still. To the first product of distillation, called low wines, is added a varying proportion of juniper berries with a little salt, and it is then redistilled. The spirit which now passes over is flavoured with essential oils or resins, derived from the juniper as well as from the rye and the barley used in brewing.

By the Sale of Food and Drugs Amendment Act, 42 & 43 Vict. c. 30, s. 6, the limit of strength below which gin is not allowed to be sold is 35 under proof, unless it is sold as diluted spirit.

The strength at which it is generally sent out by rectifiers is 17 and 22 under proof.

G. N. S.

GIROFLE. *Dimethyl phenoxylosaffranine* (*v.* Azines).

GINGELLY or **GINGILI OIL** *v.* Sesamé oil.

GLASS. Glass is a mixture of silicates, non-crystalline in structure owing to its comparatively rapid cooling and its indefinite chemical composition. Like other silicates, it is formed by fusion of silica with oxides of the metals, the silica acting as the acid, or, more strictly speaking, the anhydride, and the oxide or oxides as the base. As the bases differ in molecular weight, the percentage composition of glass does not immediately suggest its chemical relations; hence it is advisable to compare the ratio of the oxygen in the silica to that in the bases, whatever the latter may be. This is easily done by multiplying the percentage of silica by the factor 0·530; of lime by 0·285; of baryta by 0·104; of lead oxide by 0·072; of potash by 0·170; and of soda by 0·258; the total amount of oxygen in the bases is then found by addition, and its ratio to that in the silica determined.

Simple silicates. Before considering mixtures of silicates it is advisable to discuss shortly the properties of the simple silicates, a mixture of which forms glass.

Silicates of the alkalis. These are the most fusible of all the silicates. By fusing silica with two or three times its weight of potash or soda, a homogeneous transparent mass is obtained, which dissolves completely in cold water. If the weights of silica and of soda and potash are equal, the resulting compound is still easily fusible, but it is no longer completely soluble. As the proportion of silica rises, the product fuses at an increasingly high temperature; and if the proportion of oxygen in the bases bears to that in the silica a ratio such as 1:18, the highest temperature of a forge is necessary for its fusion.

Soluble glass, as silicate of potash or soda is termed, is prepared by combining the constituents in the proportion of 3 of silica to 2 of carbonate of potash, or of 1 of silica to 1 of carbonate of soda, by fusion, or by heating the silica in the form of sand with a strong solution of the alkali under a high pressure. It is soluble in 4 or 5 parts of boiling water; it is used in the manufacture of artificial stone, and is sometimes added to soap, and applied to the purpose of cleansing. The silicates of the alkalis possess the property of not crystallising on cooling; hence they do not pass rapidly from the liquid to the solid state, but assume all intermediate degrees of plasticity. They impart this property to other silicates with which they are mixed; moreover, the resulting mass is transparent, which is of extreme importance in view of the uses to which glass is put.

Silicates of calcium and barium. These silicates melt only at very high temperatures. The most fusible contain silica and base in such proportion that their oxygen ratio is 1:3; such a compound fuses at a red heat approaching whiteness. The resulting substance is crystalline when cold. With larger proportions of silica complete fusion can be induced only at the temperature of the oxy-hydrogen flame. They are slowly attacked by water.

Silicates of alumina and of magnesia are sometimes present in glass as impurities. When pure they cannot be fused at a lower temperature than that of the oxy-hydrogen flame.

Silicates of iron and of manganese are often present in glass in small amount, either as impurities, or to impart colour. They melt much more readily than the silicates of lime and baryta. Those with the formulæ $FeSiO_3$ and $MnSiO_3$ melt at a bright red heat. All of these crystallise if cooled slowly.

Silicates of lead. These silicates fuse the more easily the more lead oxide they contain. The one of the formula $PbSiO_3$ melts at a bright red heat. The colour is somewhat yellow. They crystallise only if cooled very slowly.

Mixtures of silicates melt at a lower temperature than the mean melting-point of their constituents, and often at a lower temperature than any one constituent. Those containing alkalis lose alkali by volatilisation if kept for a long time at a high temperature, and the melting-point rises; they also tend to become crystalline or 'devitrified.'

It has been mentioned that the silicates of the alkalis containing little silica are soluble in water. With a large amount of silica they are very slowly attacked, but yield to the stronger acids. The mixed silicates, on the other hand, are very slightly attacked by water or acids. The author has found that even at 270°, after exposing hard boiler-gauge glass to the action of water under great pressure, only 0·7 p.c. of solid residue was left on evaporating the water. They are, however, much more easily attacked by alkalis, and even by ammonia.

From the foregoing sketch it will have been seen that glass possesses the useful properties of being non-crystalline, hence transparent; of assuming the plastic state when heated, hence capable of being blown or cast; and of withstanding the action of water and of acids. It is also a very slow conductor of heat, and is practically a non-conductor of electricity. It is very elastic, and has a fairly high refractive index. The following table gives its more important physical properties:—

Density 2·5 to 3·0. Co-efficient of elasticity; flint glass: Young's modulus, $5·5$ to $6·00 \times 10^{11}$; simple rigidity, $2·3$ to $2·4 \times 10^{11}$; volume elasticity, $3·4$ to $4·2 \times 10^{11}$; crystal: Young's modulus, $3·4$ to $4·4 \times 10^{11}$; simple rigidity, $1·2$ to $1·7 \times 10^{11}$; volume elasticity, $3·5$ to $4·4 \times 10^{11}$. These are in the C. G. S. system of units. Velocity of sound in glass, $4·5 \times 10^5$. Mean specific heat between 0° and 100° = 0·1770; between 0° and 300°, 0·1900. Conductivity for heat, 0·0005 to 0·002. Expansion (cubical) per degree C., 0·000023 to 0·000027. Resistance (electrical) at 200°, $2·27 \times 10^{16}$; at 300°, $1·39 \times 10^{14}$; at 400°, $7·35 \times 10^{13}$ (Everett's Illustrations of the C. G. S. System of Units).

History.—The word *glass* is derived from the Saxon *gelixan*, to shine. Its Latin equivalent, *vitrum*, is believed to be connected with the root of *vid-eo*; and the Greek *ὕαλος* probably originally meant a drop of rain. These names therefore denote its shining, or transparency. Glass beads adorn Egyptian mummies which are known to be at least 3,000 years old; and pictures of glass-blowers and their operations have been found at Beni-Hassan and Thebes, dating from a period anterior to the exit of the Israelites from Egypt. Glass lenses have been discovered at Nineveh. The first to mention glass among classical writers was Aristophanes in his play of 'The Clouds.' Pliny relates a legend to the effect that some Phœnician traders, encamped on the sandy banks of the river Belus, supported their cooking utensils on blocks of soda, which they were conveying as merchandise. The heat of the fire caused the soda to melt and incorporate with the sand, forming glass; but though it can hardly be doubted that its discovery was anterior to the time of Phœnician enterprise, it may well have been made in some such manner. Both Pliny and Strabo testify to the existence of glass works at Sidon and at Alexandria. In their time it was cut, engraved, and gilt, and also coloured to imitate gems. The Romans were in the habit of using talc for windows; at Herculaneum and Pompeii, however, window-glass has been discovered which was made by blowing. The processes of glass-making were introduced into Europe at the time of the Crusades, although glass had been imported at a much earlier date. Lactantius, who lived at the end of the third century, mentions that glass was used for windows; and in 674 the Abbot Benedict caused the church and monastery of Wearmouth to be glazed. In 1334, the price paid for the glass for the windows of York Cathedral was 6*d.* per sq. foot for white, and 1*s.* for coloured glass. Until a much later date oiled paper or lattice-work was used for the windows of private houses. Venice had the monopoly of glass-making in the tenth century; it was there that glass was first silvered and employed for mirrors, which had previously been made of metal. The first window-glass was made in England at Crutched Friars, London, in 1557; the first flint-glass at Savoy House, in the Strand; and the first plate-glass at Lambeth in 1670, by workmen brought from Venice by the Duke of Buckingham. There was for long a bounty on English glass, which was repealed by Sir R. Peel.

As regards the method of manufacture, the processes have remained substantially the same as of old. Agricola describes glass furnaces, which, except in size, are of the same appearance as those of the present day. In his treatise 'De Natura Fossilium,' Lib. V. 274 (Basle, 1546), he gives as the sources of the best sand in Mount Carmel, near the column of Ptolemy, and near Tyre on the sea-shore; and in the river-beds between Cumas and Lucrinum. For alkali, he states that soda was used; or, in default of soda, rock-salt, or sea-salt, or the ashes of plants. He describes methods of producing coloured glass; for blue, cobalt (zappara) was used; for blue and green, copper oxide alone, or mixed with ochre; for green, copper and silver nitrate; for garnet, copper, stirring for twenty-four hours with an iron rod; for amethyst, manganese dioxide; for yellow, ochre or silver filings; and for ruby, gold, or a mixture of gold and copper oxides. The use of tin oxide to make opaline or white glass is also mentioned (Johann Baptiste Porta, Nuremberg, 1630; also Kunkel, Vollständige Glasmacherkunst).

Classification.—All glass contains silica, or silicic anhydride, SiO_2; as well as alkali. But it varies in the nature of the other metallic oxides which it contains. The different varieties may be conveniently divided into four classes, according to the nature of the third constituent.

1. *Alkali-lime glass.* With soda as base, this variety is used for French and English window-glass, for French, German, and English plate-glass, and for bottle-glass. With potash as base, Bohemian and German plate-glass is made, and French crown-glass; and with a mixture in which soda is present in larger quantity than potash, French, English, and Venetian plate-glass.

2. *Alkali-lead glass.* This is commonly termed *flint-glass* or crystal. Almost all makers employ potash, but a few use entirely soda.

3. *Alkali-baryta glass.* This variety is sparingly made.

4. *Coloured glass*, produced by the addition of certain oxides to one of the above varieties.

MATERIALS EMPLOYED IN THE MANUFACTURE OF GLASS.

Silica. The silica used to be obtained by grinding flint, hence the name 'flint-glass.' Sand is now invariably employed. For crown and sheet-glass, English sand may be used. It is obtained from Lancashire, where it forms shallow beds of great extent, lying close to the surface; and from Bedfordshire, where the strata vary from 40 to 50 feet in thickness. Belgian sand is also largely imported; the supplies are obtained from the neighbourhood of Waterloo, and from Moll, about thirty miles from Antwerp. A very pure sand comes from Nivelstein in Prussia. The chief impurity in sand is oxide of iron, which imparts a green colour to glass. A yellow colour does not always imply its presence, but may arise from organic matter. For window-glass, sand containing ½ p.c. of iron oxide may still be used; but for crystal and plate-glass only a trace is permissible. The effect of iron may be neutralised to some extent by addition of oxide of arsenic. In Bohemia, quartz is pulverised by heating it and dropping it into water, and subsequently grinding in wooden mortars with quartz pestles. The French use sand from Fontainebleau, Champagne, Nemours, Chantilly, &c. For coarse bottle-glass, ordinary sand is employed.

Lime. The material is chalk or limestone, either as caustic or carbonate. The former produces a harder glass than the latter, due possibly to the presence of magnesia.

Alkali. In old times kelp or barilla, obtained by incinerating seaweed, was fused with sand. The kelp contains potash, soda, and lime, and hence the necessary materials were present. Subsequently soda-ash, made by the Leblanc soda-process, was substituted for soda-glass; and in 1825 the French began cautiously to substitute sulphate for carbonate of soda, the former being a cheaper material. In 1831 English manufacturers followed their lead, and at present sulphate of soda is largely used. The sulphate must for this purpose be freed from all traces of iron by means of lime. In employing sulphate of soda, it is customary, but not essential, to add carbon in the form of anthracite coal, or charcoal, to deprive the sulphate of its oxygen. This is only possible for lime glass, for the sulphate being converted into sulphide of sodium would react with the lead, forming lead sulphide, and utterly spoil the glass. It must, however, be noted that although sodium sulphate costs only about half as much as carbonate, 71 parts of the former are equivalent to 53 parts of the latter; and, moreover, the sulphate requires a much higher temperature to react with the silica than the carbonate. In adding carbon, it is advisable to reduce the sulphate not to sulphide, which would colour the glass yellow, but to sulphite. For this purpose 3 parts of carbon are required for 71 parts of sulphate, provided carbonic anhydride is formed; and 6 parts, if carbonic oxide is the product.

Attempts have been made to introduce soda in the still cheaper form of salt; but the action of silica on salt requires a very high temperature, and salt is volatile; it would no doubt be possible to cause the reaction to take place at a lower temperature by introducing water-vapour; this, however, has not been attempted on a large scale.

Potash is invariably employed as carbonate; in the manufacture of *strass* it is rendered caustic, and purified by treatment with alcohol.

Lead. This is employed as red lead, or minium, Pb_3O_4, and sometimes, but rarely, as litharge, PbO. It is considered of advantage to employ the former in order that the oxygen evolved on heating may oxidise organic matter accidentally present, and may convert any ferrous into ferric oxide. The oxide of lead must be prepared from pure lead, and must not contain copper, which imparts to glass a greenish colour.

Barium carbonate, prepared from the sulphate, is employed in the manufacture of baryta glass, the barium wholly or in part replacing calcium. For every 100 parts of calcium carbonate 197 parts of barium carbonate must be substituted.

Cryolite, used for making white, translucent glass, is a natural product found in Greenland, and has the formula Na_3AlF_6.

As the raw materials are scarcely ever free from iron, it is necessary to convert the ferrous oxide, which colours glass green, into ferric oxide, which imparts a very pale yellow tint, so slight as to be imperceptible if the iron is present in small amount. The oxygen necessary is furnished by the red lead, as mentioned above; but for crystal, arsenious oxide, or saltpetre are often employed, and for white lime-glass, manganese dioxide (black oxide) or a trace of smalt (cobalt, or zaffre). The action of the saltpetre requires no explanation; the arsenious oxide is probably decomposed into oxygen and into metallic arsenic, which sublimes; yet too large an amount produces opalescence. The manganese dioxide serves a double object; its oxygen serves to oxidise the iron, and the manganese, if present in somewhat larger amount than is necessary, imparts to the glass an amethyst shade, which is nearly complementary to, and neutralises the yellow-green of the iron. The addition of a trace of smalt also neutralises the yellow by imparting a faint blue colour to the glass.

Cullet. In addition to the materials already described, broken-glass, or 'cullet,' is invariably added. The object of this addition is to use up the numerous fragments of glass left over during the operations of manufacture; and, what is of still greater importance, to cause the materials employed to react on each other at a lower temperature than they would do if melted together alone; in fact to serve as a flux. At the temperature necessary to produce action between the silica and the other constituents of the glass, the alkali is volatile, and much is lost before it reacts with the silica. But the cullet melts, and dissolves both alkali and silica, thus promoting their interaction. While it is stated that lime-glass deteriorates if often remelted, probably owing to the volatilisation of some of the alkali, the makers of lead-glass find that an improvement results by frequently breaking up the glass by ladling it into water, and re-melting it (this is termed to 'dragade'); it is due probably to the formation of a more homogeneous mixture; for the specific gravity and refractive index of lead-glass are so high that it is very apt to show streaks; and, moreover, the temperature of fusion is not so high as to cause any serious loss of alkali.

Mixing.—It is of the utmost importance that the constituents of glass should be thoroughly mixed. This is achieved in some works by hand, a workman turning over the powdered materials with a wooden shovel and passing them through a sieve until they are completely incorporated. Usually, however, a mechanical mixer is employed. The limestone is crushed with a 'Blake's crusher,' and subsequently pulverised by 'edge-runners.' It is afterwards sifted, and mixed. A convenient form of mixer consists of a hollow drum with blades disposed like the floats of a paddle, revolving in a box, of which the lower half has a cylindrical section. It has been recommended to mix the constituents in a wet condition, employing some of the enormous amount of heat which is wasted in all glass furnaces for the purpose of drying them after they have been thoroughly incorporated.

Proportions of constituents of glass.—It is impossible to do more than indicate the proportions in which the various ingredients of glass are mixed. A great deal depends on the temperature of firing, the length of time which the pot is exposed at different temperatures, and the amount of cullet mixed with the batch. Within certain limits, each manufacturer exercises his own judgment. An analysis of the finished glass throws little light on the amounts of the raw ingredients used. For if sulphate of soda be employed, a considerable proportion is removed by skimming, inasmuch as not all the sulphate enters into reaction with the silica. Again, a not inconsiderable proportion of alkali is lost by volatilisation; and lastly, the composition and quantity of cullet present must be a factor. However, we shall give certain general considerations which may serve as guides.

TABLE I.—POTASH-LIME GLASS.

—	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
						A—Batch						
SiO_2 .	100	100	100	100	100	100	100	100	100	100	100	100
K_2CO_3 .	50	60	50	34	35	66·75	70	60	50	52	40	42
$Ca(OH)_2$	15	20	—	15	—	—	20	CaO 10	—	—	18	—
$CaCO_3$.	—	—	20	—	26	33	—	—	22·5	11	—	17·5
As_2O_3 .	0·25	0·5	1·5	—	—	1·66	1·66	—	0·25	—	—	—
KNO_3 .	—	1	1·5	—	—	6·66	6·66	—	1·5	—	—	—
MnO_2 .	—	—	0·05	0·33	0·5	0·2	0·20	—	1·5	0·5	—	—
Smalt .	—	—	—	—	—	0·05	0·05	—	—	—	—	—
						B—Loss						
K_2O .	5	6	6	4	4	8	8·5	6	5	5	4	4
CO_2 .	14	17	25	11	23·0	36	22·5	17	24	20	11·5	19·5
Glass-gall	5	6	—	—	3·5	—	—	6	5	5	4	4
As_2O_3 .	0·25	0·5	1·5	—	—	1·66	1·66	—	0·25	—	—	—
N_2O_5 .	—	0·5	0·75	—	—	3·5	3·5	—	0·75	—	—	—
						C—Percentage of glass.						
	85 p.c.	83 p.c.	82 p.c.	90 p.c.	81 p.c.	76 p.c.	82 p.c.	83 p.c.	80 p.c.	81 p.c.	87 p.c.	82 p.c.

Of these the first five are for potash crystal; Nos. 6 and 7 for Bohemian mirror-glass; Nos. 8, 9, and 10 for Bohemian hollow-glass, for white bottles, &c. No. 11 Bohemian combustion tubes; and No. 12 Bohemian plate-glass.

TABLE II.—SODA-LIME GLASS.

—	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
					A—Batch						
SiO_2	100	100	100	100	100	100	100	100	100	100	100
Na_2CO_3	33·3	62·5	34	30	35	—	—	—	—	—	6
Na_2SO_4	—	—	—	—	—	44	50	44·6	32	30	35
CaO	14·3	—	—	—	—	6	—	—	—	—	—
$CaCO_3$	—	7·5	14·5	35	40	—	20	18	45	30	30
Coke	—	—	—	—	—	3	3	3	2	3	3
MnO_2	0·16	0·25	0·25	0·25	0·25	—	—	—	—	—	—
As_2O_3	—	0·20	—	0·20	0·20	—	—	—	—	—	—
					B—Loss						
Na_2O	3	5·25	3	5	3	3	3	3	2	2	3
CO_2	12·5	27	18·5	27	30·5	—	9	8	19·5	13	15·5
Glass-gall	3·5	6·25	3·5	3	3·5	2	2·5	2	1·5	1·5	2·5
As_2O_3	—	0·20	—	0·2	0·2	—	—	—	—	—	—
SO_3	—	—	—	—	—	23	27	23·5	17	16	18
					C—Percentage of glass						
	87 p.c.	77 p.c.	83 p.c.	79 p.c.	79 p.c.	82 p.c.	76 p.c.	78 p.c.	78 p.c.	80 p.c.	78 p.c.

No. 1 is for French mirror-glass; Nos. 2, 3, 4, and 5, French plate-glass; and the remainder for plate of second quality.

TABLE III.—BOTTLE-GLASS, AND LEAD-POTASH GLASS.

—	I	II	III	IV	V	VI	VII
			A—Batch				
SiO_2	100	100	100	100	100	100	100
Na_2SO_4	—	25	—	—	—	—	—
Coke	—	3	—	—	—	—	—
Basalt	50	5	—	—	—	—	—
Wood-ashes	160	—	—	—	—	—	—
$CaCO_3$	—	34	—	—	—	—	—
Pb_3O_4	—	—	66·6	60	55	70	42
K_2CO_3	—	—	33·3	20	36	26	33·3
As_2O_3	—	—	—	—	1	—	—
KNO_3	—	—	—	—	—	3½	16·6
MnO_2	—	—	—	—	—	—	0·5
Borax	—	—	—	—	—	4	—
			B—Loss				
Na_2O	8	2	—	—	—	—	—
K_2O	—	—	2	1	2	1·5	2
Glass-gall	20	3	—	2	—	—	—
N_2O_5	—	—	—	—	—	1·5	8
CO_2	50	15	10·5	6	11·5	8·5	10·5
O	—	—	1·5	1·5	1·0	1·5	1·0
SO_3	—	12·5	—	—	—	—	—
As_2O_3	—	—	—	—	1·0	—	—
			C—Percentage of glass				
	75 p.c.	80 p.c.	93 p.c.	94 p.c.	92 p.c.	93·5 p.c.	89 p.c.

Nos. 1 and 2 are receipts for coarse bottle-glass; the remainder for lead-glass. In all the last cullet is added, but its influence has not been taken into consideration.

The above tables show how much glass may be theoretically produced from given constituents, allowing for loss as skimmings, or as it is termed 'glass-gall,' and by volatilisation of alkali. The numbers must be taken as merely approximate; but the process is one which any manufacturer can carry out himself. These tables are abridged from *Die Glasfabrikation*, by W. Stein. Section A shows the proportions of raw constituents in the batch; section B the loss of various constituents, and section C the weight of glass obtainable from 100 lbs. of batch. Here the addition of cullet would, no doubt, considerably modify the results, as well as the temperature of the furnace, and the duration of the firing.

Glass for optical purposes may have a very varied composition. It may contain besides the usual constituents, phosphoric and boracic acids, added as phosphate or borate of sodium or potassium, and as oxides, barium, or zinc. An exhaustive statement of the refractive and dispersive indices of optical glass manufactured at the Technical Laboratory at Jena, may be found in the *Zeitschrift für Instrumenten Kunde*, 1886, pp. 338–9.

A glass has been made by Lamy in which the alkali is replaced by thallous oxide, the carbonate being substituted for potash in lead glass. It possesses of all glasses the highest specific gravity and refractive index. A special glass has recently been manufactured for the purpose of making thermometers, where it is of importance that the bulbs should not alter their capacity after frequent cooling and heating (Wiebe, Akad. d. Wissensch. zu Berlin, 1885, 629). The following receipts are given:—

	SiO_2	Na_2O	K_2O	ZnO	CaO	Al_2O_3	B_2O_3	
I.	67·5	14	—	7	7	2·5	2	=100
II.	69	14	—	7	7	1·0	2	=100
III.	52	—	9	30	—	—	9	=100

The first of these is the most easily worked.

Translucent, opalescent, or white glass may be made by means of the following mixtures.

Tin-enamel. Lead and tin are heated together; sometimes equal parts are employed, or as little as 15 parts of tin to 100 parts of lead. The metals oxidise, and the glass is produced by fusing together:—sand 100 parts, pure potash 80 parts, mixed oxides of tin and lead 200 parts.

Arsenic-enamel. Sand 100, potash 16, lime 6, red lead 130, saltpetre ½, white arsenic 10 parts; or sand 100, red lead 200, potash 60, white arsenic 30 parts.

Calcium phosphate, or bone-ash, makes glass turbid and white; thus:—sand 100, soda-ash 45, slaked lime 16, bone-ash 6, arsenious oxide 3 parts. A smaller proportion of bone-ash (2 to 4 per cent.) gives an opal glass. Such glass transmits reddish light. It may also be made, using red lead, thus:—sand 100, potash 25, red lead 75, bone-ash 8 parts. The addition of arsenious oxide to one of the above mixtures increases the fusibility while decreasing the transparency.

The presence of *fluorides* also produces milkiness. Glass rendered opalescent by them does not transmit red light, but is pure milk-white. A mixture giving good results is: sand 100 parts, red lead 32 to 35, potash 27 to 28, fluor-spar 14 to 16. Cryolite may also be employed, but the glass is apt to devitrify. The ordinary mixture consists of: sand 100, soda-ash 14·6, cryolite 14·6, chalk 6 parts. Sodium fluoride may be substituted, thus: sand 100, sodium fluoride (containing 10 p.c. of carbonate) 21, soda-ash 3, china-clay 10, and chalk 7 parts. Such opalescent glass is much used for lamp-shades, for thermometer scales, and for ornamental work. Another variety may be produced by aid of zinc oxide together with cryolite, thus:—sand 100, cryolite 40, zinc oxide 10 parts. Alabaster glass, a substance which closely resembles alabaster in its translucency and surface, may be made by the following mixture:—sand 100, potash 40, borax 5, and talc (silicate of magnesia) 5 parts.

Coloured glass. The basis of coloured glass is one or other of the varieties of soda-lime, potash-lime, or potash-lead glasses already mentioned; the colour is produced by addition of metallic oxides. Care must be taken that the glass to be coloured is essentially the same as the white glass with which it is to be united in working, else the finished articles will crack owing to difference in coefficient of expansion by heat.

Blue glass (sky) contains 8 to 12 thousandths of black copper oxide.

Deep blue contains 0·15 p.c. of pure oxide of cobalt, or 0·35 to 0·4 p.c. of zaffre. A *pale blue* glass may also be produced by partial oxidation of glass, coloured by iron.

Amethyst glass contains 2 to 2·5 p.c. of black oxide of manganese; to prevent reduction, 4 to 4½ p.c. of saltpetre is added.

Green glass is made by adding 1 to 2½ p.c. of iron oxide and the same amount of copper oxide; 1 p.c. of saltpetre should also be present to maintain the iron in the ferric state. A good green may also be produced with 0·5 to 1 p.c. of chromium oxide, or with double the amount of bichrome, or by 2 p.c. of oxide of antimony and 1 p.c. of cobalt. A bottle-green colour may be produced by adding several p.c. of iron filings.

Yellow glass. This colour may be produced by wood; for example, by adding to 100 parts of the fresh batch (a soda-lime or a potash-lime glass—not a lead-glass), 2 to 3 parts of stripped birch or alder bark, or the charcoal resulting from charring horn. The carbon is apparently here the colouring-matter. The addition of sulphur also produces a yellow colour, owing to the formation of sodium or potassium sulphide. In this case also a lead-glass must not be used. A receipt is the following: sand 100, potash 50, lime 21, sulphur 1·5 parts. A yellow colour may also be made with manganese dioxide 10 parts, ferric oxide (ochre) 8 parts; or by adding 4 to 7 parts of antimonate of lead. Glass may be painted yellow with the following mixture—silver chloride, 2 to 2·5; red oxide of iron, 10; sulphide of copper, 0·5; stannic oxide, 1 part. Bohemian lime-potash glass is best adapted for this purpose: it is fired after the design has been applied. The colour varies from pale canary to deep orange, according to the amount employed. The silver thus acts as a stain.

Uranic oxide produces a *dichroic yellow-green colour.* It is produced by the addition of 2·5 to 3 p.c. of uranate of potash or ammonia. The product is best with a potash-lime glass, free from lead. A greener shade may be obtained by adding 0·25 p.c. of yellow uranate and 0·2 p.c. of copper oxide.

Orange-coloured glass contains 2 p.c. of ferric oxide and ⅔ p.c. manganese dioxide.

Red glass may be produced by copper or by gold. The copper must exist in the cuprous state; if oxidised, the glass turns green or blue; if reduced, dull red brown. Metallic iron is added to promote reduction. To an ordinary batch, 1 p.c. of cupric oxide and 1 to 1½ p.c. of iron smithy scales are added, and the mixture is fused and well stirred with an iron rod. The glass is colourless when withdrawn from the crucible, but turns red on cooling. If it is too long exposed to heat, the copper is partially oxidised, and the red colour changes to a dull brown. Another receipt is: sand 100, red lead 166, copper scales 7, tin oxide 7 parts; if on first fusion the colour is not obtained, the mass is broken up ('dragaded') and again melted until it acquires the requisite transparency and depth.

Another variety of red glass, more crimson than the former, is obtained by the use of gold. It is generally agreed that the colour is produced by the gold in a state of extremely fine division. The gold is added to the sand of which the glass is made in the form of a very dilute solution of chloride; the sand is then thoroughly mixed and dried. The other constituents of the glass are next added. It is well to add a little red lead to other varieties of glass and to employ some nitrate of potash. The proportion of gold to other ingredients is not greater than 1 per mille, and a fine rich colour may be obtained with even much less gold. The mixture is heated in a small pot for several hours to a very high temperature. The addition of a little oxide of tin is recommended. The pot is then allowed to cool, the contents are broken up and remelted: they then acquire the fine ruby colour desired. The addition of a small trace of cobalt gives the colour a bluish tinge. This glass is never used alone, but is made to coat the surface or the interior of colourless glass. Vessels thus coated are said to be 'flashed.' Should the gold agglomerate together the glass transmits blue light and reflects a reddish-brown colour.

Black may be produced by the mixture of several oxides—cobalt, copper, iron, and manganese; the presence of excess of any one oxide causes the glass to appear black, for it does not dissolve. The addition of 7 to 10 p.c. of sulphur also yields a black glass. It is known as 'hyalithe,' and has long been made in Bohemia. It is probably due to the formation of a trace of iron sulphide.

Aventurine glass contains either finely divided copper, or, as is sometimes believed, cuprous oxide. It is deep yellow in colour, and full of sparkling metallic-looking red scales. Von Pettenkofer and also Clémandot give the following receipt:—cullet 300, cuprous oxide 40, and smithy scales 80 parts. Hautefeuille, who has conducted exhaustive experiments on the manufacture of aventurine gives this process:—crystal 2,000, saltpetre 200, copper turnings 125, ferric oxide 60; or, sand 1,500, chalk 357, dry carbonate of soda 801, carbonate of potash 143, saltpetre 200, copper turnings 125 parts; or, white soda glass 1,200, sand 600, carbonate of soda 650, saltpetre 200, copper turnings 125. When the glass is liquid, 38 parts of cast-iron filings, rolled up in paper, is thrown into the pot, and the mixture is stirred with a red-hot iron. The glass becomes blood-red, opaque, and full of small bubbles; the draught of the furnace is stopped, the pot is covered with a lid, ashes are heaped over it, and it is allowed to cool very slowly. Next day, on breaking the crucible, aventurine is found to have been produced. But it is difficult to produce a good article owing to the streaky nature of the product or to the prevalence of bubbles; the mass is sometimes striated, and sometimes the crystals are too fine. Hautefeuille finds that the crystals do not amalgamate with mercury, and hence concludes them to consist of cuprous silicate.

Chromium aventurine was discovered in 1865 by Pelouze. It is produced by heating the following mixture:—sand 250, carbonate of soda 100, calc-spar 50, bichrome 20 to 40 parts. This glass contains 6 to 7 p.c. of chromium oxide, of which not more than one half is combined; the uncombined portion is present in the form of brilliant crystals. With more than 50 parts of bichrome it becomes very difficult to fuse.

Iridescent glass, displaying prismatic colours on the surface, has evidently been produced by the action of water and carbonic acid for centuries on Roman glass. The alkali has been partially removed from the surface layers, producing interference colours caused by a thin film on the surface. This effect may be imitated by heating the manufactured article with water containing 15 p.c. of hydrochloric acid under pressure (Fremy and Clémandot); or, more easily, by exposing the glass while hot to the fumes of stannous chloride, by sprinkling a little of that salt on the ledge of the furnace while heating the vessel (Powell).

Cracked glass, in which the vessel has the appearance of small irregular cracks over its surface, may be made by plunging it while hot into water, but withdrawing and reheating it before it has sprung to pieces. Another method is to roll the glass, while soft, on a table covered with thin flat fragments of broken glass, then to heat and form the vessel. In the latter case glass of a different colour may be used and a varied effect produced.

VESSELS FOR MELTING GLASS.

Pots &c. The manufacture of pots is, as a rule, undertaken by the glass manufacturer. It is necessary that they should withstand a temperature of about 1000°C. (1832°F.) for many months, and hence they must be made of very refractory fireclay. Fireclay consists essentially of silicate of alumina; that employed for the purpose in England comes from Stourbridge; in France from Forges-les-Eaux (Seine Inférieure); and in Germany from Ardennes (Belgium), and from Klingenberg. An idea of the composition of the clays can be gathered from the following analyses:

——	No. 1	No. 2	No. 3	No. 4	No. 5
Silica	71·6	64·2	71·7	57·4	68·0
Alumina	26·0	32·2	22·3	38·0	29·0
Ferric oxide	1·2	2·4	4·5	1·8	0·2
Lime	0·1	—	0·5	1·8	—
Alkalis	1·1	1·2	—	1·0	0·8
	100·0	100·0	99·0	100·0	98·0

No. 1 clay from Forges-les-Eaux; No. 2 from Ardennes; No. 3 from Stourbridge; No. 4 from Klingenberg; No. 5 from Bohemia. All these clays in their combined state contain water, varying from 6 to 20 p.c. During firing this water is expelled and the pot contracts considerably.

As the clay may contain impurities in the shape of pyrites or lumps of limestone, these have to be removed. This is done by breaking it up into small lumps and removing the foreign substances by hand. The clay is afterwards dried and carefully sifted. Four qualities of Stourbridge clay are sold. The best quality, found below the coal-measures, is employed for glass-pots. As the clay in its pure state would contract too much on firing, and the pots would therefore be covered with small cracks, a quantity, usually one fifth of the weight of the clay, of the material of old pots, freed from adhering glass, and finely ground, is mixed with it. The mixture is tramped under foot, and is preferably left for many months to mature. This doubtless has for its object the combination with the clay of water present as such ; it renders the clay more plastic. Abroad, pots are made with help of a mould; but English manufacturers consider that better results are obtained with hand-made pots. A slab of wood or stone is sprinkled with a thin layer of sand, and, beginning at the middle of the bottom, the workman constructs a spiral of clay, each piece being thoroughly kneaded with the hand and incorporated with the clay previously laid down. Scratches are then made in the first layer, and a second layer is laid, still proceeding spirally, on the top of the first, until a sufficient thickness of clay has been accumulated for the bottom of the pot. Then the sides of the pot are built up in a similar manner, adding small rolls of clay and pressing them into the portions already laid, always proceeding spirally. The utmost care is taken that the whole structure is solid and that the clay does not inclose air. Several crucibles are kept in hand at one time, so that one may have an opportunity of setting while the workman is engaged at another.

Form of the crucibles.—These may be open, for soda or potash-lime glass, or closed, for potash-lead glass. The following woodcuts show the various forms in use, or which have been proposed:—

FIG. 1.

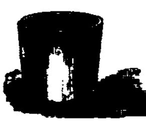


FIG. 2.

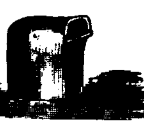
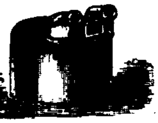


FIG. 3.



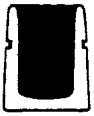


FIG. 4.

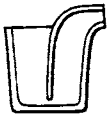


FIG. 5.

No. 1. Plate or sheet-glass crucible.

No. 2. Flint-glass crucible.

No. 3. Pot with shoulders, for supporting smaller pots for coloured glass.

No. 4. Plate-glass melting-pot: section.

No. 5. Pot with division for continuous working: section.

Other varieties of divided pots have been proposed, but these do not appear to have come into general use. They are probably less durable than those of simpler form, and are certainly not so easily constructed.

After the pots have been made they are left for a time, varying from three to twelve months, at the ordinary temperature, or in a gently warmed room. A stock of pots is always kept so as to replace any casualty without delay. When required, the pot is heated to bright redness in a small subsidiary furnace, termed a 'pot arch,' before being moved in on an iron barrow, to replace a broken pot. The heat is very gradually raised for from four to seven days before it attains its final temperature. The duration of life of a pot is, according to Peligot, from one to three months; but English pots are said to last at least six months and often a year. In some cases, where several workmen withdraw glass from one pot, a circular ring of fireclay is placed in the pot, and the glass is withdrawn from the centre. In flint-glass pots such a ring is sometimes inserted before the hood is built.

The description of Dr. Siemens' tank furnace, which supplies the place of pots, will appear below.

Furnaces. It is essential that gaseous fuel be employed in heating the glass-pots. In the old style of furnace, which with some modifications is still largely used in Britain, the grate is below the bed of the furnace, and the products of combustion pass up through a hole in the centre of the bed on which the pots rest. Various devices have been conceived to promote thorough combustion, such as the admission of air through side channels, the passage of the gases through layers of red-hot coal before they burn, and stoking from below in a methodical manner. In the Siemens furnace, his regenerative principle is applied, the gases being produced in a separate generator and burned in the chamber itself. Such furnaces are employed in heating pots. The tank furnace, which permits of continuous working, is also usually heated on the regenerative principle. A fair idea may be gained of the patterns in use by descriptions of the ordinary furnace, provided with a 'Frisbie's feeder' for stoking; Boetius's furnace; and the Siemens regenerative furnace, applied to a tank. It is necessary, however, first to consider the materials of which the furnaces are built and method of building.

Material of furnaces.—As the furnaces have to withstand intense and continuous heat for several years, they must be built of very refractory material. Fire-clay alone is not always refractory enough, and bricks composed of pure silica, obtained from Dinas, Valley of Neath, Wales, are employed for the crown or vault of Siemens furnaces. For the ordinary furnace, fireclay alone, or clay mixed with pebbles, broken up into irregular fragments by being heated and quenched in water, and then ground, is made use of. It is found that this material, owing to the angular form of the particles, causes the clay to bind together better than if sand were used. The bricks are not fired before the furnace is built; but they are dried, and during building they are made to adhere together by rubbing the brick to be added against those already laid. The adhesion of the dry clay is so considerable that very flat domed or arched roofs can be constructed without any props from below. While clay contracts during heating, bricks containing silica expand slightly, and a furnace constructed with the latter requires less patching after the temperature has been raised. It is evidently of the utmost importance, when open glass-pots or a tank is used, that no droppings from the roof should enter the pots or tank, else the glass becomes 'stony,' owing to the presence of small unfused particles.

As a rule, the furnaces are built by the same workmen who make the glass-pots; but in some parts of Germany special workmen journey about, whose sole business it is to build furnaces.

Although it is advisable to construct the domes or vaults of a furnace of siliceous bricks, the bed of the furnace must be made of bricks more basic in character, else the glass, which occasionally runs over them when a pot breaks, would corrode them and render them useless. The bed is therefore constructed of bricks of ordinary fireclay.

In some cases the necessity of specially shaped bricks for the dome of the furnace is avoided, by building up the dome-shaped part with moist clay by hand, after the circular walls have been laid in the same manner as pots are made. The disadvantage of this plan is that the furnace must lie unused for many months — even six or eight—before it can be fired, in order that the clay may dry. It is, therefore, never resorted to in this country. Moreover, the clay contracts on firing, and the cracks have to be repaired before the furnace is fit for work.

We shall now describe some of the furnaces in actual use, choosing the types previously referred to.

1. *Old-fashioned flint-glass furnace, with Frisbie's feeder.* As the glass-pots must be heated entirely with gaseous fuel, the firebox is placed below the furnace, and entrance for the stokers is through an arched passage, A, fig. 6. B, B, are the fire-bars, in the centre of which is placed Frisbie's feeder, which will afterwards be described in detail. The fuel is small coal. The flames and products of combustion pass through a short vertical shaft C into the body of the furnace, striking against the vaulted roof D, by which they are deflected downwards towards the sides of the chamber, heating the pots E. They escape through the short flues F, one of which is situated between each two pots, so that in a furnace with twelve pots there are twelve flues. The entrance from the chamber into the flues is at the bottom of each; and they pass through the side of the vaulted roof, and deliver into the wide open stack of the furnace G. It is of importance that smuts and smoke should not enter the furnace, especially when open pots are employed; and the stoking of the furnace must therefore be regular and constant. One of the best devices for achieving this is the mechanical stoker devised by Mr. Frisbie, of which a cut is given below. The object is to introduce small charges of coal in the middle and at the bottom of the heap of burning fuel, so that combustion takes place at the top. The coal introduced is heated by the fuel burning above it, and the resulting gas passes through the glowing mass and burns at the top. When the gaseous constituents of the coal have been distilled off and burned, the carbonaceous matter is pushed up by a fresh charge from below. Other advantages are, that the grate-bars are in contact with comparatively cold fuel, and thus last a long time; and that no sudden inrush of cold air takes place during stoking. This is of great importance, for the quality of the glass and the life of the pots depend on the regularity of the temperature in the furnace.

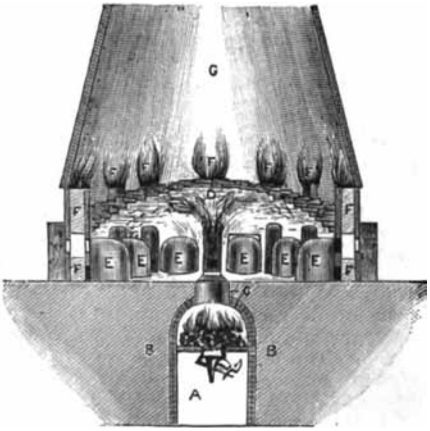


FIG. 6.

In the cut, A A are the fire-bars; B is a hole through the grate; C is a hopper with a movable bottom, D, provided with a plunger for raising and lowering it; F is a shield or apron, which closes the bottom of the grate when the coal has been charged; G is a rocking-bar, attached to H a handle, and to K, the lever which carries the hopper below the grate; L is a catch, and M the arm which supports the hopper and the apron. C is charged with fuel, and by means of the handle H forced under the fire-bars; this motion raises the movable bottom D, forcing the fuel into the aperture at the bottom of the grate; the motion is then reversed, and the hopper withdrawn.

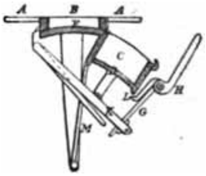


FIG. 7.

2. *Boetius's furnace.* Complete combustion is also attained in this variety of furnace, by the introduction of heated air to mix with the gases distilled from the coal and with the smoke. It is shown in fig. 8. It is employed in many glass works, and is simpler in its construction and less costly than Siemens' furnaces, although not so economical in fuel. The figure nearly explains itself. The fire is stoked through the openings A, A, air enters through passages opposite B, B, as shown by the arrows; and also through other flues C, C, so that on mixing with the gases they may be completely burned; air also enters through a perforated column standing on the hearth, opposite D. This column, however, retains any glass reaching it owing to the

breaking of a crucible, and is cleaned only with great difficulty.

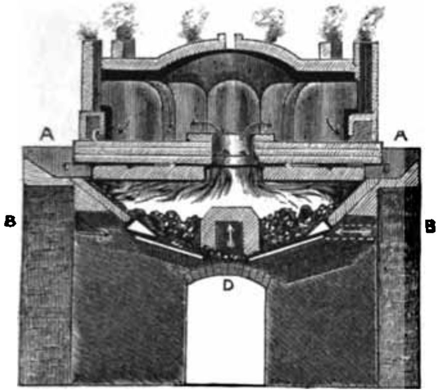


FIG. 8.

3. *Siemens' furnace.* The special feature of this furnace is that the gas is produced in a 'producer' entirely separate from the furnace; and that after the gas has been burned in the furnace, the products pass into two chambers below the furnace, filled with loosely built bricks, to which they impart their heat. After a certain time, certain valves are shut and opened by means of which gas from the producer passes through one of these chambers, and air through the other; the heated gas and air then burn in the furnace, and the products are led through two similar chambers to which they impart their heat. Again, on reversing the current, the last pair of chambers yield up their heat to the gas and the air, while the first pair are heated by spent products. By this means the heat is economised, and the furnace is heated with gaseous fuel. In Siemens' newer forms of furnace, radiant heat alone is employed.

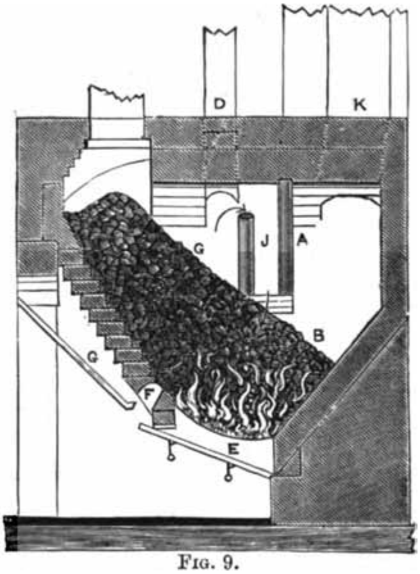


FIG. 9.

A recent form of producer is shown in fig. 9. 'The fuel B is contained in one compartment of the producer, which is divided by the curtain wall A; by this means the zone B, where carbonic oxide is mostly produced, is separated from the zone C where hydrocarbons distil from the ignited fuel. The grating E, at the bottom, admits air and allows ashes and clinkers to escape. If more air is required for combustion it may be admitted by lateral openings of which one is shown at F. Air is driven in by a steam injector G, so placed as to avoid blowing air or gases down through the grating E. The hydrocarbon gases, which collect in the chamber C, are led away by channels J which heat the hydrocarbon products from the zone C and direct them on to incandescent fuel in the zone B, whereby they are further heated and converted into permanent gases. The curtain-wall A need not absolutely separate the chambers B and C from each other, for if a small portion of the volatile gases should leak into the carbonic oxide compartment, they would come in contact with incandescent fuel, and the desired effect would thereby be ensured' (S. C. I. 1885, 441). The gases finally escape through the flue K, and are led to the regenerators.

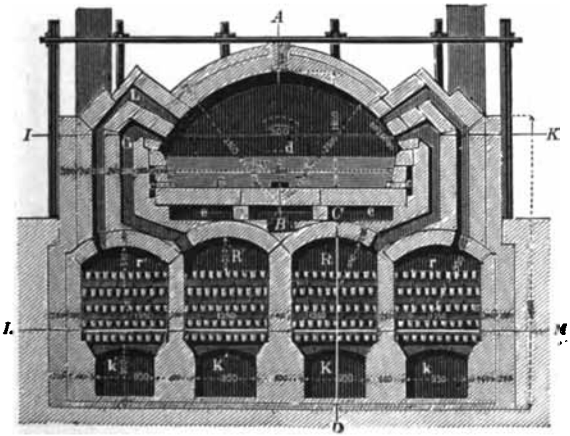


FIG. 10.

This device for heating may be applied to furnaces similar in design to those already shown, the regenerators being situated below the chamber containing the glass-pots. But in order to show the design of Siemens' tank-furnace, the regenerative process may be described as applied to that method of glass-making. The furnace is shown in the accompanying figures (10, 11, and 12). An elevation of the furnace is shown in fig. 11, along the line A B in the diagrams of the plan, fig. 12, and C D of the section, fig. 10; and the section, fig. 10, follows the line E F of the plan. The tank-furnace is divided into three compartments, A, B, C. The first serves to melt the glass; in the second it is refined; and from the third it is withdrawn for working. It passes from the first to the second compartment through an opening in the partition W; and from the second to the third through the hole *b* in the partition V. The metal is withdrawn through the working places C; while E in fig. 12 is the working platform; *e, e, e*, fig. 11, are draught-flues which serve to keep cool the bottom and sides of the trough; and *d*, fig. 11, is the opening through which the batch is introduced.

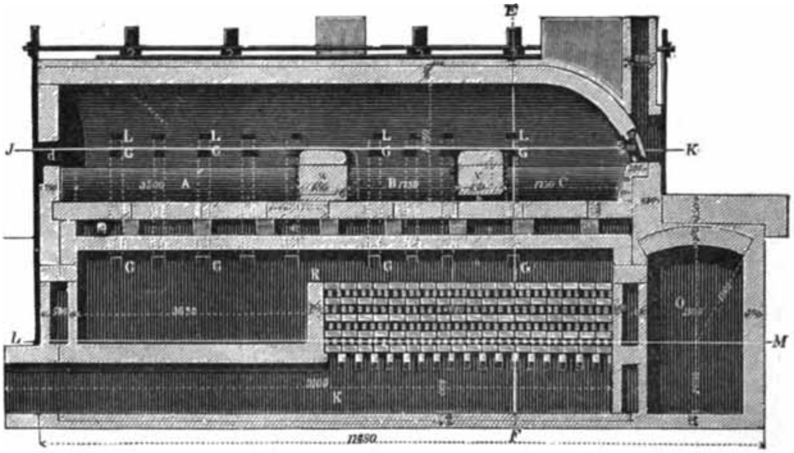


FIG. 11.

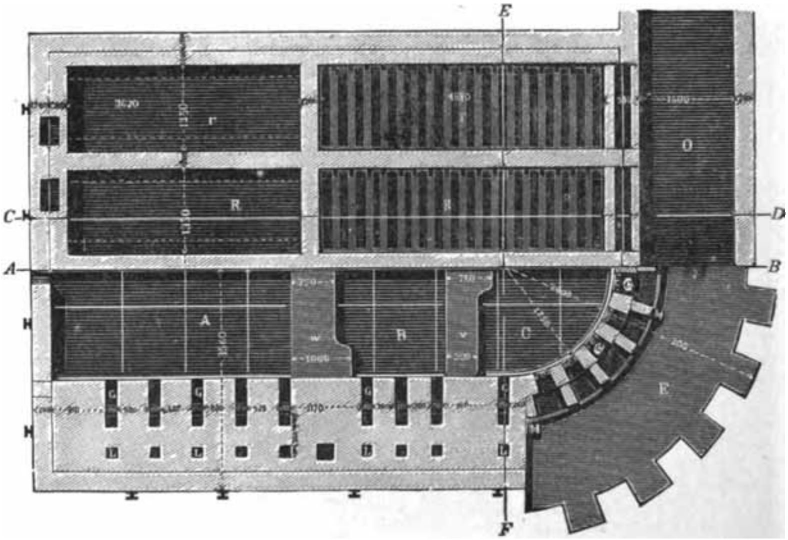


FIG. 12.

The regenerators R *r*, R *r* (figs. 10 and 12) lie below the furnace. They are worked in pairs as lettered. The chambers R R are used for heating the entering gas, and *r r* the air. The gas passes from the chambers R R through the flues O G into the furnace; and the flues L L admit the air. The openings of the air-flues lie immediately below the gas-flues, so that the flame may strike the tank as directly as possible. The chambers R R are connected with the reversing valve by means of the flue K K′ (fig. 10), which regulates the direction of the gas-stream; while the air-stream is reversed by a valve with which the flues *k k′* communicate. For purposes of repair, the regenerators are accessible through the arched way o (fig. 11). The numerals in the cuts give the dimensions of the furnace in millimetres. By his plan of employing radiant heat, Mr. Siemens claims to secure a higher temperature at a smaller expenditure of fuel. The temperature is highest at A and lowest at C. One of these furnaces employed by Mr. Siemens contains 130 tons of glass, and produces a ton of glass per hour, at an expenditure of about 14 cwt. of coal per ton. In some furnaces the second partition V is dispensed with, and floating rings are substituted, from the middle of which the glass is withdrawn. The ring is the equivalent of the second partition. Such rings or floating vessels vary in size, according to the quantity of metal to be withdrawn in a given time; for the viscous glass takes some time to replace that withdrawn. 'The second and third compartments communicate with each other at the bottom, so that glass shall be gathered only from the most dense, or in other words, the best stock in the floating vessel. For the production of window-glass of high quality vessels with loose rings are preferred, as the rings may from time to time be removed and exposed to the heat of the furnace in order to clear them of adhering matter formed by the decomposition of their interior surfaces, which otherwise would deteriorate the glass.

Preparation of 'metal,' melting, &c. The first operation is to introduce the glass-pot into the furnace. The pot is previously heated in a small baking-oven or pot arch, an arch closed with iron doors at one end and walled up at the other. In this oven the crucible stands on three fireclay bricks. The temperature is raised very cautiously, the full heat not being attained until from four to seven days. The glass furnace is urged to its utmost temperature so as to render the removal of the broken crucible which it is intended to replace as easy as possible by melting the escaped glass. The crucible is then emptied of glass by ladling. The front of the furnace is broken through, and the bed made smooth and freed from spilt glass by chipping it away with long chisel-edged bars. The broken crucible is grasped by long pincers, and tilted over on to a carriage consisting of a large three-pronged fork on wheels. The fork is inserted into the mouth of the broken crucible, which is tilted over, and by depressing the handle of the fork, the crucible is raised, and removed. The new crucible is also tilted forwards in the baking oven, and the fork inserted in its mouth; it is then lifted by depressing the handle of the carriage, and conveyed to the glass furnace. It is then tilted into an upright position by means of tongs and levers. As the operation takes place with an open furnace, and as the crucibles are white hot, it is attended with considerable difficulty and requires great skill. The front of the furnace is then built up.

The first operation is to glaze the new pot. To effect this, a charge of broken glass or cullet is melted in it. The object is to cover the wall of the crucible, so that it may not be attacked by the soda or potash introduced with the batch. When this has been accomplished, the 'founder' fills the pots as quickly as possible by means of a shovel with alternate layers of cullet and batch; and the furnace is then urged to a high temperature. In six or seven hours the charge is in quiet fusion, all effervescence owing to escape of sulphurous or carbonic anhydrides having ceased. But the pots are not nearly full, for the mixture occupies much greater space than the metal. The pots are again filled up in the same manner, and in three or four hours more the second charge is melted. A third charge is then added, and sometimes a fourth, and in two or three hours more the pot is full of glass. During the fusion, bubbles of carbonic anhydride or of sulphurous anhydride are evolved from the carbonate or sulphate of the alkali and from the limestone; the sand remains suspended, and is slowly attacked and dissolved. This process of solution is termed 'refining.' If red lead be used, oxygen is evolved also, and the organic matter which may be mixed with the sand &c. is oxidised. It is with the object of oxidising the organic matter and also of stirring the glass, that a small quantity of arsenious acid is added; its oxygen is partially consumed for that purpose, and the excess, together with metallic arsenic, is evolved as gas. The addition of nitre to the batch has a similar effect. It is customary also to add a small quantity of manganese dioxide, so as to neutralise the green colour resulting from iron in the materials employed. It also has the effect of oxidising the green ferrous silicate to pale yellowish ferric silicate. White fumes of volatilised alkali are also seen issuing from the pot during fusion, and these coat the arch of the furnace. With prolonged exposure to heat the metal becomes more liquid, less full of bubbles, and is consequently more transparent. A scum, technically termed 'glass-gall,' now floats on the top. It consists of sulphates and chlorides of the alkalis. Its composition may be seen from the following figures:—

—	Window glass	Glass for table purposes	Bottle glass
Sulphate of soda .	83·32	90·51	55·92
Sulphate of lime .	10·35	6·00	25·11
Salt . . .	1·43	0·04	0·20
Glass, clay, &c. .	3·35	3·30	17·77

This matter is removed by means of a ladle. If, as in some cases, a fireclay ring floats in the pot, it is only necessary to skim off the gall from the interior of the ring. There is also the advantage that the exterior portions of the glass near the walls of the pot, which are apt to become stringy during the long heating, do not mix with that portion in the ring.

After the glass has been refined, the temperature is allowed to fall somewhat; but before this, samples are withdrawn and carefully examined as to colour, absence of bubbles, grit, striation, &c. The processes of fusion and refining occupy twenty to twenty-four hours. When all the pots are exhausted, they are refilled and the process begins anew.

Temperature of furnace. As a general rule, the temperature is estimated by the eye, and by the appearance of the glass. It would be advisable to know more accurately the precise temperature of the furnace during each operation, thus removing the element of uncertainty which rule of thumb always introduces. A set of cones containing varying quantities of potash, lime, iron oxide, alumina, and silica has been prepared; the method of using them is described in D. P. J. 261, 35–43. These cones melt at temperatures differing by intervals of approximately 30°C. from 1,145° to 1,745°; they are furnished by the Royal Porcelain Works of Berlin at a cost of 4*s.* 6*d.* per 100.

Manufacture.—The operations necessary to give glass the required form are conveniently classified under three heads—1. Manufacture of window-glass, sheet, and crown; 2. Manufacture of hollow ware; and 3. Casting plate-glass. These will be described in their order.

1. MANUFACTURE OF WINDOW-GLASS.

a. **Crown glass.** The principle of this process is the expansion to a disc by means of rapid rotation of a globe of glass affixed to a rod, with a perforation at that portion diametrically opposite to the rod. The operations are as follows. The workman, or gatherer, collects from 16 to 20 lbs. of glass from the pot on his rod, which he then swings round, so as to collect the glass on the 'nose' or end of the rod. This takes usually two dips in the pot. After cooling his rod by applying water, the glass is rolled on the iron table or 'marver' so as to give it a cylindrical form with a slight taper, fig. 13 (*a*). The apex of the cone is termed the 'bullion point.' While the rod is being rotated, a boy blows in, and expands the glass to a small bulb (*b*). It is again heated and blown, when it resembles a flask (*c*). By a third heating it is blown into a large globe (*d*). During this operation it is necessary that the bullion point shall remain diametrically opposite the rod, and to secure this the rod is placed on a stand, and the bullion point centred by means of a support into which it is inserted. While the rod is being revolved, and after it has somewhat cooled, a boy presses a piece of wood on the point, so as to make it flush with the surface of the globe; it then forms a small lump in the interior of the globe. The globe is again heated, withdrawn from the fire, and the rod is rapidly revolved, resting meanwhile in an iron support. Another workman presses a rod, termed a 'ponty,' tipped with molten glass to which the form of a shallow cup has been given, against the bullion point, when the globe assumes the form shown at *e*. The rod is then detached by cooling the neck of the globe with a piece of cold wet iron, and by a sudden tap, and the rod is then thrown into water so as to crack off the glass still adhering to it. This glass forms 'cullet' and is used for subsequent charges of fresh pots. The rod when cool is again used for a second gathering.

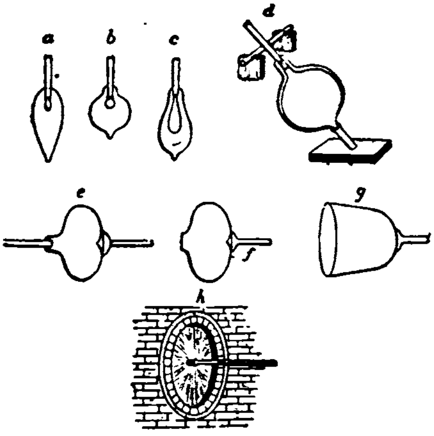


FIG. 13.

The globe now adheres to the ponty, and is open at the neck or 'nose' as shown at *f*. The globe is then inserted into the 'nose furnace' of which an outline sketch is shown at *h*. This furnace has a wide opening through which an immense body of flame is seen. With a screen before his face, the globe is revolved by the workman; the neck expands owing to centrifugal force; the intermediate form *g* is seen for an instant; and the next moment a large circular plate of glass is revolving in the flames. It is removed from the furnace still in rapid revolution, and laid on a support termed a 'whimsey;' the ponty is cut off with shears, and by help of an iron fork the plate is lifted into the annealing furnace, and piled on its edge against its neighbours. The collapse of such discs caused by their leaning on each other is prevented by the insertion at regular intervals of iron frames or 'drossers.' The temperature of the annealing furnace is gradually lowered for from 24 to 48 hours, till it reaches that of the atmosphere.

The tables are then divided in the warehouse by the 'splitter,' with help of a diamond, into two unequal parts, the larger containing the 'bull's-eye.' The size may vary from 50 to 70 inches, and its weight from 13 to 18 lbs. The usual diameter is 54 inches or thereabouts. Great judgment is required in the splitter, who has to classify the plates and split them in the most advantageous manner.

Owing to the method of manufacture, crown-glass is not quite regular in surface or thickness. There is considerable waste, the bull's-eye being re-melted; moreover, the size of the sheets is limited by the position of the bull's-eye. Yet this glass has a more brilliant surface than either sheet or plate-glass, and it is still preferred for that reason. It is, however, rapidly being ousted by its two rivals, the size of the sheets more than compensating for their lack of brilliancy. The manufacture is now, we believe, entirely confined to England.

b. **Sheet glass.** The principle of sheet glass manufacture is the blowing of a cylindrical globe, which is opened at the end and expanded into a cylinder. It is then detached from the rod, and the contracted portion near the rod cut off symmetrically; it is then split up one side by a diamond, placed in an auxiliary furnace to soften, and when soft, extended by rubbing with a flat instrument.

The preliminary operation is similar to that described for crown-glass. The clean rod being heated to redness in the 'shoe,' a small opening into the furnace at the right-hand side of the opening through which the pot is reached, the

gatherer collects a lump of glass or 'metal' weighing from 10 to 50 lbs. The usual weight is 15 to 20 lbs. It is placed on a wooden table or marver, kept moist so as to prevent its inflaming; or sometimes on a hollow iron block, kept cool by circulation of water in the interior, and covered with a layer of charcoal to protect the glass from scratches. Here it is rolled, assuming the shapes shown in fig. 14, *a*, *b*, and *c*. It is then reheated, and the workman takes his stand on a wooden frame, erected over a pit about 10 feet deep in front of the furnace. By swinging his rod and rotating it completely round his head and blowing alternately, the forms represented at *d*, *e*, and *f*, are successively taken, the cylindrical shape being given by rolling on the marver. The end of the cylinder is then opened by either heating it in the furnace and blowing it out, or, as this causes the edges of the cylinder to become thin, by applying a piece of hot glass so as to soften the closed end of the cylinder, and then blowing it. By the latter process a much smaller opening is made, and less glass wasted. A pair of widening tongs is then inserted, and the cylinder being revolved, the end takes the form shown at *g*. A ponty on which glass has been gathered, of the shape shown at *h*, forming a thick flat plate, is then pressed against the open edge of the cylinder, and the gathering-rod is cracked off by applying a cold iron. The cylinder is again heated, and the portion to which the rod was previously attached cut off with shears or cracked off by winding a thread of molten glass round it; its form is shown at *i*. It is laid on a table, and split while still hot by passing up the inside of the cylinder a diamond attached to a long handle and guided by a straight rod of wood. No time is lost in transferring it to the flattening furnace. This furnace, of which a sketch is shown at fig. 15, is conveniently heated by gas.

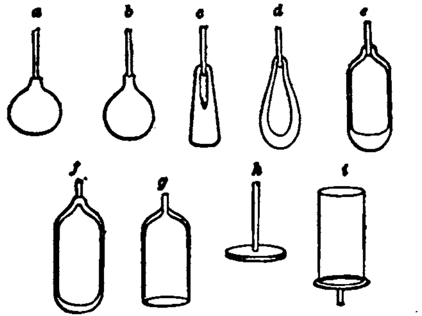


FIG. 14.

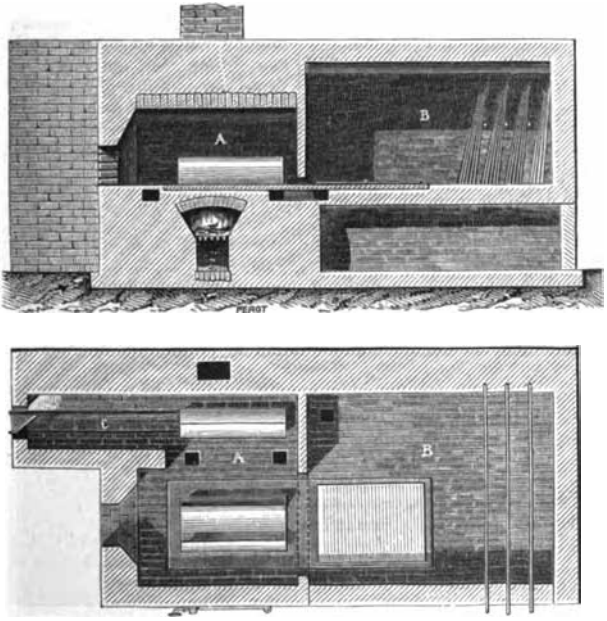


FIG. 15.

Various improvements in these furnaces have recently been introduced. Among them may be mentioned that of a revolving disc, in which the glass is placed and then brought into the warmer part of the furnace after being subjected to a preliminary heating in a cooler part. It was invented as long ago as 1826 by M. Hutter, of Rive-de-Gier. By still further revolving the disc, the plate passes again into a cooler part, and by a fourth quarter revolution, it is again brought opposite the opening, to be removed and replaced by another. By yet another plan, which is now largely used, the cylinder is placed on a platform on rails, which is gradually introduced into the hotter part of the furnace. In the figure given above, the cylinder is introduced through the flue C, supported on a clay base, curved so that the cylinder rests securely on it.

The clay support is pushed forward with an iron rod till it comes opposite the opening A. By this time it is at a red heat. From the support it is transferred by means of a long iron rod or croppie to the flattening stone, which is covered by a sheet of thick glass so as to protect the cylinder from the comparatively rough surface of the stone. The cylinder, with its cracked side uppermost, soon opens out into a sheet; it is then smoothed by aid of a 'polissoir' or rod of iron, tipped with a flat block of wood, kept moist to prevent its burning. After being flattened, it is pushed forward through the opening into the annealing chamber B, and when sufficiently rigid it is placed on its edge along with others previously flattened. As with crown glass, bars of iron are placed at regular intervals so as to furnish a support for the sheets. When the chamber is full, the fire is extinguished, and the sheets are allowed to cool for several days. The adhesion of the cylinder to the flattening plate is prevented by sprinkling the latter from time to time with a little powdered gypsum or sulphide of antimony, or by throwing in a little lime dust. It is found that a smoky flame retards the devitrification of the glass, but under any circumstances the glass plate covering the flattening sole is devitrified in a few hours and must be replaced by a fresh one. If the flattening stone runs on rails, the plate when flattened is withdrawn and transferred to the annealing furnace. Half an hour is sufficient to anneal a thin plate. The sheets are then examined and classified, according to their quality and thickness. The standards of thickness are 15, 21, 32, 36, and 42 ounces per square foot. A very large amount of such glass is now made for glazing windows and for photographic purposes. The glass is, however, not so brilliant as crown glass, and is frequently marked by faint striæ, produced during the unfolding of the cylinder.

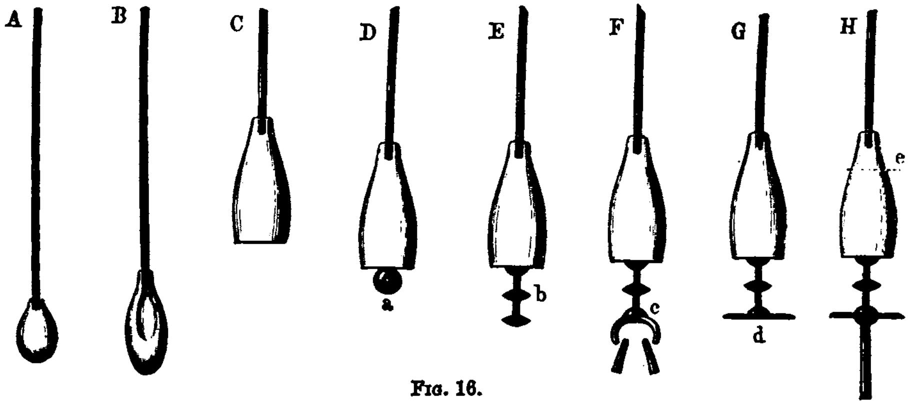


FIG. 16.

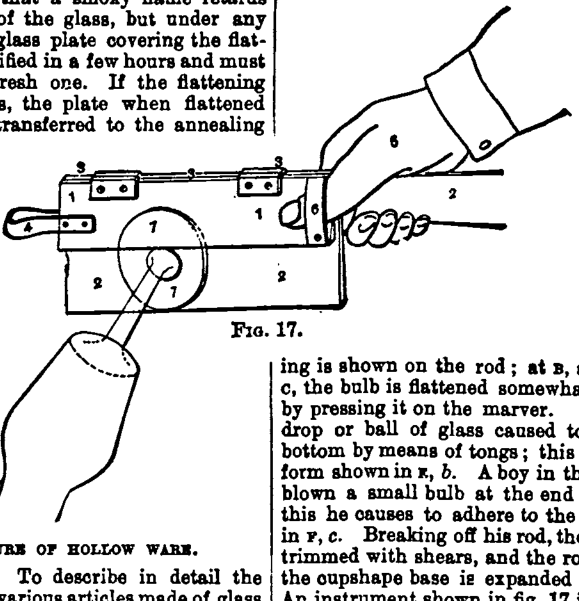


FIG. 17.

2. MANUFACTURE OF HOLLOW WARE.

a. **Blown glass.** To describe in detail the manufacture of the various articles made of glass would be beyond our province. As typical examples we shall describe the manufacture of a wineglass, and of a glass jug. The various stages are shown in figures 16 and 17. At A, a gathering is shown on the rod; at B, a small bulb; at C, the bulb is flattened somewhat on the bottom by pressing it on the marver. D shows a small drop or ball of glass caused to adhere to the bottom by means of tongs; this ball is given the form shown in E, *b*. A boy in the meantime has blown a small bulb at the end of his rod, and this he causes to adhere to the stem, as shown in F, *c*. Breaking off his rod, the rough edges are trimmed with shears, and the rod being whirled, the cupshape base is expanded into a foot G, *d*. An instrument shown in fig. 17 is often used for making the feet regular; such feet are called 'cast-feet.' The foot is now held in a spring tool (fig. 18), or in lieu of this a working rod is sealed to the foot as in H, and the bowl being detached from the rod *e*, it is trimmed even with shears and adjusted to the right dimensions by means of callipers, which, it should have been mentioned, are used at each operation to ensure uniformity in pattern. If the working-rod is used to hold the foot of the glass, as in H, its removal leaves a lump which has afterwards to be removed by grinding. The process of manufacture of a moulded jug is shown in the next figure. The bulb is blown into a mould as shown at A (fig. 19); a ball of glass is then attached, subsequently becoming a foot, as for the wineglass. The neck of the jug is then trimmed with shears (B), moulded (C), the handle attached (D), bent (E), and sealed at its other end (F).

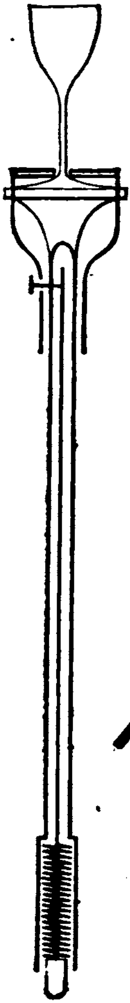


FIG. 18.

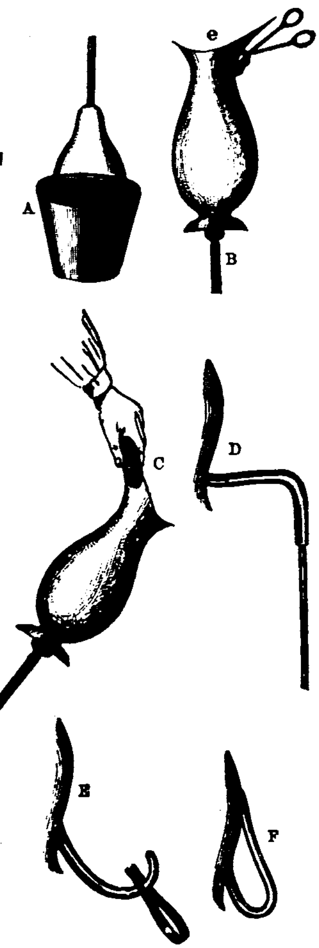


FIG. 19.

As these operations demand the utmost manipulative skill, it need not cause surprise to learn that the apprenticeship of a glass-blower lasts seven years, and that the union is one of the closest. Many men, of course, acquire the necessary dexterity in a much shorter time, and others never acquire it; the latter remain to the end of their lives 'boys,' and undertake only the minor operations requiring less skill. The exposure for many hours a day to such intense heat causes profuse perspiration, and in many works the men are provided with soda-water to restore the lost moisture. The amount drunk is often a dozen bottles a day to each man.

b. **Glass bottles** are invariably blown in moulds. For ordinary wine-bottles the glass is inferior in quality. The composition of the batches has been shown in Table III., columns 1 and 2. Slag, as it comes from the ironworks is sometimes used. At Finedon, in Northamptonshire, the glass manufactory is placed close to the blast-furnaces of the ironworks, and the molten slag is directly conveyed to the glass-furnaces, where it is mixed with alkalis and sand in the charging tank. For such coarse articles where clear colour and absence of flaws is of little moment, a tank-furnace is commonly used. In making bottles five persons are usually employed—viz. the 'gatherer,' the 'blower,' the 'wetter-off,' the 'workman,' and the 'boy.' The glass is collected by the 'gatherer,' blown and trundled on the marver to a conical form by the 'blower,' who then opens the mould, closes the mould with his foot after inserting the conical bulb, and blows the bottle so that it fills the mould. It is then passed to the 'wetter-off,' who detaches it from the rod by touching its neck with a wet tool. The 'workman' next forms a lip; the bottle is fixed in a frame, the neck is heated in the furnace, and a small band of molten glass is coiled round it and shaped by a tool for the purpose shown in fig. 20. The 'boy' then carries it on a fork to the annealing oven.

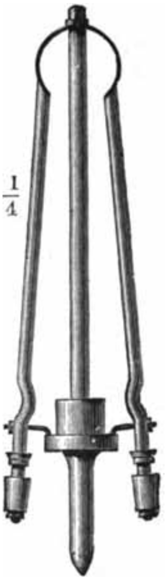


FIG. 20.

A machine has been invented and patented by Mr. Ashley by which the process of bottle-making is greatly assisted by machinery. We quote from the *Times* report of the operations (January 25, 1888): 'This machine consists first of a receptacle called a "parison," in which the exact quantity of molten metal required to form a bottle is placed, there being no overplus or waste. At the lower part of the parison is the collar mould which forms the lip. In the centre of the mould is a device for working up the metal to form the collar. This portion of the mechanism is hollow, and is in connection with a reservoir of compressed air, which is maintained at a steady pressure of about 50 lbs. per square inch. The molten metal is prevented from entering the hollow part of the mechanism by a movable button. After the collar or lip has been formed, the mould, which is in two parts and is still open, is turned upside down, and the mass of plastic molten metal begins to elongate by gravity, the air being gently admitted into the centre of the bloom. This latter having attained the required length, the mould is closed and the full pressure of air is gradually brought to bear, which causes the metal to fill every portion of the mould. The mould is then opened and the bottle removed for annealing, the result being a perfectly formed bottle having the same thickness of glass throughout, as was demonstrated by breaking and cutting several bottles.' The time occupied in making a bottle by this process is said to be fifteen seconds; the output is ten times that of the hand-made bottles, and the number of hands employed can be reduced, according to Messrs. Sykes, the licensees, from 300 to 180.

c. **Glass-tubing and rod or cane.** The method of producing glass-tubing or glass-rod or cane is to gather metal on the iron rod, attach a working rod to the end of the lump, previously rolled on the marver, and extend it by drawing apart the two rods. For tubing, the gathering is expanded into a thick-walled bulb before the mass is extended (fig. 21, *a*, *b*). To prevent too rapid cooling, the rod or tube is laid on a ladder, on which it rests; these ladders also serve as guides to the men walking backwards. If the tube or cane is thick, or if the tubing is intended to resist internal pressure—as, for instance, for boiler gauges—it is annealed; if thin, the process of annealing is dispensed with.

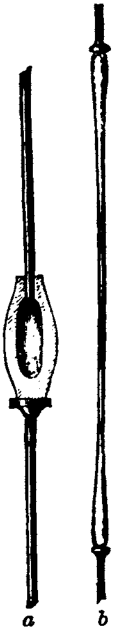


FIG. 21.

For thermometer-tubing, in which the bore is flat, a bulb is expanded on the rod, and, after being squeezed flat on the marver, a fresh gathering of metal is taken on, rolled to a cylinder, and then drawn.

Variegated cane may be produced by inserting a mass of molten glass into a mould which contains round its inner surface, in a perpendicular position, a number of short lengths of coloured canes. These adhere to the molten mass, which is then withdrawn and marvered. Some more glass is gathered from the pot to cover the coloured cane, and the whole mass may then be drawn; by twisting, spiral patterns may be produced. As glass retains the form given to it in the lump, even after drawing, varieties of cane may be made by moulding the first metal, preferably coloured, then covering it with molten glass, and then drawing it into cane.

The cane may be drawn to any desired degree of fineness by heating it before a blowpipe and spinning it on a wheel. Such fine glass is used for embroidery, and even woven into a fabric. It is also employed, under the name of 'glass wool,' for the purpose of filtering liquids which would attack ordinary filtering materials.

The manufacture of glass tube into articles of use in physical and chemical laboratories forms an art of itself.

d. **Pressed glass.** Many small articles are now pressed; among such are salt-cellars, small basins, jars, &c. The glass is gathered on the rod and dropped into the mould, the tail being cut off with a pair of shears. For small articles, hand pressure is sufficient; for larger articles a screw or a lever press is employed. The hinges of the mould are placed so as to leave marks as little visible as possible on the article produced. The moulds are made of brass, gun-metal, or iron. However smooth their surfaces may be, it is always found that the article is somewhat rough on its surface, probably owing to the contraction of the surface glass by rapid cooling. It is found that the higher the temperature of the mould, the more brilliant the surface.

As such articles are made and sold very cheaply, the expensive red lead is often replaced by barium carbonate. A good clear soft glass for the purpose may be made by a mixture of zinc oxide, cryolite, and sand. A large amount of cryolite renders the glass opaque; a smaller amount, opalescent; less than 3 parts cryolite to 1 of zinc oxide and 10 of sand gives a transparent glass of great refractive power.

Tools for working hollow glass. In fig. 22 the various tools for working hollow glass are shown. In the figure, 1 is termed the 'tool.' It is used in regulating the form of the bulb, compressing it in places and extending it, or even dividing it completely. 2 is a similar tool, the steel edges being replaced by wood; its use is in opening the bowls of tumblers and wineglasses, where steel would scratch the glass. 3 is termed the 'battledore'; it is a flat piece of polished

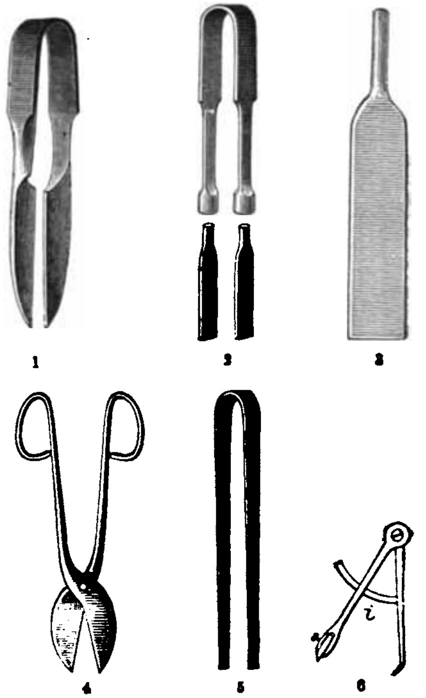


FIG. 22.

iron with a wooden handle, and is used for flattening the bottoms of vessels such as wine-decanters. 4 is a pair of shears for trimming the edges of vessels. 5 is a pair of pincers used for putting the handles on jugs and similar work; and 6 is a pair of callipers.

3. PLATE-GLASS.

Plate-glass is made by casting glass on a flat table and subsequently grinding it flat and polishing it. The form of crucible used for melting the glass is shown in fig. 4. It is grooved, so as to make it possible to raise it and tilt it so as to pour out the molten metal. It is made somewhat thicker than the usual pots so as to withstand the strain of lifting when full of metal. In Messrs. Chance's, plate-glass works at Birmingham, Siemens' furnaces are used for heating the pots; but in France, Boetius's furnaces are employed. Instead of the usual working holes, such furnaces are provided with doors made of cast-iron frames in which fireclay bricks are built, so that the pot may be removed through the doorway when its charge has been melted. The pot is lifted by means of a large fork on wheels, the prongs of which fit the groove in the pot. It is then placed on an iron barrow and run to the casting table. This table is constructed of iron plate or of phosphor-bronze. It has been found that, if made in one piece, it acquires the form of a flat arch, owing to the greater expansion of the upper surface when the hot glass is poured on it; hence it is made in segments, so that, although each segment expands, the whole table acquires the form of a number of flat arches, and less glass is lost in grinding than would be lost if the arch were a single one. The table is placed close to the door of the furnace, and it is arranged to run on rails, so that it can be brought opposite to any one of the openings through which a pot is removed. On the other side of the table is the annealing furnace. The pot having been taken out of the furnace is caught by tongs, attached to a crane, and lifted above the table; the glass is then poured as quickly as possible, and an iron roller is immediately run over it. The thickness of the plate is adjusted by causing the edges of the roller to run on rails as guides, the height of which above the level surface of the table may be altered at will. It is unnecessary to mention that the glass for this purpose must be free from air-bells, at a very high temperature, quite liquid, and that all impurities must be removed from the surface by skimming before it is poured. The surface of the glass, however smooth the surface of the table and the roller, is by no means even. Its rapid cooling, together with the operation of spreading it over the surface, causes it to become rough, and partially to devitrify. Hence it must be ground and polished. The operation of annealing must, however, precede the grinding. The plates are transferred as quickly as possible from the casting table to the annealing furnace. As such plates are often 12 to 20 feet long, and 6 to 8 feet wide, it would be impossible to stand them on their edges, and quite as impossible to support one on the top of another. Hence each plate must be annealed by itself. The flat floor of the annealing furnace is raised to a temperature higher than that of the glass; the glass plate is transferred to it; the door is shut, and the oven is cooled. But as the cooling operation, if left to itself, would take more than a fortnight. it is hastened by blowing cold air in below the floor; the time of annealing is thus reduced to four or five days. When it is removed from the oven it is known as 'rough plate,' and next undergoes the operations of grinding and polishing.

The glass plate, after it is annealed, is inspected, and if necessary cut, so that imperfect portions may be rejected. It is then embedded in plaster of Paris, so as to fix it to the grinding table. This table revolves on a central axis; and arms project over it, to the ends of which cast-iron rubbing plates are attached. These plates also revolve, and by means of screws their position can be shifted so as to bring them when desired near the centre of the table or near its circumference. Sand and water are used for grinding. The sand must be clean and sharp, and it is also of importance that the grains shall be uniform in size. Uniformity in the size of the grain is secured by washing and sifting. When the plate has been rendered comparatively plane by means of sand, powdered emery is employed to render it still smoother. Emery of various degrees of fineness is obtained by washing. The crushed emery is mixed with water, and delivered into a small tank. The larger particles sink while the smaller are carried on by the overflow. The second tank is larger, hence the overflow bears a less proportion to the total contents of the tank, and therefore a longer time is given for the emery to settle. The third is still larger, and so on. By this means emery powder of every grade of fineness may be obtained, from a comparatively coarse powder to the finest dust.

The one surface of a plate having been ground, it is reversed, and the other surface is treated first with sand and then with emery. The sand and emery after use are washed off into a tank where they settle, and are used several times.

The operation of polishing is similar in character. Instead, however, of employing cast-iron plates, one surface of glass is caused to rub against another. The preliminary smoothing is accomplished by the use of fine emery; the final operation being done by hand, so as to remove any scratches. The glass is then polished, the polishing plates being now made of wood, covered with felt and weighted. The powder employed is 'rouge' or oxide of iron, obtained by igniting sulphate of iron at a white heat for 36 hours. This rouge, mixed with water, is squirted on to the plate during its motion; the polishing plates are moved at right angles to the direction of motion of the glass plate by suitable machinery. The glass is then sorted and cut to any desired size by a diamond.

Annealing.—The operation of annealing has been frequently alluded to. It consists in slow cooling, and its object is to prevent the glass from being brittle, and even flying to pieces while it cools. It is probable that the molecules of glass are still capable of motion, even after the glass is apparently solid. Glass when quickly cooled shows certain curved markings when examined by polarised light, which reveal a state of strain. Similar markings can be produced by submitting the glass to pressure or tension, and quickly cooled glass is evidently in a state of strain and stress, some portions being unduly compressed, and some unduly extended. But when slowly cooled, it is homogeneous or nearly so. It is therefore to be presumed that a certain molecular flow has taken place during the slow cooling.

The ovens in use for this purpose are adapted to the shape of the glass objects to be annealed. For wine glasses, tumblers, jugs, &c., a wire grating, or often a train of trucks, is caused to traverse continuously a long oven of the shape of a horizontal flue. The fire being at one end, the fresh articles are placed on the grating nearest the fire; and they slowly move away from the source of heat, becoming cooler and cooler the further away they are moved. This tunnel or flue is 80 feet long. The heat is often derived from the main furnace. For small articles, 6 hours is a sufficient time for cooling. But large or, more correctly, heavy articles, of thick glass, require a much longer time; in some instances as long as 60 hours.

The annealing oven for sheet glass is often a part of the furnace itself. The annexed figure 23 gives an idea of a very advantageous arrangement

The furnace for flattening the cylinders is shown in plan. The cylinder at *d* is flattened at *e* on the flattening stone, which runs on rails. When flat, the stone is pushed into the compartment 1, whence it is moved on to the travelling plate 2, by means of a rake inserted through an opening at *f*. The flattening stone is then returned for a subsequent operation. The sheet of glass, however, does not rest on the plate, but is caught in grooves at the side. As each successive plate is introduced, the previously flattened ones travel a stage further; in 20 or 30 minutes they issue from the furnace annealed. The annealing tunnel contains nine plates.

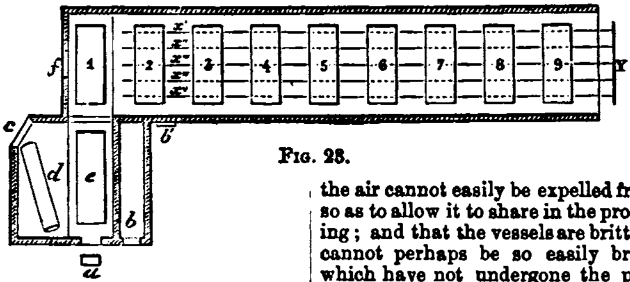


FIG. 23.

The annealing of plate-glass has already been alluded to. Each oven holds only one plate. It is a large brick chamber with a low roof, and is raised to the required temperature before the plate is introduced. The cooling, as before remarked, is accelerated by introducing cold air below the floor.

Tempering.—Of late years attempts have been made, some with success, to cool glass quickly and uniformly; it is then, of course, under a strain and stress, but these are uniformly distributed. It has long been known that if molten glass is dropped into water, each drop assumes the form of a pear with a long thin tail. Such drops are termed 'Prince Rupert's drops.' Their peculiarity is that the body of the drop is exceedingly hard, so hard indeed that it will stand a blow with a hammer without fracture, but as soon as a fragment of the tail is broken off the whole drop flies instantaneously into the minutest fragments. It was found by M. de la Bastie that glass vessels dropped into oil or melted mutton fat, which is kept at a temperature of 68–75°C. (155–167°F.) (some authorities give 350 to 400°C.), the glass being in a semi-ductile state, do not crack, but are rendered hard and difficult to break. When broken, however, the pieces are not large and irregular, as is usual when glass is fractured, but very small and angular. The process has not become a commercial success, owing to the facts that the vessels sometimes go to pieces of their own accord after a year or more; that it is difficult to apply the process to wine decanters or water-bottles, for the air cannot easily be expelled from the interior so as to allow it to share in the process of tempering; and that the vessels are brittle, though they cannot perhaps be so easily broken as those which have not undergone the process; lastly, that such vessels cannot be ground or cut without flying to pieces. This prevents ornamentation. The same remarks apply to Pieper's process, which differs only in the method of tempering—namely, by blowing into the semi-plastic glass superheated steam. It is also difficult to heat the vessels to the required temperature, still causing them to retain their shapes.

Mr. Siemens has lately described a process (Jour. Soc. Arts, 1884–85, 386), introduced by him with great success, for 'hardening' glass. It depends on the principle that glass, if evenly cooled, however quickly, is under little strain, and that the more rapidly it loses heat the harder its surface becomes. A sheet of glass, for example, loses heat more rapidly from its edges than from its surface, owing to the greater surface exposed. Hence it is under strain. But if the heat is rapidly and uniformly conveyed away from the surface, it retains its shape, and is hardened and not under strain. The cooling should be proportioned to the volume of the glass, not to its surface. The processes are adopted according to the quality of glass required. These are (1) Hardening; (2) Casting; (3) Semi-hardening. They have been carried out for six years at the Dresden glass-works, and the value of the goods thus treated has increased from 600*l.* to 7,000*l.*, and is yearly on the increase. The first process is adapted for plate. The glass, which must be without flaw, is cut, exposed suddenly and evenly to the radiant heat of a special furnace, of which the roof of the arch is three feet from the sole on which the glass lies, until the glass is soft. The plate is then withdrawn and quickly placed between metal plates. The process of heating requires one minute and the cooling half a minute. The sole of the heating furnace is smooth, and is covered with powdered talc to prevent the adhesion of the glass. The success of the process is due to the uniform temperature of the furnace, and to the fact that the heat is wholly radiant. The glass, which is difficult to handle in the soft state, is withdrawn from the furnace by means of wooden shovels soaked in silicate of soda to prevent their burning. Owing to the extremely high temperature to which the plate is exposed, hard enamels may be used for ornamenting its surface. If required of extreme hardness, thin copper plates are applied to cool it. Iron plates give a less hard glass; and the effect may be reduced by covering the surface of the cooling plates with wire gauze, or by using asbestos paper or clay slabs. Bottles may also be hardened by heating them till soft, and then placing them in a case of iron in which they stand, prevented from touching the iron in more than three places by projecting ribs, or they may be heated in the casing, and then removed from the furnace and allowed to cool in the air. The most quickly cooled of such plates withstand eight times a shock which would break an ordinary plate, and those slowly cooled or semi-hardened three times. They are not scratched by a diamond, and hence cannot be cut; but they may be polished, etched, and slightly ground if desired. The process of casting glass may be applied to the manufacture of floor plates, grindstones, pulleys, tramway sleepers, and it is hoped that it may be possible to introduce glass for use in building. The glass is melted in tank furnaces, and tapped into moulds, as in casting iron. But sand is not used as a mould. The material must have the same conductivity and capacity for heat as the glass. Mixtures of powdered glass-pots and porcelain, with metal turnings and filings, and with barium sulphate and magnetic iron ore, have been used with fair success. The mould and the glass in it are then heated together, taken out of the furnace, and cooled in the open air. The cost of casting 1 cwt. of glass is 5*s*. 6*d*.

It may be stated with fair accuracy, that hardened glass bears to ordinary glass the same relation as steel to iron. This process has been applied to military water-bottles. It is well adapted for enamelled signboards. The street lamps in Dresden, which are made of hardened glass are so much more durable than they used to be that the breakage has been reduced to one-tenth of what it previously was.

The Ornamentation of Glass.

The chief processes are—1. Painting and enamelling; 2. Staining; 3. Cutting; 4. Etching by hydrofluoric acid; 5. Etching by the sandblast. These will be shortly described in their order.

1. **Painting and enamelling.** For shading and outlines, a glass closely corresponding to the formula $K_2O,PbO,4SiO_2$ which is easily fusible, is mixed with some powder in sufficient quantity to render it opaque when fired. Such substances are ferric oxide, or the oxides of cobalt, manganese, or iridium. Care must be taken to avoid borax glass for this purpose, because, though easily fusible, it attracts water on exposure, and becomes rough and unsightly. The glass is ground to a fine powder in a mill, and finally rubbed on a glass slab with glass mullers; it is then mixed with the oxide, and again triturated with oil. It is applied with a brush. The shading may be applied by using the enamel as a paint, by cross hatching, or by stippling.

2. **Staining.** The two stains used are silver and cuprous oxides; the former varies from canary yellow to deep orange, and the latter gives a ruby colour. The stain is mixed with kaolin and water or oil and applied with a brush. The copper stain requires a reducing flame in the subsequent firing.

3. **Cutting.** Glass is cut by pressing it against an emery wheel, kept moist with water. Such wheels are of different sizes, so as to allow of large or small effects. Skilful workmen copy figures and landscapes with great accuracy; and they are aided by the effect of intaglio appearing as cameo; the deeper the cut the more the glass appears to be raised. The effect of cutting deeply is to allow light to pass more easily, and the imagination causes the belief that the high lights stand out from the surface of the glass. Flashed glass may be made to give pleasing effects, the ruby colour on the surface being removed so as to exhibit clear glass or glass of a different colour beneath. Cameos are sometimes produced on opaque glass by the laborious process of cutting away the glass and leaving the design in relief. The operation of cutting requires a very special class of skilled workmen, for the designs are executed by free hand. The cut portions are finally polished with rouge applied with wooden wheels.

4. **Etching by hydrofluoric acid.** The glass is covered with a thin layer of beeswax, by applying it with a soft brush. Designs are then drawn on the glass with a needle point, or, for objects like lamp shades, symmetrical designs are drawn by means of complicated and highly ingenious machinery. The articles are then dipped in aqueous hydrofluoric acid, contained in gutta-percha troughs with lids. Weak acid acts slowly, and produces clear designs, while strong acid roughens the glass, rendering it opaque. The length of exposure to the acid and its strength are so regulated as to suit the particular designs required. In some works mixtures such as the following are employed. 1 litre water, 250 grams acid fluoride of potassium, 250 grams commercial hydrochloric acid; the solution is saturated with potassium sulphate (acid ?) requiring about 140 grams. Another receipt is:—8 parts potassium fluoride in 100 parts water, mixed with 1 part sulphuric acid. Fluoride of ammonium dissolved in water may also be used. If flashed glass be etched with dilute acid, the coloured layer may be removed, exposing the under surface. The glass, when etched, is washed with soda and hot water to remove the wax, which is thus wasted. It would be desirable either to recover the wax or to devise a cheaper substitute.

5. **Etching by the sand blast.** The glass is pasted over with a paper stencil, exposing the surface in certain places. It is then placed under a hood fitting tightly to a base, by means of an indiarubber packing. Through this hood pass jets or nozzles, into which sand is allowed slowly to trickle. The air is exhausted from the hood, usually by means of a steam injector, and

the pressure of external air urges the sand on to the surface of the glass. Those portions unprotected by the paper stencil are subjected to the impact of the grains of sand, and are roughened. The angular fragments of sand produce such an effect that, by concentrating the blast on one spot of the glass, a hole may be drilled through a half-inch cylinder or plate in a quarter of an hour or twenty minutes. It is in this way that the holes are drilled through which the gas-pipes pass in street lamps. The graining is not so fine, nor is it possible to produce such delicate patterns as by means of etching with acid.

The silvering of mirrors.—Various metals, mercury, silver, gold, platinum, may be deposited on glass, converting it into a mirror. Usually mercury is used for the purpose. An amalgam of tin and mercury is employed. A flat surface is covered with tin foil, all creases and wrinkles being smoothed out with a soft brush. A little mercury is poured on the foil and spread over the whole surface with a woollen cloth. The table is surrounded with a beading, and mercury is poured in it until it reaches a depth of a fifth of an inch. A narrow strip of paper is then pushed in between the foil and the mercury resting on it; the edge of the glass plate, previously thoroughly cleaned, is then placed on the paper, and the plate held in a nearly horizontal position is then pushed along, the paper on which it rests slipping on the surface of the foil. When the plate rests on the mercury, the table is inclined by jack screws at one end, so that the mercury runs off, leaving the plate resting on the amalgamated foil. A woollen cover is then placed on the plate, and it is then weighted down, the weights being gradually increased. The table is gradually tilted, till after twenty-four hours it is inclined at an angle of 10 or 15 degrees. The plate is then lifted and set on its edge in a trough into which the excess of mercury drains. After about four weeks all superfluous mercury has drained off and the mirror is finished.

The silvering of glass was introduced by Drayton in 1843. His process was subsequently modified by Liebig. The following solutions are employed. 1 part of fused silver nitrate dissolved in 10 parts of water; a solution of ammonium nitrate of 1·115 sp.gr., or of ammonium sulphate of 1·106 sp.gr.; a solution of caustic soda absolutely free from chlorine, of 1·050 sp.gr. These three solutions are mixed in the proportions—100 volumes of the ammonia solution, 140 volumes silver solution, and 750 volumes soda solution. The silver solution is poured into the ammonium sulphate, and the soda added in small quantities at a time. It is then allowed to settle for three days, and the clear portion siphoned off. 50 grams of white sugar candy are dissolved and boiled with 3·1 grams of tartaric acid for an hour, and then diluted to 500 c.c., 2·857 gram of copper tartrate are dissolved in water, caustic soda is added until the initial blue precipitate is redissolved, and the solution is then diluted to 500 c.c. One volume of the sugar solution, and one volume of the copper solution are mixed, and eight volumes of water added. Immediately before use 50 volumes of the silvering solution are diluted with 250–300 volumes water at 28–30°C. mixed with 10 volumes of the reducing solution, and poured into a shallow trough; the glass plate is then laid on this solution and left for some hours. The silver is precipitated on the surface of the glass. It is then washed, dried and polished by gentle rubbing with chamois-leather. The silver deposited on a square metre of glass weighs 3 to 3·5 grams. Numerous other receipts are also given, the chief difference being in the materials used for reduction.

Glass can also be platinised and gilt, but these processes are not carried out on a large scale.

Glass beads.—1. **Hollow.** These are chiefly of French manufacture. They are produced by blowing small bulbs out of glass-tubing, plain or coloured. The interior is filled with coloured wax; or if pearls are to be imitated, with 'pearl-essence'—*i.e.*, the small scales of whitebait and similar fish, ground to an impalpable powder, and preserved in ammonium chloride solution. 2. **Solid** or **Venetian.** These are either cut from thick-walled coloured tubing by means of a guillotine cutter, the splinters being removed by a sieve, and, to round the sharp edges, heated to redness in a revolving drum, when the edges melt. To prevent adhesion, and the closing up of the perforation, they are kneaded in moist clay, or in a mixture of clay and finely ground charcoal before heating. These substances are subsequently removed by washing. They are finally polished by shaking in bags with bran. Opaque beads, like mother-of-pearl, are produced from tubes drawn from glass which has been violently stirred so as to inclose minute air bubbles. These are greatly subdivided, and drawn into streaks, thus producing the desired effect. Cut beads are made chiefly in Bohemia. Their manufacture needs no special description. Long beads are termed bugles. Large ornamental beads are made by taking the glass from the pots with a slightly conical rod covered with fine china clay. By holding the rod vertically the glass slips down the rod, and by revolving the latter, the spherical form is secured. The rod is allowed to cool, and the bead knocked off when solid. A certain amount of ornamentation can be produced by twisting coloured glass round the bead while it is still hot; or by placing small drops of coloured glass on the hot bead. Glass marbles are made from coloured glass rod; it is cut off in lengths and these are heated in a revolving drum, china-clay or talc being present to prevent adhesion. The rotatory motion causes them to assume a globular form. W. R.

GLASS OF ANTIMONY, *v. Antimony crocus,* art. ANTIMONY.

GLASS, TOUGHENED, *v.* GLASS.

GLAUBER'S SALT. *Sodium sulphate, v.* SODIUM.

GLAUBERITE *v.* CALCIUM.

GLAZES *v.* POTTERY.

GLOBULINS *v.* ALBUMINOIDS.

GLONOINITE *v.* EXPLOSIVES.

GLUCINUM *v.* BERYLLIUM.

GLUCOSAN *v.* HORSE CHESTNUT.

GLUCOSE *v.* DEXTROSE.

GLUCOSIDES. A large and important group of substances occurring almost exclusively in the vegetable kingdom, which by the operation of hydrolysis induced by fermentation or by the action of dilute acids may be resolved into sugar and another compound not belonging to the class of carbohydrates. The sugar thus formed is usually dextrose; certain glucosides yield glucoses either incapable of fermentation or optically inactive, and a few give bodies which, although carbohydrates, are not of the nature of true sugars.

This decomposition may, in a few cases, be induced by simply boiling the aqueous solution or heating it under pressure in sealed tubes. It is much more rapidly effected by the action of dilute acids, and also in many cases by that of alkalis. It may also, in a number of cases, be brought about by the action of certain ferments like 'emulsin,' 'erythrozym,' 'myrosin,' &c. Saliva is also capable of effecting the decomposition of certain glucosides. Some of the glucosides may be made to undergo the alcoholic and lactic fermentation.

In the greater number of cases only one variety of sugar is formed on hydrolysing a glucoside, although instances are known in which two different kinds of sugars are produced.

The majority of the glucosides are neutral bodies; one or two are basic and a few are acids. They are usually soluble in water and alcohol, and but very sparingly soluble in ether. They are charred when heated to a moderately high temperature, with the production, occasionally, of a sublimate of the other component. Fehling's solution is usually, although not invariably, reduced by solutions of glucosides. Many of them are optically active, and as a rule rotate the ray of polarised light to the left, although neither the amount nor the direction of the rotation has any necessary relation to the sugar present.

The glucosides are usually obtained by digesting the vegetable substances which contain them either with water or dilute alcohol, and adding lead acetate to the solution to precipitate tannin &c., removing the excess of lead by sulphuretted hydrogen, and concentrating the solution to the crystallising point. Or the glucoside may be precipitated from the aqueous solution by alumina, or by alum and ammonia, and the 'lake' or compound so formed may be subsequently decomposed by treatment with an acid.

Only the more important glucosides are here described in alphabetical order.

Æsculin $C_{15}H_{16}O_9$. Found by Minor in 1830 in the bark of the horse chestnut (*Æsculus Hippocastanum*), also present in the bark of *Hymenodictyon excelsum* (Wallich), and in the roots of the wild jasmin (*Gelsemium nitidum*, Michx. (Gray). Crystallises in colourless needles. On heating splits up into *Æsculetin* (Dioxycumarin) $C_9H_6O_4$ and glycosan. Aqueous solution has a faint acid reaction, and is highly fluorescent. Gives a yellow solution with nitric acid, which, on addition of ammonia, acquires a deep blood-red colour. Reaction characteristic and delicate.

Amygdalin $C_{20}H_{27}NO_{11}$. First found by Robiquet and Boutron, in 1830, in bitter almonds. Composition and mode of decomposition into bitter almond oil and hydrocyanic acid first indicated by Wöhler and Liebig. Contained also in the kernels of peaches, cherries, plums, apples, &c. Usually although erroneously stated to be present in all plants which yield hydrocyanic acid on distillation with water. Crystallises from water in orthorhombic prisms containing 3 mols. water; from 80 p.c. alcohol in pearly scales with 2 mols. water; odourless; slightly bitter taste; neutral reaction, and turns ray of polarised light to the left. Readily soluble in water; less soluble in alcohol; insoluble in ether. Is not poisonous. Melts at 200°, and is decomposed at higher temperatures. In contact with emulsin, or an aqueous extract of sweet almonds, pea-meal, barley-water, &c., solution decomposes, especially at about 30°, into *Benzaldehyde*, *hydrocyanic acid*, and dextrose:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

Similar reaction induced by dilute hydrochloric acid; less readily by sulphuric acid, and by water at 150°. Decomposed also by electrolysis into same products. On boiling with alkalis gives ammonia and amygdalic acid.

Antiarin $C_{14}H_{20}O_5 + 2H_2O$. The poisonous principle of an arrow poison obtained from *Antiaris toxicaria*. Crystallises from water or alcohol in colourless shining plates. Melts at 220·6°. Neutral reaction.

Apiin $C_{27}H_{32}O_{16}$. Found in the leaves and seeds of parsley (*Petroselinum sativum*); in celery (*Apium graveolens*); and other umbelliferous plants. Small colourless needles. M.p. 228. Sparingly soluble in cold, readily soluble in hot water and alcohol. Solution readily gelatinises. Soluble in alkalis, giving light-yellow solution which is strongly dextrogyratory $(a)_D = +173°$. On hydrolysis with dilute hydrochloric acid gives *Apigenin* $C_{15}H_{10}O_5$ and glucose.

Arbutin $C_{12}H_{16}O_7$. Discovered by Kawalier in the leaves of the red bearberry (*Arctostaphylos uva-ursi*). Occurs also in *Pyrola umbellata* and other ericaceous plants of which the dried aqueous extract yields *hydroquinone* on destructive distillation. Found associated with methylarbutin. Colourless silky needles. Readily soluble in boiling water and in alcohol. Solution does not reduce alkaline copper solution. Melts at 187·5°. On hydrolysis yields sugar and *hydroquinone* $C_{12}H_{16}O_7 + H_2O = C_6H_{12}O_6 + C_6H_6O_2$.

Bornesit $C_7H_{14}O_6$. Monomethyl ether of Dambose occurs in Borneo caoutchouc. Four-sided rhombic prisms; readily soluble in water; melts at 175°. Dextrorotatory. Forms an explosive compound with nitric acid.

Caïncin $C_{40}H_{64}O_{18}$. Found by François, Pelletier, and Caventou in the root of Caïnca (*Chiococca anguifuga*, Martius), a rubiaceous plant growing in Brazil, and used for the cure of snake bites; also in *C. racemosa*, used in the Antilles as a remedy for syphilis and rheumatism. Slender lustrous needles, of a bitter, astringent taste. Acid reaction; forms salts with lead and the alkalis. On hydrolysis yields glucose and *Caïncetin*, $C_{22}H_{34}O_3$.

Carminic acid $C_{17}H_{18}O_{10}$. The colouring matter of cochineal (*q. v.*) and the essential constituent of carmine (*q. v.*). Forms a dark purple brown, indistinctly crystalline mass, giving a fine red powder. Easily soluble in water and alcohol. Decomposed at 136°. On boiling with dilute sulphuric acid yields *carmine-red* and a sugar $C_6H_{10}O_5$, which is optically inactive, uncrystallisable, and unfermentable (Hlasiwetz and Grabowski):

$$C_{17}H_{18}O_{10} + 2H_2O = C_{11}H_{12}O_7 + C_6H_{10}O_5.$$

Liebermann was unable to obtain sugar from carminic acid, and doubts the glucosidic nature of the colouring matter of cochineal. Carminic acid is a feeble bibasic acid.

Chitin $C_{18}H_{30}N_2O_{12}$? The main constituent of the elytra and integuments of insects and the carapaces of crustacea. An amorphous, colourless, semi-transparent substance; insoluble in water, alcohol, ether, alkalis, and dilute acids. Soluble in cold sulphuric and hydrochloric acids, forming nearly colourless solutions which gelatinise on cautious addition of salt. By prolonged boiling with dilute sulphuric acid gives a glucose capable of reducing Fehling's solution.

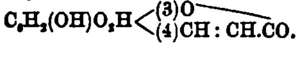
Coniferin $C_{16}H_{22}O_8$. Discovered by Hartig in the cambial sap of *Larix europæa*, and met with in the saps of the conifers in general. Found also in beetroot and in asparagus. White crystalline substance. Slightly soluble in cold, readily in hot water, and alcohol. M.p. 185°. Aqueous solution has a bitter taste. Lævorotatory $(\alpha)_D^{20°} = -66{\cdot}9$. No action on Fehling's solution. Soluble in concentrated sulphuric acid with red colour; on addition of water solution gives a resin of an indigo-blue colour. With phenol and concentrated hydrochloric acid gives, especially in sunlight, an intense blue colour. By hydrolysis with emulsin is gradually transformed into grape sugar and *Coniferyl alcohol* $C_{10}H_{12}O_3$: $C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3$. By oxidation with chromic acid yields *Vanillin* (*q. v.*).

Convolvulin $C_{31}H_{50}O_{16}$? The active principle of officinal jalap-root (the rhizome of *Ipomæa Purga* also called *Convolvulus Schiedeanus*). Colourless brittle substance melting at 150°. Sparingly soluble in water, readily soluble in alcohol and acetic acid. Dissolves in concentrated sulphuric acid with fine red colour. By the action of hydrochloric acid upon the alcoholic solution gives glucose and *Convolvulinol* $C_{13}H_{24}O_3$.?

Crocin $C_{44}H_{70}H_{28}$. Colouring matter of saffron (flowers of *Crocus sativus*) and of Chinese yellow pods, the fruit of *Gardenia grandiflora*, with which the yellow robes of the Chinese mandarins are dyed. Forms a brittle, yellowish-brown mass. Easily soluble in water and alcohol. Sulphuric acid dissolves it with a deep-blue colour, which passes through violet and cherry-red, to brown. With dilute acids it yields *Crocetin* $C_{34}H_{46}O_9$, and *Crocose*, a dextrorotatory glucose, the reducing power of which is only half that of dextrose.

Dambonite $C_8H_{16}O_6$. Dimethyl ether of dambose. Found in caoutchouc. Crystallises from water in prisms. M.p. 195°. Optically inactive, non-fermentable, and without action on alkaline copper solution.

Daphnin $C_{15}H_{16}O_9$. Constituent of the bark of certain species of *Daphne*, *e.g. D. Mezereum* and *D. alpina*. Forms colourless rectangular prisms. Melts with partial decomposition at 200°. Bitter astringent taste. Slightly soluble in cold water, more soluble in alcohol, insoluble in ether. Soluble in alkalis and their carbonates with golden-yellow colour. Slowly reduces alkaline copper solution. By hydrolysis with emulsin, or by boiling with dilute acids, is resolved into a fermentable glucose and *Daphnetin* or *Dioxycumarin*:



$$C_6H_2(OH)O_2H\Big\langle\begin{matrix}(3)O\text{———————}\\(4)CH:CH.CO.\end{matrix}$$

Digitalins. The active principles contained in foxglove (*Digitalis purpurea*) are mainly glucosides, but they have not yet been separated in a pure state, and their distinctive characters are therefore not accurately known. The digitalin of pharmacy is a white, indistinctly crystalline, intensely bitter powder consisting of at least five distinct substances, viz. digitonin, digitin, digitalin, digitaleïn, and digitoxin, mixed with the decomposition products of these bodies (*v.* DIGITALIS).

Digitalin $(C_5H_8O_2)_x$? is the essential constituent of the so-called 'French digitalin' of pharmacy, in which it occurs, together with paradigitogenin and digitoneïn, to the extent of from 2 to 3 p.c. It is a colourless amorphous powder, slightly soluble in water, readily soluble in alcohol. It dissolves in strong oil of vitriol with a bright yellow colour, and the solution in contact with vapour of bromine acquires a splendid rose-red or violet-red colour. (Characteristic reaction for digitalin.)

Digitaleïn is a yellow amorphous powder, readily soluble in water and alcohol. It gives the same reactions as digitalin, and has a similar physiological action.

Digitonin. A white amorphous powder, readily soluble in water and alcohol, constitutes the principal portion of the pharmaceutical preparations. In properties and physiological action it closely resembles saponin, from which it is distinguished by giving a fine garnet-red colour on boiling with moderately concentrated oil of vitriol or with strong hydrochloric acid.

Digitoxin $C_{21}H_{32}O_7$? Is the most poisonous of the active principles of digitalis. Crystallises in colourless foursided plates of pearly lustre, insoluble in water, soluble in alcohol and chloroform. M.p. 240°. Solution in concentrated sulphuric acid does not give the digitalin reaction.

Frangulin $C_{21}H_{20}O_9$ (Thorpe and Robinson, C. J. 1890, 38). A yellow crystalline colouring matter discovered by Binswanger in the bark of the berry-bearing alder (*Rhamnus Frangula*) (for literature *v.* Thorpe and Robinson, *l.c.*). Present also in the root-bark, and in the seeds and fruit of the same plant. Forms a citron-yellow microcrystalline mass, nearly insoluble in water, but readily soluble in alcohol and benzene. Soluble in alkalis with intense cherry-red colour. Melts at 226°. Decomposes at higher temperatures, giving a bright-red crystalline sublimate of *emodin*. On boiling with dilute acids is decomposed into emodin and a compound which reduces Fehling's solution but which is not glucose.

Helleboreïn $C_{26}H_{44}O_{15}$ and *Helleborin* $C_{36}H_{42}O_6$, two poisonous glucosides found in the roots of *Helleborus viridis*.

Hesperidin $C_{22}H_{26}O_{12}$. Discovered by Lebreton in unripe oranges. Found generally in the fruit of the Aurantiaceæ. A white, microcrystalline, tasteless, hygroscopic powder; almost insoluble in water and alcohol; readily soluble in hot acetic acid. Lævorotatory $(\alpha)_D = 89°$. M.p. 251°. Soluble in alkalis and acids. No reducing action on alkaline copper solution. On boiling with dilute sulphuric acid forms *Hesperetin* $C_{16}H_{14}O_6$, and grape sugar without assimilation of water. $C_{22}H_{26}O_{12} = C_{16}H_{14}O_6 + C_6H_{12}O_6$.

Indican $C_{26}H_{31}NO_{17}$ (?). A glucoside discovered by Schunck in woad (*Isatis tinctoria*), and in *Indigofera tinctoria* and *Polygonum tinctorium*. Forms a yellow syrup of a bitter, disagreeable taste and acid reaction; soluble in water, alcohol, and ether. Readily decomposed on heating with dilute acids. Forms *indigo-blue* and *indiglucin*. $C_{26}H_{31}NO_{17} + 2H_2O = C_8H_5NO + 3C_6H_{10}.O_6$.

Jalapin (*Scammonin*) $C_{34}H_{56}O_{16}$. The active principle of the root-stalks of *Ipomæa orisabensis*, and of scammony, the dried sap of *Convolvulus Scammonia*. Amorphous, resinous powder; translucent in thin plates; m.p. 150°; slightly soluble in water, readily soluble in alcohol and ether. Soluble in concentrated sulphuric acid with a purple or maroon-red colour, changing to brown and becoming finally black. On hydrolysis with dilute acids yields *Jalapinol* and sugar.

$$2C_{31}H_{56}O_{16} + 11H_2O = C_{32}H_{62}O_7 + 6C_6H_{12}O_6.$$

Lokaïn $C_{42}H_{48}O_{27}$. The colouring principle of 'Lokao' or Chinese green, an alumina lake said to be prepared from the bark of certain varieties of *Rhamnus*. A bluish-black mass; insoluble in water and alcohol; soluble in ammonia and alkalis with a pure blue colour. With reducing agents, *e.g.* sulphuretted hydrogen, colour changes to blood-red, quickly becoming green on exposure to air. On hydrolysis yields *Lokanic acid* $C_{36}H_{36}O_{21}$ and *Lokaose* $C_6H_{12}O_6$, a crystalline, optically inactive sugar, capable of reducing alkaline copper solution.

Morindin $C_{26}H_{28}O_{14}$ or $C_{28}H_{30}O_{15}$. One of the colouring principles of *Morinda citrifolia* and *M. tinctoria*. Silky, yellow needles; soluble in hot water and in alcohol. Dissolves in alkalis with an orange-red colour, which is not changed on boiling. Melts at 245°, and gives a sublimate of *Morindon* $C_{15}H_{10}O_5$. On hydrolysis, also yields 48·4 p.c. of morindon, together with a glucose which reduces alkaline copper solution. *Cf.* A'al (Thorpe and Greenall, C. J. 1887, 52; Thorpe and Smith, 1888, 171).

Parillin (*Smilacin*). A glucoside resembling saponin, discovered by Pallotta in sarsaparilla root. Formula unknown. Fine needles; sparingly soluble in cold, readily soluble in hot water, in alcohol, and acids and alkalis. On boiling with dilute sulphuric acid yields *parigluin* and a crystallisable glucose.

Phloridzin $C_{21}H_{24}O_{10}$. Found by De Koninck in the root-bark of the apple, pear, cherry, and plum-tree. Long, silky needles; bitter taste; sparingly soluble in cold, readily in hot water. Melts at 109°. Lævorotatory. Readily hydrolysed into *Phloretin* $C_{15}H_{14}O_5$, and a glucose, 'phlorose,' dextrorotatory and crystalline.

Picrocrocin $C_{38}H_{66}O_{17}$. Found in saffron. Fine, colourless prisms; bitter, characteristic taste; yields a *terpene* and a glucose (crocose) on hydrolysis. $C_{38}H_{66}O_{17} + H_2O = 3C_6H_{12}O_6 + 2C_{10}H_{16}$.

Quercitrin $C_{36}H_{38}O_{20}$. The colouring matter of quercitron, the bark of *Quercus tinctoria*. Forms lustrous, yellow needles containing 3 mols. of water when crystallised from water, in which it is sparingly soluble; readily soluble in alcohol. M.p. 168°, with decomposition forming a sublimate of *quercetin*. Gives an intense green colour with ferric chloride; slowly reduces alkaline copper solution. By hydrolysis with dilute sulphuric or hydrochloric acid yields *Quercetin* $C_{24}H_{16}O_{11}$ and *Isodulcite* $C_6H_{14}O_6$. $C_{36}H_{38}O_{20} + 3H_2O = C_{24}H_{16}O_{11} + 2C_6H_{14}O_6$. Is not decomposed by emulsin.

Quinovin $C_{38}H_{62}O_{11}$ (Liebermann) or $C_{30}H_{48}O_{11}$ (Oudemans). Found by Pelletier and Caventou in false cinchona bark; also present in true cinchona barks. Also in the bark of *Remijia Vellozii* and in the root of *Potentilla Tormentilla*. Occurs in two modifications, termed by Liebermann α-Quinovin (found in the cinchona barks) and β-Quinovin found in the bark known as *China cuprea*.

α-Quinovin is a white crystalline powder of a bitter taste; insoluble in water, soluble in alkalis, ammonia, lime, and baryta-water. Soluble in alcohol. Solution yields a precipitate on addition of water. Dextrorotatory: $(\alpha)_D = +58·9$ to 59·2. Does not reduce alkaline copper solution, and does not ferment with yeast. The alcoholic solution yields *Quinovic acid* $C_{32}H_{48}O_6$ and a kind of sugar, *Quinovit*, $C_6H_{12}.O_4$, *with elimination of water*:

$$C_{38}H_{62}O_{11} = C_{32}H_{48}O_6 + C_6H_{12}O_4 + H_2O.$$

β-Quinovin is distinguished from α-Quinovin by its behaviour with alcohol, with which it forms a molecular compound with 5 mols. of alcohol, crystallising in large rhombic prisms melting at 70-80° in the alcohol of crystallisation. Melts at 235° with partial decomposition. Has only half the rotatory power of α-Quinovin; by hydrolysis splits up into quinovic acid and quinovit, which are identical with those formed by α-Quinovin.

Ruberythric acid $C_{26}H_{28}O_{14}$. The constituent of madder root (*Rubia tinctorum*) which by hydrolysis yields alizarin. Yellow silky prisms; slightly soluble in cold, readily soluble in hot water, also in alcohol, almost insoluble in ether. Gives a bright-red solution with potash, which changes to a dark purple on boiling. On boiling with dilute acids or alkalis yields alizarin and saccharose.

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + C_{12}H_{24}O_{12}.$$

This decomposition is not effected by emulsin.

Rutin $C_{42}H_{50}O_{25}$ (Schunck). Found by Weiss in the leaves of garden rue (*Ruta graveolens*). Found also in capers (the flower-buds of *Capparis spinosa*), and in *Waifa*, 'Chinese yellow berries,' the undeveloped flower-buds of *Sophora japonica*, and in the leaves of *Polygonum Fagopyrum*, the common buckwheat. Pale yellow needles; readily soluble in boiling water and alcohol. Decomposed by boiling with dilute acids into *quercetin* and isodulcite.

$$C_{42}H_{50}O_{25} + 4H_2O = C_{24}H_{16}O_{11} + 3C_6H_{14}O_6.$$

Salicin $C_{13}H_{18}O_7$ $(C_6H_{11}O_5.OC_6H_4.CH_2.OH)$. Found by Leroux in the bark of the willow. Most varieties of *Salix* contain salicin. Found also in poplars and in the flower-buds of meadow-sweet (*Spiræa Ulmaria*), and in castoreum. Forms white lustrous needles, or occasionally large tables belonging to the rhombic system. Strong, bitter taste. Moderately soluble in cold, very soluble in hot water. Lævorotatory. Melts at 201°; at 240° is resolved into a mixture of glycosan and saliretin. Soluble in concentrated sulphuric acid with an intense red colour. With emulsin yields glucose and *Saligenin*. Dilute acids on warming yield the same products; on boiling they give *Saliretin*.

Salicin was formerly employed as a febrifuge.

Saponin $C_{32}H_{54}O_{18}$? Found by Schrade in common soapwort (*Saponaria officinalis*). Found also in many plants of the sapindaceous and mimoseous orders, and appears to be widely diffused in the vegetable kingdom. Is best prepared from *Quillaja-bark.* White amorphous powder, having a burning, biting taste. Produces violent sneezing. Very soluble in water, forming frothy solution. Lævorotatory $(\alpha)_D = -73°$.

Xanthorhamnin $C_{48}H_{66}O_{29}$. The yellow colouring-matter of Persian or Turkish berries, the seeds of *Rhamnus infectoria*, so-called Avignon grains, and other varieties of *Rhamnus.* Crystallises from alcohol in golden-yellow microscopic needles. Very soluble in water and alcohol and in alkaline solutions; reduces alkaline copper solution. By hydrolysis yields *Rhamnetin* $C_{12}H_{10}O_5$ and *isodulcite* $C_6H_{14}O_6$.

$$C_{48}H_{66}O_{29} + 5H_2O = 2C_{12}H_{10}O_5 + 4C_6H_{14}O_6.$$

GLUE is obtained from animal matter, the hot watery solution of which becomes jellified on cooling. The substances used in its manufacture are bones, horns, hoofs, hides, and the residual fleshings from the mills of leather-dressers.

Properties.—When pure, glue is hard, transparent, inodorous, not affected by change of temperature, and quite neutral to litmus or turmeric. When heated it intumesces and has the odour of burnt horn. It takes fire with difficulty, and leaves a very bulky charcoal, which, on incineration, produces a residue consisting principally of phosphate of lime, which always accompanies the manufacture to a small extent.

In cold water it softens and becomes opaque, but does not dissolve, and increases in weight to the extent of from 40 to 45 p.c. It, however, dissolves in hot water, and when its solution rises to a higher temperature than 100°, it begins to sour, and loses to some extent the property of forming a jelly. It is insoluble in ether and oils.

Concentrated acetic acid renders it first transparent and then dissolves it, when the solution does not become viscid, nor does it lose its adhesive property.

Its average composition is

Carbon	50·00
Oxygen	24·30
Nitrogen	18·70
Hydrogen	7·00
	100·00

Glue made from good white bones absorbs, on dissolving, thirteen times, whilst that from dark bones only takes up nine times, its weight of water.

Manufacture.—The bulk of the glue in the market is prepared from bones, principally town collected, which, after being carefully picked from rags, iron, and other refuse, are coarsely ground to the size of about 3 inches in a bone mill such as that made by Oldham & Booth, or that of Crosskill made by the Beverley Iron Company. They are then put into vats containing cold hydrochloric or sulphurous acid of 10°T., or 1·05 sp.gr., in which they are digested until they become soft and transparent, then taken out and drained over the vat, after which they are washed with clean water (which must not contain chloride of sodium, as this deteriorates the quality and appearance of the glue), in a revolving washer, till the washings are free from acid. They are now clean and ready for steaming.

The next operation is to put them into digesters (of which there are a series) of cast or wrought iron, 8 or 9 feet high and 4 feet diameter each, holding about 18 cwt. of bones. Then they are subjected to the action of high-pressure steam of 30 to 35 lbs. per square inch for three or four hours, during which time the fatty and gelatinous products are gradually run off by a pipe at the bottom of the digester into settling tanks, which are kept warm to ensure the fluidity of the liquor. If a fine pale quality of glue is required, the liquor is now bleached by sulphurous acid or other bleaching agent. After settling for two hours the fat is skimmed off the top, and used principally in the manufacture of soap and waggon grease. The manhole lid on the side of the digester is taken off, and the steamed or degelatinised bones are raked out, allowed to dry spontaneously, and used for the manufacture of bone manures. The gelatinous liquor in the settling tank is now run off and filtered through a fine wire gauze, and boiled down in wooden tanks by means of a coil of steam pipes laid horizontally on the bottom of them, to such a strength that, on a sample being taken and set aside to cool, a clear and firm jelly is formed.

It is then run into moulds of wood, zinc, or iron, of any convenient size, say 6 feet long, 2 feet deep, and 1 foot wide, which should be slightly wider at the top than at the bottom, to allow of easy removal of the cake of glue; these are kept in a room as cool and dry as possible. When the glue has set it is cut out in squares, each square deposited in a wooden box open at the back and front, and taken to a cutting-machine similar to that used by soap-makers, and cut by piano wires to the thickness required. The resulting cakes of glue are deposited upon nets made of twine in frames and removed to the drying rooms, in which they are placed in piles, leaving a space of 3 inches between each frame for the circulation of the air. The temperature of the drying rooms should not exceed 21°, because at a higher temperature the glue will become fluid again, and prevent the separation of the cakes from the net, nor must the air be too dry in the first room, or the cakes will become bent and cracked.

The first room is heated by steam pipes placed round the bottom. When the cakes are dry enough to handle they are taken to other drying rooms, where the final drying is effected by means of a current of air driven by a Blackman Air Propeller, and after several days the cakes will be found to be quite dry, hard, and of good shape, ready for the market.

Examination of glue.—(*a*) *Estimation of water.* 2 or 3 grams of glue shavings are dried at 110 to 150°C. until the weight remains constant. (*b*) *Estimation of ash.* The residue from the test *a* is burned in a platinum crucible, if necessary, with the addition of a drop of nitric acid. (*c*) *Qualitative examination of the ash.* The properties of the ash gave a clue to the origin of the glue. The ash from bone-glue fuses by the heat of the Bunsen burner; its aqueous solution is neutral, and it contains phosphoric acid and chlorine, whereas the ash from leather-glue does not fuse, owing to the presence of caustic lime. Leather-glue has an alkaline reaction, and is free from phosphoric acid and chlorine. (*d*) *The determination of the acid.* 30 grams of glue are suspended in 80 c.c. of water and allowed to stand for several hours. The volatile acids are then driven over by a current of steam. As soon as the distillate amounts to 200 c.c. the distillation is discontinued and the contents of the receiver titrated with standard alkali. Sometimes the distillate contains sulphurous acid, in which case the receiver should contain a known amount of standard alkali. (*e*) *Capacity of drying.* The solution of glue freed from volatile acids is made up with water to 150 grams and heated on the water-bath; 10 c.c. are spread on a watch-glass and allowed to stand in a room which is free from dust and not exposed to frequent changes of temperature. The change of the glue jelly is observed for several days, and if possible the behaviour of this jelly is compared side by side with glue jellies of known quality, as the temperature and amount of moisture in the air has an influence on the consistency of the jelly. (*f*) *Foreign matter.* The rest of the glue solution from the test *e* is diluted with hot water and transferred to a cylinder holding 1,000 c.c. and provided with a c.c. scale. After filling up to the top, the contents of the cylinder are allowed to subside for 24 hours and the settlement noted down as 'foreign matter.' (*g*) *Smell.* The smell of glue differs very much. Leather-glue smells least. Other glues do not smell in the solid state, while their jelly has an unpleasant odour (R. Kistling, Chem. Zeit. [11] 691 and 719–720; S. C. I. 6, 565).

Ordinary glue of good quality contains from 12 to 18 p.c. of water, and from 1·5 to 5·0 p.c. of ash.

GLUTEN. Wheaten flour when elutriated with water so as to wash out the starch, leaves on the hand or on the muslin whereon the washing may be performed, a sticky, adhesive residue. This is crude gluten. Its value in bread-making is as a mechanical agency for entangling the carbonic acid gas which is produced by the action of yeast on the starch in the flour whereby the whole mass of dough is raised. Consequently one of the objects of the baker is to obtain such flour as contains a large proportion of gluten. To ascertain this, a leading Paris baker, M. Bolland, in a practical way adopted a method by which he separated the gluten from the flour; this gluten was put into a tube and heated in the oven, the amount of its expansion deciding for him its quantity and its resisting action to steam or quality. Well-fed and well-harvested grain is richer in gluten than such as is grown upon poor land or garnered in a damp or sprouted condition; and although rye, oats, and barley are rich in albuminoid bodies, they are so deficient in crude gluten that loaves made of the flour of any of these cereals are heavy and consistent, and resemble wheat flour treated by boiling rather than by baking. If, for instance, barley-flour be washed with water very little residue of gluten is found; rye and oat flour leave practically none, and the same may be said of any other cereal. It is, therefore, its superiority in the amount of gluten contained in it which gives to wheaten flour its pre-eminence for the purpose of forming light and easily assimilated bread.

Gluten is to some extent used by itself after separation from the starch of flour for the manufacture of biscuits and loaves for use by diabetic patients when the object is to restrain the use of starch in their food.

Crude gluten when moistened with water is of a variable grey colour and coheres in a tenacious, elastic, tough mass; freed from water it is translucent and tasteless. It contains 0·8 fibrin and 0·2 of an albuminoid body called *glutin.* It was first obtained from flour by Beccaria, and its resemblance to animal substances was the subject of early chemical investigation. Later and more accurate analyses determined that its chemical composition was similar to that of egg-albumen. In its anhydrous condition it contains:

Carbon	52·6
Hydrogen	7·0
Nitrogen	16·0
Oxygen with a trace of sulphur	24·4
	100·0

If exposed to a temperature of 100° it dries into a brittle semi-transparent substance which looks not unlike glue, and in drying it strongly adheres to the substance on which it rests. After being thoroughly dried it cannot again be rendered plastic.

Gluten is insoluble in water, ether, and pure alcohol. It is soluble in alkalis and tardily in weak acid solutions. It may be heated to 150° without undergoing any sensible destructive change; but at higher temperatures it shrinks, melts, and finally takes fire.

As noted above, the quantity of gluten in wheaten flour varies considerably with the quality of the flour, but it may be said that fine wheaten flour as commonly employed in this country contains from 11 to 13 p.c.; which in bread made of such flour represents approximately 9·5 p.c.

To estmate the amount of gluten which is contained in any sample of flour, Wanklyn and Cooper (Bread Analysis, 43 *et seq.*) direct 10 grams of the flour to be taken and carefully washed free of starch. The gluten is then immersed in ether and worked by means of a glass rod, whence it is transferred to a platinum dish and spread evenly within it, so as to be easily dried. The dish is then heated in the water-bath until its contents cease to lose weight. The dried gluten having been weighed a correction of 0·3 on the flour for ash and 1·0 on the flour for fat should be made. The mechanical quality (*i.e.* its sufficient ductility) of the hydrated gluten should also be observed (*v.* ALBUMINOIDS).

GLYCERIN (*Glycerol*, *Glycyl alcohol*, *Propenyl alcohol*, $C_3H_8O_3$ or $\left.\begin{matrix}C_3H_5{}'''\\H_3\end{matrix}\right\}O_3$) is one of the results of the process called 'saponification' when applied to most natural fats and oils. The term saponification is employed chemically in the most general sense to denote the change which occurs whenever an ether is split up into an acid and an alcohol, whether the agent effecting the change be water, an acid, or a base.

The process may also be regarded as the substitution in a neutral salt (the natural fat) of a mineral, and usually a strongly alkaline, base, for the base glycerin. Whichever view be taken, it is important to remember that the elements of water are taken up during the process (which indeed only occurs in presence of water), and that the glycerin, as such, does not exist in the fat; hence the sum of the weights of the fatty acids and glycerin is always considerably greater than the original weight of the fat employed. Moreover, three molecules of a fatty acid are equivalent to one molecule of glycerin, and this proportion is necessary for the formation of a neutral fat; hence glycerin has been sometimes called a 'tri-acid base.' The analogy between the decomposition of a mineral salt and of a neutral fat by caustic potash is complete, thus:

$$\mathrm{Bi'''(NO_3)_3 + 3K(OH) = Bi'''(OH)_3 + 3K(NO_3)}$$

$$\underset{\text{Tristearin}}{\mathrm{(C_3H_5)'''(C_{18}H_{35}O_2)_3}} + 3\mathrm{K(OH)} = \mathrm{C_3H_5(OH)_3} + \underset{\text{Potassium stearate}}{\mathrm{3K(C_{18}H_{35}O_2)}}.$$

The following table, taken from Allen's Commercial Organic Analysis, 2nd edit. [2] 31, shows the composition of the leading proximate constituents of fatty oils, and the theoretical proportions of fatty acid and glycerin resulting from their decomposition:—

Glyceride	Chief sources	Formula	Molecular weight	Products of saponification 100 parts	
				Fatty acid	Glycerin
Glycyl tributyrate (butyrin)	Butter fat . . .	$C_3H_5(C_4H_7O_2)_3$	302	87·44	30·46
Glycyl trivalerate . .	Porpoise and whale oils	$C_3H_5(C_5H_9O_2)_3$	344	88·96	26·77
Glycyl trilaurate . .	Cocoa nut oil . Palm nut oil .	$C_3H_5(C_{12}H_{23}O_2)_3$	638	94·04	14·42
Glycyl tripalmitate . .	Palm oil, lard . .	$C_3H_5(C_{16}H_{31}O_2)_3$	809	95·28	11·41
Glycyl tristearate . .	Tallow, lard . Cacao butter .	$C_3H_5(C_{18}H_{35}O_2)_3$	890	95·73	10·34
Glycyl trioleate . .	Olive oil, lard oil, almond oil .	$C_3H_5(C_{18}H_{33}O_2)_3$	884	95·70	10·40
Glycyl tribrassiate . .	Rape oil . . .	$C_3H_5(C_{22}H_{41}O_2)_3$	1052	96·39	8·75
Glycyl trilinoleate . .	Linseed and drying oils	$C_3H_5(C_{16}H_{27}O_2)_3$	794	95·21	11·58
Glycyl trihomolinoleate .	Linseed oil . . .	$C_3H_5(C_{18}H_{31}O_2)_3$	878	95·67	10·48
Glycyl triricinoleate .	Castor oil . . .	$C_3H_5(C_{18}H_{33}O_3)_3$	932	95·92	9·88

Regarded as a trivalent, or triatomic, alcohol containing the radicle C_3H_5''' (a relationship indicated by the termination of the name glycerol), glycerin bears the same relation to ordinary ethyl alcohol that orthophosphoric acid bears to nitric acid. It forms three distinct classes of ethers, just as the tribasic phosphoric acid forms three distinct classes of salts, with three different proportions of the same base, or even with three different bases.

Although glycerin is almost always commercially prepared from by-products resulting from the saponification of the fixed oils (whether in the manufacture of fatty acids for candle making, or more recently in the 'spent lye' of the soap-maker) it can be obtained by various synthetical processes, and, as Pasteur has shown, it is a constant product of the alcoholic fermentation of sugar, and hence it is a natural constituent of beer, wine, &c. 100 parts of sugar produce 3·5 parts of glycerin. Recent researches also tend to show that its compound with phosphoric acid $C_3H_5(OH)_2PO_4H_2$ is the starting point to which a number of complex constituents of the brain may be referred as its derivative, and to which they tend when they decompose.

Pure glycerin is a colourless, odourless, viscid liquid, with an intensely sweet taste. It is optically inactive and neutral in reaction. Its sp.gr. may be taken as 1·2665 at 15°C. compared
—35,5° with water at the same temperature. At ~~[illegible]~~°C. it solidifies to an amorphous mass, but when this is kept for a long time at or below 0°C. rhombic deliquescent crystals are formed. Its boiling-point appears to be so constant at 290°C. that Th. Gerlach (D. P. J. 208, 255, 1885; abstracted in S. C. I. 4, 226) recommends its use for the determination of this point on high temperature thermometers. A very small addition of water, however, lowers the boiling-point very considerably, a specimen containing 5 p.c. of water boiling at 164°C. The influence of pressure on the boiling-point of pure glycerin is thus shown: at 50 mm. 210°C., at 12·5 mm. 179°C. It is not volatile at ordinary temperatures, but is appreciably so at 100°C., more especially if water be present. This fact renders its quantitative determination very difficult. Its vapour burns with a pale blue flame.

Glycerin is one of the most powerful solvents known, and some of these solutions partake of the character of definite chemical compounds, and are used in the arts; they will be described under the head of the applications of glycerin. It is sufficiently hygroscopic to absorb half its weight of water from damp air, and it mixes with water in all proportions; the specific gravity of such mixtures diminishes so regularly that, if nothing else than glycerin and water be present, their relative proportions may be determined from the following formula:

$$\frac{\text{Observed sp.gr. of mixture} - 1{\cdot}000}{2{\cdot}665} = \text{percentage by weight of glycerin.}$$

For greater accuracy, substitute 2·61 as a divisor for proportions between 60 and 30 p.c. and 2·50 below 30 p.c.

The following table by Skalweit (Repertor. d. Analyt. Chemie, 5, 18) gives the specific gravities and refractive indices for the sodium ray, at 15°C. of mixtures of glycerin and water in various proportions:—

Glycerin p.c.	Sp.gr. compared with water at 15°C.	Refractive index at 15°C.	Glycerin p.c.	Sp.gr. compared with water at 15°C.	Refractive index at 15°C.
0	1·0000	1·3330	51	1·1318	1·4010
1	1·0024	1·3342	52	1·1346	1·4024
2	1·0048	1·3354	53	1·1374	1·4039
3	1·0072	1·3366	54	1·1402	1·4054
4	1·0096	1·3378	55	1·1430	1·4069
5	1·0120	1·3390	56	1·1458	1·4084
6	1·0144	1·3402	57	1·1486	1·4099
7	1·0168	1·3414	58	1·1514	1·4104
8	1·0192	1·3426	59	1·1542	1·4129
9	1·0216	1·3439	60	1·1570	1·4144
10	1·0240	1·3452	61	1·1599	1·4160
11	1·0265	1·3464	62	1·1628	1·4175
12	1·0290	1·3477	63	1·1657	1·4190
13	1·0315	1·3490	64	1·1686	1·4205
14	1·0340	1·3503	65	1·1715	1·4220
15	1·0365	1·3516	66	1·1748	1·4235
16	1·0390	1·3529	67	1·1771	1·4250
17	1·0415	1·3542	68	1·1799	1·4265
18	1·0440	1·3555	69	1·1827	1·4280
19	1·0465	1·3568	70	1·1855	1·4295
20	1·0490	1·3581	71	1·1882	1·4309
21	1·0516	1·3594	72	1·1909	1·4324
22	1·0542	1·3607	73	1·1936	1·4339
23	1·0568	1·3620	74	1·1963	1·4354
24	1·0594	1·3633	75	1·1990	1·4369
25	1·0620	1·3647	76	1·2017	1·4384
26	1·0646	1·3660	77	1·2044	1·4399
27	1·0672	1·3674	78	1·2071	1·4414
28	1·0698	1·3687	79	1·2098	1·4429
29	1·0724	1·3701	80	1·2125	1·4444
30	1·0750	1·3715	81	1·2152	1·4460
31	1·0777	1·3729	82	1·2179	1·4475
32	1·0804	1·3743	83	1·2206	1·4490
33	1·0831	1·3757	84	1·2233	1·4505
34	1·0858	1·3771	85	1·2260	1·4520
35	1·0885	1·3785	86	1·2287	1·4535
36	1·0912	1·3799	87	1·2314	1·4550
37	1·0939	1·3813	88	1·2341	1·4565
38	1·0966	1·3827	89	1·2368	1·4580
39	1·0993	1·3840	90	1·2395	1·4595
40	1·1020	1·3854	91	1·2421	1·4610
41	1·1047	1·3868	92	1·2447	1·4625
42	1·1074	1·3882	93	1·2473	1·4640
43	1·1101	1·3896	94	1·2499	1·4655
44	1·1128	1·3910	95	1·2525	1·4670
45	1·1155	1·3924	96	1·2550	1·4684
46	1·1182	1·3938	97	1·2575	1·4698
47	1·1209	1·3952	98	1·2600	1·4712
48	1·1236	1·3966	99	1·2625	1·4728
49	1·1263	1·3981	100	1·2650	1·4742
50	1·1290	1·3996			

Where the volume of glycerin is not enough to permit an accurate determination of its specific gravity, Strohmer (C. C. 15, 397) determines it by ascertaining its refractive index with Abbé's refractometer. The relation between the amount of glycerin and the refractive index is given by the formula:

$$n(\mathrm{D}) = 0{\cdot}75875 + \frac{(\mathrm{K} + 56{\cdot}569)\mathrm{D}}{\mathrm{D}(100 - \mathrm{C}) + \mathrm{C}}$$

where D = sp.gr. of anhydrous glycerin, and C = percentage of glycerin by weight.

Glycerine also mixes in all proportions with alcohol, but is nearly insoluble in ether, from which it separates any alcohol or water. It is, however, insoluble in carbon disulphide, petroleum spirit, benzene, and (contrary to the usual text-book statements) in chloroform. In fact, a rough test of its purity is to agitate it with an equal bulk of chloroform, when the impurities collect in an intermediate layer. A mixture of two volumes of absolute alcohol and one of ether, or of equal weights of chloroform and alcohol, may be used to separate glycerin from sugars, gums, and many extractives and salts.

Glycerin dissolves many substances, such as iodine, carbolic acid, mercuric iodide, the alkaloids, &c. more readily than water does. When agitated with many ethereal solutions it will remove the substances dissolved therein; it will in some cases prevent the precipitation of metallic solutions by fixed alkalis or by ammonia. Anhydrous glycerin dissolves caustic potash and soda, lead oxides, the sulphates and chlorides of potassium, sodium, and copper, all deliquescent salts, and the vegetable acids and alkaloids. Klever gives a long table of the solubilities of different bodies in 100 parts by weight of glycerin, from which the following are taken: 98 sodium carbonate, 40 alum, 25 ferrous sulphate, 20 lead acetate, 20 sodium chlorate, 0·50 quinine, and other alkaloids, 1·9 iodine, 0·20 phosphorus, 0·10 sulphur. The solutions of alkaline earths and of lead oxide in glycerin are not decomposed by carbonic acid, and would appear to be more or less definite compounds.

Perhaps the most characteristic chemical reaction of glycerin is that when heated with a dehydrating agent, *e.g.* concentrated sulphuric acid or potassium hydrogen sulphate, irritating fumes of acrolein (acrylic aldehyde) C_2H_3,COH are given off. It is this body which is produced when fat is burned. When glycerin is heated with phosphorous iodide, allyl iodide C_3H_5I is formed; heated with solid caustic potash it forms potassium acetate and formate, and free hydrogen. It is very readily oxidised by many reagents, carbon dioxide and water being the ultimate products; in a dilute aqueous solution and in presence of excess of caustic alkali, potassium permanganate oxidises it so definitely into oxalic and carbonic acids that the reaction may be used for its quantitative determination.

The best method for the detection of small quantities of glycerin (such, for example, as are to be found in beer, wine, milk, &c.) is that founded on its reaction with borax, with which it forms a compound having an acid reaction, the original aqueous solution of borax being alkaline. W. R. Dunstan (Ph. [3] 13, 257 and 14, 41) recommends the following method of applying the test. To 2 c.c. of a solution of 1 part borax in 200 water, add enough alcoholic solution of phenol phthalein to produce a rose-red colour. The liquid to be tested for glycerin is made neutral or very faintly alkaline to litmus, and is gradually added to the solution of borax until the rose colour is discharged. The liquid is then heated to boiling, when the red colour is restored, disappearing, however, as the solution cools. With 2 c.c. of the borax solution, about 5 c.c. of a 2 p.c. solution of glycerin must be added to destroy the colour, and the limit of the reaction is practically reached with a solution of this strength. The reaction occurs also with the other polyhydric alcohols, and is more delicate with mannitol than with glycerol. Ammonium salts also discharge the red colour, but it is not restored by heat.

Owing to the volatility of glycerin in presence of water (causing loss when its solutions are concentrated), and to its great solvent power, its accurate determination in a complex mixture is an exceedingly difficult problem. Some methods aim at isolating the glycerin in an approximately pure state. Albuminous and many other organic matters may be precipitated by basic lead acetate or by zinc chloride, and a mixture of alcohol with either chloroform or ether may be used to separate the glycerin from the watery liquid. For the determination of glycerin in beer or wine, Clausnizer recommends the following method. To 50 c.c. of the liquid, previously heated to 100°, add 3 grams slaked lime, evaporate to a syrup, stir in 10 grams of powdered marble, and continue stirring and heating till the mass is dry. It is then powdered, and an aliquot part ($\frac{2}{3}$ or $\frac{1}{2}$) thoroughly extracted with 20 c.c. rectified spirit, to which is subsequently added 25 c.c. of dry ether; the extract is then filtered off into a tared flask, the precipitate washed with ether-alcohol (3 : 2), and the ether and alcohol are distilled off; the residue is then dried at 100° until the loss does not exceed 2 milligrammes in two hours. This process may, *mutatis mutandis*, be applied to the determination of glycerin in other liquids. Hydrofluosilicic acid is sometimes used to precipitate the alkali metals.

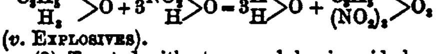
Three methods have been proposed for the determination of glycerin, based on its chemical reactions. The first, by Morowski (J. pr. 22, 401), depends on the fact that when glycerin is heated with litharge, 1 molecule of water is eliminated and monoplumbic glyceride, $C_3H_6PbO_3$ is formed. 20 or 30 times the supposed weight of glycerin is the proper quantity of litharge, the temperature is 125°, the time for heating two hours, and the increase in weight of the litharge multiplied by the factor 1·243 is the weight of the glycerin. The second, and volumetric method, which is applicable to the assay of soap lyes, and is described by Muter (An. 6, 41), is due to the fact that the solvent action of caustic potash on recently precipitated hydrated oxide of copper, is directly proportional to the amount of glycerin in the liquid. The copper in solution may be titrated with potassium cyanide, or may be precipitated by electrolysis. Within certain limits pointed out by Puls (J. pr. 15, 83), 73·5 parts of cupric oxide in solution correspond to 92 of glycerin. The third process, which under favourable conditions is very accurate, is the one alluded to above as depending on the oxidation of glycerin by potassium permanganate in presence of excess of caustic alkali:

$$C_3H_8O_3 + 3O_2 = C_2H_2O_4 + CO_2 + 3H_2O.$$

The excess of permanganate is destroyed by a sulphite, and the oxalic acid is determined by its calcium salt. The absence of other substances forming oxalic acid on oxidation—such as sugar and other carbo-hydrates, alcohol, and the acids of the acrylic or oleic series—must be ensured; if it is necessary to use alcohol in the preliminary process, methyl alcohol should be employed. This method is of very general application, and, with proper precautions, yields excellent results.[1]

Commercially, the ethers of glycerin are of the highest importance. The glycylic-ethereal salts of organic acids and of phosphoric acid have been already referred to in speaking of the natural sources of glycerin. Amongst those prepared artificially, the following may be briefly mentioned here.

(1) When glycerin is treated with a cold mixture of fuming nitric and concentrated sulphuric acid, nitroglycerin, or glycyl trinitrate $C_3H_5(O.NO_2)_3$, is formed, which is the basis of many explosives—such as dynamite, &c.—



$$\left.\begin{matrix}C_3H_5{}'''\\H_3\end{matrix}\right>O + 3\left.\begin{matrix}NO_2\\H\end{matrix}\right>O = 3\left.\begin{matrix}H\\H\end{matrix}\right>O + \left.\begin{matrix}C_3H_5{}'''\\(NO_2)_3\end{matrix}\right>O_3$$

(*v.* EXPLOSIVES).

(2) Treated with strong sulphuric acid alone, a body whose formula is $C_3H_5(OH)_2SO_4$ is produced, which forms soluble but unstable salts with barium, calcium, and lead.

(3) Glycyl arsenite $C_3H_5AsO_3$ is formed by dissolving arsenious oxide (white arsenic) in glycerin. An amber-yellow fatty substance results, melting at 50°C., which is much used as a mordant by calico-printers for fixing aniline colours. A similar compound is formed when oxide of antimony is treated with an alkaline solution (caustic soda is usually employed) of glycerin. Such a mordant is cheaper than tartar emetic (D. P. J. 1885, 258, 520).

(4) At 160°C. glycerin will dissolve two-thirds of its weight of boric acid, forming $C_3H_5BO_3$—a substance patented as a preservative agent under the name of 'boroglyceride.'

Commercially, glycerin is invariably obtained as the result of the decomposition of neutral fatty bodies in the process of manufacturing either candles or soap. In the preparation of pure fatty acids for candles, the decomposition is effected by lime in presence of water at a pressure very slightly exceeding that of the air at the time, and at about 105°C., or by water alone at a temperature above 300°C., or by a combination of both methods. Owing to the large demand for glycerin for the manufacture of explosives, the processes just alluded to did not produce a sufficient quantity, and hence manufacturers turned their attention to the enormous quantities of dilute glycerin mixed with salt which were allowed to run to waste in the 'spent lye' of the soap-maker; hence, within the last few years, a very large amount of pure glycerin has been prepared from that source by processes of quite recent invention.

The preparation of glycerin as a by-product in the candle manufacture will be first described.

In the earlier stages of the industry, the neutral fat, usually tallow, was boiled in open

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[1] A full account of the method, and references to original memoirs of investigations thereon, will be found in Allen's Commercial Organic Analysis, 1886 [2] 289–292.

vats by the injection of steam at from 105° to 110°C., with 16 p.c. of lime, previously made into a thin cream with water. The result was a hard lime soap and 'sweet water'—*i.e.* very dilute glycerin—which merely required concentration to produce a moderately pure article. Early in 1854 Tilghmann found that when an emulsion of 2 parts of tallow and 1 part of water was pumped through a coil of pipe heated to 322°C. and was then allowed to stand, it separated into two layers, the upper one consisting of fatty acids and the lower of dilute glycerin. Several modifications of this were afterwards patented, but the only one worked on a large scale was that of G. P. Wilson and G. Payne, dated July 24, 1854, under which considerable quantities of 'distilled glycerin' have been made by Price's Candle Company. In this process neutral fats are put into a still (fig. 1) provided with a fine steam-worm, and also with a fractional condensing apparatus K, of large surface; a usual form is a series of vertical copper pipes, connected at top and bottom by gun-metal bends, and mounted on an iron frame set over a series of circular iron tanks *h*. Standing in each of these tanks, and connected with the gun-metal bend above it, is a condensing worm whose temperature can be controlled by water in the surrounding tank. The contents of the still are heated, usually by an external fire, to about 300°C., when abundance of superheated steam is injected among them by the pipe and from the superheating furnace; the result is that mixed vapours of fatty acids, glycerin, and water are carried over to the upright pipes, where pure fatty acid vapours condense in the pipes nearest to the still, while those farthest from it yield fatty acids and mixtures of glycerin and water in various stages of concentration. If the temperature be allowed to rise above 300°C., some of the glycerin is decomposed, with the formation of acrolein, thus: $C_3H_8O_3 = 2H_2O + C_3H_4O$.

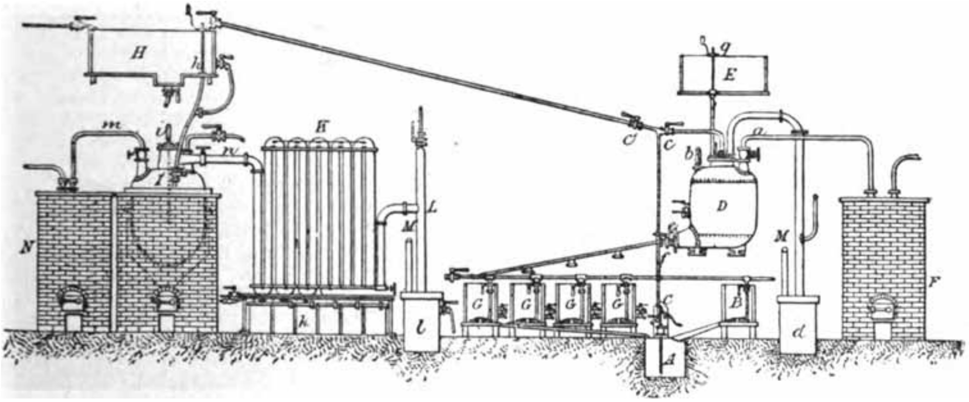


Fig. 1.

Another method of removing glycerin from neutral fats, especially palm-oil, prior to the distillation of the fatty acids for the manufacture of 'composite' candles is to treat the fat with concentrated sulphuric acid at about 175°C., and then to subject it to prolonged washing with water at, or a little above, 100°C. The acidulated water thus obtained contains nearly all the glycerin of the original fat; barium (or calcium) carbonate is added to it until effervescence ceases, the liquid is clarified by subsidence and concentrated by evaporation in open cast-iron pans till its sp.gr. is 1·240.

The apparatus used is also shown in fig. 1. D is a copper vessel to contain the neutral fat, which may be heated by an open fire, or preferably by superheated steam, through the pipe *a* from the furnace F containing a superheater. E is a lead-lined tank filled with sulphuric acid, which is admitted at pleasure into D by opening the valve controlled by the handle *g*. The vapours evolved—chiefly sulphurous acid—pass by a large pipe into a condenser *d*, meeting a shower of water on their way. C is a force pump to transfer to D the fat which is melted into A. When the 'acidification' is complete, the fat is run off into the tanks G G, where it is boiled with steam for some hours, on about one-fourth its volume of water. This last stage of the process is that in which the neutral fat is decomposed into fatty acids and glycerin.

Latterly, however, glycerin has become sufficiently valuable for candle manufacturers to adopt that method of preparing fatty acids which gives them, *cæteris paribus*, the greatest yield of glycerin. In this process, as patented by De Milly in 1856, about a ton of neutral fat is heated in an autoclave with one-third its volume of water and 2 p.c. of lime to a pressure of 8 atmospheres for four hours, a little steam being allowed to escape at the top to promote the agitation of the whole mass. The whole is then blown out into a tank, and the 'sweet-water' is run off and concentrated by evaporation till its sp.gr. is 1·220, when it is of a brownish colour and known as 'raw,' in which state it is sold for many purposes. The evaporation may be conducted in many ways. A useful form, originally devised for sugar-boilers, and termed 'évaporateur universel,' is shown in fig. 2. It consists essentially of pairs of saucers set edge to edge upon a central hollow revolving shaft, through which steam passes to their interior; the lower edges of these dip into a jacketed trough containing the liquid to be evaporated, and when they are revolved thin layers of the liquid are brought up and speedily evaporated. The apparatus may also be worked in a vacuum (fig. 3). Its further purification is conducted somewhat as follows. It is heated in a jacketed pan with that kind of animal charcoal known as ivory black, and is then distilled, this alternate treatment being repeated as often as may be necessary. The distillation is performed in an atmosphere of superheated steam, and at as low a temperature as is consistent with distillation, usually about 210°C., in a copper still heated externally, and furnished with the upright fractional condensers previously described, or with some modification thereof. The number of distillations required depends on the quality of the original raw glycerin and on the purity of the product demanded, but in all cases it is conducted very slowly. Of the six fractionating condenser coils, Nos. 1 (nearest the still), 2, and 3 usually yield pure glycerin, while the dilute products from 4, 5, and 6 are frequently returned to the still, although in some cases they are concentrated in a vacuum pan. Some stills hold as much as 3 tons, but they are usually smaller, and occasionally they are provided with a continuous feed, to avoid emptying and re-charging. A catch-box on the goose-neck, in case the contents boil over, is a useful precaution. This is shown at D, fig. 4, which is the outline of a form of still and condenser much used on the continent of Europe. External heat and injected superheated steam are both employed to effect distillation. The still-head B is unusually large, and the fractional condensers E are upright cylinders with longitudinal partitions F running nearly their whole length. The condensed liquid runs out through G into receptacles H.

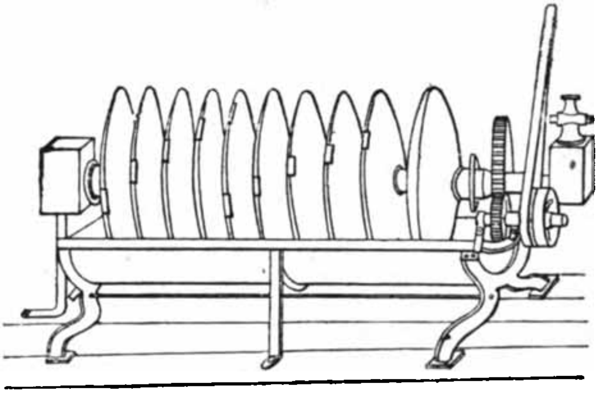


FIG. 2.

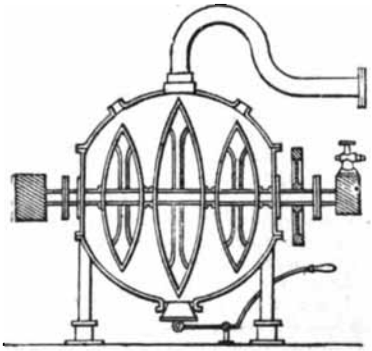


FIG. 3.

Although evaporation and distillation are the usual methods of purifying glycerin, the action of cold upon its solutions is sometimes employed in conjunction with them, especially by Sarg, at Vienna. When an aqueous solution of glycerin partially freezes, the frozen mass contains more water than the remaining liquid, and hence concentration can be effected. According to Werner, commercial glycerin will freeze more readily if chlorine gas be passed into it. In purifying glycerin by cold, the whole mass is cooled to 0°C. or below, and some crystals of glycerin are added; nearly the whole mass rapidly solidifies, and a centrifugal machine is used to separate the solid from the liquid portions. Treated in this way, glycerin at 1·240 sp.gr. can, it is said, be concentrated to 1·266 sp.gr.

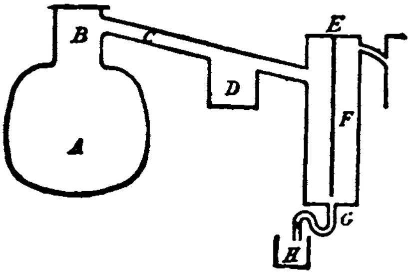


FIG. 4.

Owing to the very large demand for glycerin for the manufacture of explosives, and the great difficulty of recovering it from its most abundant source among manufacturers' by-products—viz. soap-makers' 'spent lye'—many attempts have been made within the last few years to remove glycerin from fats prior to their conversion into soda and potash soaps. The most successful of these was worked out by Messrs. Michaud Frères of Paris, and has been patented in most countries. It consists essentially in resolving neutral fat into fatty acids and glycerin by the action of water and a minute quantity of zinc oxide (or, in another modification, of magnesium carbonate) under high pressure, and it is thus described in the English Patent (Oct. 27, 1882) :—'For this purpose the fatty matter is subjected in a close vessel to the action of steam at a pressure of 100–130 lbs. per square inch, and at corresponding temperature, in presence of ¼–⅛ its weight of water, and ⅛–⅜ p.c. of its weight of the oxide of zinc commercially known as zinc white, or a like proportion of zinc powder or zinc grey, which is a residue in the treatment of zinc, being a mixture of zinc with its oxide.' It is claimed for this process that 'the reducing action of the zinc powder prevents the discolouration of the acid fats such as results from the ordinary treatment'—an expectation, however, which does not appear to have been realised commercially. Hence the soaps made from tallow &c. which has been treated in this way assume a spotted appearance after some time, and are not so good-looking as when made by the ordinary processes. This fact is almost fatal to the commercial success of the process, since the competition in the soap trade is exceedingly keen, and both the wholesale buyers and the consumers are guided to a much greater extent than they ought to be by the mere appearance of the soap. This inferiority of colour arises, in all probability, from the formation of products of oxidation of some of the constituents of the original fat, owing to the high temperature employed, and it is well known that such products, especially in the case of tallow, are apt to 'work foxy' in the soap pan —*i.e.* to form high-coloured compounds with caustic alkalis. It is also alleged that the melting-point of the fatty acids is lowered by the process, and hence that the hardness of the soap is lessened. Moreover, fatty acids prepared in this way possess the general characteristics of distilled fatty matter—viz. they resist the action of ordinary bleaching reagents, and they tend to darken on exposure to air. It cannot be said, therefore, that these methods, theoretically scientific as they are, have been, or are at present likely to be, adopted to any extent by soap manufacturers, who have, however, recently attained a large measure of success in their attempts so to modify their processes as to recover very large quantities of both glycerin and salt from the spent lye hitherto allowed to run to waste. The earliest of these attempts was by H. Reynolds in 1858, and its main features have reappeared in all subsequent processes—viz. concentration of the liquid, removal of the salts by 'fishing,' and distillation of the crude glycerin by superheated steam. The recovery of the glycerin from the spent lye has the advantage of interfering less than any other glycerin process with the ordinary methods of soap manufacture, methods which are as simple as possible, the soap being made in open vessels, and in practically one operation, since no previous manipulation of the fatty matter is required.

The spent lye contains water, glycerine, albuminous, resinous, and soapy matters (whose nature and amounts vary with the kind of fats which have been saponified), and a large number of salts of sodium, viz. sodium chloride, sulphate, hyposulphite (and other oxygen sulphur acids), carbonate, sulphocyanide, &c., as well as occasionally some caustic soda, and lastly some magnesium salts. The mineral salts depend mainly on the purity, or otherwise, of the caustic soda lye employed in saponifying, and of the common salt used in 'salting out' the soap. The exact treatment followed depends in great measure upon the composition of the spent lye. Mr. C. T. Kingzett gives the following as its average composition per gallon after concentration :

Water	7·53 lbs.
Glycerine	2·04 „
Salts	2·78 „
	12·35

and the same authority gives the annexed composition of the salts deposited during the process :

Sodium chloride	78·12
„ sulphate	8·61
Insoluble organic matter . .	0·22
Glycerin and organic matter .	3·55
Water	7·50
Alkali (calculated as sodium carbonate)	2·61
	100·61

These figures, however, must not be taken as giving more than a very general idea of the main facts, since the composition of these products is subject to very great variations, caused by local circumstances, and by the different processes employed in the manufacture of soda. The objects of the various patented processes for dealing with spent lye, in order to recover from it both the glycerin and the sodium chloride, may be reduced to three, viz.:

(1) To remove or destroy the albuminous, resinous, and soapy matters present in the lye.

(2) To economise the cost of concentration to the point at which the product may be either used as crude glycerin, or purified by distillation.

(3) To facilitate the removal of the salt employed, and to recover it in such a form that it may be used again in the ordinary process of soap-making.

It has also been proposed to 'salt out' the soap with some salt other than sodium chloride, which in the subsequent processes shall be more easily separated from the glycerine, as for example sodium sulphate. This, however, would involve greater changes in the soap manufacture than those concerned in it have yet seen their way to adopt on a large scale. Moreover, resin soaps, and those made from weak oils, cannot be salted out in this way by sodium sulphate.

To effect the first object, a large number of 'coagulating agents' have been proposed, and in many cases subsequently abandoned. Among them are fatty acids, which also removed the saponifiable sodium salts, albumen itself, blood, gelatine, salts of aluminium and of chromium, caustic lime, calcium chloride, tannic acid, &c. The second object is a matter solely of arrangement of manufacturing plant, and is, as usual in such cases, dependent mainly upon local circumstances and conditions. The third is more strictly chemical, and comprises among other things the use of hydrochloric acid gas, to render the salt more insoluble; of carbonic acid gas to precipitate the alkaline sodium salts as bicarbonate; and of copper salts to remove the sulphocyanides present. Under this head may also be classed patents for the separation of glycerine from salt by dialysis, and by solution of the former in alcohol; the expense of both these methods, however, precludes their commercial adoption, except for special purposes. Altogether, no fewer than 90 patents have been taken out for the manufacture of glycerin from soap lye, or for distilling the same. The only process, however, which appears to give practical results is that of Messrs. Domeier & Co., which consists of a combination of various patents, supplemented by modifications which are dependent on the composition of the spent lye, and hence are peculiar to each special factory where the process is carried on. This industry is a remarkable illustration of the fact often met with in manufacturing chemistry, that the best patent is of very little use without the additional knowledge necessary to work the patent, which usually can only be obtained by practical instructions given by the patentee. Messrs. Domeier's process is used by all the largest soap-makers in England, and by a large number in foreign countries. By its use, the theoretical quantity of glycerin contained in the fats and oils is recovered, and the process is not costly, since the other products obtained in working it pay for a very large proportion of the labour involved. The principal patents in use by Messrs. Domeier are No. 2,462 in 1881, and Nos. 7,972, 7,973, and 8,051 in 1885.

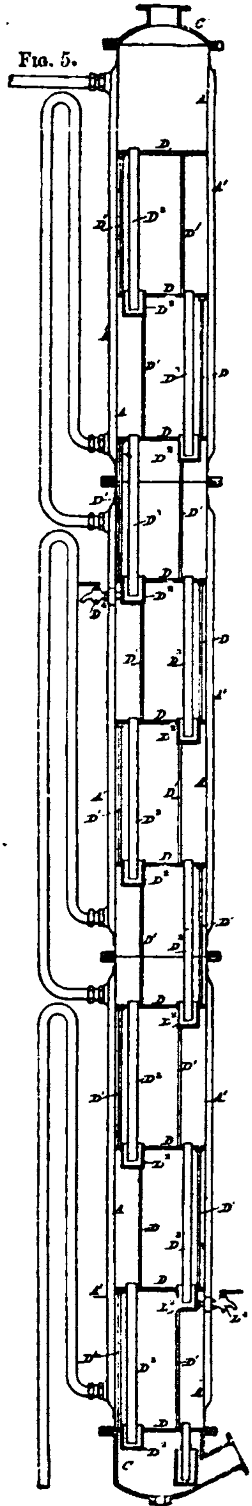
The outline of the process is somewhat as follows. Sufficient lime (usually about 1½ per cent.) is added to the lyes to convert the carbonated alkali into caustic, and the liquid is concentrated to the point when common salt begins to be deposited; the caustic alkali is then removed by boiling the liquids with rosin, and the rosin-soap which results is removed by skimming, to be subsequently incorporated with a fatty soap, for the production of the familiar household yellow or brown soap. If the original lyes were of the class known as Lancashire lyes, containing as impurities alkaline hyposulphites, sulphides, sulphocyanates, cyanides, ferrocyanides, &c., the liquid is neutralised with mineral acid, and perchloride of iron is added as long as a precipitate is formed, which is removed by subsidence; it contains fatty matter and Prussian blue, each of which can be purified by well-known methods. The sulphur has still to be separated out, for which purpose 3 or 4 per cent. of hydrochloric acid is added, the liquid is heated, and hot air is blown through it for some hours; sulphurous acid passes off with the air, and sulphur is deposited in the liquor. To render the decomposition of the oxidisable sulphur compounds as complete as possible, chlorine is introduced, usually in the form of chloride of lime, a solution of which is added until free chlorine is found in the liquor. The sulphur is removed (by subsidence) and the liquid neutralised; it is then fit to be boiled down for the recovery of common salt, and the production of glycerin by distillation.

The concentration of the lyes is one of the most important practical parts of the process. It is generally considered advisable that an ordinary concentrating pan, if used, shall be fired at the side, and not from beneath, to avoid cracking it from the deposition of salts. An evaporator much used is a conical pan, apex downwards, surrounded with circular flues, and opening into a sphere at its lowest part, in which there is a valve at the back, to facilitate the removal of the salt. The concentrated crude glycerin is pumped into cooling tanks at a temperature between 150°C. and 170°C. and at this stage it consists roughly of 10 p.c. of salt and 80 p.c. of glycerin. The salt which is 20 p.c. of water recovered is washed with brine, and is finally obtained in so pure a state that it may be used in the manufacture of even the finest soaps. Frequently the crude glycerin is 'washed' by being mechanically mixed with some suitable solvent, which will dissolve out the impurities. For this purpose the patentees use 'a hydrocarbon obtained from the distillation of coal tar, petroleum, or other mineral oil, carbon bisulphide, amylic alcohol, ether, or other suitable solvent in which the glycerin is practically insoluble.'

The crude glycerin has now to be distilled. The still employed may be of any convenient form, as shown in the preceding figures; it is provided with a special distributor for steam, and an arrangement for removing the deposited salt, in most cases periodically. The condensing apparatus, however, is different, and much resembles that employed in vaporising alcohol. It consists of an upright cylinder A A (fig. 5) or casing, containing shelves or trays, D, D, one above the other, and perforated with conical holes $\frac{1}{16}$ inch diameter at the top, in such a way that the vapour which enters at the bottom, C, is able to ascend through the apparatus. Liquid condenses on the shelves, and runs down by pipes D^2 into receptacles D^3, whence it can be drawn off by taps D^4. As the vapour progressively cools, condensation takes place, glycerin with but little water is deposited on the earlier shelves, while mixtures of glycerin and water with lower and lower boiling-points condense on the succeeding shelves; finally, at the end of the series of columns, steam blows out from the condenser, a temperature just above 100° C. being maintained even there. Two receivers are provided, one for glycerin of the purity required, the other for impure glycerin, the taps D^4, D^4, being set to run into one or the other, as may be found necessary. When the working of the still has been adjusted, the operation is continuous, care only being required to maintain the temperatures in the various parts of the condenser without change, for which purpose thermometers are employed.

The Yaryan evaporator is now being largely employed for concentrating glycerin. In this arrangement of evaporating plant, the latent heat of the vapour of liquids boiling under a low vacuum is used to boil a second vessel working under a higher vacuum, and so on in a series of three, four, or even six effects. The liquid to be concentrated flows in small thin streams through pipes surrounded with steam, and is not exposed to a high temperature for more than two minutes; the feed and discharge of liquor to and from the coils is continuous and automatic, and the quantity of liquid within the coils at any time is small, while the product is delivered con-

FIG. 5.



tinuously concentrated to the exact point desired. V. EVAPORATION.

Analysis and assay of commercial glycerin.[1]—The account above given of its manufacture will be the best guide to the impurities likely to be present, and hence a knowledge of the history of the glycerin, or of the purpose for which it is to be used, suffices to limit the numbers of impurities to be searched for. The colour is no criterion, since glycerin once distilled from soap lyes may be darker than some specimen of undistilled glycerin. Its specific gravity is best determined by Mohr's lever balance, the glass plummet of which, being totally immersed, indicates more surely than a hydrometer. The ordinary distilled product is rarely above 1·261, whereas raw glycerin from soap lyes may vary from 1·290 to 1·360. The proportion of mineral matter, ascertained by igniting about 5 grams, affords a good indication of the nature of a sample; distilled glycerin should not give more than 0·1 or at most 0·2 p.c. Distilled glycerin burns quietly, and any considerable black residue indicates organic impurity. The ash may be examined by the ordinary methods of mineral analysis. Calcium (often as calcium oleate) is a frequent impurity, best determined by precipitating the diluted glycerin with ammonium oxalate; similarly, oxalic acid may be detected by calcium chloride. Chlorides cannot be determined by direct precipitation with silver, its chloride being slightly soluble in, and its nitrate reduced by, glycerin; hence the glycerin must be burnt away, and the residue exhausted with water and titrated with decinormal silver nitrate. Sulphates may be determined by precipitating the diluted glycerin with barium chloride. The total amount of organic impurities may be determined with a fair approach to accuracy by the following method. Fifty grams are diluted with double the bulk of water, carefully neutralised with acetic acid, and warmed to expel carbonic acid; when cold a slight excess of basic acetate of lead is added, and the whole well agitated. The precipitate is washed by decantation, collected on a double counterpoised filter, dried at between 100 and 105°C. and weighed. The precipitate and filter are then separately ignited in a porcelain crucible at a very low red heat, the residues moistened with nitric acid and re-ignited. The weight of the residual lead oxide (and sulphate), deducted from that of the dried precipitate, gives the weight of organic matter precipitable by lead. This reaction is used by the officers of the United States Customs to distinguish raw from distilled glycerin.

Faint odours in pure glycerin may often be detected, and occasionally recognised, by agitating the sample with ether, allowing the liquids to separate, and then pouring the ethereal solution into a watch-glass. As the ether evaporates, the odour is developed.

The proportion of albuminous matter may be approximately determined by igniting the dried precipitate with soda-lime; the ammonia formed, multiplied by 5·09, gives the required amount. Rosin may be separated by prolonged dialysis at 100°C. (the glycerin passing through the porous septum) or by agitating the sample with ether or petroleum spirit. By agitating glycerin with chloroform, the higher fatty acids, rosin oil, and some other impurities are dissolved, while others form a turbid layer between the chloroform and supernatant glycerin. The lower fatty acids, such as formic and butyric (frequently present) are detected by gently heating the glycerin with alcohol and sulphuric acid, when the ethers are formed, which have characteristic odours. Pure diluted glycerin should give no precipitate with silver nitrate, and should not blacken when mixed with an equal volume of strong sulphuric acid; sugar and some other impurities cause a marked darkening, or even charring. Pure dilute glycerin does not sensibly reduce Fehling's copper solution when heated with it to 100°C. for a few minutes; glucose, cane sugar, and arsenious acid, if present, will do so. When mixed with an equal volume of a 10 p.c. solution of silver nitrate, and allowed to stand ten minutes in the dark, pure glycerin should show no black deposit of reduced silver.

According to H. G. von Törring the various methods for the estimation of glycerin are subject to important sources of error, which are avoided in a new method especially applicable to its determination in brandy lyes depending on the following facts—(*a*) A solution of glycerin may be evaporated, without losing a trace of glycerin,

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[1] Summarised from Allen's Commercial Organic Analysis, vol. ii., with some additions.

until the residue contains 50 p.c. of water. By mixing the residue with burnt gypsum most of the water is absorbed, and a mass obtained suitable for the extraction of the glycerin by a solvent. (*b*) The glycerin can be completely separated from the non-volatile matters by distillation *in vacuo* at a temperature of 180°. (*c*) The aqueous glycerin obtained by distillation is suitable for precipitation of the glycerin as benzoate. The method of procedure is to evaporate 30 c.c. of the filtrate from the lyes on the water-bath to 5 c.c. Then 15 grams of burnt gypsum are mixed with the residue, and when the mass begins to set it is well powdered and exhausted for six hours with alcohol in an extraction apparatus. The alcoholic solution is treated with 10–20 c.c. of water, and heated until all the alcohol is driven off, when the residue is distilled. The distillation apparatus consists of a retort resting in an air-bath, and a Liebig's condenser. The receiving flask has a neck connected with an air pump. The distillation is at first carried on at 150–170° without working the air pump, until all the water has passed over into the receiver. Then the pump is set to work, and the temperature raised to 190–210°. When all the glycerin has come over, about 3–4 c.c. of water are added to the contents of the retort, and distilled at 150–170°, under ordinary pressure, in order to wash all the glycerin into the receiver. The yellowish distillate, amounting to 10 or 15 c.c., is mixed in the receiver with 5 c.c. of benzoyl chloride and 35 c.c. of a 10 p.c. solution of caustic soda, with frequent cooling and shaking to consolidate the precipitated glycerin benzoate, which is finally collected on a weighed filter, washed with water, and dried for two to three hours at 100° (H. G. von Törring, Landw. Versuchs. 36, 23; S. C. I. 8, 424).

Glycerin intended for pharmaceutical or medical use, or for the manufacture of nitroglycerin, should be distilled, and should give no reaction with any of the tests named above. A very large proportion of glycerin produced (the total production throughout Europe being at present about 25,000 tons per annum) is converted into nitroglycerin, and thence into dynamite and other explosives. For this purpose a special 'nitrification' test is made the basis of commercial transactions in glycerin. 100 parts of pure glycerin should yield 210 parts of nitroglycerin. To perform the test 10 grams of glycerin are cautiously added to a mixture of 27 grams of nitric acid, sp.gr. 1·50, and 47 grams of sulphuric acid, sp.gr. 1·842. The purer the glycerin is, the quicker and sharper will be the separation between the nitroglycerin formed and the acid liquid. If after the operation the mixture be allowed to settle in graduated tubes, comparative results may be rapidly obtained from a number of samples. The nitrification temperature must be between 20 and 30°C. and the test should only be attempted by experts, as a slight want of caution would lead to disastrous results.

The largest dynamite manufactory in the world is that of Nobel's Explosive Company (Limited), at Ardeer, on the coast of Ayrshire, Scotland, where about 8 tons of explosives are daily manufactured, the basis of the whole being nitroglycerin. W. L. C.

GLYCOLIC ACID, *Hydroxy-acetic acid* (*Acide glycolique*, Fr.; *Glycolsäure*, Ger.), $CH_2OH.COOH$. Formed by the oxidation of glycol $CH_2OH.CH_2OH$, or by the oxidation of alcohol with nitric acid at ordinary temperatures. From chloracetic acid $CH_2Cl.COOH$ by boiling it with water.—Crystals, which if pure are permanent in air, but if impure deliquesce. Readily soluble in water, alcohol, and ether. Cannot be distilled without decomposition. Yields on oxidation oxalic acid. The glycolates of the alkalis are deliquescent; calcium glycolate $(C_2H_3O_3)_2Ca$ (with 3 and 4 aq) and silver glycolate $(C_2H_3O_3Ag)_2.H_2O$ are sparingly soluble in water (*v.* HYDROXY-ACIDS). F. R. J.

GLYCYRAMARIN *v.* LIQUORICE.

GLYCYRRETIN *v.* LIQUORICE.

GLYCYRRHIZIC ACID *v.* LIQUORICE.

GLYCYRRHIZIN *v.* LIQUORICE.

GNOSEOPINE *v.* VEGETO-ALKALOIDS.

GOA POWDER *v.* ARAROBA POWDER.

GOLD. Au (Aurum). At. wt. 196·85 (Thorpe and Laurie); 196·64 (Krüss); 196·90 (Mallet). The occurrence of gold in nature in the metallic form, the bright colour of the metal, and its resistance to atmospheric action, led to its being utilised for ornaments at very early times. The same reasons, together with the comparative scarcity of the metal, led also to its adoption for the purposes of coinage, but it was soon found necessary to add to it a certain proportion of another metal to increase its hardness and thus to impart to it a greater resistance to wear than is possessed by gold in its pure state. The metals usually employed for this purpose were then, as now, copper and silver. The use of silver as the alloying metal is accompanied by the difficulty that comparatively small quantities of this metal greatly diminish the yellow colour of gold, whilst larger quantities destroy it altogether. Native gold nearly always contains silver, and occasionally the percentage is so high as to form a true gold-silver alloy. An alloy of this kind, elektron, was used for coinage at a very early date in Greek history.

Gold is the most extensible of all metals. It may be hammered into a leaf only 0·00009 mm. thick, and drawn into wire of so small a size that 166 metres will weigh but a single gram. Its sp.gr. is 19·31 and it melts at about 1,075°C. Molten gold is green in colour, and when allowed to solidify without being disturbed it cools down to a temperature at which the surface of the metal appears quite dark, and then it suddenly 'flashes,' evolves a large amount of heat, raising the metal to a bright yellow heat again, and then solidifies. The properties of the metal are destroyed by the action of very small quantities of certain impurities, notably lead and bismuth. Gold containing 0·2 p.c. of silicon has so low a melting-point that it softens in the flame of a candle.

Gold occurs in nature chiefly in the metallic form, but occasionally in combination with other elements, especially tellurium. Iron pyrites and arsenical iron pyrites very frequently contain small, and sometimes large quantities of gold. It is believed that this gold is usually present in the metallic state. Galena, too, frequently contains gold, and it is also found in connection with zinc blende and other minerals.

Native gold. The sources of native gold are mainly two:—1. Quartz veins, and 2. Secondary alluvial deposits. It is chiefly from this latter source that the metal has hitherto been obtained, but owing partly to the gradual exhaustion of the more important of the known alluvial deposits, and partly to mining difficulties connected with their treatment, it has of late become of somewhat less importance. Quartz mining, on the other hand, has made rapid progress.

The metallurgical treatment of auriferous quartz and of alluvial gold deposits is exceedingly simple. So much so, indeed, that whilst in the case of many other metals the ores to be suitable for metallurgical treatment on a commercial scale must contain high percentages of the metal to be extracted, and even, as in the case of lead, sometimes as much as 70 p.c. or more, yet if the ton of auriferous quartz contain but 2 or 3 dwts. of gold it might (under favourable circumstances) prove profitable to work, and with 1 oz. of gold would in many cases yield large profits. This difference is still more marked in the case of the auriferous gravel worked by hydraulic mining, as a ton of such material rarely contains more than a few grains of gold. The value of the product tends, however, to counterbalance the smallness of the quantity present in the material to be treated.

The alluvial or 'placer' deposits may be subdivided into (1) shallow placers, and (2) deep leads; the former consisting of surface gravel beds, the deep leads being beds of gravel at greater depth, frequently covered over to a considerable thickness with more recent deposits. The 'deep leads' are usually the beds of ancient rivers. In working placer deposits 'false bottoms' are frequently met with. These are beds of gravel cemented together in such a way as at first sight to appear to be the bed rock. Large quantities of similar auriferous cemented material have in recent years been discovered in the Transvaal where what appear to be reefs of this cement, or highly-inclined beds—banket reefs—have been traced for very considerable distances, and worked in places to a considerable depth.

The metallurgical treatment of these deposits of gravel and of cement is intimately connected with the mode in which they are mined, and, in fact, the method of mining and the metallurgical treatment are mutually subservient to each other. The gold occurring in the deposits of gravel is obtained by washing away, by the aid of water, the lighter gravel from the gold disseminated through it. The cement has usually to be crushed to a fine state of division by the aid of stamps, by heavy rollers, or by other similar means, or its disintegration is effected by the aid of a 'puddling machine.' These latter machines vary in construction, one form consisting of a perforated iron pan with a movable bottom, in which arms carrying iron teeth are caused to revolve. The cement is charged into the machine, and water being allowed to flow into it, the teeth revolving, disintegrate the cement, the finer portions of which are carried away by the water through the perforations in the pan, and the coarser portions may then be withdrawn either by lowering the bottom of the pan or by other suitable means. In other cases the lumps of cement are forced by a current of water against an iron plate, the force of impact being sufficient to break up the material. The gold occurring in this cement is frequently in so fine a state of division, and so coated with other substances, that a large proportion of it will, if the cement is treated by the ordinary battery method, escape into the 'tailings,' and it has been shown that grinding to a fine state of division is frequently far better adapted to the treatment of the material than is a stamp battery. The Wiswell ore pulveriser and amalgamator, fig. 1 is a machine of this type.

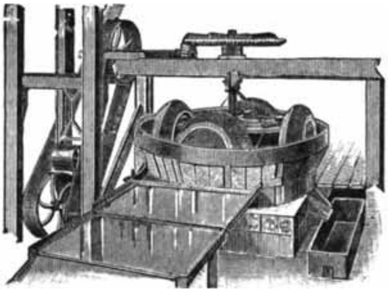


FIG. 1.

The finely divided auriferous material is either passed over amalgamated copper plates as in the stamp battery, or, in the case of coarser material, is treated similarly to the ordinary method of treatment to which auriferous gravel is subjected. This consists in passing the material to be treated through long box sluices, by the aid, it may be, of a current of water directed against the gravel bank by an iron nozzle or monitor attached to a length of piping. These sluices consist of a series of wooden troughs, each of which is from 1 foot to 5 feet wide, and 1 foot to 2 feet high, and 12 or 14 feet long. One end of such a trough is narrowed slightly so as to fit into the broad end of a similar trough, and numbers of these are connected together in this way to form the sluice, which may be as much as several thousand feet in length. The troughs are so arranged as to allow a fall of from 8 to 18 inches in the 12-foot length. Attached to the bottoms of the wooden troughs are raised projections termed 'riffles,' which usually consist of strips of wood attached longitudinally and transversely. The auriferous gravel being carried through these troughs by a current of water, the gold, owing to its greater specific gravity, settles behind the riffles whilst the gravel is carried forward by the current. Mercury is charged in at the head of the sluice to assist in the collection of the gold, and amalgamated copper plates are occasionally swung across the sluice in order to induce the amalgamation of the float gold which is carried forward by the current. The sluice is divided into lengths; at the end of each is a 'grizzly,' a perforated portion over which the coarser gravel passes, whilst the finer gravel passes through the perforations on to another portion of the sluice below it, usually at a lesser inclination, and provided with a separate water supply. These sluices are 'cleaned up' at intervals, the water being turned off, the sluices emptied of gravel and the gold and amalgam collected from behind the riffles. The greater portion of the gold is caught at the head of the sluice, and this portion is therefore cleaned up at frequent intervals, whilst the other portions are only attended to once or twice a year. The amalgam collected is squeezed through a bag, usually made of canvas or chamois leather, the solid amalgam remaining in the bag is retorted, and the residual mercury is used over again in the sluices.

In the treatment of gold quartz it is customary to stamp the quartz to a fine state of division in a stamp battery, pass it over amalgamated copper plates to collect the free gold, and then over a vanning machine to concentrate and collect the pyrites usually disseminated through the quartz, this pyrites being frequently highly auriferous. Before the quartz is charged into the stamp battery it is broken down to a suitable size by a rock-breaker. In that shown in fig. 2 the quartz is crushed between a fixed and a moving iron jaw, this latter being so placed as to admit of large-sized lumps of quartz being charged in at the top, whilst at the bottom, where the jaws close, only comparatively finely divided material can pass through, the size being regulated at will. The quartz then passes to the stamp battery, fig. 3.

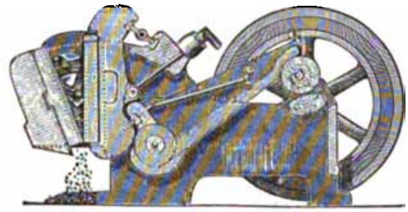


FIG. 2.

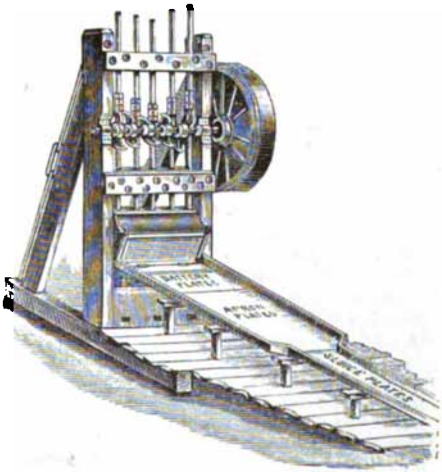


FIG. 3.

The weight of the stamps varies considerably, as also does the rapidity of the drop. Usually each stamp will weigh some 700 or 800 lbs., and will drop seventy or eighty times a minute. Both the weight of the stamp and the rapidity of the drop depending on the character of the quartz to be treated and on the degree of fineness to which it is to be reduced. A current of water introduced into the mortar carries the finely crushed quartz through a wire-gauze or perforated metal screen of the desired degree of fineness—usually 30 to 60 meshes to the linear inch—on to amalgamated copper plates in front of the battery. These plates are frequently arranged in the form of a series of steps to ensure a more thorough contact between the fine gold suspended in the current of water and the amalgamated plates. That portion, too, of the plates which immediately adjoins the stamp-battery, and on which the greater portion of the gold not caught inside the battery collects, usually consists of copper plates electro-plated with silver, the silvered plate presenting after amalgamation a much cleaner surface than does the ordinary amalgamated copper plate, in which the copper dissolved in the mercury induces the formation of a superficial film of oxide. A number of modifications of the ordinary amalgamated plates, as shown in fig. 3, are in use for this purpose. The material escaping from the plates passes to a concentrating apparatus. The most usual form is the Frue vanner, fig. 4.

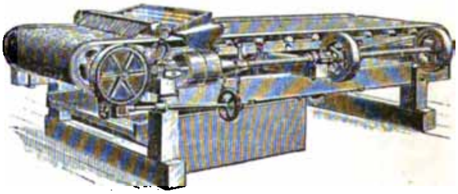


FIG. 4.

In this machine a sloping endless india-rubber belt is moved forwards in the opposite direction to that of the water current which flows from the stamps, bearing with it the suspended pyrites that it is desired to collect. The belt, besides its forward movement, has an oscillating movement imparted to it, the result being that whilst the lighter material, sand, &c., continues to be borne forwards by the current of water, the heavier material is carried in the inverse direction by the revolving belt and may be collected. In another vanning machine an end shake is imparted to the belt in the place of the side shake of the Frue vanners. The suspended matter remaining in the water-current passes to settling tanks before the water is finally allowed to escape. The gold-amalgam adhering to the amalgamated plates is carefully removed and retorted, the pyrites being treated in a manner about to be described.

Various modifications of this stamp-battery method are in use, chiefly in connection with the treatment of quartz containing finely divided gold. Fig. 5 shows the arrangement of the Huntington centrifugal mill, which has been considerably employed in cases where the quartz was not very hard. 'Dry' crushing is sometimes employed, the powdered material being then treated either by amalgamating it with mercury in iron pans or by a chlorination process; occasionally rolls are employed in the place of stamps, and it is stated with considerable advantage both as regards cost of treatment and the state in which the gold is liberated, the gold freed from the quartz by the stamp battery being less easy to amalgamate than that freed by the rolls.

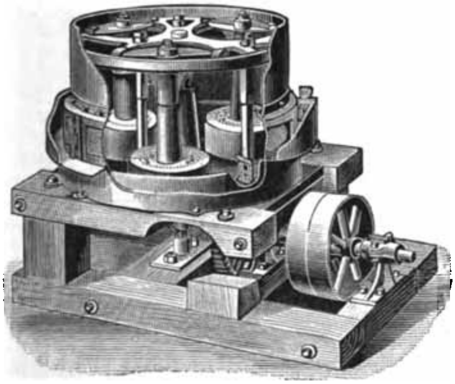


FIG. 5.

The selection of a site for the stamp battery is a matter of the greatest importance. It has been pointed out by Hammond that it should be as near the mine as possible, be readily accessible, water and wood should be abundant, and there should be a sufficient fall both to render the crushing process automatic and to allow of the escape of the waste material ('tailings') from the battery.

The battery itself should be so arranged that the ore, as it comes from the mine, is discharged upon an iron sieve or framework, termed a 'grizzly,' which separates it into two classes—(1) fine ore, of a size suitable for direct crushing in the battery, and (2) coarse ore, which must first pass through the rock-breaker; this should be placed immediately below the coarse ore-bin, the shoot from which should feed directly into the jaws of the rock-breaker, by which means labour is spared, and by a regular system of feeding the crusher is worked at its maximum capacity. The crushed ore passes to the main ore-bin, into which the fine ore passes from the grizzly. To increase the output of the stamp battery as much as possible, it is evident that the work it has to perform should be reduced to a minimum. To aid in this direction the coarse ore may be passed through two or more rock-breakers, or even a set of fine-crushing rolls, one rock-breaker crushing 'coarse' and the other 'fine,' the crushed ore from the one passing to the other by gravity, and from this to the stamp battery below.

The capacity of the battery may be further increased or diminished by the system of feeding. Thus, if too thick a layer of ore exists between the 'die' (the crushing surface attached to the stamp box) and the 'shoe' (the crushing surface attached to the 'stem' or lifting rod), the ore will cushion the blow, and the crushing capacity of the battery will be reduced. On the other hand, by keeping this layer of ore as thin as the safety from breakage will permit, the capacity of the battery is greatly increased. To effect this, a variety of mechanical arrangements—termed 'self-feeders'—have been introduced. They are mostly arranged on the principle of the shaking table.

The width of the mortar or 'stamp box,' in which the ore is crushed by the stamps, is regulated by the character of the ore. Narrow mortars increase the discharge of the pulp from the battery; but if the screens through which the pulp passes are placed too close to the stamps, they are subject to excessive breakage; if, again, the discharge is too low, the screens are rapidly destroyed, and, generally, screens last longest with high discharge and wide mortar. The feed-opening should extend for nearly the whole length of the mortar.

The screens are usually made of brass or steel wire, or of slot- or needle-punched sheet iron, the slots being either horizontal or diagonal. In front of the screen, across the mortar, a piece of heavy canvas is frequently placed; the pulp as it passes through the screen splashes against this, and the discharge on to the plates is consequently more regular.

The degree of fineness to which the ore should be stamped by the battery depends greatly on its nature. If much pyrites is present, which, from its richness in gold, has afterwards to be collected, the crushing must not be too fine, or the pyrites would not 'concentrate.' On the other hand, if the gold is present in a very fine state of division, the crushing must be fine, in order to free the gold; but excessive crushing has a tendency to flatten out the gold, and gold so hammered is found to amalgamate with difficulty. This is one of the points which has been urged in favour of rolls as compared with stamps, the rolling process leaving the gold in a state in which it may readily be amalgamated.

The height of fall or 'drop' of the stamps varies from about 4 to 9 inches. Heavy stamps should have a low drop, and light stamps a high one; but the drop must be sufficient in height or rapidity to produce a good 'splash' in the mortar, and so force the crushed ore or 'pulp' through the screens. Soft ores and those rich in sulphides should have a low drop. The order in which the stamps drop—arranged in batteries of five—is very varied, but the orders 1, 4, 2, 5, 3, or 1, 5, 2, 4, 3, are perhaps the best.

The 'duty,' or amount of ore crushed by the stamps, depends on their weight, on the height of the drop, the size of the screens, the width of the mortars, the height of the discharge, and the nature of the ore. Hard or clayey ores give the lowest results.

Heavy stamps, and those with high drops, should be driven at a low speed. With double-armed cams (lifting the stamps by raising the 'tappets' or projecting portions keyed on to the stems) the speed should not be great enough to bring the cam into collision with the falling tappet, as breakages would be sure to result. The shoes and dies were formerly made of white iron, but hard chrome steel is now being used instead. With steel shoes the dies are frequently made of iron, as they are found to wear evenly, and they are not subject to the same degree of

—	1	2	3	4	5	6	7	8	9	10	11	12
No. of stamps	10	20	40	40	40	10	10	30	60	20	20	10
Weight of stamps, lbs.	700	850	850	750	850	850	750	750	750	900	950	650
Drop of stamps, inches.	6–7½	6–6½	6½	6	6½–7	6	5½	6½	6	5	6–8	4–6½
Drops per minute	85	85–90	92	92	88	90	90	93	90	100	86	80–90
Duty per stamp in 24 hours, tons.	1½	2½	2¼	2½	2¼	1¾	2¼	2½	2½	2½	2½	1½
Shoes and dies	White iron	Chrome steel	Steel	White iron	White iron	Iron	Chrome steel	Chrome steel	White iron	Steel shoes Iron dies	Steel	White iron
Size and character of screens	No. 6 angle slot	No. 6, 7, 8 angle slot ¼ in.	No. 8 angle slot ¼ in.	No. 8 straight slot	Brass wire 20, 24, 30	No. 8 angle slot	No. 7 angle slot	Nos. 7, 8 angle slot	No. 8 slot punched	No. 9 round punched	Brass wire No. 50	Nos. 0, 1 tinned iron
Dimensions of apron, inches	48 × 48	46 × 12 and 46 × 24	42 × 48	48 × 15	46 × 30	36 × 48	24 × 48	24 × 48	48 × 84	—	48 × 168	48 × 156
Width of sluice, inches	14	15	14	14	15	14	14	15	16	—	15	Apron and sluice are in one
Length of sluice, feet	12	24	14	9	18	12	15	18	20	—	10	
Gold recovered:												
Percentage in battery	80	50–67	90	75	33–67	50	66	60	—	60	33	75
Percentage on plates.	20	50–33	10	25	67–33	50	33	40	—	40	67	25
Percentage of sulphurets	1·66	2	2	1½	1½	0·2	1½	2	2	1½	2	5
Value of sulphurets, dollars per ton	50–80	100–200	57	127	125	45	100	100	125	45	70	—
Total cost of milling, dollar per ton	1·45	1·00	0·605	0·75	0·69	1·11	0·60	0·65	0·45	0·85	0·40	1·75
The items being—												
Labour, dollar	0·64	—	0·17	0·27	0·20	0·333	0·26	0·18	—	0·45	0·16	0·69
Shoes and dies, dollar	0·14	—	0·65	0·12	0·10	0·08	0·05	0·08	—	Shoes = 0·015 Dies = 0·025	0·03	0·15
Screens, dollar	0·01	—	0·015	0·01	—	0·01	0·01	0·01	—		0·01	
Mercury, dollar	0·02	—	0·15	0·02	0·15	0·02	0·01	0·01	—	0·07	0·09	0·08
Incidental expenses, dollar	0·24	—	0·14	0·14	0·15	—	0·09	0·12	—			
Water, dollar	0·40	—	0·20	0·19	0·225	0·667	0·18	0·25	—	0·29	0·11	0·83
Number of men employed in mill.	3	6	5	9	6	2	2	5	—	9	3	3
Number of men employed in mine	10	30	70	79	60	5	18	45	30	16	22	6
Water used for milling (miner's inches)	2	—	8	—	—	2½	3	10	21	7½	6	3
Depth of mine, feet	200	700	680	1000	1125	60	620	800	240	425	400	58
Cost of mining per ton, dollars	2·50	2·50	3·35	4·00	3·00	0·94	3·00	2·50	2·00	1·50	2·05	2·20

Names of mines:—(1) Loyal Lead; (2) Gover; (3) Bunker Hill; (4) Keystone Consolidated; (5) Kennedy; (6) Sutter Creek; (7) Wildman; (8) South Spring Hill; (9) Amador; (10) Utica; (11) Stickles; (12) McCreight.

wear as are the shoes. To obtain the maximum crushing capacity of the battery the dies must be kept as high, with reference to the lower edge of the screens, as the safety of the screens will permit.

The 'stems' or lifting-rods are made of malleable iron. They usually break at the socket of the stamp-head (a mass of iron giving the necessary weight to the stamp). They are made reversible, and, being made of malleable iron, the broken parts may be readily welded together again.

The tappet is so shaped that when the revolving cam strikes it, besides being lifted and allowed to drop, it is turned through a portion of a revolution varying from one-fourth to one-eighth. This equalises the wear of the shoes, and produces a slight grinding effect on the ore.

The quantity of water fed into the battery depends on the character of the ore and on the size of the openings of the screen. Clayey and highly-sulphuretted ores require the maximum quantity of water. Usually about 1,800 gallons of water are required for every ton of ore crushed.

The feed water required for each 'concentrator,' or 'vanner,' is about one gallon to two gallons per minute, the wash water required being about a half to one gallon per minute. The total quantity of mill water required for a 40-stamp gold quartz mill with 16 Frue vanners averages about 12 miner's inches (a 'miner's' inch represents a quantity of water varying with the locality—say 16,800 gallons in twenty-four hours).

The largest portion of the amalgam is usually caught on plates placed inside the battery, but this depends on the coarseness of the gold, the quantity of mercury charged into the battery, and on the shape of the mortar. The coarser the gold the richer in gold will be the amalgam produced. The outside plates are cleaned up at regular intervals. The splash plates nearest the battery, and on which most of the gold caught on the plates is collected, are small and readily removable. The amalgam collected is ground in a clean-up pan, similar to that used in a silver mill, to clean it, and is then pressed and retorted. The floor of the clean-up room should be cemented in order to prevent loss of mercury.

The grade or inclination of the copper plates is usually 1½ inch to 1¾ inch per foot. In amalgamating the plates, after freeing them from grease by washing with caustic soda, wash with water and rub on some mercury nitrate solution before adding mercury, as copper and mercury do not, at first, readily amalgamate. Owing to the solubility of copper in mercury the surface of the mercury on the plate becomes coated by the oxidation of the copper, and this coating may be removed by the occasional use of potassium cyanide solution, but from the extremely poisonous character of this salt its use is accompanied by great danger. To avoid this, the copper plates are frequently first coated with an electro-deposited layer of silver, which amalgamates readily, and the surface of the plate so amalgamated remains clean for a considerable time. It is found that the copper plate absorbs after a time large quantities of amalgam. To collect this the plates are from time to time 'sweated' to liquate the amalgam, large quantities being recovered in this way; but even then the quantity of gold and silver retained by the plate is considerable. The best method of treating such a plate is probably electrolytic refining (COPPER).

Mercury is charged into the mortars about every half-hour. Sulphuretted ores require much larger charges of mercury than do ores containing but little sulphides. The consistency of the amalgam on the outside plates indicates whether a sufficient quantity of mercury has, or has not, been charged into the mortar; it should not be hard and dry. Usually about two ounces or less of mercury is added for every ounce of gold in the ore crushed. The loss of mercury is about half an ounce for each ton of ore crushed, the loss being mainly due to the mercury being 'floured' and carried away into the tailings.

Outside the mill the tailings sometimes pass over long lengths of blanket sluices, having a grade of about 1 inch or more in the foot. The sands collected are ground with mercury in iron pans.

Figs. 6 and 7 show the mode of erection of the small 3-head 'prospecting' mill recently erected at the Royal School of Mines.

Great care should be taken in building the foundations of the stamp-battery, owing to the continuous shaking which it will have to undergo. The mortar-boxes may rest on a log of wood, or an india-rubber cushion is sometimes placed beneath the boxes to deaden the force of the blow.

The preceding table gives details respecting a number of Californian stamp-mills. The wages vary from 2½ to 3 dollars a day in the mill and mine, and the working conditions are generally favourable, the mills being worked mainly by water power.

The 'concentrates' from the Frue vanner should be stored on an inclined concrete floor to allow them to drain as dry as possible. They consist usually for the main part of iron pyrites. If they contain much galena, or copper pyrites, they are sold to smelting works where they are treated by the ordinary methods of smelting. Otherwise the pyrites, either roasted or in its natural state, is ground up with mercury in an iron pan, or it is first roasted and then treated with chlorine or bromine. In this method of treatment the pyrites is first carefully roasted with a view to liberate the gold and to leave the iron in a state—ferric oxide—in which it will not be attacked by the moist chlorine or bromine, to the action of which it is to be subjected, and by converting the sulphide present into oxides to avoid the reprecipitation of the gold which would otherwise take place. If silver is present in the concentrates they should first be roasted nearly dead, and then, towards the end of the roasting, some salt should be charged in. If this is done too soon, gold will be volatilised. Silver chloride may be extracted from the tailings by a strong solution of brine or a weak one of sodium hyposulphite, and then precipitated by metallic copper or sodium sulphide. The roasted material is then slightly moistened, and in the older method of treatment was placed on a false bottom in a tarred wooden tank, the chlorine being introduced beneath the false bottom and allowed to gradually pass up through the ore. When it made its appearance above the ore, a cover was placed on the tank and luted down with dough, the material under treatment being allowed to remain in contact with the chlorine for a considerable time. It was then washed with water and the gold precipitated from the solution by ferrous sulphate, the chlorination of the residues being, if necessary, repeated, after first drying them.

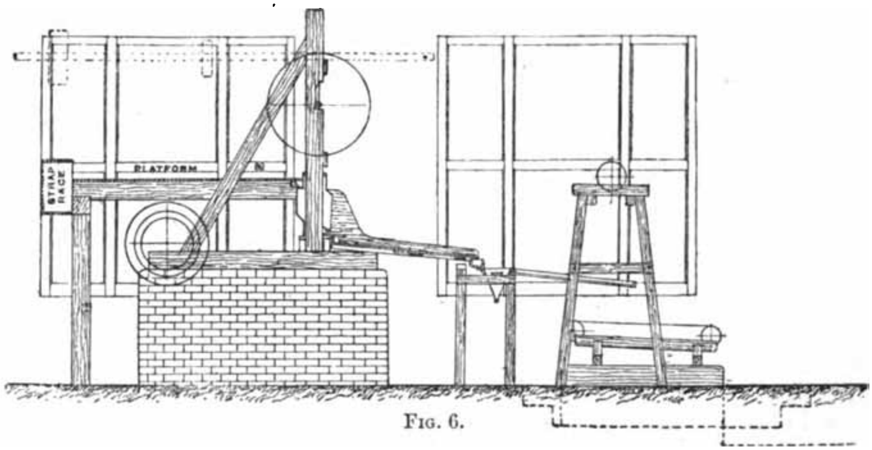


FIG. 6.

A slightly modified arrangement of this kind is shown in fig. 8: A being the chlorinating vat; B, the roaster; C, the leaden chlorine generator; D, a truck for the waste residues; and E, the precipitating tank. Instead of the fixed tank a barrel-shaped receptacle swung on trunnions was afterwards employed, and then, owing to the great loss of chlorine experienced in the older mode of treatment, the length of time which must necessarily elapse before the operation is complete, the difficulty of working in the presence of escaping chlorine, and the incompleteness of the extraction of the gold, the use of chlorine under pressure in rotating barrels was suggested and employed. The chlorine was also in some cases replaced by bromine.

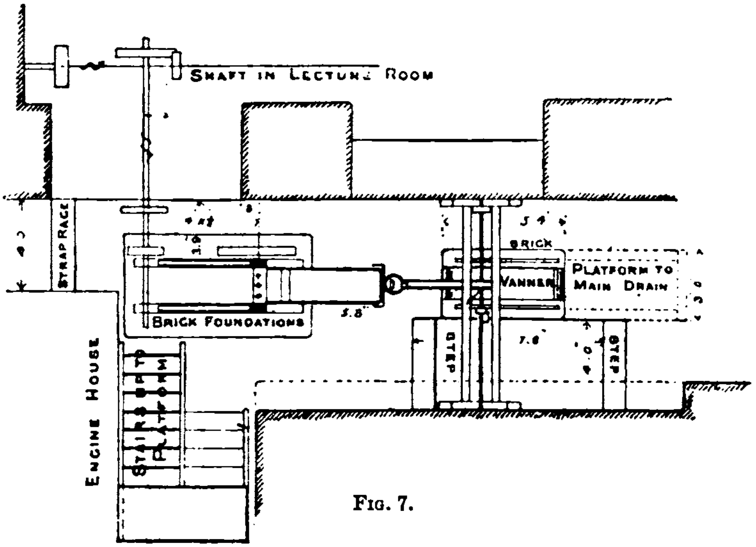


FIG. 7.

A modification of this method, fig. 9, introduced by Messrs. J. C. Newbery and C. Vautin, consists in placing the material to be treated in a lead-lined barrel which may be rotated; a solution of chloride of lime, and afterwards sulphuric acid, are then introduced into the barrel, and air is forced in at a pressure above that required to liquefy chlorine. The barrel is then rotated until the chlorination is considered to be complete, when the rotation is stopped, the gas in the barrel allowed to escape into a vat filled with milk of lime, to prevent the inhalation of chlorine by the workmen, the barrel is again closed and then again rotated, by which means the contents are thrown automatically into a filter vessel formed of iron lined with lead, and having a false bottom, the space beneath which is connected with a vacuum pump. Instead of the vacuum pump hydraulic pressure is sometimes employed. By the aid of this pump the residues from the barrel may be rapidly washed, the gold in the solution being afterwards precipitated in the ordinary way.

Where chlorination processes are not employed, the 'concentrates' are ground fine in iron pans and treated with mercury, but only a relatively small percentage of the gold can be collected by this treatment. A larger percentage is sometimes obtainable by first submitting the pyrites to a roasting process, but such treatment adds very greatly to the cost, and sometimes renders the gold more difficult to amalgamate.

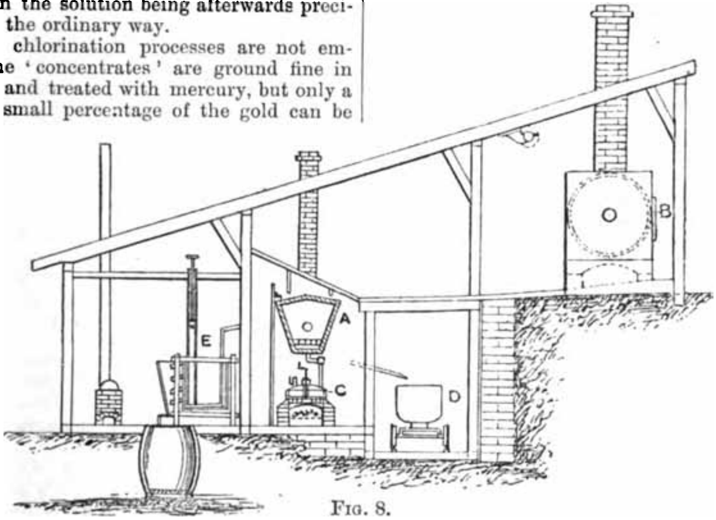


FIG. 8.

Numerous forms of amalgamating machines have also been suggested, but without any great success being obtained.

The separation of the gold found in true gold ores is frequently a matter of considerable difficulty. When such a material cannot be treated either by mercury direct, or by chlorination methods, it is customary to use it as an addition in the smelting of ores of lead, or, but more rarely, of copper. In these cases the gold passes into the metallic lead or copper or into the intermediary products that are obtained, and is collected from them simultaneously with the silver also present. In the case of metallic lead the gold may be extracted from it by the aid of metallic zinc, and in that of copper by electrolytic methods. As, however, this separation of gold from lead and from copper is intimately connected with the separation of any silver that may also be present, it will be described in the article on SILVER.

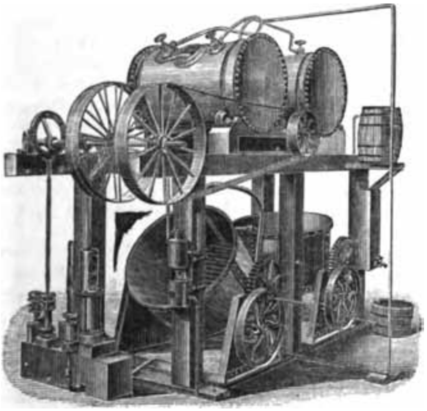


FIG. 9.

The cost of the chlorination process varies with the locality, but at the Plymouth Consolidated Mine, California, it is as follows:

	Dollars
Roasting:—	
3 men at 2½ dollars per day, per month of 30 days	225·00
1¾ cord of wood per day, do. do.	223·13
54 lbs. of salt per day, do. do.	12·15
Chlorine generator:—	
Manganese peroxide, 60 lbs. per day, per month of 24 days	33·84
Salt, 68 lbs. per day, do. do.	12·24
Sulphuric acid, 120 lbs. per day, do. do.	86·40
Acid used to clear liquor in settling tanks, 40 lbs. per day, and for $FeSO_4$ manufacture, 40 lbs. per day, do. do.	57·60
Wages for leaching	165·00
Wages of foreman.	125·00
Total	940·36

The quantity of ore treated being one hundred tons, the cost per ton was 9·4036 dollars, or less than 2*l*. per ton.

At the Amador Mine, California, the cost of treatment is about 13 dollars per ton, whether it is effected in vats or in rotating barrels. The details are as follows:

	Vats. Dollars		Barrels. Dollars
Labour	4·00		4·00
Wood	3·00		3·00
Manganese peroxide	0·65	Chloride of lime	1·20
Salt	0·35		0·15
Sulphuric acid	2·00		1·26
Incidental expenses	3·00		3·00
Power	—		0·39
Totals	13·00		13·00

Ores containing auriferous tellurides cannot be treated by ordinary amalgamation, nor yet by chlorination. Owing to the low melting and boiling points of gold telluride, if it is attempted to roast the material with which it is associated, a large part of the gold telluride is volatilised, and the gold is consequently lost. For the same reason there is much difficulty in smelting it with ores of lead or of copper. This is especially evident if the material containing the telluride is assayed by the ordinary fusion method, when very low and discordant results may be obtained, the lead button produced being also rendered brittle by the tellurium associated with the lead. Similar low results will be obtained by the scorification method of assay unless the proportion of granulated lead ordinarily used be enormously increased.

It has been proposed to treat this ore by various wet methods. One of these, in which a potassium cyanide solution is employed, appears to be efficacious as far as the solution of the gold is concerned, but the solution is difficult to effect, and the treatment is naturally accompanied by considerable danger to the workmen employed. The silver, too, which is usually associated with the gold, appears to remain to a great extent in the residues.

The gold obtained by either of these methods is not pure, but is associated with silver and other metals. To purify it, it is melted with two or three times its weight of silver; the alloy produced is granulated, and the granules are treated either with boiling sulphuric acid in white cast-iron vessels, or with nitric acid in vessels of porcelain or platinum. By this means the silver and other foreign metals, including any platinum that may be present, are dissolved away, and the gold is left undissolved. This is then collected and fused in a crucible with the addition of a little nitre or potassium bisulphate. If osmiridium was present in the original gold it will remain with the gold even after this 'parting' treatment, though in some cases it may have separated in the form of powder from the coherent gold. It does not alloy with the gold, and may be separated from it by allowing the gold, after fusion in the crucible, to stand for some time in the molten state. The osmiridium will then sink to the bottom of the crucible, and may be easily separated from the gold after the metal has solidified. Small quantities of lead and bismuth may remain with the gold, and in this case the metal would be brittle. It may, however, be readily 'toughened' by throwing on the molten metal either corrosive sublimate or cupric chloride, or by passing chlorine through it. The impurities are in this way eliminated in the form of chlorides.

In a pure state gold has a tensile strength of about 7 tons to the square inch with an elongation of 31 p.c. on 3 inches. In connection with this point Roberts-Austen has recently examined the influence exerted by the presence of small quantities of impurities on the physical properties of the metal, and finds that whilst some elements increase the tensile strength and the elongation of gold, others render it extremely brittle and reduce its tensile strength to a minimum. The experiments further showed that whilst those metals which have a higher atomic volume than that of gold render that metal brittle and diminish its tensile strength, this deleterious effect is not produced by elements having the same or smaller atomic volumes, and from a comparison of the results it is shown that the influence of an impurity on a mass of gold is in direct relation to the periodic law of the elements.

The alloys of gold with copper and with silver are of considerable importance from a commercial and artistic point of view, but those with other metals are relatively unimportant. The use of copper in intensifying the colour of gold, and that of silver in diminishing it, both these metals increasing the hardness and the durability of the gold, has led to the use of such alloys both for the purposes of coinage and for art metal-work from very early times, the number of the alloys employed being naturally exceedingly large. In Japanese art the use of a small quantity of gold in enabling a beautiful purple patina to be produced on the surface of copper has long been known. The proportion of copper alloyed with the gold for the purposes of coinage is usually such that it forms either $\frac{1}{12}$th or $\frac{1}{10}$th part of the weight of the alloy, the former being the British and the latter the most important foreign standard. The quantity of gold converted into coin in 1888 amounted to about 190,000 kg.

The annual production of gold is now about 6,000,000 ounces, but owing to the recent discoveries in the Transvaal and elsewhere it is probable that this quantity will soon be considerably increased.

A very full bibliography of gold is appended to Gold, by Alfred G. Lock, London, 1882, Practical Gold Mining, by C. G. W. Lock, London, 1889, and attention must also be drawn to a treatise on Hydraulic Mining, by A. G. Bowie, New York, 1885; The Metallurgy of Gold, by M. Eissler, London, 1889; The Reports of the State Mineralogist of California (1888, article by J. H. Hammond); Losses in Gold Amalgamation, by W. M'Dermott and P. W. Duffield, London, 1890; and to the numerous important papers relating to this subject which have appeared in the Transactions of the American Institute of Mining Engineers. E. J. B.

GOLD, MANNHEIM. A brass containing 80 p.c. of copper and 20 p.c. of zinc (v. also Copper alloys).

GOLD, MOSAIC. A fine, flaky yellow form of the bisulphide of tin; is used in the arts to imitate bronze under this title, and is preferably prepared as follows. A mixture of 7 parts of sulphur, 6 parts of ammonium chloride, and 18 parts of a powdered amalgam containing 2 parts of tin to 1 part of mercury, is heated gently until the odour of sulphuretted hydrogen is no longer perceptible. The heat is then raised to low redness, and a mixture of mercurous chloride, ammonium chloride, and cinnabar sublimes, while the mosaic gold alone remains. A fine product is also obtained by heating a mixture of 5 parts of stannous sulphide and 8 parts of mercuric chloride. The temperature should not be too elevated, as the stannic sulphide loses one equivalent of sulphur when strongly heated.

Mosaic gold is insoluble in nitric and hydrochloric acids, but dissolves in *aqua regia* and in alkaline hydrates.

A brass, introduced by Hamilton and Parker (Edinb. J. of Sc. 1826), and containing 52 to 55 p.c. of zinc, is also known by this name. A mixture of equal parts of zinc and copper is fused at the lowest possible temperature, and zinc is slowly added, with constant stirring, until the desired colour is produced. The colour passes from a brassy yellow to a purple or violet, and finally becomes perfectly white. The mass, when cooled, has the colour of gold, and is said to be peculiarly free from tarnish (*v.* also Copper).

GOLD, ORANGE *v.* Azo-colouring matters.

GOLD PURPLE (*Purple of Cassius*). This compound is obtained as a fine, flocculent purple precipitate on addition of a solution of stannous chloride containing stannic chloride, to a dilute neutral solution of gold chloride. The presence of the stannic chloride is essential, as pure stannic chloride produces only a brown precipitate.

A very fine product is obtained by adding stannous chloride to ferric chloride until the solution is of a pale-green colour, and employing the mixture to precipitate the gold solution. According to another process, 1 part of tin is dissolved in the minimum of hydrochloric acid, and 2 parts of the tin are dissolved in a cold mixture of 3 parts of nitric acid and 1 part of hydrochloric acid, the solution being finally heated to ensure conversion of all the tin into stannic chloride. A solution of 7 parts of gold in a mixture of 6 parts of hydrochloric acid and 1 part of nitric acid is diluted with 3,500 parts of water, and the solution of the stannic chloride is added, the stannous chloride being then added in drops until the required colour (from violet to purple or brown) is obtained (Baisson).

According to Pelletier, a purple of Cassius of constant composition is obtained as follows. A solution of as much gold chloride as contains 20 grains of gold is diluted to 700 or 800 c.c., and tin filings are introduced. The liquid speedily becomes brown and turbid, and finally deposits the purple, which is washed and dried. It is said to contain 32·75 p.c. of stannic oxide, 14·62 p.c. of stannous oxide, 44·77 p.c. of aurous oxide, and 7·86 p.c. of water.

Purple of Cassius may also be obtained in great beauty by treating an alloy of gold 2 parts, tin 3·5 parts, and silver 15 parts, with nitric acid to remove the silver and oxidise the tin.

This body, which is used in the manufacture of artificial gems (*v.* Gems, artificial), and for imparting a red, rose, or pink colour to porcelain or enamel, varies in colour from a violet to a purplish red or brown. While moist, it is soluble in ammonia with production of a purple colour, from which the precipitate is redeposited on addition of an acid or on boiling, and, in the latter case, is not again soluble. The ammoniacal solution precipitates gold on exposure to light.

When dried and triturated, the purple of Cassius acquires a metallic lustre. No gold is removed from it by the action of mercury. It retains water at 100°, but gives it up and acquires a brick-red colour when ignited, and loses its colour at the melting point of gold, but without evolution of oxygen.

The constitution of this substance, of which the composition, as found by analysis, is very variable, is not yet established. Berzelius, judging from the researches of Figuier, considered it to be a hydrated stannate of gold and tin. Macquer looked upon it as a mixture of stannic hydrate and metallic gold; and Proust considered it to be a mixture of aurostannous stannate and stannic hydrate.

Debray (C. R. 75, 1025) looks upon it as allied to the *lakes*, and as consisting of gold combined with stannic acid, as the colouring matter of the lake is combined with alumina, the gold being insoluble in mercury, as the colouring matter is insoluble in water. Debray has prepared the purple by boiling freshly precipitated stannic hydrate with a mixture of gold chloride and potassium oxalate. The action of ammonia on the purple is similar to its action on stannic hydrate, both being soluble while moist, but becoming insoluble when anhydrous.

The fact that the ammoniacal solution precipitates gold is in favour of the view that the gold is present in the metallic state, as ammonia is not known to precipitate precious metals by action on their oxides.

Debray has also produced a purple by replacing the stannic hydrate by *alumina*.

Müller (J. pr. [2] 30, 252) has prepared purples by several processes without the use of tin. A pale rose (containing 0·1 p.c. of gold) to deep carmine pigment is produced by igniting a well-washed and dried mixture of magnesium oxide and gold chloride. A similar result is obtained by heating the mixture in a current of hydrogen.

Lime, calcium carbonate, calcium phosphate, barium sulphate, and lead and zinc oxides give similar but less satisfactory results.

The most intense purple is, however, obtained by reducing a mixture of aluminium hydrate and gold chloride with alkaline grape-sugar solution. The mixture is agitated and heated until of a bright scarlet colour, but the colour must not be allowed to reach a purplish red, or the resultant product will be of inferior brilliancy.

Similar but less brilliant purples than those with magnesia and alumina are obtained with tin. As much stannous chloride as corresponds with 9 grams of stannic oxide, is dissolved in 200 c.c. of water, and the solution is rendered alkaline by addition of potassium carbonate. Grape sugar solution is added, and the mixture is diluted to 300 litres, and is warmed until of the best colour.

These methods of preparation uphold the view that the gold is present in the metallic state.

For the bibliography of the subject previous to 1866, *v.* Fischer (D. P. J. 182, 39).

GOLD, SALTS OF. Two oxides are known, the monoxide or suboxide Au_2O, and the sesquioxide or peroxide Au_2O_3.

The *hydrated sesquioxide* $Au(HO)_3$ is best prepared by heating a solution of gold chloride with magnesia, and washing the residue with nitric acid. It possesses a yellow, olive-green, or brown colour (according to the method of preparation) while damp, and becomes brownish or black on drying. When warmed with alcoholic potash, metallic gold is precipitated in minute scales used in *miniature painting*.

The hydroxide is soluble in potash, with formation of a very unstable *potassium aurate*. The solution may be used in electrogilding.

When acted upon by ammonia, the oxide produces a green or brown *fulminate* allied to that of silver. The fulminate may be obtained as a buff-coloured precipitate, containing some ammoniacal subchloride of gold, on addition of ammonia to gold chloride solution.

The trichloride and the trisulphide are the only salts of gold requiring description here. The use of aurous potassium cyanide and aurous potassium sulphide in electrogilding will be found described under Electroplating.

Auric sulphide Au_2S_3 is obtained as a deep yellow precipitate on passage of sulphuretted hydrogen through a solution of gold chloride. When finely divided gold is heated with sulphur and potassium carbonate, a double sulphide of potassium and gold, which resists a red heat and is soluble in water, is obtained. It is employed for the production of *Burgos lustre* in gilding china.

Auric chloride or **trichloride** $AuCl_3$ is prepared by dissolving gold in *aqua regia* and evaporating the solution to dryness at a temperature below 120°, the hydrochloric acid being always kept in excess over the nitric acid. The residue is dissolved in water and filtered from the protochloride which is always produced, and the solution is evaporated on the water-bath. Large orange-coloured efflorescent crystals of the hydrous chloride $AuCl_3.2H_2O$ are thus produced.

According to Thomsen the chloride is best prepared as follows. Powdered gold is converted by the action of chlorine into the dark-red crystalline dichloride, and a little water is added to convert it into a mixture of mono- and trichloride. The mass is heated gently to decompose the former, and the residue is dissolved in water, filtered from the reduced metal, evapoporated and heated to 150°C., with production of a brown crystalline mass of the anhydrous chloride.

When heated to 200°, the trichloride is resolved into a mixture of aurous chloride and gold. At a higher temperature the whole of the chlorine is given off.

Auric chloride is freely soluble in water, alcohol, and ether. It forms a crystalline compound, $AuCl_3.HCl.4H_2O$, with hydrochloric acid, and forms double chlorides with the alkali metals and with organic bases.

Oxalic acid, grape sugar, ferrous sulphate, and most reducing agents and organic bodies reduce this compound to the metallic condition, the metal so produced being in many cases of such tenuity as to require months to deposit from the liquid, and often possessing a ruby-red or purple colour by transmitted light.

Auric chloride is largely employed for toning silver prints in photography.

GOLD, YELLOW, *v.* Victoria yellow.

GOLDEN BROWN or **BISMUTH BROWN** *v.* Azo- colouring matters.

GOLDEN YELLOW *v.* Naphthalene.

GOMARD RESIN *v.* Oleo-resins.

GRAIN LAC *v.* *Lac resins*, art. Resins.

GRAIN OIL *v.* Fusel oil.

GRAIN TIN *v.* Tin.

GRAINS OF PARADISE *v.* Cocculus indicus.

GRANITE. A holocrystalline acid rock of plutonic origin; *i.e.* it is a rock consisting wholly of crystalline minerals, and containing from about 60 to 80 p.c. of silica, partly free and partly combined, while its texture suggests that it has slowly consolidated from a molten condition, under great pressure, at considerable depth beneath the surface. Granite is essentially an aggregate of felspar, quartz, and mica. The usual felspathic constituent is orthoclase, or common potash felspar, generally associated with more or less plagioclase; and the mica is either muscovite (white mica) or biotite (dark mica), while in many granites both micas are present. Biotite granite is now frequently known by G. Rose's name of *granitite*. Granitic rocks may contain various accessory minerals, such as hornblende, augite, and tourmaline, thus giving rise to varieties often distinguished by special names; while, on the other hand, it sometimes happens that one of the minerals of typical granite may disappear, thus producing a binary granite. *Aplite* is a name occasionally applied to a rock consisting only of felspar and quartz; but sometimes extended to all muscovite-granites. If the quartz and felspar are so intergrown as to suggest they have crystallised simultaneously, the rock is termed *graphic granite* or *pegmatite*. Under the name of *greisen*, German miners recognise a rock composed of quartz and mica, usually carrying topaz, and associated with tin-stone. An aggregate of orthoclase and black mica is known as *mica-syenite*; the typical *syenite*, sometimes distinguished as *hornblende-syenite*, being composed essentially of orthoclase and hornblende. Hornblende granites are often called, by English writers, 'syenitic.' Schorl, or black tourmaline, is not unfrequently present in granite, especially near the margin of intruded masses. Garnet is an occasional constituent, but not so commonly in true granite as in *granulite*, a rock consisting mainly of quartz and felspar in small grains, so that microscopic sections present between crossed nicols a characteristic mosaic structure. When a granitic rock becomes foliated, or its constituent minerals exhibit more or less elongation in definite directions, it is said to acquire a 'gneissoid' structure, and may pass into a true *gneiss*.

Granite occurs frequently in the form of intrusive masses, which, while coarsely crystalline in the centre, may present a fine texture towards their margin. From the main mass, veins or apophyses are thrown off into the neighbouring rocks; and these veins, having cooled less slowly, are often fine-grained, and may pass into micro-granites and quartz-porphyries. It has been asserted that certain granites may have resulted from the extreme alteration of stratified rocks; and hence geologists who hold this view recognise two types of granite, one igneous, and the other metamorphic.

It is not uncommon to find in granite nodular masses which appear as dark patches on the fractured or polished surface of the rock. While some of these inclusions seem to be fragments of foreign rock which have been caught up in the granitic magma and altered, others may be regarded as parts of the original magma differentiated during consolidation; and it is notable that the inclusions are usually more basic than the matrix. (For comparative analyses of the granite and its inclusions, *v.* J. A. Phillips in Quart. Journ. Geol. Soc., 36, 1880, 1.)

Granite is extensively employed for constructive purposes where massive work is required, as in the foundations of buildings, in docks, sea walls, the piers of bridges, and lighthouses. The specific gravity of granite is about 2·6; a cubic foot weighing about 166 lbs., and a cubic yard 2 tons.

Granite rocks are always divided by joints, which usually run in three directions, thus splitting the rock into masses of roughly cuboidal form. The stone is blasted in the quarry, and the blocks split up by 'plug and feather' wedges. When the surface is required to be dressed smooth, it is 'fine-axed' by continued tapping, at right angles to the face, with a special form of axe. Solid cylinders are turned on a lathe, and columns measuring as much as 8 feet in diameter may thus be wrought. The polishing of granite is effected by means of cast-iron planes worked over the smooth surface, first with sand and water, and then with emery, the final polish being given with putty powder applied on thick felt. In this way even elaborate mouldings may be readily polished. (For granite working, *v.* G. W. Muir, Journ. Soc. Arts, 14, 1866, 471; and G. F. Harris, Granite and our Granite Industries, London, 1888.)

Granite rocks are extensively developed and quarried in Cornwall and Devon, where they occur as a series of bosses protruding through the killas or clay-slate. The largest of these intrusions are, proceeding westwards, those of Dartmoor, Brown Willy or St. Breward district, Hensbarrow or St. Austell, Carn Menelez or Penryn, and the Land's End or Penzance district. In addition to these principal exposures there are numerous smaller masses. The granite of Devon and Cornwall is usually grey and coarse-grained, but red granite also occurs, as at Trowlesworthy in the western part of Dartmoor. A local variety, termed by R. N. Worth *Trowlesworthite*, and described by Prof. Bonney, is composed of red felspar, with tourmaline, purple fluorspar, and a little quartz. A handsome red granitic rock occurring near Luxullian, in Cornwall, and hence called by Bonney *Luxullianite*, consists of red orthoclase, in large crystals, with schorl, or black tourmaline, and quartz. This is the rock of which the Duke of Wellington's sarcophagus, in St. Paul's, is formed.

The nearest exposure of granite to London is at Mount Sorrel, in Leicestershire, where pink and grey biotite-granite, rather hornblendic, is worked for kerb-stones, paving setts, and road metal. The hornblende granites of the Channel Islands are quarried for similar purposes. Shap Fell, in Westmoreland, yields a beautiful hornblendic granite, with large crystals of salmon-coloured orthoclase, which is now largely used as an ornamental material, and has been employed for example in the posts around St. Paul's. The granites of Scotland are of much industrial importance. Aberdeen granite was brought to London for paving in the last century, but the great development of the trade dates from about 1850. The Aberdeen stone, which is of grey or blue tint, is valued for monumental work; while the Peterhead granite is usually of a fine pink colour. The Ross of Mull, in Argyllshire, furnishes a handsome red granite, yielding blocks of exceptional size. Granite is also worked in Kirkcudbrightshire, where it occurs in bosses surrounded by slates; the grey granite of Dalbeattie being well known in commerce.

In Ireland granite is very extensively developed, the chief districts being in counties Wicklow, Galway, Mayo, Donegal, and Down. The largest quarries are those near Dalkey, which yielded the stone for Kingstown Harbour. The quarry near Castlewellan, co. Down, which was opened to supply granite for the Albert Memorial, in Hyde Park, has since been closed (G. H. Kinahan, Geol. Ireland). Granite is also found in the Isle of Man, Arran, Anglesea, Lundy I., and the Scilly Isles.

It is needless to specify the numerous European localities in which granite is worked. Of late years a green 'granite' (gabbro) from Warburg, in Sweden, has been imported as a monumental stone. In the United States workings are established in a large number of localities, the granite-producing States being, in order of relative importance, Massachusetts, Maine, Rhode Island, Connecticut, Virginia, and New Hampshire (*v.* Rep. of Tenth Census, U.S., 10, 1884).

For a large collection of analyses of granites, *v.* J. Roth's Beiträge z. Petrographie d. plutonische Gesteine (Berlin, 1873–84). F. W. R.

GRAPE SUGAR *v.* DEXTROSE.

GRAPHIC TELLURIUM *v.* TELLURIUM.

GRAPHITE, an impure variety of native carbon, known also as *plumbago*, and popularly as *black lead*. It occurs usually in compact and crystalline masses, but occasionally in six-sided tabular crystals which cleave into flexible laminæ parallel to the basal plane. The crystals were referred to the hexagonal system until A. von Nordenskjöld, in 1855, after studying the crystals from Pargas, in Finland, declared them to be monoclinic. Kenngott, however, afterwards showed that they were truly rhombohedral (P. 96, 110).

Graphite is a mineral of iron-black or steel-grey colour, with metallic lustre, having a sp.gr. of 1·9 to 2·6. In consequence of its softness (H = 0·5–1) and the ease with which it produces a metallic streak when rubbed on paper, it is largely used in the manufacture of pencils, whence the name 'graphite' given to it by Werner, from γράφω (I write). It was formerly called *molybdæna*, and confused with molybdenite (MoS_2), a mineral which also gives a metallic mark on paper. Graphite seems to have been first recognised as a distinct mineral by Gesner, who figured a lead pencil in 1565 (Roscoe). Scheele in 1779 showed that graphite was a kind of mineral carbon, since it could be converted into CO_2 by the action of nitric acid. As the carbon is always associated with more or less iron, the older mineralogists described the mineral as a 'carburet of iron,' but Vanuxem demonstrated that the iron is present as Fe_2O_3 and not as a carbide. The ash left on the combustion of graphite usually contains, in addition to the ferric oxide, silica, alumina, and lime.

Exposed on platinum foil to the flame of the blowpipe, graphite burns, but often with more difficulty than diamond. When heated with a mixture of potassium bichromate and sulphuric acid, it disappears. In order to obtain perfectly pure graphite, the mineral is first ground and washed to remove earthy matter, and then treated, according to Brodie's method, with potassium chlorate and sulphuric acid; on subjecting the resulting product to a red heat, pure carbon is obtained in a remarkably fine state of division.

The following analyses are selected from a large number by C. Mène (C. R. 64, 1091):—

—	I	II	III	IV
Carbon	91·55	81·08	79·40	78·48
Volatile matters	1·10	7·30	5·10	1·82
Ash	7·35	11·62	15·50	19·70
	100·00	100·00	100·00	100·00

I. Very fine Cumberland graphite, sp.gr. 2·345. II. Graphite from Passau, Bavaria, sp.gr. 2·303. III. Crystallised Graphite, from Ceylon, sp.gr. 2·350. IV. Graphite, from Buckingham, Canada, sp.gr. 2·286.

Graphite when used for pencils is frequently mixed, in a powdered state, with pure clay, and the mixture consolidated by hydraulic pressure. It is also sometimes mixed with sulphur or with sulphide of antimony. Brockedon first suggested the use of the hydraulic press as a means of obtaining from powdered graphite a homogeneous and coherent mass, which could be readily sawn into pieces of convenient size. The finest pencil lead was yielded by the ancient mine at Borrowdale, in Cumberland, where it occurred in pipes, strings, and irregular masses, or 'sops,' associated with a dyke of diorite and with intrusive masses of diabase, in the Cambro-Silurian volcanic series known as 'the green slates and porphyries.' The Cumberland graphite was formerly termed 'wad,' a name sometimes applied also to native oxide of manganese. (For description of the old Borrowdale workings *v.* J. C. Ward in Geol. Survey. Mem. on Lake District, 1876.)

Excellent graphite is found in Siberia, especially at the Mariinoskoi mine, in the Tunkinsk Mountains, Government of Irkutsk. This deposit, discovered in 1838, occurs in gneiss, associated with diorite; and has been largely worked by M. Alibert to supply Faber's pencil factory. In 1860 graphite was discovered in granite near the river Nischne Tungusska, and workings were undertaken by M. Siderov. It is also found in the Kirgis Steppe and at several localities in the Ural mountains. (For Russian graphite *v.* N. v. Kokscharov, Materialien z. Mineralogie Russlands, 4, 1862, 153, where analyses are given.)

Most of the graphite used in this country for crucibles is obtained from Ceylon. The mineral is widely distributed through the western and north-western provinces of the island, and as many as 800 mines or pits have been opened, though these are not all working at once. Some of the mines reach a depth of 200 feet, and it is necessary to drain them by means of steam pumping machinery. It is estimated that when the trade is active, the mining and working of graphite in Ceylon employs about 24,000 men, women, and children. (Handbook to Ceylon Court, Ind. and Col. Ex., 1886, 3; F. Sandberger, N. J. 1887, 2, 12.)

In India graphite is found in several localities, chiefly in the Madras Presidency, the best coming from Travancore, but even this is far inferior to that from Ceylon. Europe does not yield much commercial graphite, except at Passau in Bavaria, where it occurs as a graphitic schist, and is largely used in the pencil factories of Nuremberg. In the United States graphite is widely diffused, but rarely in sufficient quantity to be worked. The principal locality is Ticonderoga, in Essex Co., New York, where the Dixon Crucible Co. have worked a schist containing about 10 p.c. of graphite. It has also been worked to a limited extent near Raleigh, N. Carolina; at Stourbridge, Mass.; at Cumberland Hill in Rhode I.; and at Sonora in California. The graphite 'ores' are crushed or stamped, and then washed, whereby the flakes of graphite are readily separated from the denser matrix.

In the Laurentian gneiss of Canada, graphite is of frequent occurrence, and has occasionally been worked, as at the Buckingham Mines. The mineral is usually found in veins and nodular masses, or finely disseminated through bands of limestone. The presence of graphite in the Laurentian limestones has been cited as an indirect proof of the presence of life when these ancient rocks were formed; but the organic origin of graphite, though in many cases probable, is difficult of proof. It is notable, however, that graphite frequently contains hydrogen as well as sulphur. Daubrée has obtained it artificially by decomposing carbon disulphide in contact with metallic iron at a high temperature; while H. Sainte-Claire Deville prepared it by passing vapour of chloride of carbon over fused cast iron. Crystalline graphite is often formed in blast furnace slag during iron smelting, and is known to workmen as *kish*. Graphite also occurs in certain meteoric irons, such as that of Tolucca in Mexico. A cubic form of graphitic carbon, discovered in a meteoric iron from Youndegin, Western Australia, has been described by Mr. L. Fletcher under the name of *Cliftonite* (Min. Mag. 7, 1887, 121).

In consequence of its refractory character, graphite is largely used in the manufacture of crucibles, retorts, twyers, and other objects required to withstand high temperatures. For crucibles, the powdered mineral is mixed with Stourbridge fireclay, and made into a paste with water; the kneaded mass is allowed to lie for many weeks before the crucible is moulded; the vessel when moulded is slowly dried, and carefully fired in a seggar.

As a lubricating agent graphite is highly valued, since it diminishes friction and tends to keep the moving surfaces cool. To obtain the best results the powdered mineral should be carefully selected and sized. For steam cylinders it is used dry; for heavy bearings it is mixed with grease; and for light bearings with oil. Made into a paint with linseed oil, it has been advantageously employed as a coating for metalwork. Graphite is also used dry for polishing stoves and other objects of cast iron, the thin flakes forming a lustrous coating which protects the metal. Blasting powder and heavy ordnance powders are likewise glazed with graphite, for though it slightly diminishes the explosive force of the powder it protects it from damp. Being a good conductor of electricity, graphite is used in electrotyping, as originally suggested by Murray; the moulds upon which the metal is to be deposited receiving a conducting surface by being coated with finely divided graphite.

(For a large collection of analyses of British and foreign graphites, see J. Percy, Metallurgy: Fuel, &c., 2nd ed., 1875, 104.) F. W. R.

GREEN, ANANDONIS, *v.* Chromium.

GREEN CINNABAR *v.* Chromium.

GREEN EARTH, *Terre verte*, *v.* Pigments.

GREEN, EMERALD, *v.* Chromium.

GREEN, GUIGNET'S, *v.* Chromium.

GREEN SMALT, *Cobalt green*, *v.* Pigments.

GREEN ULTRAMARINE, *Chromium sesquioxide* *v.* Chromium.

GREEN VITRIOL, *Ferrous sulphate*, *v.* Iron.

GREENLAND SPAR *v.* Cryolite.

GREENOCKITE, *Cadmium sulphide*, *v.* Cadmium.

GRENAT SOLUBLE *v.* *Picric acid*, art. Phenol and its homologues.

GREY ANTIMONY ORE, *Antimony sulphide*, *v.* Antimony.

GREY COBALT, *Cobaltine*, *Cobalt glance*, *v.* Cobalt.

GREY COPPER *v.* Copper.

GUAIACENE *v.* *Guaiacum*, art. Resins.

GUAIACIC ACID *v.* *Guaiacum*, art. Resins.

GUAIACOL *v.* *Pyrocatechol*, art. Phenol and its homologues.

GUAIACONE *v.* *Guaiacum*, art. Resins.

GUAIACONIC ACID *v.* *Guaiacum*, art. Resins.

GUAIACUM *v.* Resins.

GUAIENE *v.* *Guaiacum*, art. Resins.

GUAIOL *v.* *Guaiacum*, art. Resins.

GUANO *v.* Manures.

GUARANA (*Uarana*). Guarana is a dried paste prepared from the seeds of the *Paullinia sorbilis* (Martius; Bentl. a. T. 67), a climbing shrub inhabiting the northern and western provinces of Brazil. It is made for the most part by different sections of the Guaranis, a tribe of South American Indians, and probably by different methods. Generally, however, the ground or powdered seeds are moistened by exposure to dew, or by the addition of water, kneaded into a paste, made into cylindrical or globular masses and dried before fires, in chimneys, or by the heat of the sun. These cakes as they appear in commerce are hard, with a rough reddish-brown exterior and somewhat lighter colour inside. They evolve a chocolate-like odour and have a bitter astringent taste. In South America guarana is an article of food used much in the same manner as we employ cocoa, and in European medicine it is administered as a nervous stimulant for the relief of certain kinds of headache. For further details as to its source, preparation, and uses *v.* Cooke (Ph. [3] 1, 221); Hallawell (Ph. [3] 3, 773); Squibb (Ph. [3] 15, 165); and Rusby (Ph. [3] 18, 1050).

The physiological activity of guarana depends upon the presence of an alkaloid at first termed 'guaranine' but afterwards found to be identical with *caffeine* (*v.* Caffeine) (Martius, Kastn. Archiv, 7, 266; A. 36, 93; Berthemot a. Dechastelus, J. Ph. 26, 518). Stenhouse obtains the alkaloid by extracting powdered guarana with about fifty times its weight of boiling water and treating the solution when cold with basic acetate of lead. A precipitate of alkaloid and salts of lead falls from which repeated extraction with hot water removes the caffeine. The aqueous solution is freed from lead by sulphuretted hydrogen, evaporated to dryness, and the residue treated with hot alcohol. From this solution, on concentration, crystals of alkaloid are obtained, which may be purified by recrystallisation (Ph. [1] 16, 212). For other methods *v.* Greene (Ph. [3] 8, 87), who prefers to extract a mixture of guarana and three times its weight of litharge with boiling water; C. J. Williams (C. N. 26, 97), who exhausts a moistened and slowly dried mixture of guarana and lime with benzene; Squibb (Ph. [3] 15, 165) and Bochefontaine a. Gusset (Ch. Tech. C. Anzeiger, 4, 322), who treat a mixture of guarana and magnesia with weak alcohol and chloroform respectively. Kremel (Ph. Post, 21, 101) determines the caffeine in guarana by placing 10 grams in a flask with 100 c.c. of 25 p.c. alcohol, noting the total weight, and digesting for one or two hours at 100°. The weight lost by evaporation is made up with similarly diluted alcohol, and 50 c.c. of the solution, corresponding to 5 grams of guarana, is filtered off, mixed with calcium hydroxide, and evaporated to dryness. The residue is extracted with chloroform from which the alkaloid is obtained in crystals, dried at 100° and weighed. The following percentages of caffeine are selected from published analyses of guarana: 5·10, 5·04 (Stenhouse); 5·05 (Greene); 4·20 to 5·00 (5 samples, Feemster, Ph. [3] 13, 365); 4·5 (B. a. Gusset); 3·12, 3·80 (Kremel). Feemster found in the seeds 5·08 p.c. and Peckolt (J. 1866, 709), in the shelled seeds 4·81 p.c.; seed shells 2·44 p.c. and pulp 4·29 p.c.

Besides caffeine, guarana contains gum, starch, an acrid *green fixed oil*, a *concrete volatile oil*, and *tannin* (Fournier, J. Ph. 1861, 291). The tannin further examined by Greene (Ph. [3] 8, 328) was found to behave towards reagents unlike previously known varieties, and the term *paullinitannic acid* was therefore applied to it. Kremel found 1·3 to 2·0 p.c. of *ash* consisting chiefly of phosphates. A. S.

GUARANINE *v.* Guarana.

GUERNSEY BLUE. A colouring matter belonging to the Induline group (*q.v.*).

GUIGNET'S GREEN *v.* Chromium.

GUINEA GREEN B. The sodium salt of the disulphonic acid of diethyl- dibenzyl- diamido- triphenyl- carbinol. Is a dark-green powder resembling Light-green S or Acid Green, *v.* Triphenyl methane colouring matters.

GULAUCHA, GULOE, and GILOE. Indian names for *Chasmantera cordifolia* (*Cocculus* *cordifolius*). This plant flourishes in India, the drug being sold extensively in the bazaars as a tonic and antiperiodic, in the form of cylindrical pieces 2 to 5 cm. long and 1 to 5 cm. in diameter. It is a perennial creeper, climbing to the summit of the highest trees, its branches putting forth roots which, reaching to the ground, initiate a fresh growth. Roots, stem, and leaves are equally in demand as a drug. The Indian pharmacopœia commends its use as a tincture (4 to 8 c.c. *in die*); as an extract (0·6 gram to 1 gram *per diem* in the form of pills); and as an infusion (1:10), of which 60 c.c. to 90 c.c. are to be taken thrice a day. The stems contain verberin, an uncrystallisable bitter substance, changed by dilute sulphuric acid into a glucoside, and a bitter kind of starch meal known as 'palo' (S. C. I. 6, 49).

GUM ACACIA *v.* GUMS.

GUM AMMONIACUM *v.* GUM RESINS.

GUM ARABIC *v.* GUMS.

GUM ASAFŒTIDA *v.* GUM RESINS.

GUM BENJAMIN *v.* BALSAMS.

GUM BENZOIN *v.* BALSAMS.

GUM, BRITISH, *v.* DEXTRIN.

GUM ELASTIC *v.* INDIA-RUBBER.

GUM GALBANUM *v.* GUM RESINS.

GUM GAMBOGE *v.* GUM RESINS.

GUM KINO *v.* CATECHU and KINO.

GUM LAC or **LAC RESIN** *v.* RESINS.

GUM MYRRH *v.* GUM RESINS.

GUMMIC ACID *v.* GUMS.

GUM RESINS. This article includes the more important members of that group of products which consist essentially of a mixture of gum and resin. They are generally the exudated milky juice of plants dried by spontaneous evaporation. When triturated with water they give more or less perfect emulsions. Compare introduction to article RESINS.

Ammoniacum; *Gummi-resina ammoniacum*; *Gomme-résine ammoniaque*, Fr.; *Ammoniak gummi-harz*, Ger.

Persian ammoniacum. The ammoniacum of the early Greek physicians came from Africa and was probably that variety known as African ammoniacum. The drug, which has however since the tenth century been an article of European commerce, is obtained from Persia and neighbouring districts, reaching our markets according to Dymock (Ph. [3] 6, 321) now generally by way of Bombay. It is the inspissated juice collected from the stems of the *Dorema ammoniacum* (Don). For plates *v.* Bentl. a. T. 131. This plant attains a height of 6 to 8 feet, and the flow of juice from its stem is caused by the puncture of beetles.

The gum-resin occurs in commerce as brittle grains or tears or roundish lumps, pale yellow externally and waxy milky-white within. It softens readily when warmed. In taste it is bitter and acrid, and it possesses a characteristic odour. Triturated with water it forms an emulsion. A very complete account of the literature of ammoniacum, together with the result of the examination of some twenty specimens, will be found in the memoir of Hirschsohn (P. Z. 1875, 225; Ph. [3] 7, 612, 710, a. 770). The sp.gr. of ammoniacum is 1·207 and it is soluble 3 parts in 4 of alcohol. Hypochlorites, as for example a solution of bleaching powder, impart to it a bright orange colour, a character that serves to distinguish it from the African variety which is not affected by these reagents. The allied gum-resin galbanum also gives no colour reaction with hypochlorites.

Ammoniacum was analysed by Braconnot (A. Ch. 68, 69), and Hagen (Schwartze, Pharm. Tabel, 2te Ausg. 280) and recently by Hirschsohn (*cf.* Johnston, Tr. 1840, 350). It consists essentially of *resin*, *gum*, and a small proportion of *volatile oil*. The *resin* constitutes 70 p.c. of good specimens of the drug. Hirschsohn finds resin soluble in ether 47·1 to 69·2 p.c. It melts at from 35° to 50°, is soluble in alcohol, chloroform, glacial acetic acid, sulphuric acid, and alkalis, partly soluble in carbon bisulphide, benzene, and solution of ammonia, and insoluble in petroleum ether. Przeciszewski (Pharm. untersuch. Dorpat, 1861) states that the resin contains sulphur, but this was questioned by Flückiger and Hanbury (Fl. a. H. 326) and by Moss (Ph. [3] 3, 761) and their results are confirmed by Hirschsohn. Sommer (J. 1859, 573) was unable to obtain umbelliferone from the gum-resin, but *resorcinol*, $C_6H_4(OH)_2$, and *protocatechuic acid*, $C_6H_3(OH)_2COOH$, are formed when it is fused with potash (Hlasiwetz and Barth, A. 130, 354). It yields *styphnic acid*, *trinitro-resorcinol*, $C_6H(NO_2)_3(OH)_2$; when treated with nitric acid (Will a. Böttger, A. 58, 269; *cf.* Schwanert, A. 128, 123) and reduced by heating with zinc dust the chief product is the *hydrocarbon*, $C_{18}H_{20}$, which boils at 235°, together with (*m*) and (*p*) *xylene*, (*m*) *ethyltoluene* and (*o*) *ethylphenol-methylether*, $C_6H_4.Et.OMe$ (Ciamician, B. 12, 1658).

Ammoniacum *gum* is partly soluble and partly insoluble in water. The insoluble portion, which constitutes a fourth of the gummy constituents, appears to be identical with the similar bassorin-like gums which occur in asafœtida and galbanum. Hirschsohn obtained 9·7 to 51·8 p.c. of soluble and 2·6 to 32·6 p.c. of insoluble gum. *Volatile oil* of ammoniacum exists only to the extent of ¼ p.c. Hirschsohn obtained no volatile oil by distillation with water, but petroleum ether gave him 1·4 to 6·7 p.c. of volatile oily residues. Flückiger and Hanbury describe the oil as unlike that of galbanum, possessing in a high degree the odour of the drug, and being free from sulphur. The specimens of ammoniacum examined by Hirschsohn contained 0·8 to 3·3 p.c. of *moisture*, 2·0 to 16·8 p.c. of *ash*, and *saccharine matter* to the extent of from 1·6 to 4·6 p.c.

Ammoniacum is employed in medicine internally as an expectorant, and externally it is frequently applied as a constituent of plasters.

African ammoniacum. This, according to Hanbury (Ph. [3] 3, 741), is the ammoniacum of Dioscorides and the older writers. It is derived according to Lindley (Pereira, Mat. Med. 1853, 1715) from the *Ferula tingitana* (*Linn.*), a plant inhabiting the African coast of the Mediterranean.

African ammoniacum, which is scarcely known in European markets, is described by Pereira as consisting of dark-coloured masses which internally have much the appearance of the Persian variety. The odour is, however, quite distinct. It forms an emulsion with water. Moss examined a specimen in 1873 (Ph. [3] 3, 742) which consisted of *resin* 67·76 p.c., *gum* 9·01 p.c., *water and volatile oil* 4·29 p.c., and *bassorin and insoluble matter* 18·85 p.c. It contained 13·47 p.c. of *ash*. It softened between the fingers more readily than Persian ammoniacum. That analysed by Hirschsohn was obtained from the late Mr. Hanbury and gave similar results. By distilling it, however, the last observer obtained *umbelliferone* $C_6H_2(OH)\langle\begin{array}{l}CH{=}CH{-}CO.\\ O\rule[0.5ex]{5em}{0.4pt}\end{array}$ Goldschmiedt (B. 11, 850) announces that by fusion with potash African ammoniacum yields *resorcinol* $C_6H_4(OH)_2$, together with *an acid* $C_{16}H_{18}O_6$. This acid is not produced when the Persian drug is similarly treated.

Asafœtida; *Gummi-resina Asafœtida*; *Asafœtida*, Fr.; *Asant*, *Stinkasant*, *Teufelsdreck*, Ger.

Gum-resin asafœtida is the dried juice of the roots of two large herbaceous plants which inhabit Thibet, Afghanistan, Turkestan, and the country from the Sea of Aral to the Persian Gulf. These are the *Ferula Narthex* (Boissier) and the *Ferula Scorodosma* (Bentham a. Hooker). For drawings *v.* Bentl. a. T. 126–127, and Holmes (Ph. [3] 19, 21, 41 a. 365). Details of the mode of preparing the roots and of collecting the dried exudation are given by Flückiger and Hanbury (Fl. a. H. 316) and by Pereira (Mat. Med. 1853, 2, 1704). It is certain that asafœtida was known to the Arabian writers of the tenth century, and there is reason to believe that a knowledge of the drug is far more ancient.

Supplies of asafœtida are now almost entirely derived by way of India from Afghanistan. It occurs as tears more or less agglutinated, and sometimes as a honey-like mass. It is often largely mixed with earthy matter. A characteristic property of the drug is that when broken the milky white surface changes gradually to a pink which passes into a brown hue. Touched with nitric acid (sp.gr. 1·2) it gives a green colour. With water it forms an emulsion. The tears are brittle and may be powdered when cold. Asafœtida has a powerful alliaceous odour and an acrid bitter alliaceous taste.

The chief constituents of asafœtida are *resin*, *gum*, and *volatile oil*. For results of early investigations *v.* Gm. 17, 398. The analysis of Pelletier (Bl. Ph. 3, 556) shows that the resin amounts to 65·0 p.c., the soluble gum 19·44 p.c., the insoluble gum 11·66 p.c., and the volatile oil 3·6 p.c., or, according to Flückiger and Hanbury, 6 to 9 p.c. The *resin* is only partly soluble in ether and chloroform, but is entirely dissolved without alteration by concentrated nitric acid (*cf.* Johnston, Tr. 1840, 354). Hlasiwetz and Barth (A. 138, 64) discovered in the resin *ferulic acid*, the methylphenolic ether of oxycinnamic or caffeic acid,

$$C_6H_3.(CH{:}CH.COOH)(OCH_3).OH\,1{:}3{:}4.$$

An alcoholic solution of asafœtida is precipitated by an alcoholic solution of lead acetate, and from the insoluble lead salt the ferulic acid is regenerated. It consists of needles melting at 168–169° (Tiemann, B. 9, 416). This acid is related to vanillin $C_6H_3.(CHO).OCH_3.OH\,1{:}3{:}4$. It contains the same phenolic groups; but the formaldehyde residue (CHO) in vanillin is replaced by the residue of acrylic acid (CH:CH.COOH). Synthetically, ferulic acid may be prepared from vanillin by Perkin's condensation reaction (Tiemann and Nagai, B. 11, 647). The vanillin is treated with sodium acetate in presence of a dehydrating agent, such as acetic anhydride. Thus:

$$C_6H_3(OCH_3)(OH)(CHO) + CH_3COOH - H_2O$$
$$= C_6H_3(OCH_3)(OH)(CH{:}CH.COOH).$$

In practice acetyl-ferulic acid is formed, which is decomposed by caustic alkali. It is interesting to note in this connection that *vanillin* itself has recently been detected in asafœtida by Schmidt (Ar. Ph. [3] 24, 534). The ethereal solution shaken with water containing acid sulphide of sodium yielded aldehyde crystals, from which the vanillin was obtained and identified. When asafœtida resin is distilled alone, *variously tinted oils* are obtained, together with ¼ p.c. of *umbelliferone* $C_6H_3(OH)\langle\begin{array}{l}CH{=}CH{-}CO\\ O\rule[0.5ex]{5em}{0.4pt}\end{array}$ (Sommer, J. 1859, 573). Fused with potash *resorcinol* $C_6H_4(OH)_2$ and *protocatechuic acid*, $C_6H_3(OH)_2COOH$, are formed (Hlasiwetz a. Barth) and treated with nitric acid it yields *trinitroresorcinol* or *styphnic acid*, $C_6H(NO_2)_3(OH)_2$ (Will a. Boettger, A. 58, 269).

The *gum* of asafœtida consists of 2 parts, the one soluble and the other insoluble in water. The *volatile oil* is described by Flückiger and Hanbury as of a light-yellow colour with the odour of asafœtida. The taste is at first mild and then irritating, but it does not stimulate when applied to the skin like mustard oil. The oil is neutral, but becomes acid by exposure to the air; at the same time evolving sulphuretted hydrogen. In the fresh state it is free from oxygen, and boils at 135°–140°. The proportion of sulphur varies from 20–25 p.c., the continual evolution of hydrogen sulphide rendering it impossible to obtain an oil of constant composition. At 25° the oil has a sp.gr. 0·951, and is dextrorotatory. A drop floated on water is coloured violet by bromine vapour. Fractionated it yields at 300° a beautiful *blue oil*. When the oil is treated with metallic sodium or potassium the sulphur is removed, and the liquid which remains has the odour of cinnamon. Hlasiwetz (A. 71, 23) regards volatile oil of asafœtida as a mixture of the *two sulphides* $C_{12}H_{22}S_2$ and $C_{12}H_{22}S$.

Asafœtida is used in medicine as a nervous stimulant and antispasmodic, and in the East as a condiment.

Other varieties of asafœtida. The *Hing* used by the natives of Bombay is a variety of asafœtida. It is derived from *Ferula alliacea* (Boissier). It is more repulsive, and contains a larger proportion of volatile oil than asafœtida (Flückiger, Ph. [3] 6, 401; Fl. a. H. 319).

Bdellium.

Indian Bdellium; *False Myrrh*; *Bdellium*. This is the bdellium of the Bible, and is now used chiefly as an adulterant of myrrh. It is the product of *Balsamodendron Mokul* (Hooker) and, according to Dymock, also of the *B. Roxburgii* (*cf.* Ph. [3] 6, 661). Both are indigenous to India, but grow perhaps also in Southern Arabia. The gum-resin breaks with a flat conchoidal fracture, and though somewhat darker in colour, it resembles myrrh in appearance. It may be distinguished from myrrh by its not giving the violet colour reaction (*v.* MYRRH).

African Bdellium. A more highly esteemed bdellium, the product of *Balsamodendron africanum* (Arnott), a shrub indigenous to West Africa. It is used in France as a constituent of plasters. In fracture and other respects it resembles myrrh, but it does not give the violet colour reaction (*v. Myrrh*). African bdellium was analysed by Pelletier (A. Ch. [2] 80, 38), who found *resin* 59 p.c., *soluble gum* 9·2 p.c., *insoluble gum* 30·6 p.c., *volatile oil* and loss 1·2 p.c. The resin was further examined by Johnston (Tr. 1840, 368). *Cf.* Bley a. Diesel (Ar. Ph. [2] 43, 304).

Euphorbium. *Gomme-résine d'Euphorbe*, Fr.; *Euphorbium*, Ger. This extremely acrid drug has been known since the time of Dioscorides, but it is now very seldom employed in medicine. It is the inspissated milky juice of the *Euphorbia resinifera* (Berg), a cactus-like plant inhabiting Morocco and neighbouring districts of Northern Africa. A drawing is given by Bentl. a. T. 240. Euphorbium consists of irregular masses of a waxy-yellow or brown appearance, often inclosing spines and other fragments of the plant. It has a slight aromatic odour and an extremely acrid taste, its dust causing violent and even dangerous irritation to the nose or throat.

Flückiger (Fl. a. H. 560) found a selected specimen to consist of *amorphous resin*, $C_{10}H_{16}O_2$, 38 p.c.; *euphorbon*, $C_{15}H_{22}O$, or $C_{15}H_{24}O$, according to Hesse (A. 192, 193), 22 p.c.; *mucilage*, 18 p.c.; *malate of calcium, sodium, &c.*, 12 p.c.; *mineral compounds*, 10 p.c. It contains no volatile oil. Analyses have also been made by Braconnot (A. Ch. 68, 44), Pelletier (Bl. Ph. 4, 502), Brandes (Repert. 6, 145), Buchner and Herberger (Repert. 37, 213), Rose (P. 33, 52; 53, 369), and Johnston (Tr. 1840, 364). According to Flückiger and Hanbury, the activity of euphorbium is due to the amorphous resin which the drug gives to 70 p.c. alcohol. When it is treated with alcoholic potash a potassium salt is formed, which, when decomposed by an acid, yields an amorphous precipitate, the *euphorbic acid* of Buchheim (Wiggers and Hausemann's J. 1873, 559). After removal of the amorphous resin, ether or petroleum ether extracts from the residue, the 'sparingly soluble resin' of the older writers, which Flückiger analysed and named 'euphorbon' (J. 1868, 809; Z. [2] 4, 221). Euphorbon is crystalline, and when properly purified is free from acridity. It is insoluble in water, sparingly soluble in cold alcohol, but is readily dissolved by benzene, chloroform, ether, or petroleum ether. Flückiger finds it to melt at 116°, Hesse at 113–114°. A thin film of euphorbon, easily obtained by allowing a drop of the alcoholic solution to evaporate, gives a fine violet colour when treated successively with sulphuric and nitric acids. This reaction is, however, by no means a characteristic one. Lactucerin behaves in precisely the same manner, and myrrh contains constituents which when oxidised give similar violet colours (*cf.* Henke, Ar. Ph. [3] 24, 729).

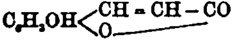
The gum of euphorbium, unlike gum arabic, is precipitated by neutral lead acetate, and by sodium silicate and borate. On the addition of alcohol to an aqueous extract of euphorbium a crystalline precipitate falls consisting of *malates.*

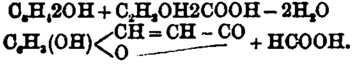
Euphorbium is now used only in veterinary medicine. Applied externally to the human subject it is irritant and vesicating, and internally administered it causes violent vomiting and purging. It is said to be an efficient preservative of iron and steel against corrosion (Year Book Pharm. 1880, 344).

Galbanum; *Gummi-resina Galbanum*; *Galbanum*, Fr.; *Mutterharz*, Ger. Galbanum has entered into the constitution of incense, and has been employed in medicine from the earliest times. It was used by the Israelites, and was well known to Hippocrates, Theophrastus, and Dioscorides, also to the Arabians, and still retains its place in the official pharmacopœias of Europe and the United States. But notwithstanding its antiquity, the precise plant or plants from which galbanum is derived still remains uncertain. It is most probably obtained from the *Ferula galbaniflua* (Boissier and Buhse), and perhaps from other allied species of *Ferula*, natives of Persia. For figure *v.* Bentl. a. T. 128 (*cf.* Holmes, Ph. [3] 19, 365).

The gum-resin occurs in commerce in drops or tears, usually adhering together into solid masses. In colour it exhibits various shades of light yellowish-brown, sometimes tinted with green. The odour of galbanum is aromatic, and the taste unpleasant, bitter, and alliaceous. Flückiger and Hanbury (Fl. a. H. 323) note that when galbanum is warmed with concentrated hydrochloric acid a red colour is developed which on the careful addition of spirit of wine turns violet or bluish. Asafœtida treated in the same manner assumes a dingy colour, while ammoniacum gives no colour change at all. Further details of the characters of galbanum and its behaviour towards reagents are given in an elaborate memoir by Hirschsohn (P. Z. 1875, 225; Ph. [3] 7, 369, 389, 429, 531, and 571). This pharmacologist divides galbanum of commerce, according to its physical character, into three varieties, one coming from Persia and two from the Levant, or, according to its behaviour towards reagents, into four sorts—one from Persia and three from the Levant.

Among the earlier investigators of galbanum are Carthaeuser (Pelletier, Bl. Ph. 4, 97), Neumann (R. P. 27, 249), Pelletier (Bl. Ph. 4, 97), Fiddechow (Berl. Jahr. Pharm. 1816, 230), and Meissner (N. J. T. 1, 1 a. 3). The inquiries of these investigators and the more recent statement of Vigier (Gommes résines des Ombellifères, Paris, 1869, 60) show that galbanum consists essentially of about 65 p.c. *resin*, 20 p.c. *gum*, and 3 to 7 p.c. *volatile oil*. The volatile oil is obtained by distillation with water or by extraction with petroleum ether. The latter method gave Hirschsohn from 3·35 to 26·9 p.c. According to Flückiger and Hanbury, the crude oil possesses an aromatic taste and is dextrorotatory. On the addition of bromine to the oil extracted from Persian galbanum a red to violet or blue colour appears. The oil consists partly of *a hydrocarbon* $C_{10}H_{16}$ which like turpentine oil gives crystalline terpenehydrate $C_{10}H_{16}2H_2O.H_2O$ and hydrochloride $C_{10}H_{16}.HCl$. The chief part, however, is a mixture of heavier hydrocarbons (*cf.* Moessmer, A. 119, 237).

After removal of the volatile oil by petroleum ether, Hirschsohn extracts the resin from the residue by ether. His results, which extend over twenty-four specimens, range from 41 to 63 p.c. The method adopted by him gives apparently rather less resin and rather more volatile oil than those employed by the older workers the averages of whose results are given above. Galbanum resin was analysed by Johnston (Tr. 1840, 362). According to Hirschsohn, it is not a single substance, but a mixture of *three or four distinct resins. Umbelliferone or oxycoumarin*  $C_6H_3OH\Big<\begin{matrix}CH=CH-CO\\O\qquad\qquad\qquad\end{matrix}$ was first obtained by Sommer by distillation of galbanum resin or the crude drug (J. 1859, 573). Moessmer (A. 119, 260) prepares it by first separating the resin, which in concentrated alcoholic solution is saturated with hydrochloric acid gas and kept at 100° for some hours (*cf.* Hlasiwetz a. Grabowski, A. 139, 100). Zwenger (A. 115, 15) obtained umbelliferone from the resin of mezereon, and it is now known to be a product of the distillation of many other resins or gum-resins, especially those of the Umbelliferæ. According to Hirschsohn, it occurs to some extent ready formed in galbanum. Galbanum yields 0·83 p.c., sagapenum 0·32 p.c., asafœtida 0·28 p.c. Synthetically, umbelliferone may be produced, as pointed out by Pechmann (B. 17, 932) by acting upon a mixture of resorcinol and malic acid with dehydrating agents such as sulphuric acid, thus:



$$C_6H_4 2OH + C_2H_3OH2COOH - 2H_2O$$
$$= C_6H_3(OH)\Big<\begin{matrix}CH=CH-CO\\O\qquad\qquad\qquad\end{matrix} + HCOOH.$$

Another product of the destructive distillation of galbanum resin is a thick *brilliant blue oil.* This was first observed by Neumann, and was examined by most of the chemists already referred to. Recently it has been studied afresh by Kachler (B. 4, 36). The oil deposits in the cold crystals of umbelliferone. It has a bitter acrid taste and aromatic odour. Kachler separated it into a *colourless hydrocarbon* $C_{10}H_{16}$ boiling at 240°, and a *blue oil* $C_{10}H_{16}O$ which boiled at 289°. The flowers of the wild chamomile *Matricaria chamomilla* (Linn.) yield a blue oil very similar to this obtained from galbanum. Both oils are converted by potassium into the hydrocarbon $C_{10}H_{16}$, which on the addition of bromine vapour gives the blue colour reaction. Hlasiwetz and Barth (A. 130, 354) have shown that by fusing galbanum resin with potash as much as 6 p.c. of *resorcinol* $C_6H_4(OH)_2 1{:}4$ is formed (*cf.* Goldschmied, B. 11, 850), and by treatment with nitric acid, Will a. Boettger (A. 58, 269) obtained *styphnic acid* $C_6H(NO_2)_3(OH)_2$ (*cf.* Schwanert, A. 128, 123).

Hirschsohn in his experiments, after removal of the volatile oil and resin and a little saccharine and astringent matter, by extraction of galbanum with petroleum ether, ether, and 85 p.c. alcohol, successively; treats the residue with water to obtain the gum. The yield was 6 to 17 p.c. The sugar obtained from this gum by the action of dilute acids is optically distinct from that produced in the same way from gum arabic. The final insoluble residues in Hirschsohn's experiments were from 8 to 24 p.c.

Galbanum is administered in medicine internally as an expectorant, and externally it enters into the composition of plasters.

Gamboge. *Cambogia, Cadis Gum, Gummi Gambogia, Gummi Gutti*; *Gomme Gutte*, Fr.; *Gutti, Gummigutt*, Ger. This beautiful orange-red gum-resin comes to us from Camboja, Siam, and Cochin China, where it is the product of a laurel-like tree, the *Garcinia Hanburyi* (Hooker); *v.* Bentl. a. T. 33. Gamboge was known to the Chinese in the thirteenth century, but it was not until the seventeenth century that it appeared in European markets. For the purpose of collecting it the trees are incised, and sections of bamboo are attached to collect the milky juice, which, hardening by evaporation, takes the cylindrical shape of the receiving vessel. Gamboge as it occurs in commerce is brittle, and may be powdered readily. In presence of water it forms at once a yellow emulsion. It has a disagreeable and acrid taste.

Among the earlier investigators who analysed gamboge are Braconnot (A. Ch. 68, 33), John (Chem. Schriften, 4, 193), Unverdorben (N. J. T. 8, 1 a. 60), Christison (A. 23, 185), Johnston (Tr. 1839, 281), and Büchner (A. 45, 72). Costelo (Am. J. Pharm. 1879, 174), who has analysed the gum-resin more recently, finds the *resin* to vary from 68–79 p.c., and the *gum* from 19–27 p.c. (*cf.* Hurst, Ph. [3] 19, 761). The gum is extracted by water. Its solution, like arabic, is not precipitated by neutral lead acetate, but its behaviour towards other reagents shows it to be a different gum. By the action of dilute acids it yields a *non-fermentable sugar*, and when oxidised by nitric acid *mucic acid* $C_4H_4(OH)_4(COOH)_2$ is formed.

Alcohol dissolves the resin. It combines with bases, and is called by Johnston *gambodic acid*. By fusion with potash, Hlasiwetz and Barth (A. 138, 68) obtained a number of interesting products. Besides several *acids of the fatty series*, these observers isolated *phloroglucinol* $C_6H_3(OH)_3 1{:}3{:}5$; *pyrotartaric acid* $CH_3.CH(COOH).CH_2COOH$; and *isomesidic, isouvitic*, or *isovitinic acid* $C_6H_4.CH_2COOH.COOH$. This last-mentioned acid has since been produced by the action of hot dilute alkali on *cyantolyl (o-) carboxylic acid*, $C_6H_4.CH_2CN.COOH$, which converts the cyanogen into a carboxylic group (Wislicenus, A. 233, 106).

For the detection of gamboge in mixtures, *v.* Hirschsohn (P. Z. 24, 609). In medicine gamboge is employed as a drastic purgative, usually in combination with other substances. It is also an important colouring agent.

Ivy gum resin. *Gummi-resina Hederæ.* In Southern Europe and in the Levant a gum-resin is obtained from the old trunks of the common ivy, *Hedera Helix* (Linn.). It consists of irregular masses of a reddish or yellowish-brown colour externally, but showing a deep red by transmitted light. The taste is bitter and acrid, but when heated it evolves a balsamic odour. Pelletier (B. Ph. 4, 504) found the gum-resin to consist of *resin* 23 p.c., *gum* 7 p.c., and 70 p.c. of woody fibre. Examined by Sommer (Ar. Ph. [2] 98, 11) it gave no umbelliferone.

Besides the gum-resin the leaves, berries, and the wood itself of ivy have been used in medicine and they have been examined by chemists. Hartsen (J. 1875, 827) found ivy leaves to contain a glucoside allied to saponin, and this has been since studied by Davies and Hutchinson

(Ph. [3] 7, 275), Davies (Ph. [3] 8, 205), Kingzett (Ph. [3] 8, 206), Vernet (J. 1881, 91), Vincent (Bl. 35, 231), and Block (Ar. Ph. [3] 26, 953). Most of these observers obtained the glucoside from ivy berries. Davies and Hutchinson regard it as identical with the *hederic acid* which, together with *hederotannic acid*, Posselt found in ivy berries (A. 69, 62).

Hederic acid or *ivy glucoside*, $C_{32}H_{54}O_{11}$, is obtained from ivy berries after they have been exhausted with ether by treatment with alcohol, which, on evaporation, deposits it in needles (D. a. H.), or the berries are exhausted with alcohol, and the residue, after the alcohol has been removed by distillation, is washed in the cold with benzene and extracted with hot acetone. On concentrating the solution a crystalline mass is obtained which is purified by recrystallisation from alcohol (Vernet; Vincent). The glucoside forms silky needles which melt at 233°. It is insoluble in water, chloroform, and petroleum ether, is slightly soluble in the cold in acetone, benzene, and ether, and very soluble in hot alcohol and alkalis. It is inodorous, but possesses the taste of the berries. By the action of dilute acids it breaks up into a crystalline *compound* $C_{26}H_{42}O_{6}$ (?), which melts at 278-280°, and a non-fermentable *sugar* which reduces Fehling's solution.

The alkaloid 'hederine' of Vandamme and Chevallier (B. J. 21, 325) has not been confirmed by subsequent investigation.

Myrrh. *Myrrha, Gummi-resina Myrrha*; *Myrrhe*, Fr.; *Myrrhe*, Ger. Together with olibanum, myrrh has been used as a constituent of incense from the earliest times. It is mentioned in Genesis and in other places in the Bible. The Egyptians employed it not only in fumigations, but also in embalming and in medicine. It has retained its place down to the present day, and is included in all the pharmacopœias. Myrrh is the spontaneous gum-resinous exudate of the shrubs or small trees of the *Balsamodendron myrrha* (Nees), an inhabitant of the Somali coast of the Gulf of Aden and of the Red Sea coast of Arabia (Trimen, Ph. [3] 9, 893). A drawing of the tree is given by Bentl. a. T. 60. The exudate is allowed to harden on the tree before collection. According to Dymock (Ph. [3] 6, 61), it is now shipped, together with allied gum-resins, to Bombay, where a sorting takes place and the better varieties are re-shipped to Europe. It occurs in irregular-shaped masses of a red-brown colour and dusty appearance. When cold it is brittle, and breaks with an uneven, waxy, oily-looking fracture, often exhibiting lighter-coloured semicircular striations. With water it readily yields an emulsion. The odour of myrrh is fragrant and agreeable, and the taste bitter, aromatic, and acrid.

The chief constituents of myrrh are *gum*, *resin*, and *volatile oil*. The relative proportions, even in the case of true myrrh, vary greatly with different specimens. Generally the gum constitutes 40-65 p.c., the resin 25–40 p.c., and the volatile oil is said to reach 4·4 p.c. Among the earlier analyses are those of Pelletier (A. Ch. 80, 45), Braconnot (A. Ch. 67, 52), and Brandes (B. J. 22, 275). Flückiger and Hanbury (Fl. a. H. 143) found 27 p.c. of resin in a good specimen. Brückner's analysis (N. R. P. 16, 76) gave: soluble in water, gum, 67·76 p.c.; resin soluble in carbon bisulphide, 14·06 p.c.; resin soluble in ether, 12·57 p.c.; resin insoluble in ether, 4·81 p.c.; substances soluble in diluted alcohol, 0·43 p.c.; insoluble (sand, bark, &c.), 0·38 p.c.

Myrrh resin is soluble in alcohol and chloroform, but it is only partly soluble in ether, carbon bisulphide, and alkalis. It gives a violet colour when a fragment moistened with alcohol is treated with nitric acid, but not so marked as in the case of galbanum (*cf.* Ruickholdt, Ar. Ph. [2] 41, 1; Held, A. 63, 59; Hager, Ph. Centh. 1865, 58). Distilled, it gives no umbelliferone, but by fusion with potash Hlasiwetz and Barth (A. 139, 78) obtained small quantities of *catechol*, $C_6H_4(OH)_2$1:2, and *protocatechuic acid* $C_6H_3(COOH)(OH)_2$1:3:4. The property of giving a violet colour when oxidised by nitric acid, or better, by bromine vapour, is confined to that resin which dissolves in carbon bisulphide, and which, according to Brückner, contains 75·6 p.c. of carbon.

Brandes and Braconnot found the gum of myrrh to be three-fourths soluble in water (*cf.* Pelletier; Heckemeijer, J. 1858, 482). It has not been recently examined.

The quantity of volatile oil in myrrh varies very greatly. Brandes gives 2·6 p.c.; Braconnot 2·5 p.c.; Ruickholdt (Ar. Ph. [2] 41, 10) 2·18 p.c.; Bley and Diesel (Ar. Ph. [2] 43, 304) 1·6 to 3·1 p.c.; and Flückiger 0·75 p.c.; while Fritzsche, who worked on a large scale, obtained 4·4 p.c. (Fl. a. H. 144). The oil, according to Ruickholdt, has the composition $C_{10}H_{14}O$. Gladstone (C. J. 17, 11) describes it as a viscid brownish-green oil that, boiling at 266°, gave an oxidised product. Its sp.gr. was 1·0189. The oil prepared by Flückiger (*cf.* B. 9, 471) had different characters. It was lighter than water, the sp.gr. at 13° being 0·988, and the boiling-point 270–290°. Redistilled in a current of carbonic anhydride it passed over between 262 and 263°, and on analysis gave the formula $C_{22}H_{32}O$. After redistillation the oil, on addition of a drop of nitric acid, gave after an hour or two a permanent violet hue, but this is better observed when bromine vapour is applied to a solution of the crude oil in carbon bisulphide.

According to Flückiger, the *bitter constituent* of myrrh is a glucoside.

Myrrh is a reputed stimulant and tonic, but its employment in medicine depends chiefly on its aromatic properties.

Other varieties of myrrh. Several gum-resins more or less resembling true myrrh are occasionally found in commerce. Two are described by Flückiger and Hanbury. One of these, often incorrectly called *East Indian myrrh*, but which is really an African drug, is known as *bissa-bol* or *hebbakhade*. In outward appearance it is very similar to true myrrh, but it is more acrid, and its resin, soluble in carbon bisulphide, gives no violet colour with bromine vapour.

The other variety is *Arabian myrrh*. It is collected in Southern Arabia east of Aden, and is probably the product of a distinct species (Hanbury). It is very nearly related to true myrrh in appearance, and some specimens give the violet colour reaction.

Olibanum. *Frankincense*; *Gummi-resina Olibanum*; *Thus masculum*; *Encens*, Fr.; *Weirauch*, Ger. Olibanum or frankincense has been the favourite basis of incense from the earliest times. It is frequently referred to in the Bible, and the Egyptians employed it for fumigations and for embalming.

Duemichen, in his book on the Paintings of the Temple of Dayr el Báhri in Upper Egypt, which represent the traffic between Egypt and a land called Punt as early as the seventeenth century B.C., has shown that these paintings include, not only representations of olibanum in bags, but boxes or tubs containing living olibanum trees. Tribute offerings of frankincense were common throughout the ancient world. At the present day the incense of the Roman and Greek Churches is largely composed of olibanum.

The gum-resin is the dried exudated juice of several species of *Boswellia*. These trees, the fragrance of which is noticeable even at a distance, inhabit Eastern Africa, near Cape Gardafui, and the southern coast of Arabia. They were studied by Birdwood (Trans. Linn. Soc. 27, 111, 148). One of them is figured by Bentl. a. T. 58 (Fl. a. H. 134). Olibanum is a solid which softens in the mouth, and has a slightly terebinthinous, not disagreeable, taste. It consists of tears of various shapes, generally detached. The odour, especially on heating, is pleasantly aromatic. It has a pale yellow or brown colour, and the larger fragments are more or less milky and translucent. Triturated with cold water it yields an emulsion.

The chief constituents of frankincense are *resin*, *gum*, and *volatile oil*. The oil is obtained by distillation; alcohol dissolves the resin and water the gum. Braconnot (A. Ch. 68, 60) found resin 56 p.c., soluble gum 30 p.c., insoluble gum 6 p.c., and volatile oil 8 p.c.; while the analysis of Kurbatow gave resin 72 p.c., gum 21 p.c., and volatile oil 7 p.c. (Z. [2] 7, 201). The resin was regarded by Johnston (Tr. 1839, 301) as a mixture of two compounds; but Hlasiwetz considers it a single substance, having the formula $C_{20}H_{32}O_2$ (Fl. a. H.). It does not dissolve in alkalis, and examined by Sommer (J. 1859, 573), gave no umbelliferone. According to Kurbatow, an *oil boiling at* 360° is obtained when the resin is subjected to destructive distillation.

The gum of olibanum behaves towards reagents exactly as gum arabic, with which it is most likely identical (Heckmeijer, J. 1858, 482).

Volatile oil of olibanum, examined by Stenhouse (A. 35, 306), boils at 179·4°, and has a specific gravity of 0·866. This oil Kurbatow has succeeded in separating into a hydrocarbon $C_{10}H_{16}$ *olibene*, which boils at 156°–158°, has the odour of turpentine, and the specific gravity at 12° of 0·863, and an *oxidised oil* boiling above 175°. Olibene is soluble in alcohol and ether, and gives a crystalline hydrochloride $C_{10}H_{16}HCl$, which melts at 127°. Wallach (A. 252, 94), who has recently examined olibanum oil, finds that olibene is identical with *lævopinene*, and that *dipentene* is contained in the higher boiling fractions. At the present day olibanum is seldom employed in medicine. It is used almost exclusively in the preparation of incense.

Opopanax. A bright orange-brown gum-resin occurring in hard nodular or earthy-looking lumps. It was used by Hippocrates, and several varieties were known to Theophrastus and Dioscorides. It is said to be derived from the *Opopanax Chironium* (Koch), a native of Southern Europe; but Powell (Economic Products of the Punjab, 1, 402) and others regard it as a product of Persia. Flückiger and Hanbury (Fl. a. H. 327) describe a specimen of Persian opopanax, that of the *Opopanax persicum* (Bois.), which is altogether different in odour and appearance from the officinal variety.

Opopanax consists essentially of *resin*, *gum*, and a little *volatile oil*. Pelletier (Bl. Ph. 4, 49) analysed a specimen which contained resin 42 p.c., gum 33·4 p.c., starch 4·2 p.c., extractive 1·6 p.c., wax 0·3 p.c., malic acid 2·8 p.c., lignin 9·8 p.c., volatile oil and loss 5·9 p.c. Hirschsohn (P. Z. 1875, 225; Ph. [3] 7, 772) who examined twelve specimens found: soluble in petroleum ether, volatile oil, 1 to 6 p.c., resin 1 to 3 p.c.; soluble in ether, resin 14·8 to 38·8 p.c.; soluble in 85 p.c. alcohol 10·1 to 16·7 p.c.; soluble in water, gum, 11·0 to 33·4 p.c.; gummy residue, 16·3 to 58·0 p.c.; moisture, 1·3 to 4·0 p.c. The large percentage of matter soluble in alcohol obtained by Hirschsohn is a characteristic of opopanax which serves to distinguish that drug from its allies. It is never less than 10 p.c., whereas, similarly treated, the highest percentage obtained from sagapenum was 3·5 p.c., from ammoniacum 4·59 p.c., and from galbanum 4·22 p.c. This extract is also quite different in the case of opopanax from the extract derived from the other drugs mentioned. It is not saccharine, nor does it contain a variety of gallic acid. Hirschsohn notes that the resin of opopanax gives no umbelliferone when distilled (*cf.*, however, Sommer, J. 1859, 573). When fused with potash, Hlasiwetz and Barth (J. 1866, 630) found the resin to yield *catechol* $C_6H_4(OH)_2 1:2$ together with *protocatechuic acid*, $C_6H_3.COOH.OH.OH, 1:3:4$ (Hl. a. B., A. 139, 78). The resin was examined by Johnston (Tr. 1840, 352).

So highly esteemed as opopanax was in ancient medicine it has now gone entirely out of use.

Sagapenum. This gum-resin, which, like galbanum and asafœtida, has been known from the earliest times, is now seldom met with. Its botanical origin is unknown. Flückiger and Hanbury (Fl. a. H. 324) describe sagapenum as consisting of a tough, softish mass of closely agglutinated tears. The tears are brownish, not milkwhite as asafœtida, and when broken do not acquire a pink tint, and are without alliaceous odour. The specimen of sagapenum examined by these observers contained no sulphur, but yielded *umbelliferone*  $C_6H_3OH{<}^{CH:CHCO}_{O}$. Seven out of the eight specimens examined by Hirschsohn (P. Z. 1875, 225; Ph. [3] 7, 771), however, contained sulphur, and this character served to distinguish sagapenum from ammoniacum, galbanum, and opopanax. Umbelliferone was always obtained. *Resorcinol* $C_6H_4(OH)_2$ is formed when sagapenum is fused with potash (Hlasiwetz a. Barth, A. 139, 78), and *styphnic acid*, $C_6H(NO_2)_3(OH)_2$, by treatment with nitric acid (Boettger a. Will, A. 58, 269). When some specimens of sagapenum are immersed in hydrochloric acid (sp.gr. 1·13) they acquire a permanent blue colour, but others do not exhibit this behaviour.

Sagapenum was analysed by Pelletier (Bl. Ph. 3, 481) and Brandes (N. J. T. [2] 2, 97). These observers found *resin* 50–54 p.c., *gum* 32 p.c., and *volatile oil* 4–8 p.c. The resin consists of two portions, one soluble, the other insoluble in ether (Pereira, Mat. Med. 1853, 1712). The resin was analysed by Johnston (Tr. 1840, 361). Hirschsohn has recently examined eight specimens of sagapenum with the following results: soluble in petroleum ether, volatile oil, 5·98 to 16·94 p.c., together with non-volatile resin, 0·3 to 12·86 p.c.; soluble in ether, resin 27·21 to 58·9 p.c.; soluble in 85 p.c. alcohol, saccharine matter 2·06 to 3·5 p.c.; soluble in water, gum 10·74 to 29·23 p.c.; insoluble residue 5·18 to 30·09 p.c.; moisture, 1·18 to 3·72 p.c.

Scammony. *Scammonée*, Fr.; *Scammonium*, Ger. A purgative gum-resin derived from the *Convolvulus scammonia* (Linn.), a native of Greece, Asia Minor, Syria, and Southern Russia. Scammony consists of 10 to 20 p.c. *gum* and 80 to 90 p.c. *resin*. The resin is *jalapin*, and is a glucoside (*v.* GLUCOSIDES).

A. S.

GUMS. Gums are amorphous carbohydrates, for the most part of vegetable origin, which are insoluble in alcohol, and either dissolve in water or take up enough of that solvent to become glutinous and form a mucilage. They are either derived from plants by spontaneous exudation and evaporation, or are extracted by means of solvents. They are generally convertible into sugars by heating with dilute acids, and when oxidised they yield in the first instance oxalic or mucic acids or both. With one or two exceptions they are not coloured by iodine. Many drugs known as gums in commerce, and not included in this article, will be found by reference to BALSAMS or GUM RESINS.

The finer gums are used in pharmacy in the preparation of emulsions and pastilles, and as a constituent of emollient medicines, while the commoner qualities are used in the arts as adhesive agents, in the finishing of cloth, in the preparation of ink, of water-colours, and in calico-printing.

ACACIA AND ALLIED GUMS.

Gum acacia. *Gum arabic*, *Acaciæ gummi*; *Gomme arabique*, Fr.; *Arabisches gummi*, Ger. Gum acacia is the exudation from the stems and branches of various species of *Acacia*, notably the *A. Senegal* (Willd.), which inhabit Africa from Senegambia in the West to Kordofan, Southern Nubia, and the region of the Atbara in the East (Bentl. a. T. 94; Höhnel, Ph. [3] 18, 1089; Fl. a. H. 233). The drug has been known from the earliest times, having been an article of Egyptian commerce in the seventeenth century B.C.

The most esteemed variety is *Picked Turkey* or *White Sennaar gum*, which, on account of the political disturbances in the Soudan, is not just now obtainable. It consists of lumps of various sizes, sometimes as large as a walnut, and has a white or nearly white colour. The unbroken masses are rounded, and traversed by numerous minute fissures. They are brittle and break with a vitreous fracture, exposing a transparent and, in the finer varieties, quite colourless interior. *Senegal gum* is derived from the same species of acacia as that which yields the Sennaar or Kordofan gum, but is much darker in colour and the surface of the lumps is unbroken by cracks or fissures. It is chiefly imported into France. *Suakin*, *Talca*, or *Talha gum* comes from Alexandria. It is so brittle that commercial specimens have usually, for the most part, fallen to powder. The particles exhibit a great variety of colour. *Morocco*, *Mogador*, or *Brown Barbary gum* consists of light dusky brown tears or vermiform pieces. It is supposed to be derived from the *Acacia nilotica* (Desfont.). *Cape gum* is the product of the *Acacia horrida* (Willd.) and a native of Cape Colony. Its colour is amber-brown. *East India gum* comes from East Africa by way of Bombay. It consists of tears, often as large as an egg, and of a pale amber or pinkish hue. *Australian* or *Wattle gum*, the product of several Australian species of acacia, occurs in large hard globular tears or lumps, varying in colour from pale yellow to deep reddish-brown (*v.* Maiden, Ph. [3] 20, 869; *cf.* Fl. a. H.).

The sp.gr. of gum arabic is 1·487 (dried at 15°) or 1·525 dried at 100° (Fl. a. H.). It is not much more soluble in hot than in cold water. In alcohol it is insoluble. The aqueous solution is precipitated by basic acetate of lead, but not by neutral acetate. It is also thickened or rendered turbid by the addition of borates or ferric salts or soluble silicates. Oxalate of ammonium renders the solution turbid from precipitation of calcium oxalate. Salts of mercury or silver have no action on the solution, neither is it coloured blue by iodine. Dried in the air the gum retains $3H_2O$, which it loses at 100°. At a higher temperature another molecule of water escapes (*cf.* Fl. a. H.). Gum arabic yields about 3 p.c. of ash, consisting of calcium, magnesium, and potassium carbonates (Guerin, A. 4, 249). For analytical distinctions between pure arabic and gums with which it is sometimes associated, *v.* Hager (Fr. 11, 350; Ph. Centh. 1885, 388); Schlosser (C. N. 20, 120); Roussin (J. Ph. [4] 7, 251); Elwood (Ph. [3] 19, 339).

The chief constituent of gum arabic is *Arabic acid*, *Arabin*, or *Gummic acid*, $C_{12}H_{22}O_{11}$, combined with calcium and also perhaps with magnesium and potassium. For earlier work on acacia and arabic acid *v.* Gm. (15, 194). Arabic acid occurs also in the mucilage of the sugar-beet (Scheibler, B. 6, 612) and of the cherry tree (Martin, Phytochem. Untersuch., Leipzig, 1880, 72); in the animal economy (Staedeler, A. 111, 26), and it appears to be identical with Fremy's metapectinic acid (A. 67, 257). The crude acid is precipitated when alcohol is added to an aqueous solution of gum arabic previously acidulated with hydrochloric acid. By successively redissolving in water and reprecipitating, a fairly pure product is obtained. Thus prepared it is, however, a mixture of at least two compounds. One of these is *lævorotatory*, and when heated with dilute acids yields crystallisable *arabinose*, the other is *dextrorotatory* and is converted by treatment with dilute acids into an uncrystallisable sugar. To obtain lævo-arabic acid by itself it is more advantageous to employ cherry-tree gum (Scheibler). *Cf.* Neubauer (J. 1854, 624; A. 102, 105), and as to the constitution of arabic acid, O'Sullivan (C. J. 45, 41).

Arabic acid is amorphous, soluble in water and insoluble in alcohol. The aqueous solution is, however, not precipitated by alcohol until it has been first acidulated (Neubauer). Heated to 100° it is converted into insoluble *Meta-arabic acid* (Neubauer; Gelis, J. 1857, 496), or the same change may be effected by treatment with concentrated sulphuric acid (Fremy, J. 1860, 503). Meta-arabic acid is readily changed back again to soluble arabic acid by the action of alkalis. Heat of combustion *v.* Stohmann (J. pr. [2] 31, 289). Action of light, *v.* Eder (J. pr. 19, 299).

From the gum distilled with chalk Fremy obtained *acetone* and *metacetone* (A. 15, 281). Melted with potash it yields *succinic acid* together with the products obtained in the case of sugar (Gottlieb, A. 52, 122; Hlasiwetz a. Barth, A. 138, 76). With ordinary nitric acid, gum arabic yields *oxalic*, *mucic*, *tartaric*, and *racemic acids* (Guerin, A. 4, 255; Liebig, A. 113, 4; Kiliani, B. 15, 35; Hornemann, J. 1863, 381). Fuming nitric acid gives *nitro- derivates*, $C_{12}H_{18}(NO_2)_2O_{10}$ and $C_{12}H_{16}(NO_2)_4O_{10}$ (Béchamp, J. 1860, 521). Similarly acetic anhydride reacts, forming *acetyl derivates*, $C_{12}H_{18}Ac_4O_{10}$ and $C_{12}H_{14}Ac_6O_{10}$ (Schutzenberger a. Naudin, Z. 1869, 265). For metallic salts *v.* Neubauer (J. 1854, 624), Hechmeijer (J. 1858, 482), O'Sullivan (J. C. 45, 54). (*Cf.* Bn. 1, 877). An *isoarabin* (Balls, Ph. [3] 19, 992).

Allied gums. *Chagual gum* is obtained from Chili, where it is produced by the *Pourretia lanuginosa* (Ruiz a. Pavon). It is partly insoluble in water (*cf.* Pribram, J. 1867, 747). *Feronia* or *Wood apple gum* is chiefly met with in Europe as an adulterant of gum arabic. It is derived from the Indian tree *Feronia Elephantum* (Correa) (*cf.* Fl. a. H. 239). *Ghatti* and other Indian substitutes for gum arabic (Mander, Ph. [3] 18, 876; 20, 781). *Hog* or *Doctor gum* consists of reddish tears. It is derived from the *Rhus metopium* (Linn.) or perhaps the *Moronobia coccinea* (Aublet), natives of South America. This gum is quite distinct from the Hogg or Kuteera gum of India (*cf. Tragacanth*). Plants containing gums similar to acacia *v.* Gm. 15, 195. *Para* and other gums (Ph. [3] 18, 623, 745 a. 1009).

TRAGACANTH AND ALLIED GUMS.

Tragacanth. *Tragacantha*; *Gomme adragante*, Fr.; *Traganth*, Ger. A gummy exudate consisting in part of altered cells obtained either spontaneously or by means of incisions from the stems of various species of *Astragalus*, notably the *A. gummifer* (Labill.), inhabitants of the old world from Greece and Turkey to Armenia, Syria, Persia, and Kurdistan. Tragacanth was described as early as the third century B.C. by Theophrastus (Bentl. a. T. 73; Fl. a. H. 174; Schmidt, A. 51, 33; Frank, J. pr. 95, 480).

Tragacanth enters commerce mostly by way of Smyrna, where it is sorted into *Flaky* or *Leaf gum*, *Vermicelli* and *Common* or *Sorts*. The first is the most highly esteemed. It consists of thin flat pieces 1, 2, or 3 inches in length and ½ to 1 inch in width. It is nearly white, dull, translucent, horny, and marked by arched or concentric wavy elevations. Inferior specimens have a darker colour (Fl. a. H.).

When tragacanth is treated with water, one part dissolves and the other swells up, absorbing water, to the extent of even fifty times the weight of the gum used, the whole forming a thick mucilage. This may be diffused through more water when on filtering a soluble gum distinct from gum arabic passes through, and there remains on the filter a slimy non-adhesive mucilage, *bassorin*, *tragacanthin*, or *adraganthin*, $C_{12}H_{20}O_{10}$. The soluble gum behaves towards reagents in a different manner to gum arabic (*cf.* Maisch, Ph. [3] 19, 762; Ogle, Ph. [3] 20, 3). The insoluble bassorin is converted by dilute acids into sugar and by nitric acid into oxalic and mucic acids. In presence of alkalis the whole of the gum dissolves readily in water. (Fl. a. H. 178; Sandersleben, Phytochem. Untersuch. Leipzig, 1880, 90; Fremy, J. 1860, 504). For an account of earlier investigations of tragacanth and bassorin *v.* Gm. 15, 206.

Allied gums. *Bassora*, *Kuteera* or *Caramania gum*, *Hogg Gum Tragacanth* consists of yellow or brown waxy masses. It comes from Persia, where it is said to be derived from almond and plum trees, and is employed mostly in Smyrna to adulterate tragacanth (Fl. a. H.). *Cashew gum* is the exudation of the *Anacardium occidentale* (Linn.), a small tree indigenous to tropical America. *Cherry-tree gum* behaves towards water in a similar manner to tragacanth. The insoluble portion is, however, not bassorin but *meta-arabic acid* or *cerasin*, combined with metals of the alkalis or alkaline earths (Fremy, J. 1860, 504; *cf. Arabic acid*). *Linseed*, *marshmallow*, and *fleaseed gums* closely resemble tragacanth (Schmidt, A. 51, 50; Frank, J. pr. 95, 484; Kirchner a. Tollens, A. 175, 215). *Persian gum* (*v.* Ph. [3] 20, 793). *Wood gum* has been extracted from birch, ash, alder, oak, beech, and willow. It resembles cherry-tree gum (Th. Thomsen, J. pr. [2] 19, 146; Poumarède a. Figuier, A. 64, 338; S. C. I. 1890, 335; *cf.* Bn. 880). Hydrolysed it yields *Xylose* (Wheeler a. Tollens, B. 22, 1046 23, 127; A. 254, 320).

OTHER GUMS.

Agar agar gum, *Bengal Isinglass Gum.* The jelly which the dried seaweed, which, under the name of agar agar, is obtained from China, forms with water is largely composed of the *gum gelose* (Payen, J. 1859, 562) or *pararabin* (*cf.* sugar-beet gum) the latter being contained also in the carrot and the sugar-beet. Gelose is insoluble in cold water, alcohol, dilute acids, and alkalis. 1 part in 500 of boiling water forms a jelly on cooling (Morin, J. 1880, 1010; Porumbaru, J. 1880, 1011; Bauer, J. pr. [2] 30, 375). *Galactin*, a very similar gum to gelose, is found in the seeds of the Leguminosæ (Müntz, Bl. 37, 409).

Amyloid gums. These are distinguished from most gums by being coloured blue by iodine. The more important are: *Amyloid* (distinct from that derived from cellulose), the soluble gum of the cotyledons of the tamarind and other plants; *Quince gum*, which breaks up into cellulose, gum, and sugar when heated with dilute sulphuric acid; and *Salep gum*, derived from the bulbs of orchids (Frank, J. pr. 95, 479; Bn. 882).

Animal gum. A gummy substance having the composition $C_{12}H_{20}O_{10}2H_2O$ has been isolated from the secretions of the salivary glands, from the brain, pancreas, kidneys, and other parts of the body. It is unaffected by the digestive ferments, but is converted into sugar by dilute acids. It reduces ammonio-nitrate of silver solution with formation of a mirror. With water it gelatinises, forming a mucilage. It is insoluble in alcohol and ether. When pure it is distinguished from mucin, paralbumin, and metalbumin by not changing the colour of a dilute solution of methyl violet. *Nitro- derivative*, $C_{12}H_{18}(NO_2)_2O_{10}$ (Landwehr, H. 8, 122; 9, 367; 13, 122; Fr. 23, 601; 24, 640; Pouchet, C. R. 20, 21).

Fermentation gum. This gum, *Dextran* or *Viscose*, which occurs in the unripe sugar beet, (Scheibler, W. J. 1875, 790) is formed in the lactic fermentation of cane sugar by the action of the bacterium *Leuconostoc mesenteroides* (Teighem, Jahresb. agrik. Chem. 1879, 544; Béchamp, J. Th. 1881, 85; Brüning, A. 104, 197). Formed also in mucic fermentation (Nägeli, J. pr. [2] 17, 409). Dextran $C_6H_{10}O_5$ (130°) is amorphous, soluble in water and precipitated therefrom as an elastic threadlike mass by alcohol. By treatment with dilute sulphuric acid, sugar is obtained, and oxalic but no mucic acid, when oxidised with nitric acid.

Dextrin *v.* DEXTRIN.

Iceland moss gum. Two gums have been isolated from the jelly of Iceland moss, *Cetraria islandica* (Acharius). The one, *lichenin* $C_6H_{10}O_5$, is unaffected by iodine, while the other, *isolichenin*, is coloured blue by that reagent. Lichenin is a transparent brittle mass which dissolves in hot water, the solution gelatinising on cooling. It is soluble in solution of ammonio-sulphate of copper; combines with bases; is converted by dilute acids into sugar; oxidised by nitric acid it yields oxalic acid, and it reacts with glacial acetic acid, forming *triacetyl-lichenin* $C_6H_7Ac_3O_5$ (Knop a. Schnedermann, A. 55, 165; J. 1847–8, 831; Errera, Inaug. Dis. Brussels, 1882, 18; Mulder, A. 28, 279; Hilger a. Buchner, B. 23, 461). Isolichenin is soluble in water, and unlike lichenin forms no acetyl- derivative, nor is it soluble in ammonio-sulphate of copper solution (Berg, J. 1873, 848; Errera; Hönig, M. 8, 452).

The lichen *Evernia Prunastri* contains a gum resembling lichenin, *everniin* $C_6H_{14}O_7$ (Stüde, A. 131, 241).

Irish moss gum. The Irish moss, *Chondrus crispus* (Lyngbye), contains a gum which is soluble in water, insoluble in ammonio-sulphate of copper, is not coloured blue by iodine and yields mucic acid when oxidised with nitric acid (Blondeau, J. 1865, 659; Flückiger a. Obermeyer, J. 1868, 805; Painter, Ph. [3] 18, 362).

Sterculia gum, derived from various species of *Sterculia*, *v.* Maiden (Ph. [3] 20, 381).

Sugar-beet gum. Several forms of gum have been separated from the juice of the sugar-beet. *Arabic* or *meta-arabic acid* (*cf. Gum acacia*), Dextran (*cf. Fermentation gum*), *pararabin* (Reichardt, B. 8, 808) and *Lævulan* (Lippmann, B. 14, 1509). Pararabin is a powder which forms a jelly with water of quite a different appearance to that obtained with meta-arabin. It is soluble in dilute acid solutions from which alkalis or alcohol precipitate it. By heating with alkalis it is converted into arabic acid. Lævulan is a by-product in the extraction of crystallisable sugar from beet-sugar molasses. When anhydrous it is insoluble in water, but in its hydrated form it dissolves readily. When oxidised by nitric acid it yields mucic acid, and heated with dilute sulphuric acid it is entirely converted into lævulose.

Wine gum *v.* Béchamp (J. 1875, 987), Chancel (J. 1875, 987), Neubauer (Fr. 15, 194). A. S.

GUM THUS *v.* RESINS.

GUN COTTON *v.* EXPLOSIVES.

GUN METAL *v.* TIN.

GUNPOWDER *v.* EXPLOSIVES.

GURHOFITE *v.* DOLOMITE.

GURJUN BALSAM. *Wood-oil* *v.* OLEO-RESINS.

GURJUNIC ACID *v.* OLEO-RESINS.

GUROLITE or **GYROLITE** *v.* CALCIUM.

GUTTA PERCHA; from the Malay terms, *gutta*, gum, and *perchâ* or *pârcha*, the name of the tree—the gum of the percha tree—is a coagulated sap resembling caoutchouc. (Faraday found caoutchouc to contain 87·2 carbon and 12·8 hydrogen; Soubeiran found pure gutta percha to contain 87·8 carbon and 12·2 hydrogen.) It is collected from various trees belonging to the natural order Sapotaceæ, growing in Malacca, Borneo, and other islands of the Indian Archipelago; but mainly from *Dichopsis gutta* (Bentl. a. T.). The geographical distribution of the trees producing gutta percha is limited within latitudes 4°N. and 3°S. (Lingard). Its collection is effected by felling the trees immediately after the rainy season. The branches are removed and the bark cut away in strips, and below each incision a vessel is placed to catch the gutta as it slowly exudes from the lactiferous tissue; sometimes the bark is bruised by beating it with mallets to hasten the flow. The milky juice condenses rapidly and assumes colours varying from a yellowish-white to red or brown, the higher colour arising from the admixture of fragments of bark or other foreign matter with the sap. A moderately large tree at the age of 25 to 30 years yields only from 2 to 3 lbs. of gutta percha, whilst a tree of double or treble the age gives from 20 to 30 lbs. (Montgomerie). The material is next boiled in water alone, or in water to which lime-juice or cocoanut oil is added (*v.* Ency. Brit., art. Gutta Percha, for classification of products). It is then ready for export. Gutta percha has long been known to the Chinese and the Malays, but the credit of calling the attention of this country to its possible uses rests with Dr. Montgomerie, a surgeon of the East India Company, who in 1843 sent specimens to the Society of Arts of London. The imports into Great Britain were for the years 1882-1886:

	Cwts.	£
1882 . . .	62,951	463,505
1883 . . .	51,276	381,929
1884 . . .	62,713	462,746
1885 . . .	53,894	348,104
1886 . . .	40,697	269,808

At a temperature of from 0°C. to 27°C. gutta percha resembles leather in substance, although it is not so flexible and exhibits no elasticity. From this temperature it becomes softer until at about 65°C. it is plastic and capable of being rolled out or moulded; on cooling it again loses its elasticity. It is inflammable, burning brightly, and giving off black resinous drops. Payen determined the constituents of ordinary gutta percha to be three substances, which have been termed *gutta*, *alban*, and *fluavil*, existing in somewhat variable proportions, the average being:—

Gutta . . .	78 to 82 p.c.
Alban . . .	16 to 14 „
Fluavil . . .	6 to 4 „

By his process these three constituents were separated in the following manner. The gutta percha is boiled with absolute alcohol so long as the alcohol dissolves anything, when the residue is pure *gutta*. The alcoholic liquid contains *alban* and *fluavil*; *alban* is precipitated upon cooling and can be removed by filtration, and the *fluavil* can be obtained by evaporating the remaining alcoholic liquid. '*Gutta* is insoluble in alcohol, and in ether when it has previously been treated with alcohol. It is also very slightly soluble in either benzol or oil of turpentine at a temperature of 0°C., but its solubility in these substances increases with the rise of temperature. Carbon bisulphide and chloroform dissolve pure gutta as well as gutta percha at the ordinary temperature. Pure gutta is not attacked either by the caustic alkalis or by dilute acids; concentrated sulphuric acid or nitric acid, however, exerts a powerful action upon it. Concentrated hydrochloric acid acts upon gutta very slowly, colouring white gutta brown, the colour increasing gradually in intensity.

'*Alban* separates out from a hot alcoholic extract of gutta percha on cooling. It forms a white crystalline powder, or sometimes wart-like lumps. It may be easily obtained in the latter form by allowing its alcoholic solution to evaporate in the air. Examined under the microscope the crystals are seen to be transparent or translucent and in radiating groups. Alban may be heated up to 100°C. without undergoing any change; it begins to melt at 160°C. and is entirely liquid and transparent at 175° to 180°C. When again cooled it contracts considerably, forming a solid transparent mass specifically heavier than water. Hydrochloric acid and dilute acids, as well as alkaline liquids, exert no action upon alban, but like gutta it is violently attacked by concentrated nitric acid or sulphuric acid. Alban is soluble in benzol, oil of turpentine, carbon bisulphide, ether, and chloroform. It may be obtained in a crystalline condition from its solutions in the last two solvents.

'*Fluavil.*—This substance is resinous and of a yellow colour, a little heavier than water, and hard and brittle at a temperature of 0°C. At higher temperatures it is soft; at 60° it assumes a doughy consistency, melting completely when heated to 100° or 110°. When exposed to a still higher temperature it boils, at the same time undergoing decomposition, the products of its distillation consisting of acid vapours and a number of hydrocarbons. Fluavil is soluble in hot and cold alcohol, also in ether, oil of turpentine, carbon bisulphide, and chloroform. When its solutions in these solvents are evaporated, fluavil is deposited in the amorphous condition only. As obtained by evaporation from an alcoholic solution it retains very energetically the last portions of the solvent, from which it can be separated only by protracted heating at 100°C. Fluavil is not attacked either by dilute acids or solutions of caustic alkalis, but is attacked energetically by concentrated nitric acid or by sulphuric acid.

'Gutta percha being a mixture of the three substances gutta, alban, and fluavil, its properties may be deduced from a consideration of these three bodies. Gutta percha is not attacked either by alkaline liquids or by dilute acids. It is, however, energetically attacked by concentrated nitric acid, yielding upon protracted boiling with the reagent, nitric oxide, nitrous acid, camphresinic acid, and other products of oxidation. Concentrated sulphuric acid causes gutta percha to swell and converts it into a mucilaginous mass.'

It was noticed very early in the use of gutta percha that it was peculiarly liable to oxidation, the substance assuming a yellowish-grey colour and becoming exceedingly brittle. From this M. Baumhauer has arrived at results somewhat differing from those of M. Payen; his analysis showing that the chief constituent of gutta percha is a hydrocarbon represented by $C_{10}H_{16}$, which is identical with the gutta of M. Payen and is the sole constituent of fresh gutta percha sap, other constituents, if existing, being merely the products of oxidation: alban being $C_{20}H_{32}O_2$ and fluavil $C_{27}H_{32}O$. Oxidation occurs with the greatest vigour when gutta percha is exposed to a temperature of 25° to 30°C. and when subject to strong sunlight; Dr. Miller finding that when the coating of telegraph-wires and submarine cables had been protected from the light, no sensible deterioration had taken place. Dr. Hofmann's experiment with a piece of oxidised gutta percha showed, under treatment with cold alcohol, a brittle substance containing on the average 62·79 p.c. carbon, 9·29 hydrogen, and 27·92 oxygen. From the residue boiling alcohol extracted a substance of similar physical character showing 67·72 p.c. carbon, 10·09 hydrogen, and 22·19 oxygen. The final residue, insoluble in cold or in boiling alcohol, was unchanged, gutta percha showing 88·12 p.c. carbon and 12·49 hydrogen; unchanged gutta percha being free from oxygen (Chem. Soc. Qu. J. xiii. 87).

For manufacture and use of gutta percha *v.* Ure's Dict. vol. ii. 769; Payen's Industrial Chemistry, ed. by Paul, p. 748; Collins on Gutta Percha in British Manufacturing Industries.

GYROPHORIC ACID $C_{36}H_{16}O_{15}$, an acid regarded by Gerhardt as identical with evernic or lecanoric acid, and obtained from *Gyrophora pustulata* and *Lecanora tartarea*, lichens used in the manufacture of archil. Forms small crystals, nearly insoluble in water and but sparingly soluble in alcohol and ether. Decomposed by boiling alkaline solutions into orcin and carbon dioxide, and becomes purple when moistened with ammonia solution and exposed to the air (Stenhouse, P. J. 1849, 393)

H

HAARLEM BLUE. *Antwerp blue v.* PIGMENTS.

HÆMATEÏN *v.* LOGWOOD.

HÆMATIN *v.* HÆMOGLOBIN.

HÆMATITE *v.* IRON, ORES OF.

HÆMATOXYLIN *v.* LOGWOOD.

HÆMOGLOBIN (*Hæmato-globulin*; *hæmatocrystallin*). A pigmentary matter constituting the greater part of the solid substance of the red blood corpuscles of vertebrates; found also in the blood plasma of many invertebrate animals, and in the red corpuscles of the hæmolymph of a few invertebrates. Found also in muscle plasma. For methods of preparation *v.* Gamgee, Physiol. Chem. 85-88. A yellowish red to purple crystalline body, the form and colour varying with the origin of the substance, but usually obtained in plates or prisms belonging to the rhombic system. Composition $C_{712}H_{1130}N_{214}S_2FeO_{245}$ (Zinoffsky, Zeits. Phys. Chem. 10, 16). According to Lemann, hæmoglobin is not an individual substance, but a colouring-matter hæmatin $C_{68}H_{70}N_8Fe_2O_{10}$ mechanically associated with a crystallisable proteid. Hæmoglobin gives all the tests for proteids. It combines with oxygen to form oxyhæmoglobin, which constitutes the oxygen-carrier to the tissues. Unites also with carbon monoxide; the formation of this substance (carboxyhæmoglobin) is the cause of the poisoning which results from breathing air mixed with carbonic oxide. It has a bright red colour, and is more stable than oxyhæmoglobin. Similar compounds are formed with nitric oxide, acetylene, and hydrocyanic acid. For further particulars relating to hæmoglobin and its derivatives *v.* WATTS' DICTIONARY OF CHEMISTRY, vol. ii. 660.

HAIDINGERITE *v.* CALCIUM.

HALFA. *Alfa*, *alva*. Arabic name for *Stipa* or *Macrochloa tenacissima*; especially applied to the Esparto grass from Algeria (Lunge, D. P. J. 243, 396).

HALOGEN. A term originally applied by Berzelius to the group of non-oxygenated electronegative radicles, simple and compound, which combine with metals to form salts known as *haloid salts*. Usually restricted to the four elements—Fluorine, Chlorine, Bromine, and Iodine.

HAMBURGH LAKE *v.* PIGMENTS.

HARDITE *v.* RESINS.

HARDWICKIA RESIN *v.* OLEO-RESINS.

HARMALA. The seeds of the wild rue, *Peganum Harmala* (Linn.), or harmal seeds have been employed from the earliest times in Eastern medicine as a stimulant, anthelmintic, or even as a narcotic. They are said to be the source of a red dye produced in Southern Russia, and they have been used in the manufacture of oil. Wild rue is an odoriferous herbaceous plant, 1 to 3 feet high, and inhabits Southern Europe, Asia Minor, Egypt, North-western India, and Southern Siberia (Flückiger, Ph. [3] 2, 229).

Harmal seeds contain about 4 p.c. of two alkaloids, probably in combination with phosphoric acid, and residing for the most part in the outer portions of the seed. The first of these, *harmaline* $C_{13}H_{14}N_2O$, was discovered by Göbel (A. 38, 363), the second, *harmine* $C_{13}H_{12}N_2O$, by Fritzsche (A. 64, 360; J. 1847-8, 639; A. 68, 351; 68, 355; 72, 306; 88, 327; 88, 328; 92, 330; J. 1862, 377), who studied both alkaloids, and obtained numerous derivatives. Fritzsche extracts the seeds with water containing acetic or sulphuric acid, and saturates the solution obtained with common salt, which causes the alkaloids to precipitate in the form of hydrochlorides. The precipitate is dissolved in water, decolourised by treatment with animal charcoal, and the solution obtained is fractionally precipitated by ammonium hydroxide at 50-60°. The first portion of the precipitate is harmine, and the last portion harmaline. The crude harmaline is best purified by recrystallisation from methylic alcohol (O. Fischer a. Täuber, B. 18, 400). From methylic alcohol harmaline crystallises in small tables, or from ethylic alcohol in rhombic octahedra. It melts with decomposition at 238°. It is very slightly soluble in cold water or ether, but readily dissolves in hot alcohol. It forms a well-defined crystalline *hydrochloride*, $C_{13}H_{14}N_2O, HCl, 2H_2O$; *hydrocyanide*, $C_{13}H_{14}N_2O, HCN$; *chloroplatinate*, $(C_{13}H_{14}N_2O, HCl)_2PtCl_4$; *methiodide*, $C_{13}H_{14}N_2O, MeI$; *chromate*, $(C_{13}H_{14}N_2O)_2H_2CrO_4$; and *nitro-derivative*, $C_{13}H_{13}(NO_2)N_2O$. Both the hydrocyanide and the nitro- derivative are bases, and combine with acids to form crystalline salts. Nascent hydrogen converts harmaline into a *dihydride*, $C_{13}H_{16}N_2O$ (O. Fischer, B. 22, 638). By the action of hydrochloric acid on harmaline, Fischer a. Täuber obtained a brick-red crystalline powder *harmalol*, $C_{12}H_{12}N_2O$, which melts at 212° with decomposition, and closely resembles a yellow colouring-matter found in the seeds.

Harmine exists in harmal seeds in much smaller proportion than harmaline. It may, however, be prepared from the latter by simple oxidation, either by the action of heat on the dry chromate, or by heating an alcoholic solution of harmaline nitrate to which hydrochloric acid has been added. Harmine crystallises in four-sided prisms (Schabus, J. 1854, 525). It melts with decomposition at 256-257° (F. a. T.). It is very slightly soluble in water or alcohol, and slightly soluble in ether. The salts of harmine are crystalline and colourless, and in acid solution exhibit an indigo blue fluorescence. The more important are the *hydrochloride*, $C_{13}H_{12}N_2O,HCl,2H_2O$; the *chloroplatinate*, $(C_{13}H_{12}N_2O,HCl)_2PtCl_4$; the *methiodide*, $C_{13}H_{12}N_2O,MeI$ (F. a. T.); and the two *sulphates*, $(C_{13}H_{12}N_2O)_2,H_2SO_4,H_2O$, and $C_{13}H_{12}N_2O,H_2SO_4$. Fritszche prepared the following halogen and nitro-derivatives of harmine, all of which are bases and form crystalline salts: *dichloroharmine*, $C_{13}H_{10}Cl_2N_2O$; *nitroharmine*, $C_{13}H_{11}(NO_2)N_2O$; *chloronitroharmine*, $C_{13}H_{10}Cl(NO_2)NO_2$; and *bromonitroharmine*, $C_{13}H_{10}Br(NO_2)N_2O$. A *tetrabromide*, $C_{13}H_{12}N_2O,Br_4$, has been obtained by Fischer.

When harmine is treated with concentrated hydrochloric acid at 140°, Fischer and Täuber find that it breaks up into *methyl chloride* and a new phenolic compound *harmol*, $C_{12}H_{10}N_2O$, which crystallises in needles and melts at 321°. When harmol is fused with potash it yields a compound possessing both basic and acid properties, *harmolic acid*, $C_{12}H_{10}N_2O_3$, which melts at 247° (Fischer, B. 22, 637). Fischer a. Täuber, by acting on harmine in acetic acid solution with chromic acid, obtained dibasic *harminic acid*, $C_8H_5N_2(COOH)_2$. It forms silky needles, melting at 345°, at which point it decomposes into carbonic anhydride and a crystalline basic sublimate of *apoharmine*, $C_8H_8N_2$, which, further studied by Fischer, gave a well-defined gold salt, and melted at 183°. A *tetrabromide*, $C_8H_8N_2Br_4$, and a *dihydride*, $C_8H_8N_2H_2$, were also obtained. A. S.

HARMALIN. *Fuchsin* v. TRIPHENYL METHANE COLOURING MATTERS.

HARMALINE v. HARMALA.

HARMALOL v. HARMALA.

HARMINE v. HARMALA; also VEGETO-ALKALOIDS.

HARMINIC ACID v. HARMALA.

HARMOL and **HARMOLIC ACID** v. HARMALA.

HARTIN v. RESINS.

HARTITE v. RESINS.

HAUERITE. *Manganese sulphide* v. MANGANESE.

HAUSMANNITE. *Manganese tetroxide* v. MANGANESE.

HAYTORITE v. DATOLITE.

HAZELINE. Trade name for a fragrant essence obtained from the fresh bark of *Hamamelis Virginica*, or witch-hazel. Is probably analogous to eucalyptol. Is a colourless oil, possessing a pleasant pungent smell and sweet astringent taste. Is used in the treatment of eczema, ulcers, burns, &c., and as a substitute for arnica.

HEAVY SPAR. Native barium sulphate v. BARIUM.

HEBBAKHADE v. GUM RESINS.

HECLA POWDER v. EXPLOSIVES.

HEDERIC ACID. An acid contained in ivy berries; v. *Ivy gum resin*, art. GUM RESINS.

HEDERO-TANNIC ACID v. GUM RESINS.

HEDGE-MUSTARD OIL. An oil manufactured from the so-called hedge-mustard or bank-cresses—*Raphanus Raphanistrum* or *Raphanistrum arvense*—cultivated in Hungary, and used as a substitute for rape-seed oil. The oil is brought to the market either by itself or mixed with rape-seed oil, and is occasionally sold under this latter name. The siliquous fruit of the plant mentioned bears little seeds which contain 30–35 p.c. oil. This can be for the most part obtained by pressing. It has a dark olive-green colour, and an odour and taste very similar to rape-seed oil; its density and faculty for saponifying with alkali is also nearly the same, so that it is difficult to recognise it in a mixture of the two oils. Valenta has tested the two oils as regards their behaviour with the usual reagents. On acting upon them with acids of different strength, such as sulphuric and nitric acids, a mixture of these, *aqua regia*, phosphoric acid, &c., as well as with oxidising mixtures, as potassium bichromate and sulphuric acid, or concentrated nitric acid saturated with nitric oxide, various colours are produced with both oils, by the shade and intensity of which they can be pretty well distinguished. The following reaction is most characteristic for hedge-mustard oil. About 5 grams of the oil are saponified with potassium hydrate and spirit with warming, and the soap thus obtained is filtered from the unchanged oil, which is golden-yellow, and almost odourless and tasteless. The concentrated filtrate, on adding hydrochloric acid to strongly acid reaction, assumes a distinct green colour if a somewhat large portion of hedge-mustard oil be present (S. C. I. 11, 181).

HELIANTHIC ACID $C_{14}H_{18}O_8$. A body found in sunflower seeds (Ludwig and Kromayer, Ar. Ph. [2] 99, 1285).

HELIANTHIN v. AZO- COLOURING MATTERS.

HELIOCHRYSIN v. NAPHTHALENE COLOURING MATTERS.

HELIOTROPE v. AZO- COLOURING MATTERS.

HELLEBOREÏN and **HELLEBORIN** v. BLACK HELLEBORE ROOT; also GLUCOSIDES.

HELLEBORESIN v. BLACK HELLEBORE ROOT.

HELLEBORETIN v. BLACK HELLEBORE ROOT.

HELL-HOFFITE v. EXPLOSIVES.

HEMIPIC ACID. An acid obtained by the oxidation of opianic acid, narcotine, narceïne, berberine, and papaverine v. VEGETO-ALKALOIDS.

HEMLOCK. *Spotted hemlock*; *Conium*; *Grande ciguë*, Fr.; *Schierling*, Ger. Hemlock, *Conium maculatum* (Linn.; Bentl. a. T. 118) is an erect biennial herbaceous plant which inhabits the temperate portions of Europe and Asia as well as of North and South America. It was the essential ingredient in the poison potion administered to condemned criminals by the Greeks, and from that period to the present day it has been a well-known article of materia medica. The leaves gathered from wild British plants at the time when the fruit begins to form, and the fruits collected when fully developed, but before they have lost their green colour, are employed in medicine in this country (Brit. Pharm. 1885, 124; Smith, Ph. [2] 10, 489; Harley, Ph. [3] 1, 584). The root possesses little or no activity (Lepage, J. Ph. [5] 6, 10). The action of hemlock on the system is that of a sedative to the motor nerves (Christison, J. Ph. 22, 413; A. W. Hofmann, B. 14, 705; Kuhlmann, Ar. Ph. [2] 23, 38), to which end the leaves are administered, preferably as juice or solid extract, and the fruits in the form of tincture. For further botanical and historical particulars, and the mode of detecting the accidental admixture of allied umbelliferous plants v. Fl. a. H. 299-302.

The physiological activity of both the leaves and fruit of hemlock depends upon the presence of the strong-smelling volatile liquid alkaloid *coniine*, *conine*, *conicine*, or *circutine* $C_8H_{17}N$, together with smaller proportions of three nearly related bases (Geisecke, Brandes Ar. Ph. 20, 97;

Geiger, B. J. 12, 220; Planta a. Kekulé, A. 89, 129; Wertheim, A. 100, 328; 123, 157). Coniine has been prepared synthetically by Ladenburg (B. 19, 2579; 22, 1403) and proved to be *dextro-(α) propylpiperidine* 
$$\begin{array}{l} CH_2.CH_2.NH \\ CH_2.CH_2.CHPr \end{array}$$
For properties and reactions *v.* ALKALOIDS. When hemlock leaves or fruit are triturated with an alkali a strong odour is given off, due to coniine and the other bases together with some ammonia, and by distilling such a mixture, using suitable precautions, the alkaloids are obtained. Geiger, for instance, distils the fruit with potassium carbonate or calcium hydroxide, and then by a series of operations separates the bases from the distillate. Christison distils in a similar way an alcoholic extract. Wertheim extracts with water acidulated with sulphuric acid, supersaturates the extract with lime or potash, and distils. The distillate is then neutralised with sulphuric acid, evaporated to a syrup, and treated with alcohol, which dissolves the alkaloidal sulphates, and leaves the ammonium salt, which is insoluble in that liquid. The alcohol is then removed by distillation, the residue supersaturated with potash, and extracted with ether. The ethereal solution is distilled. After the ether has come over, the distillation is conducted in a stream of hydrogen, when the first portions of the distillate contain the coniine, which may be purified by conversion into hydrochloride, recrystallisation, and regeneration by means of an alkali. Together with the coniine are found varying but small proportions of *methyl coniine* $C_8H_{16}MeN$ and the *homologue* $C_7H_{15}N$ (Planta a. Kekulé). Towards the end of the distillation colourless laminæ of *conhydrine* $C_8H_{17}NO$ collect in the neck of the retort. Another method of isolating the alkaloids from the fruit is to extract with dilute acetic acid, evaporate the solution to a syrup in a vacuum, mix with excess of magnesia, and extract with ether (Schorm, B. 14, 1766). The percentage of alkaloids obtained varies, 0·2 p.c. of coniine being a good yield from the fruit.

Conhydrine, which is much less active physiologically than coniine, melts at 120·6°, and boils at 224·5° (719·8 mm.) (Wertheim, J. 1863, 435). Treated with phosphorus pentoxide or concentrated hydrochloric acid it loses the elements of water, and is converted into the two isomerides (α) and (β) *coniceïn* $C_8H_{15}N$ (Hofmann, B. 18, 7; Lellmann a. Müller, B. 23, 680). For estimation of the alkaloids in hemlock *v.* Cripps (Ph. [3] 16, 12 a. 511) and Kremel (Ph. Post, 20, 521). Hofmann (B. 17, 1922) discovered *caffeïc* or *dioxycinnamic acid*, $C_6H_3(OH)_2.CH:CH.COOH$ in hemlock. It contains also a *volatile oil*, said to be the product of fermentation (Landerer, R. P. 94, 237) and the leaves yield on ignition 12·8 p.c. of *ash* (Wrightson, Ph. 5, 40). A. S.

HEMLOCK SPRUCE RESIN *v.* RESINS.

HEMP. The name of various plants and of the fibres derived from them. The following list embraces these fibres under their commercial denominations, with the names of the plants which produce them:

Common hemp is . .	*Cannabis sativa.*
African hemp is .	*Sanseviera zeylanica* and others.
Bastard hemp is . .	*Datisca cannabina.*
Bengal or Bombay hemp is	*Crotalaria juncea.*
Bowstring (of Java and Southern China) hemp is	*Sanseviera zeylanica* and others.
Bowstring (of India) hemp is	*Calotropis gigantea.*
Brown hemp is . . .	*Crotalaria juncea.*
Brown Indian hemp is	*Hibiscus cannabinus.*
Indian hemp is . .	*Apocynum cannabinum.*
Jubbalpore hemp is .	*Crotalaria tenuifolia.*
Madras hemp is . .	*Crotalaria juncea.*
Manilla hemp is . .	*Musa textilis.*
Sisal hemp is . . .	*Agave Sisalana.*
Sunn hemp is . . .	*Crotalaria juncea.*
Virginian or Water hemp is	*Acnida cannabina.*

Of these, *Cannabis sativa*, nat. ord. *Urticaceæ*, allied to the hop plant, furnishes the true hemp. The plant is an annual, growing ordinarily to the height of 8 or 10 feet, but sometimes exceeding that limit by several feet; and it doubtless owes its origin to some part of temperate Asia. On extending its habitat, the character of the plant changed with soil and climate, giving origin to the supposed varieties *C. chinensis* and *C. indica*.

Hemp fibre examined by the microscope resembles that of flax in being round and ribbed; it has a mean diameter of 0·2 mm., and exhibits small, hairy appendages at the joints. According to Haberlandt, the breaking strain of a cord of 1 sq. mm. section is on the average 34·5 kilos. In *Manilla* hemp the fibrous bundles are oval, nearly opaque, and surrounded by a number of rectangular cells composing a dried tissue. The bundles are smooth. *Sisal* hemp forms oval fibrous bundles surrounded by cellular tissue; a few smooth ultimate fibres projecting from the bundles. It is more translucent than Manilla, and is characterised by the large quantity of spiral fibres in the bundle.

Hemp is cultivated—(1) for its fibre; (2) for its resin; (3) for the oil contained in its seed (4) for the seed itself. The tough, elastic, and durable fibre is better adapted for the manufacture of cordage and sail-cloth than any other known material. It is, moreover, employed for canvas, tarpaulin, and towelling. The finest qualities for these purposes are imported from Italy and Russia. The preparation of the fibre is similar to that of flax; the stems being bruised and 'retted' or fermented in water, after which they are again beaten out and finally 'scutched' and 'hackled' or combed (*v.* FLAX). The water in which hemp has been steeped produces no evil effects on the health of a district when allowed to flow into running water, but it always destroys the fish together with certain vegetable growths (Renouard, Bied. Centr. 1880).

The resin of hemp is employed in India as *charas*, *bhang* or *siddhi*, and *gánjá*, in which form it is used for its intoxicating and narcotic properties. *Charas* is the resin itself; *bhang* or *siddhi* consist of the dried resinous leaves and stalks; it is used for smoking, for making sweetmeats along with honey and sugar, or for forming a potable infusion. *Gánjá* is composed of the resinous fruiting heads of the female plant, and is similarly employed. In A Report on Indian Fibres and Fibrous Substances, Spon, 1887, it is stated that *Cannabis sativa* is chiefly, if not exclusively, cultivated on account of its narcotic principle. It has been found that the narcotic-yielding plant affords only a worthless fibre, and it is presumed that the climate of India favours the production of narcotic at the expense of the fibre. To attempt an extension of its cultivation, fiscal difficulties of a very formidable character would also have to be overcome, for the Government of India would never permit a plant of which the leaves and flowers yield so pernicious a narcotic to be widely grown. According to Hunter (The Indian Empire, and its People, History, and Products, 2nd ed. p. 455), excise duties are levied upon these resinous products; the hemp which furnishes them is chiefly confined to a limited area in Rájsháhí district, Bengal, and to the inner valleys of the Himalayas. The use of them is a frequent cause, not only of crime, but also of insanity. Government attempts to check consumption—first, by fixing the retail duty at the highest rate that will not encourage smuggling; and secondly, by continually raising that rate as experience allows.

The effect of hemp-resin and its compounds on the consumer is at first to exhilarate and to promote appetite. Further doses produce delirium, sleep, and sometimes catalepsy.

Hemp-resin examined by T. a. H. Smith is soluble in alcohol, and has a warm, bitter, acrid taste with a slight odour. It melts between 70° and 90°C., and has a pale brown colour. It is called *cannabin*.

The oil is obtained by expression from the seed, which yields from 25–30 p.c. of oil, and 70–75 p.c. of residual cake used for cattle feeding, although sparingly on account of its laxative properties. This oil has a sp.gr. of 0·9307.

The essential oil of *C. sativa* was prepared by L. Valenta (Gazzetta, 10, 479–481) by distilling the fresh leaves with water and agitating the resulting milky distillate with ether. The oil dried over calcium chloride and distilled repeatedly from sodium is colourless and mobile (b.p. 256–258°). The sp.gr. referred to water is 0·9292. The analysis agreed with the formula $C_{15}H_{24}$; the vapour density could not be determined, as it decomposes at 300°. The essential oil mixes in all proportions with alcohol, ether, and chloroform.

The seeds themselves are used as food for birds, some kinds of which are inordinately fond of them. They are roundish, ovate, of a grey colour, and contain 34 p.c. of oil and 16 p.c. of albuminoids.

HENBANE. *Hyoscyamus*; *Jusquiame*, Fr.; *Bilsenkraut*, Ger.

Henbane, *Hyoscyamus niger* (Linn.; Bentl. a. T. 194), is one of the group of poisonous plants belonging to the natural order Solanaceæ and is nearly related to belladonna, stramonium, and duboisia. It has been employed in medicine since the seventh century and an allied species, having similar properties, *H. albus* (Linn.) was known to Dioscorides. There are two varieties of *H. niger*, one an annual and the other a biennial. Both are to be obtained in the market, but the leaves or green tops of second year plants of the biennial variety are the most active and should alone be employed in medicine. The seeds possess still greater activity, but they are only used in the manufacture of alkaloid. Henbane is a coarse hairy erect herb with pale yellow flowers marked with purple veins, and the whole plant evolves an unpleasant odour. It occurs wild throughout Britain and most parts of Europe, Asia, and Northern Africa, and has been naturalised in North and South America. Henbane is employed as a sedative, anodyne, or hypnotic, and, like belladonna and stramonium, it dilates the pupil of the eye. Its activity is destroyed by the presence of free alkali, with which it should therefore not be administered (Garrod, Ph. 17, 462; 18, 174).

The active constituents of henbane are two isomeric alkaloids. The one, *hyoscyamine* $C_{17}H_{23}NO_3$, was first obtained in a pure state by Geiger and Hesse (A. 7, 270) and more completely studied by Höhn and Reichardt (A. 157, 98); the other, present in much smaller proportion, *hyoscine* $C_{17}H_{23}NO_3$ was discovered by Ladenburg (A. 206, 282). Hyoscyamine also occurs, together with atropine in belladonna and stramonium (*v.* DATURA), and 'duboisine,' the alkaloid of *Duboisia myoporoides* (Brown), is identical with hyoscine (Ladenburg a. Petersen, B. 20, 1661). Both hyoscyamine and hyoscine, like atropine, are mydriatic alkaloids.

To obtain hyoscyamine from henbane seeds Höhn and Reichardt first deprive them of fixed oil by treatment with ether and then exhaust by means of alcohol acidified with sulphuric acid. The clear extract, after removal of the alcohol by distillation, is almost neutralised by soda and precipitated with tannic acid. The moist precipitate is mixed with lime and extracted with alcohol. The alcoholic solution is acidified, concentrated, and purified by washing with ether. The alkaloid is then set free by the addition of soda and isolated by extraction with ether. Other somewhat similar methods have been suggested by Rennard (N. R. P. 17, 91), Thorey (Ph. [3] 12, 874), and Thibaut (C. C. 1875, 565). Duquesnel (J. Ph. [5] 5, 131) extracts the seeds with hot 90 p.c. alcohol containing tartaric acid, and from the solution obtained removes the alcohol by distillation. There remains a residue of two layers, a lower syrupy and an upper oily layer, which latter is found to contain most of the alkaloid, perhaps in combination with a fatty acid. This is extracted by treating the oil with water acidulated with sulphuric acid. The solution is nearly neutralised with potassium bicarbonate, concentrated to a syrup, and extracted with alcohol, which leaves potassium sulphate undissolved. The alcohol is removed from the solution by distillation, and the residue, diluted with water and treated with a slight excess of potassium bicarbonate, is extracted with chloroform. The crude hyoscyamine is removed from the chloroformic solution by water acidulated with sulphuric acid, is purified by treatment with animal charcoal, and the solution is then concentrated to a syrup. The alkaloid is set free by an excess of calcium carbonate and mixed with sand is dried over sulphuric acid. Finally, treatment with chloroform extracts the hyoscyamine and yields it on evaporation in large prismatic needles.

Hyoscyamine melts at 108·5° (Ladenburg) and dissolves more readily in water and dilute alcohol than atropine. It is lævorotatory. By the action of barium hydroxide or hydrochloric acid hyoscyamine yields, in the same manner as atropine, *tropine* $C_8H_{15}NO$ and *tropic acid* $C_9H_{10}O_3$ (Ladenburg, B. 13, 254 a. 607) but is distinguished from that base by its metallic derivatives. *Hyoscyamine aurochloride* $C_{17}H_{23}NO_3,HCl,AuCl_3$ melts at 159° while the isomeric atropine aurochloride melts at 137°. The appearance and solubility of the two salts is also different (Ladenburg). Hyoscine, which is obtained from the mother liquors after crystallisation of hyoscyamine, is a syrupy liquid (*cf.* Schmidt, Ph. [2] 1889, 583) which yields a gold salt melting at 198° and different from that of hyoscyamine or atropine, and when boiled with water breaks up into *pseudo-tropine* and *tropic acid* (Ladenburg), *cf.* ALKALOIDS.

Brandes, who analysed henbane seeds, found 24 p.c. of *fixed oil* (B. J. 21, 280); a substance 'hyoscypicrin,' supposed to be a glucoside, was obtained by Höhn and Reichardt; and the presence of nitrate of potassium in the leaves was pointed out by Thorey and in the medicinal extract by Attfield (Ph. 3, 447). A. S.

HENDECATOIC ACIDS *v.* FATTY ACIDS.

HENDECENOIC ACID $C_{11}H_{20}O_2$ an acid boiling at 250-260° found in petroleum; known also as *petroleumic acid* (Hell and Medinger, B. 7, 1217; 10, 451).

HEPTOIC ACIDS *v.* FATTY ACIDS.

HERACLEUM OIL *v.* OIL, ESSENTIAL.

HERCULES METAL *v.* ALUMINIUM.

HERCULES POWDER *v.* EXPLOSIVES.

HESPERIDIN *v.* GLUCOSIDES.

HESSIAN PURPLE *v.* AZO- COLOURING MATTERS.

HESSIAN RED *v.* AZO- COLOURING MATTERS.

HESSIAN YELLOW *v.* AZO- COLOURING MATTERS.

HEXAHYDROBENZENE *v.* PHENOL AND ITS HOMOLOGUES.

HEXOIC ACID *v.* FATTY ACIDS.

HIGHGATE RESINS *v.* RESINS.

HING *v.* GUM RESINS.

HIPPURIC ACID *Benzamido-acetic acid* $C_9H_9NO_3$ or $NHC_7H_5O.CH_2.CO_2H$, an acid found in the urine of horses and cows and other herbivora and in human urine when benzoic acid is taken internally. May be prepared by action of benzoic anhydride on glycocoll. Crystallises in large trimetric prisms, soluble in water and alcohol. Has a slightly bitter taste and reddens litmus. Decomposes on heating, forming benzonitrile and benzoic acid. Its aqueous solution boiled with mineral acids yields glycocoll and benzoic acid.

HOANG-NAN *v.* NUX VOMICA.

HOFMANN'S VIOLET *v.* TRIPHENYL METHANE COLOURING MATTERS.

HOG GUM *v.* GUMS.

HOLMIUM *v.* CERIUM METALS.

HOMATROPINE *v.* VEGETO-ALKALOIDS.

HOMBERG'S PHOSPHORUS *v.* CALCIUM.

HOMOFLUORESCEÏN *v.* PHTHALEÏNS.

HOMOGUAICOL *v.* *Homopyrocatechol*, PHENOL AND ITS HOMOLOGUES.

HOMOPYROCATECHOL, HOMOCATECHOL *v.* PHENOL AND ITS HOMOLOGUES.

HOMOQUININE *v.* VEGETO-ALKALOIDS.

HOMORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

HONEY. Honey is the substance secreted by the working-bee (*Apis mellifica*) from the nectar of flowers, and deposited by the insect in the wax-cells forming the honeycomb. Its essential constituents are varying quantities of the sugars, dextrose, lævulose, and sometimes cane-sugar, together with a small quantity of water. It also contains very small quantities of wax, colouring matters, aromatic substances, phosphoric acid, nitrogenous compounds, and occasionally mannitol.

The relative proportions in which the three above-named sugars occur is very variable. Thus Hehner (An. 9, 164) obtained the following results from the analysis of 25 different varieties:

	Maximum	Minimum	Mean
Moisture . .	23·26	12·43	19·3
Glucoses . .	75·34	61·42	67·2
Other constituents	16·51	8·48	13·5

In 8 cases the amount of glucoses was unaltered by inversion, in 7 increased, and in the remainder slightly diminished.

Sieben (B. C. 1885, 134) analysed 60 specimens of honey, and states that the quantity of cane-sugar may amount to as much as 4 or even 8 p.c., and that the ratio of dextrose to lævulose varies considerably, the total amount of these two sugars being 68–78 p.c. The average composition of the 60 specimens was as follows:—

Dextrose . . .	34·71 per cent.
Lævulose . . .	39·24 „
Saccharose . . .	1·08 „
Water	19·98 „
Non-saccharine matter	5·02 „

Turning now from average results to the composition of the several varieties, we find the following table of the analysis of 9 specimens of honey from different localities (J. C. Brown, An. 1878, 257).

—	England	Wales	Normandy	Germany	Greece	Lisbon	Jamaica	California	Mexico
Water expelled at 100° . .	19·10	16·40	15·50	19·11	19·80	18·80	19·46	17·90	18·47
Water expelled at a high temperature and loss	7·60	6·56	4·95	11·00	7·80	6·66	7·58	8·13	10·03
Lævulose . .	36·60	37·20	36·88	33·14	40·00	37·26	33·19	37·85	35·96
Dextrose . .	36·55	39·70	42·50	36·58	32·20	34·94	35·21	36·01	35·47
Cane-sugar . .	?	—	—	—	—	1·20	2·20	—	?
Wax, pollen, and insoluble matter	trace	trace	trace	trace	0·05	1·00	2·10	trace	trace
Mineral matter .	0·15	0·14	0·17	0·17	0·15	0·14	0·26	0·11	0·07

Erlenmeyer and v. Plata (R. P. 23, 610) found that in 6 samples of good honey the amount of water varied from 17·5–19·5 p.c., whilst a liquid honey from Senegal contained as much as 25·6 p.c. The amount of phosphoric acid present (calculated on the dried subtance) varied from 0·0123 to 0·883 p.c.

Sumatra honey, formed by *Apis indica*, contains water, dextrose, lævulose, a little wax and pollen, and 0·23 p.c. ash, but no cane-sugar or dextrin (Franchimont, R. T. C. I. 223). An Ethiopian honey, made in hollows without wax by a kind of mosquito, gave the following result on analysis (C. R. 88, 292):

Water	25·5
Lævulose and Dextrose ($\frac{1}{3}$)	32·0
Mannitol	3·0
Dextrine	27·9
Ash	2·5
Other constituents	9·1

It has also been shown (Vogel, B. 15, 2271) that all honey contains a small quantity of formic acid, derived from the stings of the bees, and that to this is due the fact that honey keeps so well.

If bees be fed on dextrose only, the honey formed contains that sugar alone. Heather-fed honey, on the other hand, contains invert sugar only, whilst Cuban honey contains dextrose in larger quantity than lævulose (Röders, C. C, 1864, 1002).

In the honey of *Polybia apicipennis* large crystals of cane-sugar are frequently found (J. pr. 71, 314). The honey of the Mexican honey-ant is almost a pure solution of lævulose, and, when dried *in vacuo*, has the composition $C_6H_{12}O_6 + H_2O$. It contains traces of a volatile acid which reduces silver salts (J. pr. 58, 430).

To obtain honey the syrup is first simply allowed to flow from the comb at the ordinary temperature, the portion thus collected being known as 'virgin-honey.' As soon as the flow ceases, the residual comb is heated and pressed, by which means a darker and less pure variety is obtained. According to Zwilling (B. C. 1885, 67) it is best to gather the honey when it has thickened and the cells are sealed, as then sufficient sugar and formic acid are present.

The honey-syrup remains clear for a long time if kept in the dark, but on exposure to light dextrose gradually separates, and such varieties as contain that sugar in the largest quantity become sufficiently solid to be cut with a knife into pieces which are not hygroscopic. As, however, the composition of honey is so variable, the consistency and colour likewise differ considerably in the different samples. Thus Narbonne honey has a light yellow colour, and forms an almost solid mass, whereas Cuban honey is a clear and almost colourless syrup.

Honey has a sp.gr. of from 1·439–1·448. When diluted with water it gives a somewhat cloudy, faintly acid solution, the cloudiness being due to small quantities of proteid matter. Its specific rotatory power varies from $-5·5$ to $+2$, but dextrorotatory honey is exceptional.

A pure solution of honey does not readily undergo alteration in the air, but when impure, both acid and alcoholic fermentation speedily take place. An alcoholic liquor known as 'mead' (Germ. *Meth*; Fr. *Hydromel*) has long been prepared from honey by fermentation. The process is, however, frequently unsuccessful, owing to the fact that honey does not usually contain sufficient nitrogenous food for the sustenance of the ferment. If a suitable food be added, the fermentation proceeds smoothly and with certainty (Gastine, C. R. 209, 479). According to Boussingault (A. Ch. [4] 26, 362) the quantity of carbon dioxide formed during fermentation is greater, and the quantity of alcohol less, than would be expected from the amount of sugar fermented. Thus, instead of the calculated quantities of 193·6 parts of alcohol and 170 parts of carbon dioxide, he obtained 177·6 parts of alcohol, and 190 parts of carbon dioxide.

For medical purposes honey is purified by warming on the water-bath, and straining it through flannel which has been previously moistened with hot water. The purified compound is known as *Mel depuratum*. Dietrich (C. C. 1877, 318) brought a filtered solution of 1 part of honey in 3 parts of water on to a dialyser, and found that 50 p.c. of the honey passed through. The solution of the crystalloids gave on evaporation a honey having an unusually pleasant aromatic taste. The colloidal liquid, in which gummy flocculæ remained suspended, gave on evaporation a syrup possessing a purely sweet, insipid, non-aromatic taste.

In order to purify honey Riecker (J. 1873, 1066) adds a little precipitated aluminium hydroxide, which carries down any foreign substances present. If ordinary honey be shaken with absolute alcohol, dextrose remains behind. Ether precipitates lævulose from the alcoholic solution, and the ethereal solution when shaken with lime loses tannic acid, whilst wax remains in solution (Scheiz and Ludwig, Ar. Ph. [3] 1423).

Honey is frequently adulterated with starch-sugar, which always contains gypsum and dextrin. The addition of this substance always raises the dextrorotatory power of the honey, and may therefore be readily detected by the polariscope. Dextrin may be detected as follows: 3 grams honey are dissolved in 3 c.c. of water, and mixed with 20 c.c. of alcohol, sp.gr. 0·83. If dextrin is present white flocculæ are precipitated, and are then filtered off. These may, however, consist of glutinous substances, which can be detected by the ammoniacal decomposition products evolved on heating (Flückiger, Pharmaceut. Chemie [2] 267). Or the honey may be dissolved in 5 parts of warm water, and the cooled solution shaken with a little iodine. If the honey be pure no colouration is produced, whereas if dextrin is present it assumes a reddish or violet tint, and becomes blue if starch is present. The gypsum present may be detected in the ash in the usual way, the latter, however, being first moistened with nitric acid to reconvert into sulphate any calcium sulphide which may have been formed during incineration. It must nevertheless be borne in mind that honey always contains small quantities of gypsum. Adulteration with cane-sugar may be detected by determining the reducing power of the honey for Fehling's solution, both before and after inversion. The amount of cane-sugar in genuine honey never rises higher than 10 p.c., and rarely above 5 p.c., whereas an adulterated sample frequently contains as much as 25 p.c. (F.).

Sugar in honey is estimated by dilution with twice its volume of water, and ascertaining the sp.gr. This varies between 1·101 and 1·115. The first number corresponds to 24 p.c., and the latter to 27 p.c. of sugar in the solutions, or to 72 p.c. and 82 p.c. in the original honey (F.).

HOPEINE $C_{19}H_{23}NO_4$? An alkaloid said to occur in small quantity in hops. Its existence is doubtful (*v.* Ladenburg, B. 19, 783).

HOPS *v.* Brewing.

HORDEIC ACID *v.* Fatty acids.

HOREHOUND *v.* Marrubium.

HORN LEAD *v.* Lead.

HORN QUICKSILVER. *Calomel v.* Mercury.

HORN SILVER. Native silver chloride *v.* Silver.

HORSE-CHESTNUT. *Hippocastanum*; *Marronier d'Inde*, Fr.; *Rosscastanien*, Ger. The well-known horse-chestnut tree, *Æsculus hippocastanum* (Linn.), is a native of Persia and Northern India. It was introduced into Europe in the sixteenth century, and is now largely cultivated for ornament throughout the temperate regions of the world. It is unimportant in medicine; but it is interesting chemically as the source of several glucosides and allied compounds.

Besides tannin (Rochleder, Z. 1867, 76), fat, and constituents common to plants, horse-chestnut bark contains the glucoside *æsculin*, $C_{15}H_{16}O_9$ (Minor, B. J., 12, 274; Jonas, A. 15, 266) and in smaller proportion *æsculetin*, $C_9H_6O_4$ (Rochleder, J. 1863, 589) which is also a product of the action of dilute acids or emulsin on æsculin (Rochleder a. Schwartz, A. 88, 356). *Fraxin* or *paviin* $C_{16}H_{18}O_{10}$ a glucoside occurring in the bark of the common ash, *Fraxinus excelsior* (Linn.), is another constituent of horse-chestnut bark (Stokes, C. J. 11, 17; 12, 126) accompanied by *fraxetin* $C_{10}H_8O_5$ (Rochleder, C. C. 1864, 415), also produced when fraxin is boiled with dilute acids.

To obtain *æsculin* Rochleder (W. A. B. 23, 1) extracts the bark with hot water, precipitates the solution with alum and a slight excess of ammonia, filters, and evaporates the filtrate to dryness at 100°. The residue yields æsculin to hot alcohol, when it may be purified by successive crystallisations. Another method (Fairthorne, C. N. 26, 4) consists in exhausting the bark with dilute ammonia, evaporating to dryness; mixing the residue with alumina, and extracting with 95 p.c. alcohol. The alcoholic solution yields crystals of æsculin which are purified by washing with water, ether and benzene. Æsculin forms colourless prisms which lose water of crystallisation at 120–130°, and melt with decomposition at 160° (Zwenger, A. 90, 65). It is soluble in glacial acetic acid, acetic ether, and in hot alcohol; very slightly soluble in cold water and nearly insoluble in ether. The aqueous solution has a blue fluorescence. Heated to 230° it breaks up into *æsculetin* and *glucosan* (Schiff, B. 14, 303). Emulsin or dilute acids convert it into *æsculetin* and *glucose* (Rochleder a. Schwartz). Heated with baryta water it yields *æsculetic acid* and *glucose* (Rochleder, J. 1856, 678). Sodium amalgam reacts forming *hydræsculin* (Rochleder, Z. 1868, 727). A characteristic colour reaction is obtained by agitating æsculin with nitric acid, when a yellow solution results which on the addition of ammonia turns deep red (Sonnenschein, B. 9, 1182). Concentrated sulphuric acid followed by solution of sodium hypochlorite strikes a violet colour (Raby, J. Ph. [5] 9, 402).

Æsculetin is usually prepared by the action of dilute acid on æsculin (Zwenger, A. 90, 63). It crystallises in shining needles or scales containing a molecule of water. It melts with decomposition above 270°. It is soluble in hot but only slightly soluble in cold water and alcohol, and nearly insoluble in ether. The aqueous solution has a slight blue fluorescence. Sodium amalgam converts it into *æsciorcin* (Rochleder, J. 1867, 751).

By the action of aqueous sodium hydrogen sulphite on æsculetin the compound *paraæsculetin* is formed which treated with ammonia yields *æsciorceïn* $C_9H_7NO_4$, a compound resembling orceïn.

Fraxin crystallises in colourless needles containing half a molecule of water of crystallisation. By the action of dilute acids it is converted into *fraxetin* and *glucose* (Salm, J. 1859, 576). Fraxetin consists of tables (from alcohol) very slightly soluble in water, but soluble in ether and hydrochloric acid.

Horse-chestnut cotyledons were found by Rochleder (J. pr. 87, 1; 101, 415) to contain three componnds. *Argyræscin* $C_{27}H_{42}O_{12}$ a crystalline glucoside converted by dilute acids into *glucose* and *argyræscetin*, $C_{21}H_{30}O_6$, and by potash into *propionic acid* and *æscinic acid* $C_{21}H_{40}O_{12}$, a compound found ready formed in the cotyledons. The third constituent of the cotyledons is the glucoside *aphrodæscin* $C_{52}H_{82}O_{23}$, which, acted on by potash, also yields *æscinic acid*, the second product being in this case *butyric acid*, or when heated with dilute acids *glucose*, and *telæscin* $C_{18}H_{30}O_7$. Telæscin acted on by hydrochloric acid gas gives up another molecule of *glucose* and forms *æscigenin* $C_{12}H_{20}O_2$ (Rochleder, J. 1862, 491; 1867, 751).

The leaves of the horse-chestnut contain the glucoside *quercitrin* $C_{33}H_{35}O_{20}$ and the flowers *quercetin* $C_{24}H_{16}O_{11}$ (Rochleder, J. 1859, 522). *Quercitrin* is usually prepared from black oak bark, *Quercus tinctoria* (Bartram) (Liebermann a. Hamburger, B. 12, 1179) and from this compound by treatment with dilute acids *quercetin* together with *isodulcite* is obtained.

For other reactions and the constitution of these compounds *v.* Glucosides.

The cotyledons of horse-chestnuts contain a peculiar *starch* (Gm. 15, 77) and a yellow *fatty oil* (Gm. 17, 97). The *ash* of different parts of the tree has been analysed by Wolff (J. pr. 44, 385) and Staffel (A. 76, 379). A. S.

HUMIC ACID or **ULMIC ACID.** The brown or black substance produced by the decay of vegetable matter. Its composition is $C_{60}H_{54}O_{27}$ (Detmer) or $C_{24}H_{16}O_8$ (Thenard).

HUNGARIAN TURPENTINE *v.* Oleo-resins.

HUNGARY BLUE. *Cobalt blue v.* Pigments.

HUNGARY GREEN. *Malachite green v.* Pigments.

HYACINTH *v.* Zirconium.

HYÆNASIC ACID *v.* Fatty acids.

HYALINE CORUNDUM *v.* Aluminium.

HYDRÆSCULIN *v.* Horse-chestnut.

HYDRASTINE *v.* Vegeto-alkaloids.

HYDRAULIC CEMENTS *v.* Cements.

HYDRAULIC LIME *v.* Cements.

HYDRAZINES. The name 'hydrazine' was applied by Emil Fischer to the then hypothetical *diamidogen* $H_2N.NH_2$, which he regarded as the parent substance of the *hydrazines*, a large and important class of bases discovered by him, derived from diamidogen by the replacement of either one or two atoms of hydrogen by monad hydrocarbon radicles. The name was intended to indicate the connection of these bases with the azo- and diazo- compounds, and in particular with hydrazobenzene $C_6H_5.NH.NH.C_6H_5$ (symmetrical diphenylhydrazine) the oldest known member of the class of the hydrazines; whilst at the same time the termination 'azine' was formed on the analogy of 'amine,' in order that a parallel nomenclature might be employed in the case of corresponding derivatives of the hydrazines and amines: thus the *hydrazonium* compounds would correspond with the ammonium compounds (A. 190, 70).

Hydrazine itself has recently been prepared by Curtius (B. 20, 1632).

The hydrazines are divided into primary and secondary, according as one or two hydrogen atoms in the original diamidogen molecule have been replaced by hydrocarbon radicles. If the two radicles are attached to different nitrogen atoms the resulting secondary hydrazine is termed *symmetrical*; if to the same nitrogen atom, *unsymmetrical*. The unsymmetrical secondary hydrazines behave like tertiary amines: they unite with the halogen compounds of the alkyls to form *hydrazonium salts*:

$$NR'_2.NH_2 + R'I = N{\cdot}R'_3I.NH_2.$$

Phenylhydrazine, $C_6H_5.NH.NH_2$, the most important of the hydrazines, is most simply obtained by reducing diazobenzene chloride with stannous chloride:

$$C_6H_5.N{:}NCl + 2SnCl_2 + 4HCl$$
$$= C_6H_5.NH.NH_2,HCl + 2SnCl_4.$$

In order to prepare phenylhydrazine on a small scale by this method, 10 grams of aniline are dissolved in 200 grams of concentrated hydrochloric acid and diazotised by the gradual addition of a solution of 7·5 grams of sodium nitrite in about 50 c.c. of water to the liquid previously cooled by ice. To the cooled solution of diazobenzene chloride thus obtained, which is somewhat turbid owing to the separation of sodium chloride, a cold solution of 45 grams of stannous chloride in 45 grams of concentrated hydrochloric acid is added. The whole solidifies to a magma of phenylhydrazine hydrochloride, which is separated by filtration, dissolved in water, and decomposed by alkali. The liberated base is extracted with ether, dried with potassium carbonate, and purified by distillation (V. Meyer and Lecco, B. 16, 2976). According to Schultz (Chemie des Steinkohlentheers, 2nd ed. 472) the large excess of hydrochloric acid prescribed in the foregoing receipt is unnecessary.

The method originally employed by E. Fischer (A. 190, 71 and 78), in which sodium sulphite is used to reduce the diazo- salt, is more complicated. 20 parts of aniline are dissolved in 50 parts of hydrochloric acid (sp.gr. 1·19) diluted with 80 parts of water, and diazotised by the addition of 1 molecular proportion of sodium nitrite dissolved in twice its weight of water slightly acidified with hydrochloric acid, cooling with ice during the operation. The solution thus obtained is added, with constant stirring, to a concentrated solution of sodium sulphite (2 mols. of the sulphite to 1 mol. of aniline). The solution turns reddish yellow and deposits crystals. On testing a portion by warming, the crystals should dissolve in the supernatant liquid to a clear yellow solution without evolution of gas, otherwise insufficient sodium sulphite has been employed. The whole is then gently warmed on the water-bath until nearly everything has dissolved; the solution is carefully neutralised with hydrochloric acid, acidified with acetic acid, and the warm solution treated with zinc-dust until quite colourless. The solution is filtered hot, heated to boiling and mixed with one-third of its volume of fuming hydrochloric acid. Phenylhydrazine hydrochloride crystallises out, is separated by filtration, and decomposed with alkali. A further quantity of the hydrochloride is obtained by evaporation of the mother-liquors. The yield of pure base is 70 p.c. of the theory.

In the foregoing process the diazo- salt is first converted by the sodium sulphite into sodium benzenediazosulphonate:

$$C_6H_5.N_2Cl + Na_2SO_3 = C_6H_5.N_2.SO_3Na + NaCl.$$

On the addition of hydrochloric acid another molecule of sodium sulphite is decomposed, and the liberated sulphurous acid or acid sulphite reduces the reddish-yellow sodium benzenediazosulphonate to the colourless sodium phenylhydrazine-sulphonate:

$$C_6H_5.N{:}N.SO_3Na + NaHSO_3 + H_2O$$
$$C_6H_5.NH.NH.SO_3Na + NaHSO_4,$$

the reduction being completed by the zinc-dust and acetic acid. Finally the sodium phenylhydrazine-sulphonate is hydrolysed by the fuming hydrochloric acid, yielding phenylhydrazine hydrochloride:

$$C_6H_5.NH.NH.SO_3Na + HCl + H_2O$$
$$= C_6H_5.NH.NH_2,HCl + NaHSO_4.$$

Reychler (B. 20, 2463) has modified Fischer's method in a way which avoids the previous preparation of the diazo- salt. Sulphur dioxide is passed into a mixture of 28 grams of aniline and 21 grams of potassium carbonate in 300 c.c. of water until the whole of the aniline has gone into solution. The liquid is then gradually poured, with constant stirring, into a solution of 21 grams of sodium nitrite in 200 c.c. of water which has been exactly neutralised with acetic acid, and the whole is allowed to stand for some hours, after which it is warmed to dissolve potassium benzenediazosulphonate, acidified with dilute acetic acid, and decolourised with dilute hydrochloric acid and zinc-dust. The solution is filtered, mixed with more hydrochloric acid and evaporated to half its bulk, after which phenylhydrazine hydrochloride is precipitated by the addition of fuming hydrochloric acid. The yield is the same as in Fischer's process.

When diazo-amidobenzene is treated in alcoholic solution with zinc-dust and acetic acid, the diazo- group is reduced and phenylhydrazine is formed together with aniline:

$$C_6H_5.N_2.NH.C_6H_5 + 2H_2$$
$$= C_6H_5.NH.NH_2 + C_6H_5.NH_2$$

(E. Fischer, A. 190, 77); but this reaction is not of practical importance.

Properties.—When freshly distilled, phenylhydrazine is an almost colourless oil with a faint unpleasant smell; but on long standing it solidifies gradually, or in a freezing mixture it solidifies at once, to a mass of tabular monoclinic crystals, melting at 23°. It readily absorbs oxygen, assuming a red or dark-brown colour. It boils, with very slight decomposition and evolution of ammonia, at 241–242° (cor.), but distils without decomposition under reduced pressure; sp.gr. 1·097 $\frac{22·7°}{4°}$ (E. Fischer). Volatile with steam, but less readily than aniline. Sparingly soluble in cold, more soluble in warm water; almost insoluble in concentrated aqueous solutions of the alkalis; miscible in all proportions with alcohol, ether, acetone, chloroform, and benzene; not so soluble in light petroleum.

Reactions.—Phenylhydrazine is very susceptible of oxidation: thus Fehling's solution is reduced by dilute solutions of phenylhydrazine, even in the cold, with evolution of nitrogen, precipitation of cuprous oxide and formation of aniline and benzene. This property of reducing Fehling's solution in the cold is characteristic of the primary hydrazines, whereas the secondary hydrazines only reduce it on warming. Mercuric oxide, when shaken with solutions of phenylhydrazine salts, oxidises them to the corresponding salts of diazobenzene (E. Fischer, A. 190, 99). Phenylhydrazine is very stable towards reducing agents, but by the protracted action of zinc-dust and concentrated hydrochloric acid it is converted into aniline and ammonia. Many of the reactions of phenylhydrazine correspond with those of the amines: thus by the action of chlorides of acid radicles or alkyl haloids, acid radicles and alkyl groups respectively may be made to replace the amidic or imidic hydrogen of phenylhydrazine. One of the most important reactions of phenylhydrazine is that in which it reacts with compounds containing carbonyl groups:

$$C_6H_5.CHO + H_2N.NH.C_6H_5$$
$$= C_6H_5.CH{:}N.NH.C_6H_5 + H_2O$$

Benzylidene-phenylhydrazine
(Benzaldehydrazone).

$$(C_6H_5)_2CO + H_2N.NH.C_6H_5$$
$$= (C_6H_5)_2C{:}N.NH.C_6H_5 + H_2O$$

Benzophenone-phenylhydrazone

In this way phenylhydrazine may, like hydroxylamine, be employed in testing for the presence of carbonyl groups in compounds (E. Fischer, A. 190, 134; B. 17, 572). The compounds thus formed are known as hydrazones (*q. v.*). By the action of sulphuryl chlorhydrol (Limpricht, B. 18, 2196), or by heating with sulphuric acid, phenylhydrazine is converted into a sulphonic acid $C_6H_4(SO_3H)N_2H_3$; this compound was first obtained by Strecker and Römer (B. 4, 784) by diazotising *p*-amidobenzenesulphonic acid and reducing with hydrogen sodium sulphite the compound thus formed.

Phenylhydrazine is a monacid base and forms crystalline salts with acids.

Uses.—Phenylhydrazine is employed in the manufacture of antipyrine. Emil Jacobsen has proposed to use it as a developer in photography (Ger. Pat. 34,342, of March 5, 1885). Both phenylhydrazine and its mono-sulphonic acid, but especially the latter, are employed in the manufacture of colouring matters belonging to the class of the 'tartrazines.'

Methylphenylhydrazine $C_6H_5.N(CH_3).NH_2$ is obtained by the reduction of nitroso-methylaniline:

$$C_6H_5.N(CH_3).NO + 2H_2$$
$$= C_6H_5.N(CH_3).NH_2 + H_2O.$$

20 parts of zinc-dust are mixed with 35 parts of water, and to this mixture a solution of 5 parts of nitroso-methylaniline in 10 parts of glacial acetic acid is gradually added, stirring all the time and never allowing the temperature to rise above 10–20°, for which purpose it is necessary to cool the liquid with ice. After standing for some hours the whole is heated to boiling and filtered hot, extracting the zinc-dust on the filter with hot very dilute hydrochloric acid. The united filtrates are supersaturated with caustic soda so as to redissolve the zinc hydroxide, which is precipitated, and extracted with ether. A mixture of methylphenylhydrazine with regenerated methylaniline is thus obtained, from which the methylphenylhydrazine may be separated by the sparing solubility of its sulphate in absolute alcohol.—Colourless liquid, boiling with slight decomposition and evolution of ammonia at 227° (cor.) under 745 mm. pressure; under a pressure of 75 mm. it boils without decomposition at 131° (cor.). Like all secondary hydrazines, and in contradistinction to the primary hydrazines, it does not reduce Fehling's solution until warmed with it. Monacid base; its salts crystallise with difficulty.

The isomeric symmetrical methylphenylhydrazine reacts with aceto-acetic ether, yielding antipyrine (G. P. 40,377 of Nov. 1886).

F. R. J.

HYDRAZONE COLOURING MATTERS. The hydrazones, or compounds formed by the union of carbonyl compounds with phenylhydrazine and its analogues, are for the most part coloured—the colour varying from a pale yellow in the case of the hydrazones of aldehydes and ketones to orange or even deep red in the osazones (dihydrazones of α-dicarbonyl compounds) of some of the orthoquinones. These substances are insoluble in water and are therefore not directly available as dyestuffs; but by employing in their preparation phenylhydrazine-sulphonic acids, instead of phenylhydrazine itself, compounds are obtained which, in the form of their alkali salts, possess the necessary solubility in water and may be used in dyeing. Not only the phenylhydrazine-sulphonic acids, but also the tolylhydrazine-sulphonic acids, the hydrazines obtained from the naphthylamine-sulphonic acids and from benzidine-disulphonic acid, &c., may be used in these reactions. Among the carbonyl compounds which have been employed in the preparation of hydrazone colouring matters may be mentioned dihydroxytartaric acid, isatin, phenanthraquinone, and benzil; but only the osazone-sulphonic acid from the first of these—known as 'tartrazine'—is at present manufactured.

As regards the constitution of these compounds, they will, in the present article, be represented, for the sake of simplicity, as hydrazones; but it is an open question whether, in spite of their mode of formation, some of them are not in reality azo- compounds. It has been experimentally proved that the hydrazone-group $=C:N.NH.C_6H_5$ readily changes into the isomeric azo-group $=CH.N:N.C_6H_5$, and the reverse change may also occur (*cf.* Zincke and Bindewald, B. 17, 3032; Japp and Klingemann, B. 20, 3192, 3284; V. Meyer, B. 21, 12; Bernthsen, B. 21, 743; E. Fischer, B. 21, 984; Beyer and Claisen, B. 21, 1697).

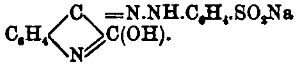
Tartrazine, *Sodium dihydroxytartrate-diphenylosazone-disulphonate*

$$\begin{array}{l} C_6H_4(SO_3Na).NH.N:C.CO_2Na \\ \qquad\qquad\qquad\qquad\quad\;\, | \\ C_6H_4(SO_3Na).NH\cdot N:C.CO_2Na. \end{array}$$

This colouring matter was discovered by Ziegler. Dihydroxytartaric acid $\begin{array}{l} C(OH)_2.CO_2H \\ | \\ C(OH)_2.CO_2H \end{array}$ behaves like the dihydrate of a diketonic acid $\begin{array}{l} CO.CO_2H \\ | \\ CO.CO_2H \end{array}$ and reacts with 2 mols. of a hydrazine to form an osazone. Ten parts by weight of sodium dihydroxytartrate are mixed with 16 parts of water and warmed to 40°; sufficient hydrochloric acid is added to dissolve the salt, and the liquid, after filtering, is heated for some time to about 80° with a solution of 20 parts of phenylhydrazine-*p*-sulphonic acid (prepared from sulphanilic acid) in 60 parts of water and 10 parts of 30 p.c. caustic soda lye. After allowing to cool, the yellow colouring matter is filtered off, pressed and dried.

Dissolves in water, giving a yellow solution which turns darker on addition of caustic soda, but is not changed by dilute acids. Alcohol gives a crystalline precipitate with the aqueous solution; stannous chloride, a yellow precipitate soluble in oxalic acid. Concentrated sulphuric acid dissolves it with a yellow colour. Dyes silk and wool pure yellow and is very fast to light (Badische Anilin- und Soda-Fabrik, Eng. Pat. 9,858 of August 19, 1885; S. C. I. 1886, 427; W. H. Richardson, Journ. Soc. Dyers and Colourists, 1887, 2 and 132; Ziegler and Locher, B. 20, 834).

Isatin yellow, *Sodium isatin-phenylhydrazone-p-sulphonate*



Ten kilos. of phenylhydrazine-sulphonic acid and 7·8 kilos. of isatin are mixed with 500 litres of water, gradually warmed, and finally heated to boiling. The solution is neutralised with sodium carbonate and the colouring matter precipitated by the addition of common salt. Orange-yellow powder, soluble in water with a yellow colour. Addition of hydrochloric acid to the aqueous solution produces no change; but caustic soda turns it browner. Dissolves in concentrated sulphuric acid with a yellowish-brown colour, which becomes yellow on dilution with water. Dyes wool and silk greenish-yellow in an acid bath. Discovered by G. Schultz (Actiengesellschaft für Anilinfabrikation, Ger. P. 40,746 of Jan. 27, 1887). A precisely similar colouring matter is obtained from methylisatin.

Phenanthraquinone red. *Sodium phenanthraquinone-di-α-naphthylosazone-disulphonate*

$$\begin{array}{l} C_6H_4.C:N.NH.C_{10}H_6.SO_3Na \\ |\qquad\;\; | \\ C_6H_4.C:N.NH.C_{10}H_6.SO_3Na. \end{array}$$

This compound is prepared like the foregoing, employing two molecular proportions of α-naphthylhydrazine-α-sulphonic acid (from naphthionic acid) and one of phenanthraquinone. Brownish-red powder, soluble in boiling water with a cherry-red colour; from the solution hydrochloric acid precipitates the yellowish-brown free acid, whilst caustic soda changes the colour of the liquid to yellowish-brown. Concentrated sulphuric acid dissolves it, yielding a blue solution, which on dilution with water gives a yellowish-brown precipitate. Dyes wool red in an acid bath. Discovered by Schultz (Actiengesellschaft für Anilinfabrikation, Ger. Pat. 40,745 of Jan. 27, 1887).

This colouring matter has valuable properties, but cannot be profitably manufactured owing to the difficulty in obtaining phenanthraquinone.

R. Meyer (Ger. Pat. 45,272 of March 6, 1888, *expired*) prepares similar yellow and yellowish-red colouring matters by the condensation of benzil $C_6H_5.CO.CO.C_6H_5$ with sulphonic acids of hydrazines of the benzene and naphthalene series. Their constitution corresponds with that of phenanthraquinone red. F. R. J.

HYDRAZONES. The compounds formed by the condensation of substances containing the carbonyl group CO with phenylhydrazine were named by many chemists 'phenylhydrazides,' or merely 'hydrazides.' E. Fischer (B. 21, 984) has pointed out the inaccuracy of this term. A 'hydrazide' corresponds with an 'amide': the phenylhydrazido- group is $C_6H_5.N_2H_2$; thus the phenylhydrazide of benzoic acid is

$$C_6H_5.CO.N_2H_2.C_6H_5.$$

In order to avoid this ambiguity, Fischer has proposed to name the compounds in which the dyad group $C_6H_5.NH.N=$ replaces the oxygen of a carbonyl group 'phenylhydrazones'—the termination *one* serving to suggest their connection with ket*ones* or with carbonyl compounds generally. Further, as in the very great majority of cases it is *phenylhydrazine* which is employed in the preparation of these compounds, the abbreviated form 'hydrazone' may be applied in all such cases and is to be taken to signify 'phenylhydrazone' unless the contrary is stated. The name 'osazone' is, for reasons to be explained presently, applied to compounds containing two dyad groups $C_6H_5.NH.N=$ attached to two contiguous carbon atoms. Thus in the case of the two compounds obtained from glyoxal CHO.CHO and phenylhydrazine we have:

$$\text{Glyoxalhydrazone} \begin{array}{l} CHO \\ | \\ CH:N.NH.C_6H_5 \end{array}$$

$$\text{Glyoxalosazone} \begin{array}{l} CH:N.NH.C_6H_5 \\ | \\ CH:N.NH.C_6H_5 \end{array}$$

(E. Fischer, B. 21, 985).

Formation.—The fact that phenylhydrazine reacts with aldehydes was first pointed out by

E. Fischer (A. 190, 134); thus with benzaldehyde:

$$C_6H_5.CHO + H_2N.NH.C_6H_5$$
$$= C_6H_5.CH{:}N.NH.C_6H_5 + H_2O$$

Benzylidene-phenylhydrazine
(Benzaldehydrazone).

Later (B. 16, 661, footnote; 17, 572) he extended the reaction to ketones, diketones, ketonic acids, and carbonyl compounds generally and proposed the use of phenylhydrazine as a reagent, analogous in its action to hydroxylamine, for ascertaining the presence of carbonyl groups in compounds. At first (B. 17, 573) he recommended that the compound to be investigated should be heated with an aqueous solution of phenylhydrazine hydrochloride mixed with excess of sodium acetate, to which alcohol might be added to dissolve the compound; but later (B. 22, 90, footnote), he substituted a mixture of equal volumes of free phenylhydrazine and acetic acid of 50 p.c. strength. The formation of a hydrazone under these circumstances is a proof that the compound under examination contains at least one carbonyl group in the ketonic or aldehydic form, *i.e.* attached with both its affinities to carbon atoms, or to a carbon and a hydrogen atom, or to two hydrogen atoms. Carbonyl groups attached with one or both affinities to oxygen or to nitrogen—as in CO.OH, $CO.NH_2$, &c.—do not react with phenylhydrazine. In some respects phenylhydrazine is to be preferred as a reagent to hydroxylamine: it is more readily obtained, and compounds containing more than one carbonyl group frequently react with two mols. of phenylhydrazine, thus showing the presence of two carbonyl groups, when they would react with only one mol. of hydroxylamine. The hydrazones of the various mono-carbonyl compounds are formed like the aldehydrazones already mentioned: thus *acetonehydrazone*

$$(CH_3)_2C{:}N_2H.C_6H_5,$$

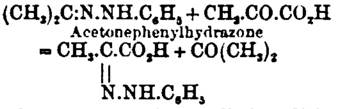
and *phenylhydrazonepyruvic acid*

$$CH_3.C(N_2H.C_6H_5).COOH.$$

The action of phenylhydrazine on dicarbonyl compounds is, however, occasionally more complex and varies with the relative positions of the two carbonyl-groups.

A few of the hydrazones are liquid, but the majority are crystalline solids. By warming the solution of a carbonyl compound with phenylhydrazine and determining the melting-point of the hydrazone formed, the hydrazone, and thus the carbonyl compound from which it is derived, may frequently be identified. Many of the hydrazones decompose on melting: in determining the melting-point, therefore, the temperature must be raised as rapidly as is consistent with accuracy, otherwise too low a melting-point will be found (E. Fischer, B. 17, 573; 20, 827).

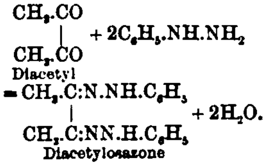
The hydrazones are readily reduced, either with sodium amalgam and acetic acid, or with zinc-dust and acetic acid. According to the length to which the reduction is carried, the hydrazone takes up either two, or four, atoms of hydrogen—in the latter case with disruption of the molecule at the point of union of the nitrogen atoms. Thus phenylhydrazonepyruvic acid $CH_3.C(N.NH.C_6H_5).COOH$, yields in the first stage of the reduction benzenehydrazopropionic acid $CH_3.CH(NH.NH.C_6H_5).COOH$, and this, by further reduction, breaks up into alanine $CH_3.CH(NH_2).COOH$ and aniline. This latter mode of reduction into a mixture of two bases was discovered by Tafel (B. 19, 1924) who proposed to employ the reaction as a means of obtaining primary amines from carbonyl compounds: thus benzaldehyde could be converted, by the reduction of its hydrazone, into benzylamine. By the action of acids the hydrazones may generally be hydrolysed into phenylhydrazine and the carbonyl compound from which they have been formed; but other complex products are formed at the same time. Pyruvic acid, however, has the property of decomposing the hydrazones, appropriating the phenylhydrazine to form with it phenylhydrazonepyruvic acid and liberating the carbonyl compound in a state of purity:


Acetonephenylhydrazone

$$(CH_3)_2C{:}N.NH.C_6H_5 + CH_3.CO.CO_2H = \underset{\underset{\textstyle N.NH.C_6H_5}{\|}}{CH_3.C.CO_2H} + CO(CH_3)_2$$

(E. Fischer, A. 253, 63). Alkyl radicles and acid radicles may be introduced into the molecule of the hydrazones in place of the imidic hydrogen by the action of alkyl haloids and anhydrides of acids, the reaction being aided in the former case by first replacing the hydrogen atom by sodium, which is effected by treating the hydrazone either with metallic sodium or with sodium alcoholate. By heating with zinc chloride, certain hydrazones are converted, with elimination of ammonia, into indoles (*v.* INDOLES).

Osazones. As already mentioned, the name *osazone* denotes a compound containing in its molecule two dyad groups $C_6H_5.NH.N=$ attached to two contiguous carbon atoms. E. Fischer (B. 17, 579) obtained from carbohydrates a series of characteristic compounds formed by the introduction of two phenylhydrazone groups into the molecule of a carbohydrate. The compound from dextrose was termed *phenylglucosazone*; that from galactose *phenylgalactosazone*, and so on. Later, when it was found that in these compounds the two phenylhydrazine-residues were in contiguous positions, the name *osazone* was applied to all compounds containing this particular grouping (E. Fischer, B. 21, 985). Osazones are formed by the action of two mols. of phenylhydrazine on *a*-dicarbonyl compounds, *i.e.* such as contain the group CO.CO;


Diacetyl

Diacetylosazone

$$\begin{array}{l} CH_3.CO \\ \quad\;\; | \\ CH_3.CO \end{array} + 2C_6H_5.NH.NH_2 = \begin{array}{l} CH_3.C{:}N.NH.C_6H_5 \\ \qquad | \\ CH_3.C{:}NN.H.C_6H_5 \end{array} + 2H_2O.$$

The yellow colouring matters known as 'tartrazines' are osazones formed in this way from dihydroxytartaric acid.

Osazones are also formed by the action of phenylhydrazine on compounds containing the group —CH(OH).CO—, thus on *a*-ketone-alcohols and *a*-aldehyde-alcohols; and it is the members of the carbohydrate family belonging to these classes which yield osazones. In the cold, unless on long standing, only the carbonyl group reacts with phenylhydrazine, and a hydrazone containing the group $—CH(OH)·C(N_2H·C_6H_5)—$ is formed; but this compound, on heating with excess of phenylhydrazine, is converted into an osazone, the alcohol group also taking part in the reaction. The mol. of hydrogen which is removed in this process reduces a mol. of phenylhydrazine to aniline and ammonia. Thus with dextrose—

$$\underset{\text{Dextrose}}{CH_2OH.(CHOH)_4.CHO} + 3C_6H_5.NH.NH_2$$
$$= \underset{\text{Phenylglucosazone}}{CH_2OH.(CHOH)_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)}$$
$$+ NH_2.C_6H_5 + NH_3 + 2H_2O$$

These osazones have proved of great use in identifying various sugars. Sometimes, however, two distinct sugars yield the same osazone: thus lævulose, like dextrose, gives phenylglucosazone:

$$\underset{\text{Lævulose}}{CH_2OH.(CHOH)_3.CO.CH_2OH} + 3C_6H_5.NH.NH_2$$
$$= \underset{\text{Phenylglucosazone}}{CH_2OH.(CHOH)_3.C(N_2H.C_6H_5).CH(N_2H.C_6H_5)}$$
$$+ NH_2.C_6H_5 + NH_3 - 2H_2O,$$

the *α*-aldehyde-alcohol and the *α*-ketone-alcohol yielding the same osazone.

The osazones are crystalline compounds, of a yellow colour, and generally have a definite melting-point, by means of which they may be identified. Concentrated sulphuric acid dissolves the various osazones, giving characteristic colourations, and the solution generally exhibits some particular colour-change on standing (Japp and Klingemann, B. 21, 549). Fuming hydrochloric acid hydrolyses the osazones in the cold into phenylhydrazine and the *α*-dicarbonyl compound from which they are derived (E. Fischer, B. 21, 2631). F. R. J.

HYDRIODIC ACID *v.* IODINE.

HYDROBROMIC ACID *v.* BROMINE.

HYDROCARBOSTYRIL *v.* QUINOLINE.

HYDROCHLORIC ACID *v.* CHLORINE.

HYDROCOTARNINE *v.* VEGETO-ALKALOIDS.

HYDROCURCUMIN *v.* TURMERIC.

HYDROCYANIC ACID *v.* CYANIDES.

HYDROFLUORIC ACID *v.* FLUORINE.

HYDROGEN. At. w. 1 (taken as unity). Symbol H. Paracelsus, in the sixteenth century, distinctly recognised the existence of this gas; its combustible property was discovered in the following century by Turquet de Mayerne, and in 1700 Lemery observed the detonating property of a mixture of air and hydrogen.

Cavendish in 1766 showed that when the gas was produced from dilute acid and one of the metals, iron, zinc, or tin, it was obtained in amount varying with the metal used.

Hydrogen was for a time confounded with other combustible gases, such as marsh-gas, carbonic oxide, and vapour of ether; all were supposed to contain the same inflammable principle, phlogiston, modified by variable amounts of other substances.

Macquer and De la Metherie first observed, in 1766, that water was produced by a burning jet of hydrogen, but it was then thought that other products than water were produced at the same time, and Lavoisier made many experiments with the object of detecting the presence of an acid which he imagined should be among the products of combustion, as was the case in the combustion of such bodies as sulphur, carbon, phosphorus, &c. Cavendish, however, in 1781, proved conclusively that water was the only product of combustion when hydrogen burns in air or oxygen, and that if a mixture of hydrogen and oxygen in the proportion of two volumes of the former to one of the latter were burnt the whole of the gases were converted into water.

Sources. Hydrogen is found free in nature among the gases evolved from certain volcanoes. It accompanies the jets of steam, known as *fumerolles* which occur in various parts of the world, as in Tuscany; also in the gases given off from the oil-wells of Pennsylvania. It is one of the many gases of which coal-gas is a mixture. It occurs in the carnallite of the Stassfurt potash mines; it is found among the gases evolved during alcoholic fermentation, especially under diminished pressure. The human breath under certain conditions contains traces of the gas, and it is found among the intestinal gases of many animals. Hydrogen occurs in an occluded state in many meteorites; commercial zinc-dust also contains it in considerable quantity. Hydrogen is evolved during the growth of fungi; carpets dyed with arsenical dyes, or wall papers coated with arsenical pigments, give rise to hydrogen arsenide on account of the liberation of hydrogen and consequent combination with arsenic; decaying wood and fungi in contact with nitrogen for the same reason give rise to ammonia (Selmi, B. 7, 80).

Spectroscopic observations have shown that hydrogen completely surrounds the sun, forming an envelope which has received the name of the *chromosphere.* Hydrogen also occurs in certain stars and nebulæ.

In a state of combination hydrogen forms one-ninth the weight of water and one fourth the weight of marsh-gas. It also occurs in smaller quantities in combination with phosphorus, sulphur, iodine, bromine, carbon, and nitrogen. It is an essential constituent of all acids; most animal and vegetable substances contain it, and it is a constituent of many minerals. It exists in the air in small quantities, in combination with nitrogen as ammonia; and in certain mineral and volcanic springs it is found in combination with sulphur and chlorine as sulphuretted hydrogen and hydrochloric acid respectively.

Preparation of hydrogen. (1) Hydrogen is obtained pure by the electrolytic decomposition of water; for this purpose the water is mixed with one-tenth its volume of sulphuric acid, and a battery of four or five Bunsen's or Grove's cells may be employed.

(2) By the decomposition of water by passing a current of steam over iron turnings contained in an iron tube and heated to redness in a furnace, the iron combines with the oxygen and forms magnetic oxide of iron, Fe_3O_4, while the hydrogen passes on and may be collected at the pneumatic trough; $3Fe + 4H_2O = Fe_3O_4 + 4H_2$.

(3) By the action of sodium or potassium on water or alcohol;

$$Na + OH_2 = NaHO + H$$
$$Na + C_2H_6O = C_2H_5NaO + H.$$

(4) By heating sodium in gaseous hydrochloric acid: $2HCl + Na_2 = 2NaCl + H_2$.

(5) By dissolving magnesium in dilute sulphuric acid: $SO_4H_2 + Mg = SO_4Mg + H_2$. The gas obtained by this process is very pure.

(6) By dissolving zinc in dilute sulphuric or hydrochloric acid. This is the most convenient mode of obtaining the gas for the lecture table or for laboratory purposes: $SO_4H_2 + Zn = SO_4Zn + H_2$ and $2HCl + Zn = ZnCl_2 + H_2$.

(7) By dissolving zinc in contact with iron or platinum in a solution of caustic potash: $2KHO + Zn = ZnOK_2O + H_2$. The iron and zinc form an electric couple, and the latter, being the positive element, is attacked.

(8) By heating in a combustion tube a mixture of 20 grams of zinc-dust with 22·8 grams of calcium hydroxide. The hydrogen obtained by this method is pure (H. Schwarz, B. 19, 1140, 1141).

(9) By projecting jets of superheated steam upon incandescent coke; equal volumes of hydrogen and carbonic oxide are thus obtained, and are led over heated bricks or other refractory material contained in a second retort, into which steam at high temperature is passed; the carbonic oxide robs the steam of its oxygen and hydrogen is liberated. About 3,200 cubic metres of hydrogen are obtained per ton of coke (F. Hembert and Henry, C. R. 101, 797), *v.* GAS, WATER.

(10) By heating a mixture of slaked lime and anthracite coal in an iron retort: $C + CaO + OH_2 = CaCO_3 + 2H_2$. By passing steam over the residue carbon dioxide is driven off, so that if enough coal be used the process can be carried on indefinitely by alternate steaming and heating (Bloxam).

(11) By heating formates or oxalates with excess of sodic, potassic, or calcic hydrate:

$$2CHKO_2 + 2KHO = 2K_2CO_3 + 2H_2.$$
$$C_2K_2O_4 + 2KHO = 2K_2CO_3 + H_2.$$

(12) By the action of potassium hydrate on certain organic bodies having a tendency to form acids by oxidation:

$$\underset{\text{Benzoyl hydride}}{C_7H_6O} + KHO = \underset{\text{Potassic benzoate}}{C_7H_5KO_2} + H_2.$$

(13) By immersing zinc in an aqueous solution of a salt of ammonia, or in methylamine, ethylamine, aniline, or naphthylamine. Ammonium nitrate is an exception to this general rule.

Purification.—The hydrogen obtained from zinc and sulphuric acid is generally contaminated with the following impurities, some of which give to the gas an unpleasant odour, viz., sulphurous acid, oxides of nitrogen, sulphuretted hydrogen, arsenetted hydrogen, phosphuretted hydrogen, and carbon dioxide. To remove these substances Dumas passed the gas through two U-tubes filled with broken glass, the first of which was moistened with a solution of lead nitrate, and the second with silver sulphate; by this means sulphuretted hydrogen and arsenetted hydrogen were removed. He then passed it through a third U-tube containing pumice stone moistened with a strong solution of caustic potash; and, lastly, through a fourth containing phosphorus pentoxide. To prevent the formation of the oxides of nitrogen, sulphuric acid free from these compounds should be employed. Hydrogen obtained by the action of sulphuric acid on iron may also contain the vapours of hydrocarbons, which vary in amount with the quantity of carbon in the iron employed; these may be removed by passing the gas through alcohol. Small quantities of atmospheric air are always present whatever means are adopted for the preparation of hydrogen; this is due probably in part to diffusion through the joints of the apparatus, and partly to the liquids employed in its preparation containing air in solution. There is no method known whereby the nitrogen may be removed, but the oxygen is extracted by leaving the gas in contact with spongy platinum.

Hydrogen may also be freed from phosphuretted hydrogen, arsenetted hydrogen, and antimonetted hydrogen by passing it through a saturated solution of permanganate of potash, and from sulphuretted hydrogen by passing through soda ley (Schobig).

Kolbe states that when pure sulphuric acid is diluted with twice its volume of water, the hydrogen evolved on dissolving zinc in it is quite free from sulphuretted hydrogen. Hydrogen in the nascent condition reduces sulphuric as well as sulphurous acid to hydrogen sulphide; the hotter and the more concentrated the acid is the more hydrogen sulphide is produced.

According to Döbereiner, the gas is deprived of all odour by leaving it in contact with moistened charcoal powder for twenty-four hours.

Properties.—Hydrogen, when pure, is a colourless invisible gas without smell or taste; it is the lightest body known, and has a specific gravity of 0·0693 (air = 1); a litre of the gas at standard temperature and pressure weighs 0·0896 gram. Hydrogen is slightly soluble in water, 100 c.c. of water dissolving 1·93 c.c. of the gas at all temperatures between 0°–20°. When inhaled it imparts a peculiar squeaking tone to the voice, due to the extreme tenuity of the gas; small animals when put into it die instantly. Hydrogen, however, is not directly poisonous, but may cause death by preventing access of oxygen to the lungs. It has not yet been liquefied.

Hydrogen burns in air with an almost colourless flame, but under certain conditions, even when pure, the centre of the flame is coloured green while the external portions are of a violet-blue colour. On reducing the pressure the blue colour is transformed to green, and from that successively to yellow, orange, and red. The refrangibility of the emitted light becomes less when the intensity of combustion is reduced by a diminution in the supply of oxygen or by a reduction of pressure (S. Santini, Gazzetta, 14, 142–146). A lighted taper is extinguished on being placed in a jar of hydrogen, and the gas burns at the mouth of the jar, rapidly if the jar be mouth upwards, slowly if mouth downwards.

Hydrogen when mixed with air or oxygen is explosive; the loudest explosion is obtained by mixing together two volumes of hydrogen and one volume of oxygen. The maximum explosive effect with air is obtained by mixing one volume of hydrogen with two and a half volumes of air, and applying a light as before; the explosion in this case is not so powerful on account of the nitrogen present. In each of these cases the two gases are present in the proportion in which they unite to form water. This mixture of hydrogen and oxygen is not explosive at greatly reduced pressure; a rarefaction produced by diminution of pressure is more effective in weakening the force of an explosion than diluting the mixture with an indifferent gas (C. J. 1884, 81).

The combination of a gaseous mixture of hydrogen and oxygen may also be effected by passing an electric spark through the mixture; a red-hot piece of wire or a glowing coal will cause their union. The heat generated by suddenly compressing the mixed gases is sufficient to cause the combination (Biot). Platinum black or a perfectly clean plate of the metal, spongy iridium and osmium, finely divided palladium, gold leaf, and silver leaf answer the same purpose.

Hydrogen and chlorine when mixed together in equal volumes in the dark will not combine, but if exposed to diffused daylight combination takes place slowly, and if exposed to direct sunlight, the electric light, or limelight, combination takes place with violence, the product being gaseous hydrochloric acid. A lighted taper or hot brick in contact with the mixture will bring about the combination. Charcoal absorbs chlorine gas with a rise in the temperature, so that, if dry hydrogen be passed over it, even in the dark, combination takes place with formation of hydrochloric acid gas.

Hydrogen does not combine with bromine vapour at the ordinary temperature even in direct sunshine, but a red-hot wire causes partial combination.

Hydrogen combines with iodine vapour on passing the mixture through a red-hot tube, and at ordinary temperature under the influence of spongy platinum.

Hydrogen combines directly with fluorine without the application of heat, even in the absence of daylight (A. Ch. 6, 472-538).

The spectrum of hydrogen consists of four bright lines, one in the red corresponding to C, one in the greenish-blue corresponding to E, one in the blue, and another in the indigo. The F line of hydrogen may be reversed by taking induction sparks between aluminium or magnesium poles in hydrogen. At a pressure of half an atmosphere above the ordinary pressure the line widens, and a dark streak is seen in its centre; at two atmospheres the reversal is well marked. With a dispersion of more than one prism C also is reversed. If drops of water are allowed to fall into a lime crucible between the poles in air, each drop causes an explosion with much widening of the hydrogen lines, but without reversal, the effect being comparable with the outburst of hydrogen in the sun's atmosphere (Liveing and Dewar, Pr. 35, 74-76).

Occluded hydrogen. Iron and platinum at a red heat absorb hydrogen gas, but palladium possesses this property in the highest degree; these metals absorb the gas while hot, and retain it when cold, to which property Graham gave the name *occlusion*. To exhibit this phenomenon the metal, *e.g.* palladium, is placed in a glazed porcelain tube, which is then exhausted by means of the Sprengel pump and heated to redness; hydrogen is now admitted and passed over the metal for some time; and the metal is allowed to cool in the gas. The tube is now exhausted a second time and again heated to redness, by which means the occluded hydrogen is expelled, pumped off, collected, and measured in a tube at the bottom of the fall tube of the pump. Graham in this way showed that palladium at a red heat occluded over 900 times its volume of hydrogen; even at ordinary temperatures the metal occludes not less than 376 times its volume. In order to denote the metallic character of this hydrogenised palladium Graham called it *hydrogenium*; its density, tenacity, and electric conductivity are less than those of palladium itself.

Graham, on examining the meteoric iron of Lenarto by means of the Sprengel pump, found that it yielded a gas when heated to redness equal to 2·85 times its own volume, and that this gas contained 85·68 p.c. of hydrogen; and as red-hot iron at ordinary atmospheric pressure only absorbs about half its own volume of hydrogen, it was concluded that this meteorite had come from some extra-terrestrial region where hydrogen exists at greater pressure than the atmosphere of our earth.

Hydrogen, as has already been mentioned, is found occluded in zinc-dust. By heating 6·749 grams of this substance in a hard glass retort to the greatest heat of a Bunsen burner, Williams obtained 47·4 c.c. of hydrogen. 6·479 grams of zinc-dust which had been moistened with water, then dried at 100°C., increased 0·1742 gram, and on heating 89·4 c.c. of hydrogen were obtained. 6·479 grams of zinc-dust which had been exposed to a moist atmosphere till the weight was constant and then dried, gave on heating as much as 362·8 c.c. Zinc-dust, therefore, takes up water and decomposes it, and gives up its hydrogen on heating (Abst. C. S. J. 1886, 15).

Hydrogen when passed through a solution of silver nitrate, sulphate, or acetate precipitates metallic silver; the amount of silver precipitated is small in comparison with that in solution. The precipitation takes place independent of light, is expedited by heat, and the silver thrown down is of a very pure quality. Platinum, palladium, and gold are also precipitated by hydrogen at ordinary temperature and pressures from their respective solutions.

Hydrogen when passed over sesquioxide of iron or oxide of copper in a tube which is heated to a moderate temperature reduces these oxides to the metallic condition. Advantage is taken of the reducing properties of hydrogen in the detection of arsenic by what is known as the Marsh's test. The manufacturing chemist also avails himself of the use of hydrogen in the manufacture of aniline, indigo, &c.

Hydrogen is used in conjunction with oxygen for the production of the Drummond or oxy-hydrogen lime light. For this purpose the gases are compressed in iron bottles furnished with taps and jets, so that the gases can be allowed to escape, and burned as required. They are allowed to impinge on a cylinder of lime which is thereby heated to whiteness, and gives a light almost equal to the electric arc.

Döbereiner's lamp.—When a jet of hydrogen is made to impinge upon spongy platinum the gas is enabled to combine with the oxygen of the air at ordinary temperature, and the platinum becomes red-hot by the heat generated. Upon this principle Döbereiner's lamp depends. It consists of a hydrogen generator provided with a horizontal exit-tube with stopcock. Attached to this tube is a bent arm on the end of which is fixed a ball of spongy platinum; the arm is so fixed that it can be brought in front of or away from the hydrogen jet at pleasure.

Autogenous soldering.—The hydrogen flame is much used for uniting the edges of the sheets of lead which are employed in making vessels for the purpose of holding acids. Joints made in this way are much more durable than those made with solder. The apparatus for this purpose is made so that hydrogen can be generated at pleasure, and when not in use the pressure of gas inside the apparatus lifts the acid out of contact with the zinc. The hydrogen generator consists of a cylindrical copper vessel lined with lead; there is an upper and lower chamber connected by a pipe, and they are filled with arrangements which admit of easy renewal of acid or zinc and the removal of the zinc sulphate formed. The apparatus gives a very constant flame, which may be used with advantage in soldering lead in the way which is practised in the construction of sulphuric acid chambers. The hydrogen is delivered from a platinum-tipped nozzle through which a jet of air also issues from a foot bellows; this is effected by attaching the nozzle by means of india-rubber tubing to a tube which branches out V-shaped into two limbs each provided with a stopcock; each of these limbs is provided with an india-rubber tube, one of which is attached to the bellows and the other to the delivery tube of the hydrogen generator. The operator can, therefore, carry the nozzle in his hand and direct the flame where he pleases, and by means of the stopcock he can readily regulate the supply of air or hydrogen.

Hydrogen for balloons.—Soon after Cavendish published his researches on 'inflammable air,' M. Charles, in 1783, suggested the application of hydrogen for the inflation of balloons. Montgolfier had, during the same year invented the balloon which he inflated with rarefied air. In hydrogen, however, M. Charles recognised a much more suitable means of inflation, although the cost was very considerable, 500 lbs. of sulphuric acid and twice that amount of iron being consumed in the inflation of a balloon about 13 feet in diameter.

The first balloon sent up from English soil, on Nov. 25, 1793, was inflated with hydrogen. In the following year the French Government instituted a series of experiments at Meudon under Guyton de Morveau, Contelle, and Comté with the view of perfecting the balloon for reconnoitring, signalling, and other warlike purposes. They made many balloons, the first of which, the *Enterprenant*, was 27 feet in diameter, and able to support 500 lbs. at a height of 1,500 feet. The authorities, however, forbade the use of sulphuric acid in the production of hydrogen for inflating balloons, as all the available sulphur was required for the manufacture of gunpowder. Guyton de Morveau suggested a method invented by Lavoisier, that of passing steam over red-hot iron, and a furnace was accordingly built, which after many trials, was capable of producing sufficient gas to fill the balloon in four hours. This balloon with one filling remained in use for a month. During that time many ascents were made, and it was towed from Maubeuge to Charleroi, a distance of 30 miles, floating in the air at such a height as to permit the cavalry and other troops to pass beneath.

Balloons inflated with hydrogen were used in the American Civil War in 1861. The gas was generated from old scrap iron and sulphuric acid in wooden tanks lined with lead: the apparatus was carried from place to place on two carts.

In 1878 Giffard made a gigantic captive balloon for the Paris Exhibition. It was spherical in form, 118 feet in diameter, and had a capacity of 882,902 feet. When filled with hydrogen it had a lifting power of 27 tons, and was estimated to carry safely 52 persons. It was made of 7 layers of muslin, india-rubber, and canvas put in alternate layers; and the seams were covered with the same materials. To fill this great aerial ship with hydrogen gas, 190 tons of sulphuric acid and 80 tons of iron were consumed (Jour. United Service Inst. 27, 735–756).

Hydrogen was also used in the Soudan War for inflating balloons. For this purpose the gas was compressed in strong iron cylinders, 12 feet long by 1 foot in diameter; these were for a reserve supply, and weighed half a ton each. A gas factory and pumping station were put up. To meet first requirements about 100 lighter cylinders, 9 feet long, and containing 120 feet of gas in a compressed condition, were taken out; these were so constructed as to be easily carried by men. One waggon containing a ton of stores was sufficient for a balloon ascent; a volume of gas occupying 4,150 feet was sufficient to lift a man 1,000 yards (Illus. Nav. and Mil. Gaz. 11, 172).

HYDROGENIUM *v.* HYDROGEN.

HYDROGEN PEROXIDE. Symbol H_2O_2. This compound was discovered in 1818 by Thenard. It occurs at times in small quantities in the atmosphere, in dew, in rain, and in snow. It is also contained in solution in the water produced by the combustion of hydrogen in oxygen (Schuller).

1. By passing a copious stream of well-washed carbon dioxide through distilled water in a beaker surrounded by ice-cold water, to which is added very gradually pure barium peroxide, finely powdered and suspended in water. The cautious addition of the barium peroxide is necessary, as an excess of it would cause the decomposition of any hydrogen peroxide formed, with evolution of oxygen and formation of water. After allowing the gas to pass some considerable time, the barium carbonate is filtered off, and the solution evaporated *in vacuo* over sulphuric acid until it acquires a syrupy consistency; $BaO_2 + CO_2 + OH_2 = H_2O_2 + BaCO_3$.

2. The preparation is also effected by the decomposition of barium peroxide with hydrofluoric, silicofluoric, or phosphoric acid, but preferably by one of the two latter. The barium peroxide, which must be of the purest quality, is made into a thin paste with water, and introduced very gradually into the acid solution, the temperature of which must never exceed 20°C. and

must be constantly agitated. When the solution is nearly neutralised, the liquid is decanted from the precipitate and freed from dissolved baryta by the addition of sodium sulphate. The most stable peroxide is that prepared with phosphoric acid, and contains a small amount of that acid in the free state (C. Z. 9, 949 and 976).

3. Thomsen recommends that moist hydrated barium peroxide be added to dilute sulphuric acid. The peroxide of barium is added slowly to a mixture of 1 part of strong sulphuric acid to 5 parts of water, the acid being always in excess on account of the tendency of the hydrogen peroxide to decompose in presence of free barium peroxide. The precipitated barium sulphate is filtered off, and excess of acid removed by exact neutralisation with baryta water, when the liquid is again filtered. The solution of hydrogen peroxide thus obtained is concentrated *in vacuo* over sulphuric acid as before.

4. It may be readily prepared by adding potassium peroxide (obtained by directing a stream of air upon fused potassium contained in a porcelain crucible) to a well cooled and moderately strong solution of tartaric acid, when potassium tartrate is precipitated, the hydrogen peroxide remaining in solution.

Hydrogen peroxide is also formed under several other circumstances, as, *e.g.*, when freshly ignited bone-black is moistened with as much water as it will take up, and exposed to light and air. Even in a few minutes a perceptible amount of hydrogen peroxide is formed (D. P. J. 256-519). A carbonic oxide flame (when the gas has been previously passed through water) is said to produce it in quantity, or if burnt in contact with the surface of water the same effect is produced (S. C. I. 3, 490).

When turpentine oil or any other hydrocarbon containing a terpene is air-oxidised in the presence of water, peroxide of hydrogen is formed and passes into solution in the water. In this way it is possible to prepare a solution of two volumes strength, that is to say, of such a strength that when fully decomposed it is capable of yielding twice its own volume of oxygen gas (Kingzett).

Commercial hydrogen peroxide is liable to contain hydrochloric, sulphuric, phosphoric, and hydrofluoric acids, alumina, lime, magnesia, potash, and soda, derived from water or other materials used in its manufacture, while baryta and traces of iron, copper, lead, and manganese are sometimes found if it has been carelessly made.

When these last are present, the product is tolerably stable only if it be sufficiently acid, though even then it is less stable than in the absence of these impurities.

The commercial liquid of so-called 10 volume or about 3 p.c. strength may be purified by the addition of about ¼ p.c. of concentrated phosphoric acid (preferably pure) to precipitate iron, copper, lead, and manganese, and prevent the subsequent formation of their peroxides which would otherwise take place. Saturated baryta water (hot or cold) is then added very gradually, until neutrality is reached. No excess must be used or hydrated BaO_2 will be precipitated, which will induce decomposition of a portion of the hydrogen peroxide.

The clear liquid is now drawn off, and is poured into an excess of cold saturated baryta water, when hydrated BaO_2 is thrown down, and is then washed until no metal except barium can be detected in the washings.

The BaO_2 is then suspended in water and added drop by drop to a solution consisting of 90 parts of distilled water to 10 parts of pure concentrated sulphuric acid until only traces of acid remain free; these are best removed by weak baryta water, for an accidental excess of BaO_2 will induce decomposition of some of the already formed hydrogen peroxide, while an excess of BaO will have no such effect. The barium sulphate is allowed to settle, and the clear liquid drawn off, if found free from both barium and sulphuric acid. The resulting product is about 3 p.c. strength, fairly stable and of great purity (Mann, C. Z. 12, 857; S. C. I. 8, 640.

The amount of hydrogen peroxide in an aqueous solution may be conveniently determined by titration with a solution of potassium permanganate containing 7·9 grams $KMnO_4$ per litre. 2 c.c. of peroxide of hydrogen solution are introduced into a graduated tube of 35 c.c. capacity, 5 or 6 drops of hydrochloric acid are added, and then the solution of permanganate is gradually introduced with constant agitation until the contents of the tube are of a red or brownish colour; the quantity of solution is then read off, 5 c.c. representing 1 p.c. of hydrogen peroxide. The results are accurate to within 0·1 p.c. and can be obtained in a few minutes[1] (C. Z. 9, 940 and 976).

Another and more accurate method is to strongly acidify the solution of hydrogen peroxide with sulphuric or hydrochloric acid, then add solution of potassium iodide free from iodate, and determine the iodine liberated by means of a standard solution of sodium thiosulphate (Kingzett, C. J. (Trans.) December, 1880, and The Analyst, 1888, 13, 62).

A third method is sometimes recommended, viz., to put the solution of hydrogen peroxide in a small retort, boil gently, and collect the oxygen evolved over mercury. The volume of oxygen in terms of the volume of solution taken is supposed to represent the strength of the solution, but this method is entirely fallacious, as weak solutions are not readily decomposed even on boiling, unless the operation be continued for a very long period.

Properties.—Hydrogen peroxide in the pure condition is a colourless, odourless, and syrupy liquid, of sp.gr. 1·4532, and possesses a strong, bitter taste, resembling that of tartar emetic. It remains unfrozen at −30°C. The compound is very unstable, bubbles of oxygen being given off at about −20°C. When heated to the boiling-point of water it decomposes with explosive violence into oxygen and water. The liquid evaporates slowly *in vacuo* without the residue undergoing any change (Thenard). It bleaches organic colouring matters, but not so quickly as

[1] The reaction between peroxide of hydrogen and potassium permanganate in acid solution may be utilised for preparing oxygen gas. In this way a good stream of tolerably pure oxygen may be readily prepared. Crystals of the $KMnO_4$ should be placed in a Woulff's bottle containing 1 : 9 sulphuric acid and the 3 p.c. solution of H_2O_2 allowed to drop regularly into the solution from a suitable reservoir.

chlorine when brought in contact with the skin it produces a white blister, which, after a time, produces an irritable, itching sensation. One volume of the concentrated solution yields at 14°C. and 760 mm. pressure, 475 volumes of oxygen, the theoretical amount being 501·8 volumes (Thenard). The compound is most stable in dilute aqueous solution; when the solution is subjected to great cold, part of the water freezes out; the addition of acid has also the effect of rendering the hydrogen peroxide more stable.

Hydrogen peroxide is a remarkable oxidising agent. It converts arsenious into arsenic acid, and sulphurous acid into sulphuric acid; lead sulphide into lead sulphate; protoxide of manganese into peroxide, and protoxides of iron and cobalt into the sesquioxides. The monoxides of barium, strontium, and calcium are converted by it into their respective peroxides. The concentrated solution of hydrogen peroxide acts with violence on selenium, arsenic, molybdenum, and chromium, converting them at once into their peroxides.

In presence of certain solid substances, especially when finely divided, hydrogen dioxide undergoes violent decomposition, the substances themselves remaining unchanged. This is the case with carbon, many metals, and oxide, but gold, platinum, and particularly silver, act most violently and evolve great heat. The presence of acids retards this decomposition, while the presence of alkalis facilitates it.

Hydrogen peroxide also acts as a deoxidising agent; thus silver oxide when brought in contact with it causes a mutual decomposition of the two compounds $Ag_2O + H_2O_2 = OH_2 + O_2 + Ag_2$, an atom of oxygen is liberated from each compound, and a molecule of free oxygen is thus obtained. A similar reaction occurs when hydrogen peroxide and ozone are brought together, $H_2O_2 + O_3 = OH_2 + 2O_2$.

An acidulated solution of potassium bichromate in presence of hydrogen peroxide gives rise to an unstable combination of chromic acid and the dioxide; this, on mixing with ether, can be extracted from the aqueous solution, imparting to it a beautiful and characteristic blue colour.

Hydrogen peroxide is reduced by manganese dioxide and peroxide of lead in presence of an acid, $H_2O_2 + MnO_2 = OH_2 + MnO + O$.

Hydrogen dioxide is easily dissolved by ether, and if the aqueous solution is shaken up with ether, the hydrogen peroxide dissolves in it to some extent, forming a more stable solution than the aqueous one, and can be distilled without decomposition.

A solution of guaiacum mixed with a small amount of blood gives a blue colouration on addition of hydrogen peroxide. This is a delicate test for the compound, and serves also as a test for blood.

When hydrogen peroxide is added to a solution of potassium iodide, even in presence of ferrous sulphate or copper sulphate, iodine is set free, which may be shown by the colouration of starch. Hydrogen peroxide is the only compound known which can liberate iodine in presence of ferrous sulphate (*cf.* Traube, B. 17, 1062).

Technical applications.—Moistened lead sulphide in contact with hydrogen peroxide is quickly oxidised to lead sulphate. This fact has led to the employment of hydrogen peroxide as a *picture restorer.* The painting darkened by age or by exposure to air containing sulphuretted hydrogen, owing to the white lead employed as body colour being partially converted into lead sulphide, after careful treatment with an aqueous solution of the peroxide is found to be greatly improved in colour from the oxidation of the sulphide to the white sulphate.

Dilute solutions of hydrogen peroxide mixed occasionally with nitric acid, are also used as 'auricome,' 'golden hair water,' &c., for imparting a light colour to the hair.

Peroxide of hydrogen may be used for bleaching in many cases where other agents, as bleaching powder, sulphurous acid, chlorine, would be injurious. It is particularly valuable for bleaching ostrich feathers, bones, ivory, silk, wood, cotton, the teeth, &c.

In the case of wool, articles to be bleached are first carefully washed till free from dirt and grease in a solution of soap in water and dilute ammonia, and afterwards rinsed in water. A mixture consisting of 10 litres of the peroxide solution (3 p.c.) with 200 grams of dilute ammonia (sp.gr. 0·985) is placed in an earthenware vessel, and the cleansed wool is put in this solution, which is kept at about 20°C. for 10 hours. It is then pressed through a wringing machine and dried at a temperature of 15° to 17°C., and preferably in the sunlight. The process as described applies to wool in particular, but the same method, with slight modifications, answers for cotton goods, feathers, ivory, bone, wood, silk and hair, &c. For bleaching delicate materials it should not be too strong; a solution of 1 in 10 is strong enough, and a bleaching vat of this solution may be used for quite a long time if the strength be kept up by fresh additions of hydrogen peroxide. The purer the peroxide is the better it will work, and care should be taken to avoid the presence of things which decompose it and, of course, render it useless, such as metals—even a nail, iron rust, &c. In bleaching dead hair, it is first digested for twelve hours in a solution of 3 parts carbonate of ammonia in 100 of water at a temperature of 30°C., rinsed, then washed with soap and treated with ammonium carbonate till all fatty matter is removed. Thus prepared it is treated in a bath of hydrogen peroxide and water as in the first case.

Medicinal and surgical applications.—The use of hydrogen peroxide in medicine has been hitherto retarded owing to the difficulty of obtaining pure and cheap solutions. As an antiseptic and disinfectant it has the advantage of

(1) Being odourless; (2) Yielding oxygen without leaving any residuum but pure water; (3) Absence of injurious influence on the organism

The antiseptic properties of the solution were first discovered by Kingzett, who gave an account of his first experiments at the British Association Meeting in 1876. These observations were subsequently confirmed by the investigations of MM. Paul Bert and Regnard (C. R. 94, 1383-1386).

M. Baldy, M. Péan (of the Hospital of Saint-Louis), Professor Hofmooke, and Dr. Hasse, of Hanover, have used it in the treatment of syphilitic and scrofulous sores, alveolar abscesses, and purulent discharges. M. Landolt, of Paris, and Dr. Adams, of the London Hospital, have also used it with great success in cases of purulent discharge from the conjunctiva, while Dr. E. R. Squibb, of Brooklyn, and many others have employed the peroxide for efficiently destroying diphtheritic membranes. Its action is that of a powerful oxidising agent, but on healthy skin its action is slow, while in contact with fistulous wounds or pus it is rapidly decomposed with effervescence, which continues till the wound is cleansed or the diseased secretion is destroyed.

Sauer has made use of hydrogen peroxide in bleaching discoloured teeth. In cases where the teeth are covered with coloured matter (*Lichen dentalis*, &c.) he employs peroxide of hydrogen in conjunction with finely levigated pumice-stone as a means of cleaning, in place of water. A suitable liquid for cleansing the teeth and mouth is prepared by mixing 1 part of 3 p.c. peroxide of hydrogen with 9 parts of water (C. N. 45, 71; and Ch. Trade J. April 14, 1888).

Hydrogen peroxide has the power of freeing water from living organisms, a property which has been utilised in brewing. It also destroys in the wort the acid and mould ferments. In stronger doses it destroys the alcoholic ferment and stops fermentation (G. Reisenbichler, C. N. 56, 219).

It has been tried with success in the preservation of beer: after a month the taste and aroma of the beer remained good (Weingartner, Bied. Centr. 1884, 428).

Hydrogen peroxide is used to a considerable extent in the laboratory; thus it has been employed in the valuation of bleaching-powder, the principle depending upon the fact that hypochlorites, when mixed with hydrogen peroxide, instantly evolve all their oxygen, at the same time liberating the oxygen of the peroxide (S. C. I. 5, 391). It is also employed in estimating the amount of active oxygen in permanganate of potash and in manganese dioxide. The amount of sulphur in sulphides is also determined by first oxidising the sulphate and then proceeding as usual (G. Lunge, B. 18, 1872).

Hydrogen peroxide has been employed with success in determining the amount of sulphur in coal gas. The solution used for this purpose consists of the commercial product diluted to a 1 p.c. solution. This solution is run into the Referees' 'apparatus,' through which the coal gas passes at a measurable rate, and the sulphurous acid gas in it is oxidised to sulphuric acid $SO_2 + H_2O_2 = SO_4H_2$. The amount of sulphur is then determined by titration or precipitation (S.C.I. 5, 285).

The feature that has told most against the more extended adoption of peroxide of hydrogen both in medicine and the arts is the instability of the solution as ordinarily prepared.

Kingzett has quite recently made an extensive investigation upon this subject, and has succeeded in preparing solutions which may be kept even in the warmest weather for many months with hardly any appreciable loss of strength. An account of his observations will be found in S. C. I. for January, 1890, and the article as made by his process is now to be obtained in commerce as 'patent preserved peroxide of hydrogen.'

HYDROGEN SULPHIDES *v.* SULPHUR.

HYDROLITES *v.* AGATE.

HYDROMAGNESITE *v.* MAGNESIUM.

HYDROMETER *v.* SPECIFIC GRAVITY.

HYDROQUININE *v.* VEGETO-ALKALOIDS.

HYDROQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

HYDROTOLUQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

HYDROXY-ACIDS. *Oxy-acids.* The organic hydroxy-acids are derived from the corresponding non-hydroxylated acids by the replacement of one or more hydrogen atoms in the hydrocarbon radicle of the acid by the same number of hydroxyl groups. According as the hydroxyl group is introduced into a fatty radicle or into a benzenoid radicle, the resulting acid is an alcohol-acid or a phenol-acid.

HYDROXY-ACIDS OF THE FATTY SERIES.

Examples of hydroxy-acids of the fatty series are glycolic acid, lactic acid, malic acid, tartaric acid, and citric acid. These acids will be described under their respective headings.

HYDROXY-ACIDS OF THE BENZENE SERIES.

If the hydroxyl group is attached to the benzene nucleus of a carboxy-acid derived from benzene or its homologues, the acid thus formed is a phenol acid. Examples of this class are the three isomeric hydroxy-benzoic acids, which have the formula $C_6H_4(OH)COOH$. When these acids react with carbonates only the hydrogen of the carboxyl group is replaced by metal; but with alkaline hydroxides they behave like feeble dibasic acids, and the hydrogen of the phenolic hydroxyl is also replaced: thus in *disodium salicylate* $C_6H_4(ONa)COONa$. On the other hand in the case of carboxy-acids derived from homologues of benzene, a hydroxyl group may be introduced into a fatty lateral chain, and in such a case the resulting acid is an alcohol acid; such an acid is *mandelic acid* $C_6H_5.CHOH.COOH$. The alcoholic hydroxyl group has no acid function.

Salicylic acid, *o-Hydroxybenzoic acid* $C_6H_4(OH)COOH$ (1, 2), occurs in the blossoms of the meadow-sweet (*Spiræa ulmaria*), and as methyl ether in oil of winter-green, an essential oil obtained from *Gaultheria procumbens*, in which it occurs along with a terpene. It is formed by the fusion of salicylaldehyde with caustic potash (Piria, A. 30, 165); and, by the same process, from salicin, coumarin, indigo, *o*-cresol, and *o*-toluenesulphonic acid. By the action of nitrous acid on *o*-amidobenzoic acid. Kolbe and Lautemann (A. 115, 201) obtained it by passing carbon dioxide into a heated mixture of sodium and phenol. Kolbe afterwards found that dry sodium phenylate, prepared from phenol and caustic soda, could be substituted for the sodium and phenol in the foregoing reaction, and patented the following process, by which salicylic acid was until lately manufactured on a large scale (Ger. Pat. 436, of July 3, 1877).

Crystallised phenol is dissolved in the equivalent quantity of concentrated caustic soda, and the solution is evaporated to dryness in shallow iron vessels, stirring thoroughly to prevent charring, and finally grinding it with a heavy pestle to a dry powder. The dry sodium phenylate $C_6H_5.ONa$, which is always of a reddish-yellow colour and very hygroscopic, is heated in a metal retort at first to 100°, and a current of dry heated carbon dioxide is passed in, constantly stirring the mass. The temperature is gradually raised, so that after a lapse of several hours it rises to 180°. After the heating has been continued for some time phenol begins to distil over, at first in small quantity, afterwards more abundantly. Finally the temperature is raised to 200°, and the operation, which lasts from six to eight hours, is interrupted when no more phenol distils over at that temperature. It is necessary to keep up a rapid current of heated carbon dioxide in order that the liberated phenol may be removed as rapidly as possible from the retort, otherwise the mass cakes together, preventing further absorption. Half of the phenol originally present as phenylate distils over during the process. The reaction takes place according to the equation

$$2C_6H_5.ONa + CO_2$$
$$= C_6H_4(ONa)COONa + C_6H_5.OH.$$

Disodium salicylate (1, 2).

The greyish white mass of disodium salicylate remaining in the retort is, after cooling, dissolved in water and freed from resinous matters and coloured impurities by fractional precipitation with hydrochloric or sulphuric acid, after which the salicylic acid itself is precipitated by a further addition of the mineral acid. The salicylic acid is purified by repeated recrystallisation from water.

The reaction which occurs was first explained by R. Schmitt (J. pr. 31, 397), who showed that when carbon dioxide acts on sodium phenylate in the cold, sodium phenyl carbonate is formed

$$C_6H_5.ONa + CO_2 = CO(ONa)(OC_6H_5).$$

When this compound is heated under ordinary pressures carbon dioxide is given off and only a small quantity of salicylic acid is formed, but when it is heated under pressure to 120–140° it is converted quantitatively into the isomeric sodium salicylate

$$CO(ONa)(OC_6H_5) = C_6H_4(OH)COONa.$$

In this process the whole of the phenol is converted into salicylic acid, and it has the further advantage that, the temperature employed being lower, a purer product is at once obtained. Schmitt describes (Ger. Pat. 29,939, of June 24, 1884) three methods of carrying out the process: (1) The dry alkaline phenylate (phenylates of the alkaline earths may be substituted) is treated with carbon dioxide at ordinary temperature and pressure as long as absorption takes place, and the resulting compound is then heated in an autoclave for some hours at 120–140°. (2) Carbon dioxide is pumped under pressure into an autoclave containing the alkaline phenylate, cooling during the process, after which the autoclave is closed and left for some hours in order to allow the formation of the alkaline phenylcarbonate to be complete. It is then heated. (3) Instead of pumping in the carbon dioxide it is introduced in the form of solid carbon dioxide, and the autoclave is then quickly closed. The rest of the process is as in the preceding case (*v.* also S. C. I. 1885, 551). It has since been found, however (Ger. Pat. 38,742, of May 30, 1886; Eng. Pat. 7,801, of June 10, 1886; S. C. I. 1886, 501), that the process may be simplified by subjecting the alkaline phenylate to the action of carbon dioxide under pressure at a temperature of 120° to 140°, instead of at ordinary temperatures. These limits of temperature must not be exceeded, otherwise phenol is split off and the reaction takes place according to Kolbe's process. The alkaline phenyl-carbonate is converted, at the moment of its formation, into salicylate, thus completing the action in one stage instead of in two.

Other processes which have been patented, in which phenyl carbonate $CO(OC_6H_5)_2$ is heated with caustic alkali, or phosgene gas is made to act on sodium phenylate in presence of a slight excess of caustic soda, are not of practical importance (S. C. I. 1884, 115 and 646; 1885, 135 and 364).

Salicylic acid is formed, along with parahydroxybenzoic acid, the latter predominating, when an alkaline solution of phenol is boiled with carbon tetrachloride: $C_6H_5.ONa + 5NaOH + CCl_4 = C_6H_4(ONa)COONa + 4NaCl + 3H_2O$ (Reimer and Tiemann, B. 9, 1285).

Salicylic acid crystallises from hot water in slender needles and by spontaneous evaporation of its alcoholic solution in monoclinic prisms. Sparingly soluble in cold water (100 parts of water at 15° dissolve 0·225 part), readily in boiling water (100 parts of water at 100° dissolve 7·925 parts); soluble in 60 parts of glycerin; very soluble in alcohol and ether. Melts at 155–156° and when carefully heated sublimes without decomposition, but when quickly distilled breaks up into phenol and carbon dioxide. The same decomposition occurs when salicylic acid is heated to 140° with concentrated hydrochloric or hydriodic acid, or with dilute sulphuric acid. A dilute aqueous solution of salicylic acid gives an intense violet colouration with ferric chloride. Free acids, especially hydrochloric and acetic, interfere with this reaction. Salicylic acid (but not its metallic salts) is a powerful antiseptic.

The monobasic salicylates, of the formula $C_6H_4(OH)COOR$, are mostly soluble in water, the dibasic salicylates $C_6H_4(OR)COOR$ mostly insoluble. Sodium salicylate breaks up on heating to between 200° and 300° into phenol, carbon dioxide, and disodium salicylate: $2C_6H_4(OH)COONa = C_6H_4(ONa)COONa + C_6H_5.OH + CO_2$; whilst potassium salicylate when heated breaks up in the same way, but the residue consists of the di-potassium salt of the isomeric parahydroxybenzoic acid. In like manner, if potassium phenylate is substituted for sodium phenylate in Kolbe's method of preparing salicylic acid, a salicylate is formed up to a temperature of 150°; above that temperature a parahydroxybenzoate is formed at the same time; and at 220° nothing but the latter compound is produced (Ost, J. pr. [2] 11, 392).

Salicylic acid which is intended for use in medicine should be white and should show the proper melting-point. It should dissolve in cold concentrated sulphuric acid to form a colourless solution, and should leave no residue on ignition. Another method of testing the acid consists in dissolving the sample in absolute alcohol, allowing the solution to evaporate spontaneously and observing the points of the crystals formed: these will be colourless if the acid is pure, violet or pink if it contains iron, yellow or brown if resinous impurities are present.

In order to ascertain the presence of salicylic acid the acidified liquid (wine &c.) containing it is extracted by shaking it with chloroform, and the residue left after evaporating the chloroform is tested with ferric chloride. If tannin and other substances which give colourations with ferric chloride are also present, it is frequently necessary to remove them first. (For an account of the methods to be employed in testing for salicylic acid in *wine*, *v.* Fr. 19, 45; 23, 394; 24, 284; in *beer*, Fr. 25, 591; S. C. I. 1886, 618; 1887, 389; in *milk*, Fr. 22, 277; 23, 524; S. C. I. 1882, 30 and 467). In *urine* it may be tested for directly with ferric chloride, which first precipitates the phosphoric acid, an excess of the reagent then giving the characteristic violet colouration with the salicylic acid (Blas, Fr. 19, 105). A colorimetric method for the determination of salicylic acid by means of the ferric chloride reaction, has been devised by Rémont (C. R. 95, 786; S. C. I. 1883, 187; *v.* also Frehse, S. C. I. 1887, 148).

Salicylic acid is employed in medicine, externally for the antiseptic treatment of wounds, and internally as a febrifuge and antirheumatic, the sodium salt and some of the ethers being preferred for internal use. Its chief application is as an antiseptic for the preservation of articles of food. Its antiseptic action is analogous to that of phenol, over which it has the advantages of being tasteless, inodorous, and non-poisonous. It is also used in the preparation of *chrysamin* and similar azo-colours, as a substitute for benzoic acid in the preparation of aniline blue, and in the manufacture of ink (with ferric salts). Various ethers of salicylic acid are manufactured: thus the methyl ether (artificial oil of winter-green) which is used as a perfume, and the phenyl ether (*salol*), the β-naphthyl ether (*betol*) and the cresyl ethers, which are employed in medicine.

'*Salol*' (phenyl salicylate)

$$C_6H_4(OH)COOC_6H_5$$

was first prepared by Von Nencki by the action of the chlorides or oxychloride of phosphorus, or of sulphuryl chloride, on a mixture of salicylic acid, or a salicylate, with phenol (Ger. Pats. 38,973, of April 23, 1886, and 1622, of July 21, 1887): $2C_6H_4(OH)COOH + 2C_6H_5.OH + POCl_3$

$$= 2C_6H_4(OH)COOC_6H_5 + HPO_3 + 3HCl.$$

Eckenroth (Ger. Pat. 39,184, of August 11, 1886; Arch. Pharm. [3] 24, 928; S. C. I. 1886, 677) has shown that it may be obtained, possibly more economically, by the action of phosgene gas on a mixture of sodium salicylate and sodium phenylate: $C_6H_4(OH)COONa + C_6H_5.ONa + COCl_2 = C_6H_4(OH)COOC_6H_5 + 2NaCl + CO_2$. The product is steam-distilled and finally purified by recrystallisation from dilute alcohol. Rhombic tables, melting at 43°. Very soluble in alcohol, insoluble in water. Salol is an excellent antipyretic and antirheumatic. When taken internally it passes unaltered through the stomach, but is hydrolysed in the duodenum by the pancreatic ferment into salicylic acid and phenol. It has thus the effect of these two substances, but may be taken in large doses without producing any disturbance of the digestive functions such as is observed with salicylic acid (S. C. I. 1886, 577).

In a similar manner, by substituting in the foregoing reactions resorcinol, or α- or β-naphthol or *o*-, *m*-, or *p*-cresol, for phenol, salicylates of the corresponding radicles have been obtained. *β-Naphthyl salicylate* ('*betol*') has been employed medicinally for the same purposes as salol (S. C. I. 1889, 565).

Isomerides of salicylic acid. The two isomerides of salicylic acid—*m-hydroxybenzoic acid* $C_6H_4(OH)COOH$ (1, 3), and *p-hydroxybenzoic acid* $C_6H_4(OH)COOH$ (1, 4)—are not of practical importance. The former may be obtained by the action of nitrous acid on *m*-amidobenzoic acid, and crystallises in microscopic laminæ, melting at 200°; the latter is formed when potassium phenylate is substituted for sodium phenylate in Kolbe's process for the manufacture of salicylic acid (*v. supra*); it crystallises in monoclinic prisms containing 1 mol. of water and melts with decomposition at 210°. Neither of these acids gives any colouration with ferric chloride.

Protocatechuic acid, *Dioxybenzoic acid*

$$C_6H_3(OH)_2COOH(1, 3, 4 : COOH \text{ in } 1).$$

This acid is of interest from the number of vegetable principles from which it may be obtained and which may therefore be regarded as containing the same grouping of the substituted radicles in the benzene nucleus. It is formed by fusing with potash oil of cloves, vanillin, piperic, caffeic, ferulic, hemipic and other acids, and a large number of natural resins. Best prepared by fusing East Indian kino with caustic soda. Monoclinic needles, melting at 199°. Readily soluble in boiling, less soluble in cold water; very soluble in alcohol, less soluble in ether. Decomposes on distillation, or on heating with potash, into carbon dioxide and pyrocatechol. Gives with ferric chloride an intense bluish green colouration, which on addition of sodium carbonate changes to a deep red.

Gallic acid $C_6H_2(OH)_3COOH$ (1, 3, 4, 5:COOH in 1) occurs in sumach, dividivi, Chinese tea, and various other plants. Formed from tannin (digallic acid, *v.* following paragraph) by boiling with dilute sulphuric acid, or when solutions of tannin become mouldy. In order to prepare it, finely-powdered gall-nuts are macerated for some days with cold water, and the decanted liquid is exposed to the air and allowed to become covered with mould. An addition of yeast is advantageous. The gallic acid, which separates, is purified by recrystallisation from boiling water. Silky needles, or triclinic prisms. Soluble in 3 parts of boiling, in 130 parts of cold water. Crystallises from water with 1 mol. H_2O, which it loses at 120°. Melts at 222-240°, and when heated to a higher temperature decomposes into carbon dioxide and pyrogallol. When heated with concentrated sulphuric acid it yields *rufigallic acid* (hexahydroxyanthraquinone) $C_{14}H_2O_2(OH)_6$, and with benzoic acid and sulphuric acid it forms *anthragallol* (trihydroxyanthraquinone) $C_{14}H_5O_2(OH)_3$. With solutions of gallic acid, ferric chloride gives a blue-black precipitate, but gallic acid does not precipitate gelatine.

Digallic acid (*gallotannic acid, tannin*)

$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH$$

occurs in various plants—most abundantly in Turkish and Chinese gall-nuts. The powdered gall-nuts are extracted with a mixture of 30 vols. of ether, 1 vol. of 90 p.c. alcohol, and 4 vols. of water. The syrupy aqueous layer, which contains the tannin, is separated, shaken with twice its volume of ether (to remove impurities), and finally evaporated to dryness on the water-bath. It may be purified by dissolving it in a dilute solution of common salt (a saturated solution of common salt diluted with an equal volume of water), and re-precipitating it from the filtered solution by dissolving in it solid salt. Amorphous yellowish powder or mass, with an astringent taste. Very soluble in water, less soluble in alcohol, almost insoluble in ether. Boiling with dilute sulphuric acid hydrolyses it, yielding gallic acid

$$C_6H_2(OH)_3CO.O.C_6H_2(OH)_2COOH + H_2O$$
$$= 2C_6H_2(OH)_3COOH.$$

Ferric salts give a black precipitate of ferric tannate, the pigment of ordinary black ink. Solutions of gelatine and albumen are precipitated by tannin.

A process has been introduced by Scherer, of Berlin (Germ. Pat. 10,076, of Dec. 10, 1879), for enabling tannin to simulate a crystalline form. A solution of tannin, concentrated until it solidifies to a brittle mass on cooling, is pressed warm through sieve-like perforations in metal. It thus forms glassy threads, which, when broken into short lengths, have the appearance of crystalline needles.

Tannin is used in medicine, in dyeing, in the manufacture of ink, and in the preparation of gallic acid and pyrogallol.

By warming gallic acid with phosphoryl chloride or with an aqueous solution of arsenic acid, H. Schiff has obtained a digallic acid which he regards as identical with natural tannin (A. 170, 49; B. 12, 33; 13, 455. Compare, however, Freda, B. 11, 2033; 12, 1576).

F. R. J.

HYDROXYBENZENES *v.* PHENOL AND ITS HOMOLOGUES.

HYDROXYLAMINE or **OXYAMMONIA** NH_2OH, or $HO.H_2N—NH_2OH$. Discovered by Lossen in 1865, who obtained it by the action of nascent hydrogen (from tin and hydrochloric acid) upon ethyl nitrate. May also be prepared by the reduction of certain metallic nitrates and nitrites, and by the action of hydrogen upon nitric oxide; also by the reduction of various nitro-paraffins. For details *v.* Lossen, A. Suppl. 6, 220; Von Dumreicher, Sitz. W. 82, 560; V. Meyer, B. 15, 2789. Known only in solution. The aqueous solution is colourless and odourless, has a strong alkaline reaction, and gives precipitates, insoluble in excess, with salts of Zn, Ni, Fe, Al, Cr, but not with those of the alkaline earths. In its general reactions resembles a solution of ammonia, although it is less basic than that substance. It acts as a strong reducing agent, *e.g.* with $CuSO_4$ solution it gives a red precipitate of Cu_2O; it reduces $HgCl_2$ to HgCl, and precipitates the metals from solution of $AgNO_3$, $AuCl_3$, and $PtCl_4$. In these reactions the hydroxylamine is decomposed into N_2O and H_2O (Meyeringh, B. 10, 1940).

The salts of hydroxylamine are readily soluble in water and alcohol, and they crystallise well and are anhydrous.

Hydroxylamine may be estimated by titration with a standard solution of iodine in presence of magnesia,

$$2NH_3O + 2I_2 = N_2O + H_2O + 4HI.$$

It may also be determined by heating with a solution of ferric sulphate to 80–90°, and determining the amount of ferrous sulphate formed by a standard potassium permanganate solution

$$2Fe_2(SO_4)_3 + 2NH_3O$$
$$= 4FeSO_4 + 2H_2SO_4 + N_2O + H_2O$$

(*v.* Meyeringh, B. 10, 1940).

Schaeffe (Bl. de Mulhouse, 1883) has applied the reducing properties of hydroxylamine in order to discharge manganese brown. The hydrochloride $NH_2OH.HCl$ must be used. On printing this upon a manganese ground the latter is instantly reduced to manganese chloride. A very dark indigo, blue-dyed on manganese, is lowered to a lighter and brighter blue by the elimination of the MnO_2. In like manner nankin, chamois, and similar colours can be discharged white (S. C. I. 3, 166).

Hydroxylamine and its salts have been used as developers in photography.

HYDROXYQUINOL, HYDROXYHYDROQUINONE *v.* PHENOL AND ITS HOMOLOGUES.

HYGRINE *v.* VEGETO-ALKALOIDS.

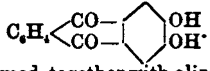
HYOSCYAMINE and **HYOSCYAMUS** *v.* DATURA; HENBANE; and VEGETO-ALKALOIDS.

HYOSEINE *v.* VEGETO-ALKALOIDS.

HYPOSULPHITES *v.* SULPHUR.

HYPOXANTHINE or **SARCINE** $C_5H_4N_4O$. A crystalline substance found in the spleen of men and oxen (Scherer, A. 73, 328), and in the bone marrow of men and oxen (Heymann). Occurs also in the muscular tissue of horses and oxen, and is formed from blood fibrin (nuclein) by the action of pancreas-ferment. Accompanies caffeine and xanthine in tea, and is contained in extract of meat. May be formed by the action of chlorine-water on carnine $C_7H_8N_4O_3$ (Weidel, A. 158, 362). For method of preparation from meat extract *v.* Neubauer, Fr. 6, 41.

HYSTAZARINE



This substance is formed, together with alizarine, when a mixture of pyrocatechol and phthalic anhydride is treated with sulphuric acid—5 grams of pyrocatechol, 6·8 grams phthalic-anhydride and 75 grams sulphuric acid are heated for 4½ to 5 hours to 140–150° on a sand bath.

The resulting product, while still warm, is poured into ¾ litre of water, heated to boiling and filtered hot.

The dark-green precipitate thus obtained is well washed with hot water, dissolved in dilute potash, and the dark-blue solution precipitated by dilute sulphuric acid. The precipitate is washed with water, dried on a porous plate, and treated with boiling alcohol in an extraction apparatus, by which means a considerable portion is dissolved.

The dark-red solution on evaporation yields an orange-red mass, which consists of alizarine and hystazarine. These two substances are readily separated by treatment with boiling benzene, which dissolves the alizarine and leaves the hystazarine; the latter may then be further purified by recrystallisation from acetone.

Yield 1½ p.c. alizarine and 12 p.c. hystazarine of pyrocatechol used.

Hystazarine crystallises from acetone in orange-yellow needles, which do not melt at 260°. It is almost insoluble in benzene, difficultly soluble in xylene, soluble in hot alcohol, ether, glacial acetic acid, and acetone.

It dissolves in alkalis with a blue (cornflower) colour, in ammonia with a violet colour, and in concentrated sulphuric acid with a blood-red colour. The barium salt is a blue precipitate, the calcium salt a violet precipitate; both are insoluble in water.

Hystazarine possesses only very feeble tinctorial properties. The faint red colour produced with an aluminium mordant differs in shade from the alizarine red. The solution of hystazarine in dilute sodium hydrate absorbs the yellowish red and violet rays of the spectrum. A very dilute solution shows two lines in the yellow $\lambda = 619{\cdot}8$, $\lambda_1 = 587{\cdot}4$. Distilled over zinc-dust, hystazarine yields large quantities of anthracene.

Diacetyl hystazarine $C_{14}H_6O_2(OC_2H_3O)_2$, crystallises from acetic acid in needles, which melt at 205–207°.

Literature. — Liebermann and Schoeller, B. 21, 2501–2505.

A dioxyanthraquinone $C_{14}H_8O_4$, of unknown constitution, but different in its properties from any of the above, has been obtained by Lifschütz, by treating dinitroanthraquinone with concentrated sulphuric acid. It crystallises from alcohol and ether in deep-red needles, which melt at 175–180°. It dissolves in alkalis and in ammonia with a reddish violet colour, and in sulphuric acid with a reddish yellow colour. When heated it sublimes readily, and at a comparatively low temperature, in orange-red plates or needles. It does not dye mordanted cloth.

The *diacetyl compound* melts at 160–165°.

Literature.—Lifschütz, B. 17, 897.

W. H. P. jun.

I

ICACIN *v.* Oleo-resins.

ICELAND SPAR *v.* Calcium.

ICE-SPAR *v.* Cryolite.

ICICA and **ICICIN** *v.* Oleo-resins.

ICOSANE $C_{20}H_{42}$. A hydrocarbon found in paraffin. M.p. 36, b.p. (under 15 mm. pressure) 205°, sp.gr. $0{\cdot}778^{37}_{4}$. Formed by the action of sodium on normal decyl iodide.

ICOSONENE *v.* Resin oil.

IDRIALIN *v.* Resins.

IDRYL *v.* Fluoranthene.

ILICIC and **ILICYLIC ALCOHOLS** *v.* Birdlime.

ILMENITE *v.* Iron; also Titanium.

IMPERIALINE $C_{35}H_{60}NO_4$. An alkaloid discovered by K. Fragner in *Fritillaria imperialis*. It is a heart-poison, and is probably closely related to the older alkaloid *Tulipine*, discovered by Gerard in *Tulipa Gesneriana*.

IMPERIAL GREEN. *Emerald Green v.* Pigments.

IMPERIAL SCARLET *v.* Azo- colouring matters.

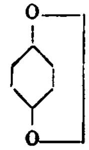
IMPERIAL YELLOW *v.* Aurantia.

INACTIVE CAMPHOR *v.* Camphors.

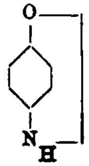
INCENSE TREE RESINS *v.* Oleo-resins.

INDAMINES and **INDOPHENOLS.**

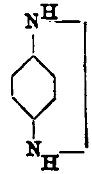
Constitution and mode of formation.—The indamines and indophenols are colouring matters which are built up on the type of benzoquinone; they are, in fact, derivatives of benzoquinonediimide and benzoquinonimide, substances which have hitherto not been prepared in a free state, but the existence of which is highly probable.



Quinone



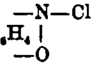
Quinonimide



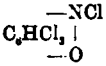
Quinonediimide

The action of gaseous ammonia upon quinone which has been studied by Woskresensky (B. 26, 801) and the action of alcoholic ammonia upon quinone, investigated by Knapp and Schultz (A. 210, 178) have failed to supply us with these interesting imido- derivatives.

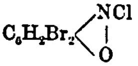
We know, however, the chlorine and bromine derivatives of quinonimide and diimide.



Quinonechlorimide $C_6H_4\begin{array}{l}-N-Cl\\ \mid\\ -O\end{array}$ has been obtained by Schmitt and Bennewitz (J. pr. [2] 8, 2). It is prepared by acting with a solution of bleaching-powder on a 25 p.c. solution of paramidophenol hydrochloride in the cold. The mixture of ingredients should be kept slightly acid (Schmitt and Andresen, J. pr. [2] 23, 435). The quinonechlorimide is extracted by ether and recrystallised from glacial acetic acid (Hirsch, B. 13, 1903). It forms yellow crystals, melting at 85°; it is slightly explosive, volatile with aqueous vapour, and resembles quinone in many of its properties.



Trichloroquinonechlorimide $C_6HCl_3\begin{array}{l}-NCl\\ \mid\\ -O\end{array}$ is prepared in the same manner from trichloramidophenol hydrochloride (Schmitt and Andresen, J. pr. [2] 23, 438; 24, 429). Yellow needles m.p. 118°, similar to quinonechlorimide.



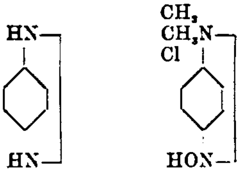
Dibromoquinonechlorimide $C_6H_2Br_2\left\langle\begin{array}{l}NCl\\ \mid\\ O\end{array}\right.$ is obtained by adding a solution of bleaching-powder to an aqueous acidulated solution of the double salt of dibromamidophenolhydrochloride and tin chloride. It settles out in flesh-coloured crystals, melting at 80° (R. Möhlau, B. 16, 2845).

Quinonedichlorodiimide is formed by acting with a solution of bleaching-powder upon a solution of paraphenylenediamine hydrochloride

(Krause. B. 12, 47). White needles, insoluble in water, soluble in alcohol, benzene, &c., and exploding at 124°.

Quinonedibromodiimide may be prepared by acting with bromine water upon paraphenylenediamine hydrochloride (Kranse, B. 12, 50). It is similar to the chlorine derivative, and explodes at 86°.

These substances are not colouring matters, as may be seen from the above description. They cannot be colouring matters, because they are indifferent, whilst every dyestuff must be either an amine or a phenol (Witt, Bau und Bildung färbender Kohlenstoffverbindungen, B. 9, 522). Their chromophoric character, however, becomes apparent in those of their derivatives which are endowed with either basic or acid properties. Nitrosodimethylamine, which may be looked upon as a substitute for the missing quinonediimide, because it is endowed with properties similar to those which this diimide should possess, has basic properties, and is an intensely coloured substance, possessing affinities for animal fibres.

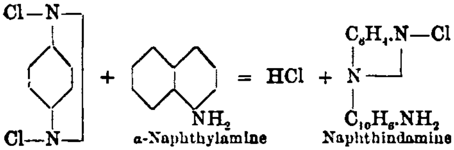

Quinonediimide (hypothetical)

Quinonedimethyl-amidoxime chloride (Nitrosodimethylaniline hydrochloride)

Owing, however, to the tendency possessed by nitrosodimethylaniline to sublime off the fibre, it cannot be used, practically, as a dyestuff.

We may, however, obtain real colouring matters, many of which have proved useful and interesting, by preparing substitution products of the quinonimides in which the substituting radicle is attached to nitrogen. Such products may be prepared by acting with amines or phenols upon quinonimides, or their equivalents, quinonamidoximes (nitroso- bases). Various cases may here be distinguished:

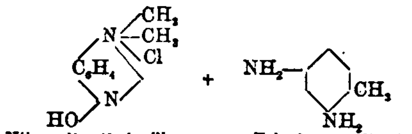
1. By acting with aromatic amines upon quinone-dichlorodiimides, indamines are formed, thus:


Dichloroquinone diimide

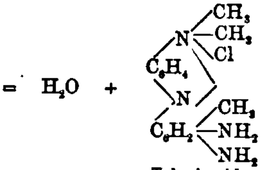
a-Naphthylamine

Naphthindamine

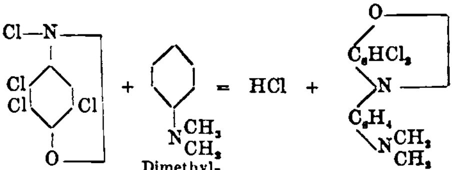
2. By acting with aromatic amines upon quinone-amidoximes (nitroso- bases) indamines are formed likewise:


Nitrosodimethylaniline

Toluylenmetadiamine


Toluylen-blue

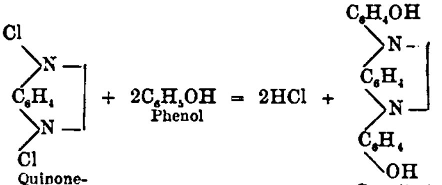
3. By acting with aromatic amines upon quinonechlorimides normal indophenols are formed:


Trichloroquinonimide

Dimethylaniline

Dimethyltrichlorobenzindophenol

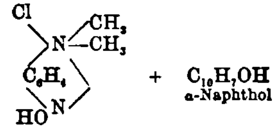
4. By acting with phenols upon quinonedichlorodiimides indophenols of a more complicated nature are formed:


Quinonedichlorodiimide

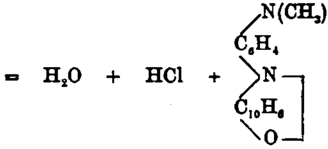
Phenol

Complicated indophenol

5. By acting with phenols upon quinonamidoximes (nitroso- bases) normal indophenols are formed:

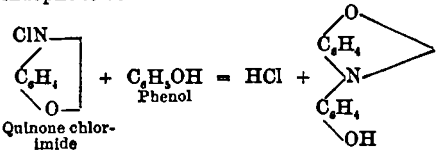

Nitrosodimethylanilinehydrochloride

a-Naphthol


Normal naphthindophenol

It will be observed that a migration takes place in this reaction, the connection between the two nitrogen atoms being severed, and a new connection between oxygen and nitrogen being established.

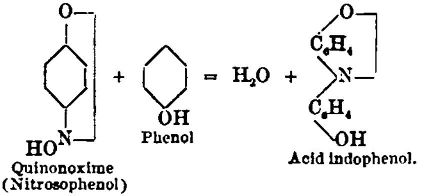
6. By acting with phenols upon quinonechlorimides colouring matters are formed, which although practically belonging to the indophenols, may be designated by the generic name of acid indophenols:


Quinone chlorimide

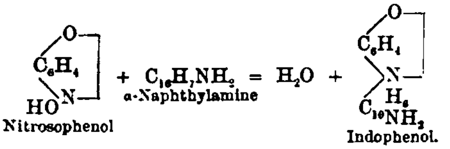
Phenol

Acid indophenol

7. The same result takes place if the equivalents of quinonimide, viz. the quinonoximes or nitrosophenols be acted upon with phenols:



8. If, however, amines be acted upon with nitrosophenols, a normal indophenol is the result:

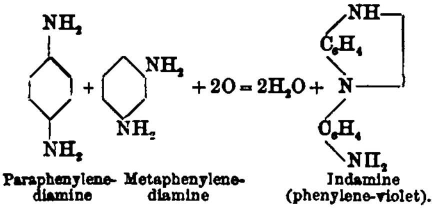


It will be noticed that all these reactions are strictly analogous to the formation of the quinone anilides and their congeners from the various quinones and aromatic bases. The discussion of these compounds will be found in another chapter.

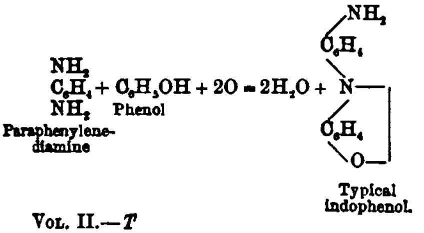
For the production of indamines and indophenols it is, however, not necessary to start from ready-formed quinonimides and diimides. It is also possible to prepare these substances by the joint oxidation of amines or phenols with compounds which are capable of producing a quinonimide or diimide.

In this process we may assume that the hypothetical quinonimides and diimides are formed as intermediate products which immediately react upon the amines or phenols present in the mixture, forming indamines or indophenols, as the case may be. Every paramidophenol or paradiamine is capable of being used for this reaction, and a large variety of colouring-matters may thus be produced. The following combinations may take place:

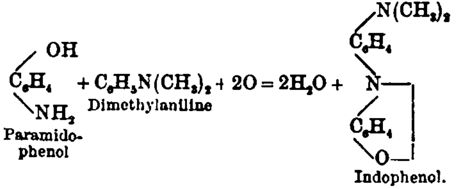
9. Paradiamines simultaneously oxidised with aromatic amines give rise to the formation of indamines.



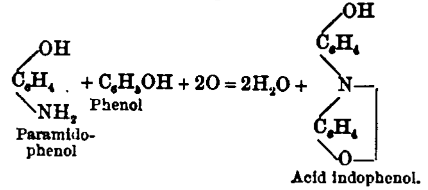
10. Paradiamines oxidised with aromatic phenols produce normal indophenols:



11. Paramidophenols oxidised with aromatic amines produce normal indophenols:



12. Paramidophenols oxidised with aromatic phenols produce acid indophenols:



From the above it will be seen that all the various colouring matters prepared by these reactions and built up on the quinone type may be subdivided into three varieties:—

a. True *indamines* containing no oxygen, and having the generic formula:

$$\begin{array}{l} R^{II}-NH \\ \vert \qquad \vert \\ N-\!-\!-\!\rfloor \\ \vert \\ R^{II}-NH_2 \end{array}$$

Amido- derivatives of substituted quinonediimides.

b. Normal indophenols, containing oxygen in their chromophoric group, being amido-derivatives of substituted quinonimides of the generic formula:

$$\begin{array}{l} R^{II}-O \\ \vert \qquad \vert \\ N-\!-\!-\!\rfloor \\ \vert \\ R^{II}.NH_2 \end{array}$$

With these the oxy- derivatives of quinonediimides are practically identical, being transformed into normal indophenols *in statu nascendi.*

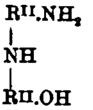
c. Acid indophenols, hydroxyl derivatives of quinonimides of the generic formula:

$$\begin{array}{l} R^{II}-O \\ \vert \qquad \vert \\ N-\!-\!-\!\rfloor \\ \vert \\ R^{II}.OH. \end{array}$$

Like all colouring matters the indamines and indophenols are capable of being reduced by the action of nascent hydrogen, of which two atoms are taken up. The connection of the chromophoric groups is severed, and colourless compounds are formed which stand in the same relation to the original dyestuff as hydroquinone stands to quinone itself:

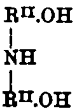
$$\begin{array}{l} R^{II}.NH_2 \\ \vert \\ NH \\ \vert \\ R^{II}.NH_2 \end{array}$$

Leucoindamine



$$\begin{array}{l} R^{II}.NH_2 \\ \vert \\ NH \\ \vert \\ R^{II}.OH \end{array}$$

Normal leucindophenol



$$\begin{array}{l} R^{II}.OH \\ \vert \\ NH \\ \vert \\ R^{II}.OH \end{array}$$

Acid leucindophenol.

It will be clearly seen that these formulæ of the leuco- derivatives are identical with the formulæ of paradiamido, amido- oxy- and paradioxy- derivatives of secondary aromatic bases. Now as the leuco- derivatives of indamines and indophenols are capable of reoxidation into the original dyestuff, it is quite apparent that we have by this means three additional methods for the production of such colouring matters:

13. Diparamido- derivatives of secondary aromatic bases may be oxidised into indamines.

14. Paramidoparoxy- derivatives of secondary aromatic bases may be oxidised into normal indophenols.

15. Diparaoxy- derivatives of secondary aromatic bases may be oxidised into acid indophenols.

The conditions under which these various reactions should be executed are stated below. (Literature on the Constitution of Indamines and Indophenols, Otto N. Witt, S. C. I. 1882, 255; R. Möhlau, B. 16, 2843; Otto N. Witt, British Association, 1887; Journ. Soc. Dy. Col. 1887; R. Nietzki, Organische Farbstoffe, 106 ff.)

History.—The first indamin observed was the intermediate product obtained in the production of saffranine, of which, however, no account was published. In 1879 Otto N. Witt prepared the first indamine in a state of purity by acting with nitrosodimethylaniline hydrochloride upon metatoluylendiamine (B. 12, 931; C. J. 1879, 1, 356). In 1881 Otto N. Witt and Horace Köchlin obtained patents for the production of normal indophenols. The production of 'acid indophenols' by the reaction of quinone chlorimide upon phenol was first mentioned by Hirsch (B. 13, 1909), and discussed by Möhlau (B. 16, 2845). The normal indophenols only have found a practical application in dyeing and calico-printing. Owing, however, to their insufficient resistance to the action of acids and to the difficulties in their application, their use has remained very restricted until quite recently, when a novel mode of their use produced a very large consumption.

Properties.—The properties of the indamines and indophenols are more uniform than those of other classes of colouring matters. It has consequently been necessary to prepare only a small number from the host of possible members of this group in order to obtain a fair notion of the properties of the whole group. With very few exceptions their shade is blue or violet; in some cases a bluish-green. The shade of the dyestuff is exhibited:

a. In the indamine group by the normal salts of the indamine bases.

b. In the group of normal indophenols by the free bases.

c. In the group of acid indophenols by the alkaline salts of the indophenol acids.

All the indamines and indophenols possess the generic character of the quinone group. They are therefore capable of acting as oxidising agents if brought together with oxidisable substances. In such reactions they take up hydrogen and are transformed into their leuco- derivatives. So considerable is their tendency to act as oxidising agents that, under suitable conditions, an indamine or indophenol will attack its own molecules, when a mixture of its oxidation products and its leuco- compounds is the result (*v. Saffranines*, art. AZINES). The conditions under which such reactions take place are, an elevated temperature and the presence of mineral acids. The indamines and indophenols are consequently unstable in the presence of acids, whilst in alkaline and neutral solution they display but little tendency to decompose. A similar decomposition is caused by the action of the violet rays of the spectrum, and this is the reason why some of these dyestuffs, especially the indamines, are rather unstable in the sunlight; the normal indophenols form, however, an exception to this rule.

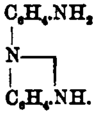
Very similar to the indamines and indophenols, as far as their constitution is concerned, are the derivatives of secondary thiobases, such as thiodiphenylamine, its homologues and congeners, known as thionine or Lauth's purple, methylene-blue, &c. As, however, the properties of these substances are vastly different from those of the indamines, they will be discussed hereafter.

The following is an account of those members of the indamine group of dyestuffs which have been more closely examined:—

I. INDAMINES.

Phenylene-blue $C_{12}H_{11}N_3$

Constitution



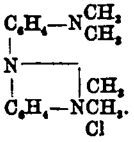
$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ N\text{——}\urcorner \\ | \qquad | \\ C_6H_4.NH. \end{array}$$

This compound is best prepared by oxidising a mixture of paraphenylendiamine and aniline hydrochloride in equal molecules in the cold, with the theoretical quantity of potassium bichromate. A greenish-blue liquid is formed, from which the iodide of phenylene-blue may be precipitated by the addition of potassium iodide solution. This salt forms long needles with a green metallic lustre. It is soluble in water with a greenish-blue colour, which turns into green on the addition of mineral acids. Acid solutions decompose very rapidly, a considerable quantity of benzoquinone being formed in this decomposition. On reduction phenylene-blue yields dipara-amidodiphenylamine, from which phenylene-blue may be regenerated by simple oxidation. Phenylene-blue is transformed into saffranine on being boiled in a neutral solution with aniline hydrochloride (*v.* SAFFRANINE).

Literature.—1. R. Nietzki, B. 16 (1883), 464; 2. R. Nietzki, Organ. Farbstoffe, Breslau, 1886, 109.

Tetramethyl derivative of Phenylene-blue. (*Dimethylphenylene green.*)

$C_{16}H_{20}N_3Cl$. Constitution



$$\begin{array}{l} C_6H_4\text{—}N{}^{CH_3}_{CH_3} \\ | \\ N\text{————} \\ | \qquad\quad |\,CH_3 \\ C_6H_4\text{—}NCH_3. \\ \qquad\quad\;\; Cl \end{array}$$

This interesting compound, which is the completely methylated derivative of the preceding one, is formed by the joint oxidation of asymmetrical dimethylparaphenylenediamine with dimethylaniline, in equal molecules, with potassium bichromate in the presence of zinc chloride (Bindschedler, B. 13, 207). The zinc double salt is at once deposited from the liquid. According to the quantity of zinc chloride present the crystals are either of a copper colour or have a metallic green lustre. These crystals are freely soluble in pure water, with a fine green colouration. Potassic iodide precipitates from this solution the methylene-green iodide $C_{16}H_{20}N_3I$ in beautiful green needles, which are easily soluble in pure water, very insoluble in the presence of an excess of potassic iodide. (*Literature*, 2.) The platinum double chloride has the composition $(C_{16}H_{20}N_3Cl)_2PtCl_4$; dimethylphenylene-green is more stable than the majority of indamines. On reduction it yields tetramethyldiamidodiphenylamine from which the green may be regenerated by oxidation.

Dimethylphenylene-green dyes silk and other fibres a yellowish shade of green. It has, however, found no application as a colouring matter, being rather unstable to light.

Its solution, on being boiled with the solution of an equal molecule of the hydrochloride of a primary amine, yields the corresponding saffranine. (Also SAFFRANINE.)

Literature.—1. Bindschedler, B. 13, 207; 2. R. Nietzki, B. 16, 464; 3. Bindschedler, B. 16, 865.

Diethylphenylene-green $C_{20}H_{28}N_3Cl$ is obtained by oxidising diethylparaphenylenediamine with diethylaniline in the presence of mercuric chloride. Very similar to the methyl derivative, but less stable.

Literature.—Bindschedler, B. 16, 867.

Homologues of phenylene-blue. These are formed by the joint oxidation of paraphenylenediamine and the homologues of aniline or of paratoluylene diamine with aniline and its homologues. They play an important part in the manufacture of the commercial saffranines, in which they are obtained as intermediate products.

Literature.—1. O. N. Witt, S. C. I. 1882, 256; 2. R. Nietzki, Organ. Farbstoffe, 110.

Witt's phenylene-violet $C_{12}H_{12}N_4.HCl$. This substance is obtained by the joint oxidation of paraphenylene diamine with metaphenylene diamine. Its aqueous solution, which exhibits a fine purple shade, is decomposed on boiling, when a corresponding diamido-azine or eurhodine is formed. Similar compounds are obtained by the joint oxidation of other paradiamines with metaphenylene diamine. This reaction is, therefore, applicable as a test for both para- and metadiamines.

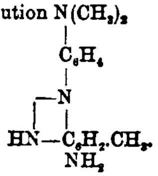
O. N. Witt, unpublished observations.

Witt's phenylene-blue $C_{14}H_{16}N_4HCl$. The dimethyl derivative of the preceding substance is formed either by the joint oxidation of dimethylparaphenylenediamine and metaphenylenediamine hydrochloride, or by mixing together lukewarm solutions of nitrosodimethylaniline hydrochloride and metaphenylene-diamine, both dissolved in glacial acetic acid. It forms bronze-coloured crystals, readily soluble in water, with a purplish-blue shade. On the addition of mineral acids unstable diacid salts of a yellowish-brown colour are formed. The aqueous solution is decomposed by prolonged boiling, yielding neutral violet, a colouring matter of the eurhodine group (*v.* SAFFRANINE).

Literature.—1. Otto N. Witt, German Patent, No. 15,272, Nov. 1880, English Patent, No. 4846, 1880; 2. Otto N. Witt, unpublished observations.

Toluylene-blue $C_{15}H_{18}N_4.HCl$

Constitution



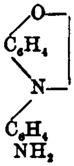
$N(CH_3)_2$ — C_6H_4 — N — $HN—C_6H_2.CH_3$, NH_2

This is the most thoroughly investigated member of the group. It is formed by the action of oxidising agents upon a mixture of dimethylparaphenylenediamine and metatoluylenediamine, or by the direct combination of nitrosodimethylaniline hydrochloride and free metatoluylenediamine. It is best prepared by the latter method. On mixing lukewarm aqueous solutions of the two ingredients in the proportion of equal molecules the blue is formed at once, and on cooling settles out in the shape of glistening bronze-coloured crystals which have the composition $C_{15}H_{18}N_4.HCl$. On adding hydrochloric acid to an aqueous solution of this compound a much more soluble diacid salt $C_{15}H_{18}N_4.2HCl$, of a reddish-brown colour, is formed. By the action of reducing agents, especially tin bichloride, the leuco- derivative of toluylene-blue, dimethyltriamidotolylphenylamine $C_{15}H_{20}N_4$ is formed. An aqueous solution of the blue is decomposed by prolonged ebullition. The products of this decomposition are leucotoluylene-blue and dimethyldiamidotoluphenazine (*Toluylene red*, *v.* AZINES).

Literature.—Otto N. Witt (B. 12, 931; C. J. 1879, 356; German Pat. No. 15,272, Nov. 1880; S. C. I. 1882, 256). R. Nietzki (B. 16, 1883, 475).

II. INDOPHENOLS.

The simplest *indophenol*, $C_{12}H_{10}N_2O$,

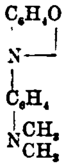


has been prepared, but it has not yet been thoroughly investigated. It is easily obtained in the shape of a violet precipitate by adding potassium ferricyanide to an alkaline mixture of paraphenylenediamine and phenol in molecular proportions. It is insoluble in water, readily soluble in alcohol, ether, and benzene. Acids dissolve it readily with a yellow colour. The solution is quickly decomposed on standing.

A very similar dyestuff of a bluer shade may be obtained by the joint oxidation of a mixture of paraphenylene diamene and xylenol in molecular proportions.

Literature.—Otto N. Witt, unpublished observations.

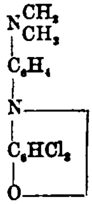
Dimethyl derivative of the above, $C_{14}H_{14}N_2O$,



is obtained like the preceding compounds from a mixture of phenol and dimethylparaphenylenediamine, or by oxidising a mixture of dimethylaniline and paramidophenol; it crystallises from alcohol in glistening green needles. Its alcoholic solution is of a brilliant greenish blue colour.

Literature.—Horace Köchlin and Otto N. Witt, Germ. Pat. No. 15,915, March, 1881. Leop. Cassella & Co. Second addition to Germ. Pat. No. 15,915.

Dimethyl-trichloroindophenol $C_{14}H_{11}Cl_3N_2O$,



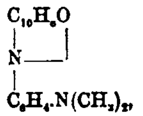
is obtained by mixing the alcoholic solutions of trichloroquinonimide (1 mol.) and dimethylaniline (2 mol.), according to the equation:

$$C_6HCl_2(NCl)O + 2C_6H_5.N(CH_3)_2 = C_{14}H_{11}Cl_3N_2O + C_6H_5N(CH_3).HCl.$$

Recrystallised from alcohol, it forms long green glistening needles, which have the general character of the indophenols and are comparatively stable. On reduction it yields the corresponding leuco- compound, dimethylamidooxytrichlorodiphenylamine, $C_{14}H_{13}Cl_3N_2O$.

Literature.—Schmitt and Andresen (J. pr. [2] 24, 435).

Indophenol of commerce, *Naphtindophenol* $C_{18}H_{16}N_2O$,



is the most important member of this group, the only one which has become a commercial dye-stuff of importance. It is prepared from an alkaline mixture of dimethyl paraphenylendiamine and α-naphthol in molecular proportions by oxidation. On a small scale potassium ferricyanide is the most convenient oxidising agent, whilst on the manufacturing scale air is pressed through the liquid, or a solution of bleaching powder is employed. It may also be prepared by adding potassium chromate to the alkaline mixture of the ingredients and acidulating with acetic acid. Another process consists in simply heating on the water-bath an alcoholic solution of free nitrosodimethylaniline and naphtholsodium; or in bringing together, in an aqueous solution, α-naphthol, nitrosodimethylaniline, and caustic soda; this mixture, is rapidly transformed into indophenol if a small quantity of a reducing agent, such as sodic stannite or glucose, be added.

Indophenol forms a dark-blue microcrystalline powder with a coppery metallic lustre, exactly resembling indigo. It is quite insoluble in water, soluble in spirit, ether, or benzene. It dissolves in dilute mineral acids, forming salts of a yellow colour, which are, however, quickly decomposed. In this decomposition α-naphthoquinone is formed as one of the products. Indophenol is slightly volatile; on being strongly heated it forms a sublimate resembling sublimed indigo. By reducing agents it is transformed into its leuco- derivative $C_{18}H_{18}N_2O$, dimethyl oxynaphthylphenylamine. This forms an article of commerce under the name of indophenol-white. It is quite stable in an acid state, but in the presence of alkalis it rapidly absorbs the oxygen of the air, indophenol being regenerated.

The application of indophenol to dyeing and calico-printing is based either on the formation of the dyestuff on the fibre, or on the oxidation of its ready formed leuco- derivative after fixing the latter on the fibre. The first class of methods is rarely employed. As an example the following description, taken from the patent specification, may serve. Bleached calico is printed with a thickened mixture of amidodimethylaniline and naphtholsodium; after drying and steaming it is passed through a solution of potassium bichromate, when the blue is instantaneously developed. As a rule ready-formed indophenol is employed for printing; it is reduced by being mixed with a solution of stannous acetate; it is then thickened with starch paste and printed on the fibre. The colour is developed by steaming and exposure to the air. Indophenol-blue on calico is very fast to the action of soap, fairly so to the action of light, and rather susceptible to acids. A new and very important use of indophenol has been discovered recently by the Swiss manufacturing firm L. Durand, Huguenin & Co. It is based on the fact that indophenol, mixed with indigo, assumes the properties of the latter. An excellent dyeing vat may be prepared with this mixture, which dyes at a much reduced cost shades which cannot be distinguished from pure indigo. The hydrosulphite process is especially applicable to this mixture.

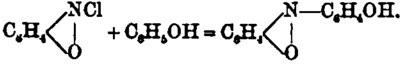
This remarkable behaviour of a mixture of indophenol and indigo is no doubt due to the fact that the leucoindophenol formed in the vat combines chemically with the reduction product of indigo. The new leuco- compound thus formed, possesses strong affinities for textile fibres, and especially cotton.

Literature.—Otto N. Witt and Horace Köchlin Germ. Patent No. 15,915, March 19, 1881, with several additions; and corresponding patents in England, France, the United States, Sweden, Belgium, and Austria. Otto N. Witt, S. C. I. 1882, 255, 144, 405. R. Möhlau, B. 16, 2845.

III. Acid Indophenols.

The colouring matters of this group are very unstable and very few of them have consequently been prepared.

Typical acid indophenol. This compound, which in all probability has the formula $C_{12}H_9NO_2$ is formed by adding caustic potash to a solution of chloroquinonimide in phenol, when a blue colouration appears instantaneously:

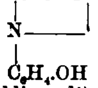


$$C_6H_4<\overset{NCl}{\underset{O}{|}} + C_6H_5OH = C_6H_4<\overset{N—C_6H_4OH.}{\underset{O}{|}}$$

It is impossible to isolate this colouring matter.

Literature.—R. Hirsch (B. 13, 1909).

The *dibromo- derivative* of the preceding compound, $C_{12}H_7Br_2NO_2$,



is obtained by adding dibromo-quinonechlorimide, suspended in alcohol, to an alkaline solution of phenol. The sodium salt of the indophenol separates out in green glistening needles, which are soluble in water and alcohol with a pure blue colour. On adding acetic acid to the solution the free indophenol settles out in dark-red, almost black prisms with a metallic lustre. It is soluble in alcohol with a magenta colour. Mineral acids decompose this compound into dibromo-amidophenol and benzoquinone. If a current of sulphurous acid gas be introduced into the solution of the sodium indophenolate, the corresponding leuco- compound $C_{12}H_9Br_2NO_2$, dioxydibromodiphenylamine, is formed. It crystallises in white glistening needles, melting at 170°.

This dibromindophenol may also be obtained by the joint oxidation of a mixture of dibromamidophenol and phenol in molecular proportions.

Literature.—R. Möhlau, B. 16, 2843.

O. N. W.

INDAZINE *v.* AZINES.

INDIA-RUBBER or **CAOUTCHOUC.** The raw india-rubber as imported into Europe is the coagulated juice of at least six different genera of trees or plants, belonging to three different natural orders, viz. Landolphia and Willughbia in *Apocynaceæ*, Castilloa and Ficus in *Artocarpaceæ*, and Hevea and Manihot in *Euphorbiaceæ*. The native countries, with the india-rubber-producing genera, are given in the following table:—

Order	Genera	Number of species	Native country
Apocynaceæ	Willughbia	9	Tropical Asia.
,,	Landolphia, including Vahea	16	Africa and Madagascar.
,,	Hancornia	1	Brazil.
,,	Urceola	7	Malay Peninsula and Archipelago.
,,	Dyera	3	Malay Peninsula.
,,	Couma (Collophora)	4	Guiana and Brazil.
,,	Alstonia	3	Malaya and Fiji.
,,	Cameraria	2	West Indies.
Artocarpaceæ	Castilloa	3	Central America and Cuba.
,,	Ficus	2	Africa and Tropical Asia.
Euphorbiaceæ	Hevea	9	Brazil, Amazon region.
,,	Manihot	1	Brazil.

Of these the Artocarpaceæ and Euphorbiaceæ furnish the best quality of caoutchouc. Owing to the largely increasing demand for india-rubber articles it is becoming a serious question how to keep up the supply of the best raw material. The British Government have caused experiments to be made in the cultivation of caoutchouc-yielding trees in Ceylon, Singapore, Madras, and in the forests of Moulmein.

The mode of the collection of the caoutchouc juice varies according to the source from which it is obtained. If the source is a *tree*, an incision is made through the bark, and the outflowing milky juice is collected in tin cups or clay cups, which, when filled, are emptied into large tin cans, and these are afterwards transported on mules to the magazine, where the juice undergoes a further treatment to be described later.

If the source of the caoutchouc is any of the climbing plants already referred to, they are cut into short lengths (about 2 feet or so), when the milky juice flows out and is collected in cans. This variety of caoutchouc juice is generally coagulated by pouring it into boiling water and stirring the mixture until the caoutchouc has become firm. A description of the *modus operandi* in collecting the juice from the *Hevea brasiliensis* will really suffice, as all the other varieties of *trees* are treated in much the same manner by the collectors.

The collector commences operations very early in the morning. He is equipped with an axe or tomahawk, a wicker basket containing a supply of soft clay, and the tin or clay cups in which he collects the outflowing juice on the trees. Having selected the tree to be tapped, he strikes the tomahawk through the bark about 6 feet from the ground, and regulates the number of incisions according to the diameter of the trunk: a tree 1 foot thick will bear six incisions round it in each row. Immediately after the incision is made a clay or tin cup is placed below the bleeding wound and supported in its place by a piece of the soft clay brought for the purpose. The collector then proceeds to other trees and treats them in the same manner, arranging his operations in such a manner that he can empty the filled vessels adhering to the trees at the end of ten hours or so. The small clay or tin vessels are emptied into a large tin collecting vessel. On the following day the collector again attacks the trees, making the incisions 8 inches below the previous ones; this operation he repeats daily until he reaches the ground. As a rule the two first rows of incisions do not furnish much good milk, it being of a watery character, but the lower rows of incisions furnish the best milk, the quality improving the lower the incision is made.

The large tin collecting vessels are now emptied into a large flat earthen vessel. A fire is lighted underneath a dome-shaped earthenware oven, supported on stones, there being a narrow opening on the top of this oven about 2 inches in diameter. A quantity of the nuts of the *Attalea* and *Euterpe edulis* are dropped down the narrow opening on to the fire below until the oven is filled within four inches of the narrow neck. Dense volumes of smoke arise, and into this the operator holds a shovel-shaped wooden tool (previously dipped in clay and then into the caoutchouc milk) until the milk solidifies and assumes a yellowish tinge, when the operator again dips the shovel into the milk and repeats the drying process, and so on until the caoutchouc attains a thickness of about 1½ inches, when it is slit up on one side and hung up to dry. A good workman can dry from 5 to 6 pounds of caoutchouc per hour. The odd scraps and fragments of caoutchouc are kneaded into balls, occasionally as large as a man's head, and come into the market under the name 'negrohead.'

The most valuable caoutchouc is that which comes from the Amazon region called Para, the negrohead-rubber being also Para, and of excellent quality. Next to these ranks Ceara rubber, from the province of Rio Janeiro, and nearly equal to it is the caoutchouc from Madagascar. Mozambique and African rubbers have an inferior character for manufacturing. The various kinds of india-rubber exported from the producing countries all have more or less a dark colour, and some, *e.g.* the African, have a disagreeable smell, due to the presence of fermentation products.

Carthagena caoutchouc comes from New Granada in sheets about three quarters of an inch thick, having a rough indurated appearance on the surface and a tarry consistency. Guayaquil caoutchouc comes in large flakes of a dark colour. African caoutchouc (Mozambique &c.) comes into the market in small balls and sausage-shaped masses. The latter are formed by rolling the caoutchouc exuding from the plants in fine threads around small sticks. Assam caoutchouc comes into the market in irregular masses, called 'loaves'; it is glossy in appearance, and of a mottled pink colour. Madagascar caoutchouc is exported in balls and lumps. The finest Para caoutchouc comes into the market in rather flat, bottle-shaped masses, showing the shape of the paddle-shaped tool upon which the milk had been dried. On cutting into the mass it is at once seen that it has been dried in layers on the tool, because the smoke has darkened the outer surface of each layer as it dried.

On cutting a piece of Para rubber it is seen that the interior is white or yellowish-white, but the surface of the rubber soon deepens in tint and eventually becomes brown. Pure caoutchouc consists of

Carbon	87·27
Hydrogen	12·73
Total	100·00

But the best 'Para rubber' it is possible to obtain always contains about 0·5 p.c. of a resinous body (soluble in alcohol, benzol, or ether) containing about 27 p.c. of oxygen. This resinous body is an oxidation product of the caoutchouc. Pure caoutchouc has a specific gravity of 0·925. It consists in reality of two gums or resins, one fibrous the other viscous, the latter being the most soluble in solvents. Consequently it is possible to separate one variety from the other by solution, providing, however, that the caoutchouc mass is not stirred up. The amount of the viscous kind varies with the quality of the caoutchouc, the percentage ranging from 30 to 70. It can be almost completely separated from the fibrous gum by repeated treatment of the caoutchouc with benzol in excess, the viscous caoutchouc only swelling up and absorbing the solvent. The peculiar smell of crude caoutchouc is due to the presence of minute traces of ethereal oils; it also contains small amounts of albuminous bodies, fatty acids such as propionic and butyric acids, and traces of wax-like resinous bodies, which are most probably the products of a partial oxidation of the caoutchouc. Masticated, washed, and dried caoutchouc is soluble in varying amounts in different solvents. From the table given below (as determined by Hanausek, C. Z.) it will be seen which are the most efficient solvents of this substance:—

Table of solubility of masticated caoutchouc in solvents.

Kind of caoutchouc	Ceara	Negro-head	Sierra Leone
100 parts of ethyl-ether dissolve	2·6	3·6	4·5
100 „ turpentine oil „	4·5	5·0	4·6
100 „ chloroform „	3·0	3·7	3·0
100 „ petroleum benzene dissolve . .	1·5	4·5	4·0
100 „ coal-benzene dissolve . . .	4·4	5·0	4·7
100 „ carbon bisulphide dissolve . .	0·4	None	None

From these results it is evident that turpentine-oil and coal-benzene are the best solvents of caoutchouc, but for manufacturing purposes the only solvents used are coal-naphtha and light petroleum spirit, the others being either too expensive or unsuitable for the purpose.

On examining a section of caoutchouc under the microscope it appears to be full of small irregular pores which are partially in communication with each other, and it is owing to this structure that it swells up on being immersed in water, alcohol, and the various solvents given above. On being immersed in water it increases 15 p.c. in volume, in alcohol 9 p.c., and in coal-naphtha much more. Further, on account of the porous structure a caoutchouc membrane allows gases to pass through it in varying amounts. Graham gives the following numbers showing the relative rate of osmotic action, viz.:

Carbon dioxide	1·0
Hydrogen	2·4
Oxygen	5·3
Methan	6·3
Air	11·8
Carbon monoxide	12·2

Graham found, however, that oxygen passes through a caoutchouc membrane much more rapidly than nitrogen does, for on dialysing atmospheric air he found that the air which had passed through contained 42 parts of oxygen and 58 parts of nitrogen.

Caoutchouc is gradually oxidised in moist air, especially in presence of light. Spiller showed that a shellac-like body is produced having the composition, viz.:

Carbon . . .	64 to 67 p.c.
Hydrogen . . .	8·4 to 9 „
Oxygen . . .	27·6 to 24 „

(Spiller, J. pr. 94, 502).

It will be shown further on that *vulcanised* caoutchouc also is very liable to the same decomposition by oxidation. On warming caoutchouc it becomes gradually softer and more elastic, but on cooling to the original temperature it regains its hardness and is less elastic. If it is heated to 120°C. caoutchouc commences to melt and decomposes completely into a black, sticky, viscous substance which does not harden for years. On increasing the temperature to 200°C., the decomposition is complete and the viscous mass never again becomes hard or even dry. This product makes an excellent 'soft lute' on being mixed with half its weight of dry calcium hydroxide. Glass vessels can be closed by means of a glass plate placed upon them and the covering rendered absolutely air-tight by means of this 'lute.'

Caoutchouc is resolved into volatile bodies of an oily nature on being submitted to careful dry distillation, the oil thus obtained in its *crude* state being called caoutchoucin. It is an excellent solvent of caoutchouc and other resins, and consists of the following bodies—viz. *tetrylene* (C_4H_8) a volatile body which boils at 0°C. and does not solidify by cold (Bouchardat, J. Ph. 23, 457); *caoutchene* isomeric with tetrylene, boiling at 14·5°C. and crystallising in needles at −15°C., which melts at −10°C.; *caoutchin* ($C_{10}H_{16}$) an oil which distils over between 160° and 180°C. On rectifying this last oil, pure caoutchin, a transparent, colourless mobile liquid, smelling like oil of citron, is obtained, boiling constantly at 175·5°C. (Greville Williams, Pr. 10, 517; Himley, A. 27, 41) and not solidifying at −39°C. On placing a drop of this substance on paper, and allowing it to evaporate, a greasy spot is left behind on the paper. Caoutchin dissolves in 2,000 parts of water, and easily in alcohol and ether. Oxygen gas is absorbed by it rapidly in large amount, a resinous body being the product of its action. Caoutchin is also converted into a resinous body by most oxidising substances. With chlorine, bromine, and iodine it forms substitution products. By the alternate action of bromine and sodium upon caoutchin, two atoms of hydrogen are eliminated and cymene ($C_{10}H_{14}$) obtained. Strong sulphuric acid acts upon caoutchin, producing a sulpho- compound $C_{10}H_{15}SO_3$.

The last product of the dry distillation of caoutchouc in the above-mentioned oil is *heveene*, a clear yellow oil belonging to the camphene group, boiling at 315°C. and not solidifying at the lowest temperatures.

Gladstone (C. J. 1886, 618) found the specific refractive energy of caoutchin to be 0·554 and the specific dispersive energy to be 0·0366, whence he is inclined to think that caoutchin is a *citrene*. On dissolving some good white caoutchouc in chloroform and fractionally precipitating out the dissolved substance with alcohol, he obtained a body which dissolved in benzene and exhibited a specific refractive energy of about 0·55 and a specific dispersive energy of 0·037. From these results he considered that the dissolved body contained two pairs of doubly-linked carbon atoms. He further compared some specimens of pentine derived by heat from turpentine, with isoprene (polymeric with caoutchin) derived from caoutchouc by dry distillation, both having the formula C_5H_8. The optical properties of these bodies were identical, viz.:

	Specific refractive energy	Specific dispersive energy
Pentine . . .	0·5922	0·0479
Isoprene . .	0·5922	0·0460

Whence the author concludes that four of the five carbon atoms are doubly linked and caoutchouc is allied to the aromatic hydrocarbons.

The use of caoutchouc as an article of commerce of *general* utility does not date further back than 1823, but Herrera mentions in his description of the second voyage of Columbus, that the Indians used the gum of a tree for the manufacture of balls 'which were elastic and better than the wind balls of Castile.' Again, Juan de Torquemada in 1615, in his work De la Monarquia Indiana, mentions the same fact and describes how the natives obtain the gum from the trees (which, by the by, was identical with the method used to-day), and also says 'the Spaniards used it for waxing their cloaks, which were made of canvas, so as to make them resist water, and in truth it is of great effect in resisting water, but not so the sun, for the rays thereof melt it.'

It was not until near the commencement of the present century that any use was made of caoutchouc in England or elsewhere in Europe. A patent was granted to Samuel Peal in 1791 for the application of caoutchouc to waterproofing cloth, &c., the hot gum being spread upon the goods by means of a brush. This is the first European application of caoutchouc to waterproofing. The next step was taken by John Clark in 1813, by discovering that turpentine dissolved caoutchouc. He applied this solution to the manufacture of air-beds. Several patents were taken out by Thomas Hancock about 1820 for various applications of caoutchouc, but the first real commencement of the manufacture of this substance dates from the summer of 1820, when Hancock invented and privately used his 'masticator' or 'pickle,' a machine designed to work up odd scraps of waste caoutchouc or irregular fragments of imported caoutchouc, and convert them into a homogeneous solid mass. This machine as now used is described under the heading 'Fine cut sheet and surgical rubber' (fig. 12). The next step in the development of this manufacture was the discovery made by Charles Macintosh, of Manchester, in 1823, that india-rubber was soluble in coal-naphtha. He applied the solution thus obtained to the waterproofing of cloth, and originated the waterproof garments which are still named after him. It was subsequently discovered that the solution of caoutchouc in coal-naphtha was rendered more easy of accomplishment by a previous mastication of the caoutchouc in Hancock's 'masticator.'

There then followed two most important inventions by Hancock, viz., the 'spreading-machine' in 1837, and the 'process of vulcanisation' in 1843. The use of the 'spreading-machine' (figs. 4 and 4*a*) is described further on. It is well known that ordinary pure caoutchouc which has not been submitted to the vulcanising process is affected by cold and heat, becoming hard and inelastic by the action of cold, and viscous and sticky by the action of considerable heat. The first discovery of the remarkable change effected by the action of sulphur upon caoutchouc (in conjunction with a considerable heat), was accidentally made by Charles Goodyear of Newhaven, U.S.A., but Hancock was unacquainted with that fact, and can undoubtedly claim to have made the discovery a practical success. Vulcanisation in all probability consists in the alteration of the caoutchouc resin through the production in it of a 'sulpho- compound,' a certain amount of hydrogen in the caoutchouc being replaced by sulphur. The 'sulpho- compound' is absolutely insoluble in all the solvents of caoutchouc, and up to the present time has not been isolated. Vulcanisation, as discovered by Hancock, was produced by mixing different quantities of 'flowers of sulphur' with the caoutchouc dough, and submitting the mixture to a temperature of 138°C. (280°F.) for some time. By this treatment caoutchouc is vulcanised, being rendered almost insoluble in solvents of caoutchouc, and much more elastic, neither reasonably increased heat nor increased cold affecting it in the least. Since Hancock's discovery many improvements have been made in the process, the most scientific and useful being that of Mr. Alexander Parkes, in 1846, now known as the 'cold-curing process.' It simply consists in the immersion of the caoutchouc articles in a solution made by mixing 1 part of chloride of sulphur with 60 parts of carbon bisulphide, no heat being applied to the articles during vulcanisation. The action of this mixture is exceedingly simple and effectual. The carbon bisulphide softens or swells out the caoutchouc surface, thus enabling the chloride of sulphur to perform its function, viz. the elimination of a certain amount of hydrogen in the caoutchouc and its combination with its equivalent of chlorine (from the chloride of sulphur), forming hydrochloric acid, and the replacement of the eliminated hydrogen by its equivalent of sulphur (from the chloride of sulphur). As a rule goods which are vulcanised by this process are only vulcanised on the surface and are slightly inelastic on being exposed to great changes of temperature. It has been found advisable in some manufactures to use certain metallic sulphides containing a varying excess of free sulphur in the vulcanising process, such as thiosulphate of lead (commonly called hypo) PbS_2O_3 and pentasulphide of antimony ('orange antimony' or golden antimony) Sb_2S_5. The first-named compound is used in black goods, whilst the latter is always used in the coloured india-rubber articles, but neither of these compounds can be used for the production of vulcanisation unless the goods are 'steam-vulcanised,' that is subjected to the action of heat produced by the presence of steam or dry heat at a temperature of from 137°C. to 204°C. (280°–400°F.) in a space surrounding the chamber containing the goods. It is also impossible to produce effectual vulcanisation with these sulphides in the absence of free sulphur.

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Having now described the elementary principles of the india-rubber manufacture from their inception at the commencement of this century to the present period, we will follow the treatment the material undergoes from its arrival in the works through all its stages of manufacture into articles of commerce.

The raw caoutchouc, as bought by the manufacturer, always contains more or less foreign matters, which must be eliminated before it can be used for manufacturing purposes. Some qualities of raw caoutchouc are very dirty, for instance, in the so-called 'African-rubber;' the impurities often consist of clay, stones, fragments of woody-fibre, resinous substances, albuminous bodies, fatty acids, &c. All raw caoutchouc contains albuminous and resinous bodies, but good samples do not contain any of the other impurities mentioned above.

To get rid of these impurities the raw caoutchouc is placed in a large wooden or iron tank containing water, and boiled for some time. This process softens the lumps, opens up the material, and dissolves out a good deal of impurity, but a large amount of impurity still remains, therefore mechanical means are applied to assist the washing out of these matters. The boiled rubber is taken out in lumps and passed through the machine called 'the washing-rollers' (fig. 1). The rollers B B, as will be seen from the engraving, are fluted, they run at equal speeds and are set close to each other, and are driven by straps running on the pulleys A A. A stream of water is kept running upon the rubber the whole time it is passing between the rollers. The lumps on passing through these rollers are squeezed together and become a rough, corrugated sheet. This sheet is passed through many times until considered sufficiently washed, it is then taken to a stoving-room to dry. Good washed sheet is simply hung upon lines or wooden bars in the chamber to dry, but sheets

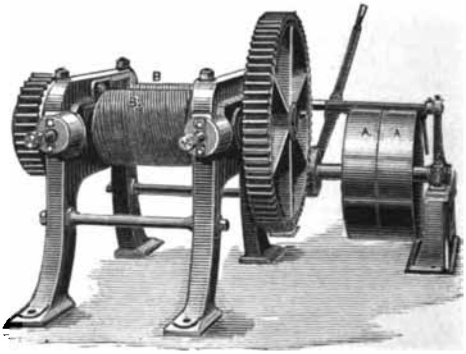

Fig. 1.

made from common 'African-rubber' become so soft and sticky by the action of the heat, that they have to be placed separately upon boards or racks to support them, otherwise they would relapse into lumps again. Having now dried the washed rubber sheet it is ready for being manufactured, but its subsequent treatment varies considerably, according to the class of goods into which it has to be made.

If the caoutchouc is going to be manufactured into 'surgical rubber' or 'fine-cut sheet' it undergoes a treatment in the 'masticator;' on the other hand, if it is going to be manufactured into any other articles, it is put through the 'mixing rollers.' As the latter class of goods are of more importance than the 'surgical-rubber' or 'fine-cut sheet' it will be more convenient to consider their manufacture first. Fig. 2 shows a 'mixing machine.' There are two rollers in the machine working at different speeds so that there is a sort of grinding effect produced. A tray or box is placed upon the bars *c c* to catch the sheet as it passes through the rollers A and also any of the dry ingredients which may fall through during the mixing process. B is a bar or backing of metal or wood placed behind the rollers A to prevent the loss of the ingredients to be mixed with the caoutchouc.

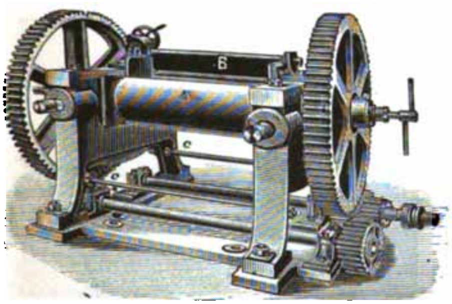

FIG. 2.

We will suppose that the manufacturer wishes to spread the mixed and compounded rubber on to cloths, and that the 'spread cloth' is to be 'steam cured,' or vulcanised by steam or dry heat. The workman takes the dry washed sheet obtained in the first process and places it between the rollers of the mixing machine *from above*. In the tray below the rollers he has the proper proportion of the mineral materials or 'compound' to be mixed with a certain weight of the india-rubber. the machine is set in motion, and handsful of the 'compound' are placed upon the india-rubber sheet as it is being drawn through the rollers. The sheet passes through the rollers below, is caught by the workman, returned to the rollers above and more 'compound' added to it, and so on until all the materials are thoroughly mixed. In the supposed case, of course, a proper amount of free sulphur or one of the sulphides mentioned above is contained in the 'compound,' which also may contain zinc oxide, calcium carbonate, steatite, litharge, ferric oxide, and lamp-black. If the sheet is to be white, then the 'compound' will contain mostly zinc oxide, and of course no lamp-black, or lead thiosulphate. Very often much heat is generated in the process of mixing, and the workman must take care not to allow it to rise too high, otherwise the 'mixing,' as it is technically called, would be spoiled. The mixed material in the form of a sheet is now taken to another pair of rollers called 'immersing rollers' and rolled out into a thinner and smoother sheet, and placed into a zinc or tin-lined box containing solvent naphtha' or some other solvent of caoutchouc. The amount of the naphtha placed into the box varies with the class of goods to be spread. If a thin varnish is to be obtained much more naphtha will be required than if the object is a thick dough. The dough-like consistency is the general rule, therefore it will be taken first. The box has a lid upon it which is kept closed during the immersion of the sheet in the solvent. The immersed sheet swells out into a bulky mass, and when it has absorbed all or nearly all the solvent, the dough is taken out of the box and placed between the 'dough-rollers' (fig. 3) which run at equal speeds (and with a very small amount of friction), the rubber dough is placed between the rollers A from above, and the machine set in motion and a tray placed again below the rollers. The mixed dough is continually scraped up by the 'doctor' or knife B. When thoroughly incorporated and made of equal consistency throughout, the dough is ready for the next process, viz. 'spreading.' This is effected by means of the spreading-machine (figs. 4 and 5). The fabric which has to be coated with the mixture is placed upon the roller A, then attached to a piece of calico or other cloth and the last-mentioned cloth carried over the roller B, under the knife or 'doctor' C, over the table K, over the roller L, until it is wrapped round the roller H. A small portion only of the fabric to be 'spread' is passed underneath the 'doctor' before commencing the process of spreading. The workman now takes the dough mixture obtained from

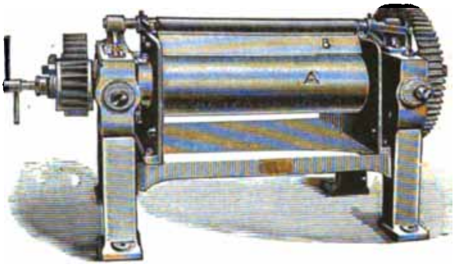

FIG. 3.

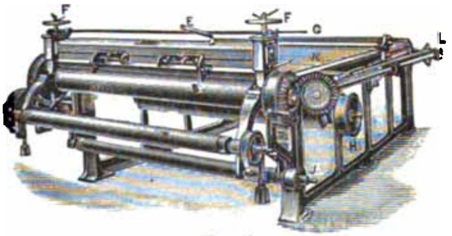

FIG. 4.

the last process and places it in a thick roll upon the fabric between the 'ears' D, resting upon the roller B and against the 'doctor.' By bringing the 'ears' closer together a narrower sheet can be coated and *vice versâ*. Everything is now ready, so the lever G is pulled and the machine set in motion. The wheels marked F are connected with the 'doctor,' which can be pressed more tightly down upon the fabric or raised higher by their manipulation. If a thinner film is required it can of course be obtained by increasing the pressure of the 'doctor' upon the cloth. As the cloth passes under the knife it draws with it upon its surface a film of caoutchouc dough. The spread cloth as it passes over the surface of the steam-heated table K has the solvent evaporated off from the dough on its surface, so that by the time it has arrived at the end of the drying table it is sufficiently dry to be rolled upon the 'taking-up roller' H having first passed over the roller L. Generally several coatings or spreadings have to be made on the fabric in order to obtain a suitable thickness, and in order to repeat the spreading all that is necessary is to replace the empty roller A by the full roller H after each spreading. The roller J in the engraving is a spare one, placed there for convenience. The spread fabric is now taken to the vulcanising chamber and heated to the required temperature to vulcanise it. If the fabric is woollen, then a lower temperature acting in a longer interval of time must be the rule, otherwise the wool would be damaged if we vulcanised in the usual time and at the usual temperature suitable to cotton or other goods. In waterproofing garments it is generally the rule to spread a dough containing more or less of the various ingredients mentioned above, *with the exception of the intermixture of sulphur or other vulcanising medium*, because in this class of goods the cold vulcanisation process is sufficient. The fabrics vary of course very much in quality according to the prevailing fashions; they are generally specially manufactured for waterproofing and are thin and flimsy in texture. If a garment has india-rubber on one side and cloth on the other, it is called a 'single texture,' if it has the india-rubber coating placed between two cloths it is called a 'double-texture.' The 'cold cure' or vulcanisation is carried out by means of a mixture of 60 parts or so of carbon bisulphide with 2 parts of chloride of sulphur, this mixture being contained in a lead-lined wooden trough. The following diagram will show the principle of the process (fig. 6).

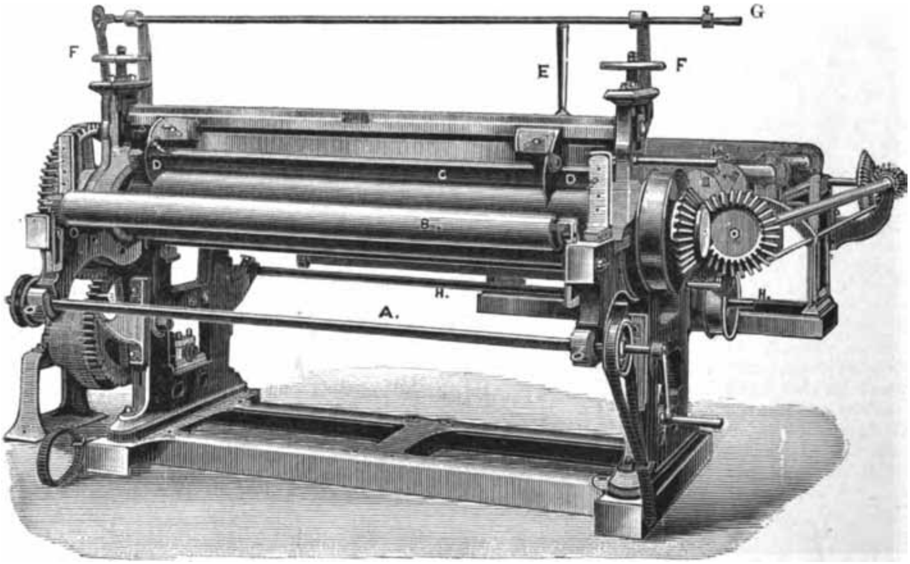

Fig. 5.

The calico tacking cloth on roller No. 1 is passed under the binding-roller *a'*, over the roller *b*, under the second binding roller *a''*, and on to the 'taking-up roller' No. 2. The roller *b* just dips into the vulcanising solution *c*, and on setting the machine into motion the spread cloth on roller No. 1 passes *with its spread surface downwards* over the roller B, by which means it becomes wet on that surface with the vulcanising solution on the roller, and by the time it arrives at the roller No. 2 it is vulcanised and sufficiently dry to roll up. The binder-rollers are placed there to keep the cloth in position and properly taut. When a 'double-texture' has to be made and vulcanised by this process, it is necessary to have the two spread cloths passing over *two* vulcanising troughs *towards each other from opposite* sides, and immediately passed through the

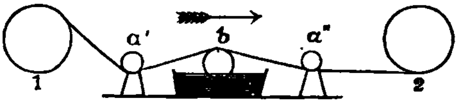

Fig. 6.

'doubling-rollers' before the vulcanisation has completely taken place. This operation will be understood from the following diagram (fig. 7).

The two sets of vulcanising plant are marked A and B respectively; they are identical with the apparatus shown in fig. 6, but the cloths after passing over the vulcanising troughs are brought on to the roller D in the manner shown, and the proofing or india-rubber mixture on their surface being still soft and sticky from the solvent action of the carbon bisulphide, and not at this stage completely vulcanised, therefore on emerging from the upper surface of roller D they are squeezed together and united, the union being rendered afterwards more complete by the vulcanisation of the india-rubber which is generally finished by the time the 'doubled' texture arrives on the 'taking-up roller' F.

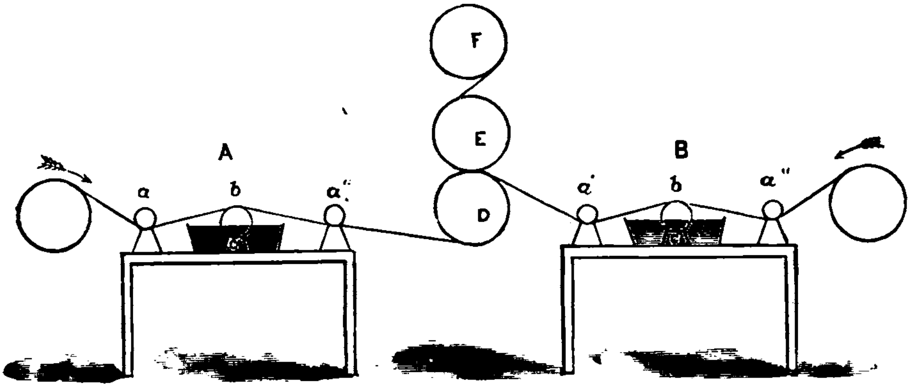

Fig. 7.

Doubling rollers are used, of course, for uniting all kinds of goods both for steam-vulcanising and cold-curing. In the first case they spread the two textures with the mixture containing the vulcanising medium, and whilst they are still slightly soft and sticky from the spreading machine are passed through the 'doubling-rollers' and united, the union being rendered permanent and complete by subsequent vulcanisation. Calendered india-rubber sheets (as described below) are doubled by the same means.

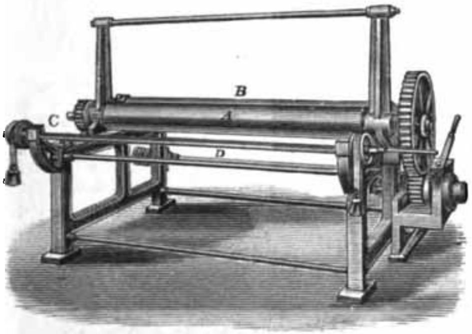

Fig. 8.

Fig. 8 represents a doubling machine by Francis Shaw. The 'doubling rollers' are marked A and B. The materials to be doubled are placed on the roller C and a corresponding roller to it on the other side of the roller B (not shown in the engraving), then passed with their rubber surfaces uppermost over the rollers A and B and between them, and the doubled fabric on emerging below is wrapped upon the 'taking-up roller' D.

Elastic Thread Manufacture.

In order to produce this the manufacturer spreads a coating or coatings of india-rubber mixture of good quality upon a roll of sized calico, or it may be spread upon cloth having a coating of vulcanised india-rubber as a foundation. The coatings of the 'thread rubber' are applied to the *sized* surface of the calico. When the required thickness of india-rubber has been spread upon the calico, the fabric is passed under rollers or brushes which distribute and rub finely divided steatite (French chalk) over the india-rubber surface in order to prevent the same adhering when separated from the sized cloth, and rolled up. The next operation is the stripping off the india-rubber sheet from the cloth. This is accomplished by running the fabric through a trough of cold water from a 'giving out roller' to a 'taking up roller,' when the size in the calico sheet softens and allows it to be separated from the india-rubber sheet by hand; thus, the roller holding the fabric is placed between two other rollers (one on each side of it), the workman then separates or lays bare a small length of the calico-sheet and the india-rubber sheet, and rolls them respectively on the outer rollers. These outer rollers have windlasses attached to them, and on turning them the calico sheet rolls upon one roller and the india-rubber on the other. The uneven outer edges of the roll of india-rubber are then cut off until quite true at both ends of the roller, then the whole is re-rolled gradually on to a large cylinder or drum in such a manner that the surface which has not been coated with steatite has a quantity of that substance applied to it (mixed with water) as it is passing to the cylinder. The workman squeezes out any air-bubbles or water which may lodge between the rolls and obtains a perfectly smooth surface all over the cylinder; if he did not the sheet would be completely spoilt in the process of vulcanisation by the expansion of the air-bubbles and water between the rolls of india-rubber. Having obtained the proper surfaces and rolled up all the sheet, he encases the whole most carefully in calico or other cloth in such a manner as to prevent all possibility of the entrance of water between the layers of india-rubber in the next process, viz., vulcanisation, which in this case is brought about in specially constructed vessels containing water which can be superheated under pressure to 280°F. (137·7°C.), into which the cylinder containing the roll of thread rubber is immersed. After the vulcanisation is complete the vulcanised rubber sheet is taken off the cylinder, washed, dried, and rolled up on another roller, from which it passes into a trough containing a rather strong solution of shellac in methylated spirit, both surfaces being wet with this solution. The wet sheet is now rolled up upon a wooden drum or roller (which is covered with a layer of unvulcanised india-rubber sheet about a quarter of an inch thick in order to preserve the edge of the thread-cutting knife from damage), when it dries and sets into a solid block. This roller is then placed into the cutting lathe and the thread cut to the gauge required and tied up in the form of hanks. The cut thread is grey owing to the excess of sulphur in it; if it is required black it is placed in a boiler and boiled with a moderately strong solution of caustic soda until it is the right colour, the excess of sulphur being thus extracted. After washing and drying, the thread is ready for sale.

Some manufacturers do not *spread* cloth for thread-making, but pass the india-rubber mixture through a calendering machine, wrapping up along with the india-rubber sheet a calico sheet in order to prevent the india-rubber surfaces adhering together. (The process of calendering india-rubber sheet is described below.) The subsequent treatment which the calendered sheet undergoes closely resembles that described above for 'spread-thread.' It is said that 'calendered thread' is sounder and better than the other, because it contains less intermixture of 'air-blebs' and is less liable, therefore, to deterioration by oxidation. Probably this opinion is correct.

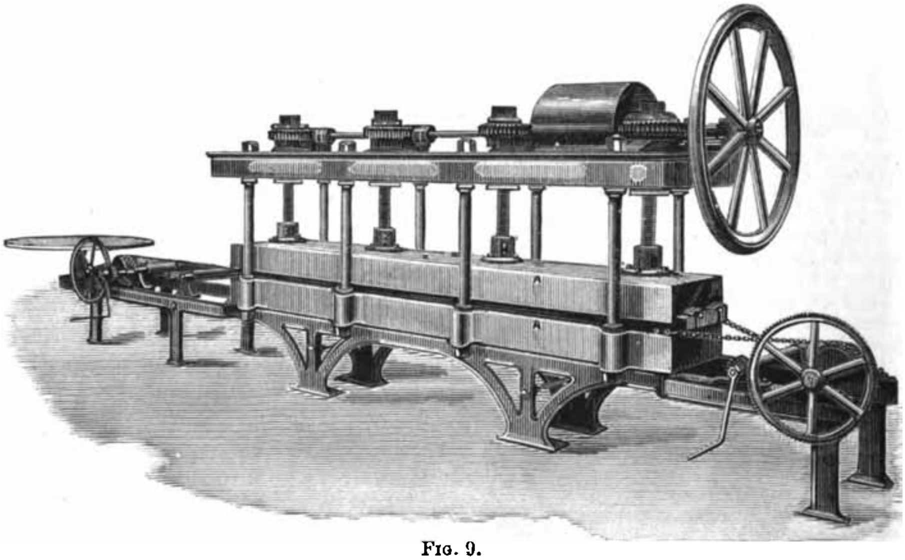

FIG. 9.

Driving-bands, straps, or belting. This manufacture is exceedingly simple. Strong canvas sheets are spread on both sides with a thin coating of india-rubber dough of a suitable quality, mixed with a proper amount of sulphur or some other vulcanising medium to produce thorough vulcanisation. The canvas sheet thus coated with india-rubber is then cut up into strips of the width required to make the strap and pressed one on the other by hand until the requisite thickness has been attained in this way. The band or strap has a thicker coating of india-rubber on the outer surface of the outer strips than the inner strips. The band is now ready for vulcanisation. This is carried out in presses, as shown in fig. 9, by Joseph Robinson & Co., Salford. The strap is placed into a trough-like receptacle or mould, seen in the engraving as a dark division between the two steam presses A. These presses have a projection on the surface adjoining the upper and lower surface of the strap, which just fits into the mould and presses the strap together. On applying the vulcanising temperature to the mould which is cast hollow for the reception of steam, the india-rubber mixture on the canvas vulcanises, and in doing so expands, but cannot increase in bulk on account of the action of the projections on the presses, consequently the whole mass becomes a solid mass of great strength.

Railway-buffers, valves, &c. As these articles must be very strong and of good quality, only very good india-rubber should be used in their manufacture, and the 'compound' or mineral matter added to the 'mixing' should not exceed a certain percentage. A good article should contain at least 65 p.c. of pure india-rubber. The india-rubber mixture is taken *whilst hot* from the 'mixing rollers' to a calendering machine. Generally enough heat is produced in the mixture by the action of the mixing process, but it is occasionally assisted by having steam passed inside the hollow rollers. The process will be better understood on examining the diagram, fig. 10.

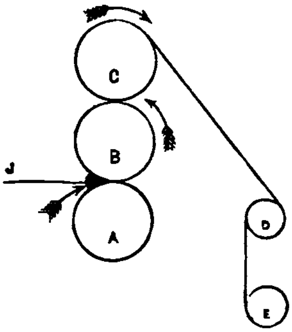

Fig. 10.

The hollow rollers of the calendering machine are marked A, B, and C. The warm india-rubber mixture from the mixing rollers is shown at the spot, marked J, on the top of roller A. On setting the machine in motion, the mixture passes through the rollers in the direction of the arrows, and arrives at the roller D. The last-mentioned roller has previously had a few laps of calico wrapped round it from a roll of that material on the roller E, and as the roller D revolves it wraps up the calendered sheet of india-rubber in a wrap of calico. Suppose a sheet of india-rubber half an inch thick and 10 feet long is required, and the first calendering produces a sheet of say ¼ of an inch thick and 20 feet long. The workman draws off the calico sheet from the india-rubber sheet, and takes the latter to the doubling rollers (fig. 8), first doubling back one half of the sheet on the other half, and then passing this doubled sheet between the rollers to squeeze the whole together into one homogeneous sheet. The resulting sheet is now 10 feet long and ½ an inch thick. In order to make a cylindrical buffer, a solid cylinder is produced from the calendered sheet by rolling up the right length of it to make a buffer of a certain size. The layers or rolls adhere together and a solid mass is obtained, but not as yet sufficiently homogeneous to be suitable for a buffer. The cylinder is therefore placed into an iron mould into which it just fits, and it is then submitted to vulcanisation and pressure in the same way as in the case of the belting described above. The resulting buffer is homogeneous, and does not exhibit the slightest trace of the rolls or layers originally there, owing to the expansion in the mould. India-rubber valves are made in a similar manner, the article being first fashioned out by the workman, and afterwards vulcanised in a mould in a vulcanising press. A good example of a vulcanising press is shown in fig. 11. Sheets are vulcanised in this press, the sheet being placed in a mould in the space between the steam-heated presses A. The upper portion of the press is then screwed down on to the sheet, and the steam turned on, when vulcanisation commences.

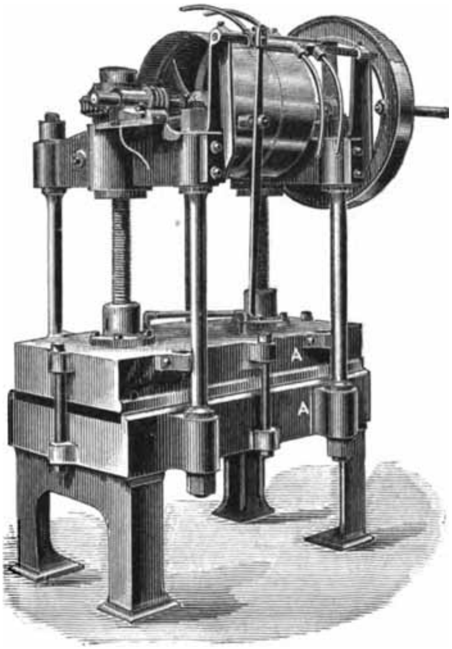

Fig. 11.

TUBING.

Tubing is manufactured by two distinct methods, viz.:

1. By squirting or squeezing through a die.

2. By joining mechanically india-rubber hollow cylinders.

1. To make tubing by the first method the india-rubber mixture containing all the necessary ingredients and the vulcanising medium is taken whilst hot or warm to the tube or cord-making machine (fig. 12) by Francis Shaw, and placed through the hopper A into the machine. The cylinder B is kept warm all the time by steam. A 'die' is placed in the nozzle C, when by the forcing action of the rod or piston D, the warm india-rubber is squeezed through the die and emerges at E, when it is rubbed over with steatite coiled upon a tray containing a layer of 2 or 3 inches of steatite, and afterwards vulcanised in a vulcanising chamber, in a *dry* heat.

India-rubber tyres for carriage wheels and bicycles, cording, &c., are also made by this machine of any length.

2. India-rubber mixture is spread upon sized cloth and stripped into sheets as described above in the manufacture of elastic thread, or else india-rubber sheet is calendered in the same manner as described, and longitudinal strips cut from the sheet thus obtained of the right width to furnish a tube of the required diameter when doubled into a cylindrical form. The cut edges of the indiarubber are bevelled, which causes the surfaces to unite better when brought into con-

tact with each other. The workman then passes the strip of sheet, doubled into cylindrical form, through a die of the proper size, and squeezes the bevelled edges of the cylinder together on its emerging from the die, thus producing a tube, which is rubbed all over with steatite, and coiled upon a tray covered with a layer of steatite, and then vulcanised as in the tubing produced by the first-mentioned process. The red-coloured tubing is manufactured by adding orange-red coloured antimony pentasulphide to the mixing; this tubing is said to be more durable than the black tubing; the durability does not depend, however, upon the *colour*, but upon the *quality* of the mixing.

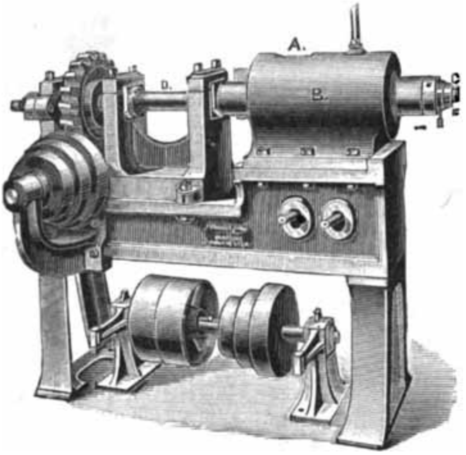

Fig. 12.

Fine-cut Sheet and Surgical India-rubber, Ebonite, etc.

This branch of india-rubber manufacture deals principally with india-rubber of first-rate quality. The india-rubber is taken from the washing rollers and passed through the masticator (fig. 13) until the mass has become thoroughly homogeneous. The action of this machine will be better understood after examining the diagram (fig. 14). The mass of india-rubber to be masticated is marked c.

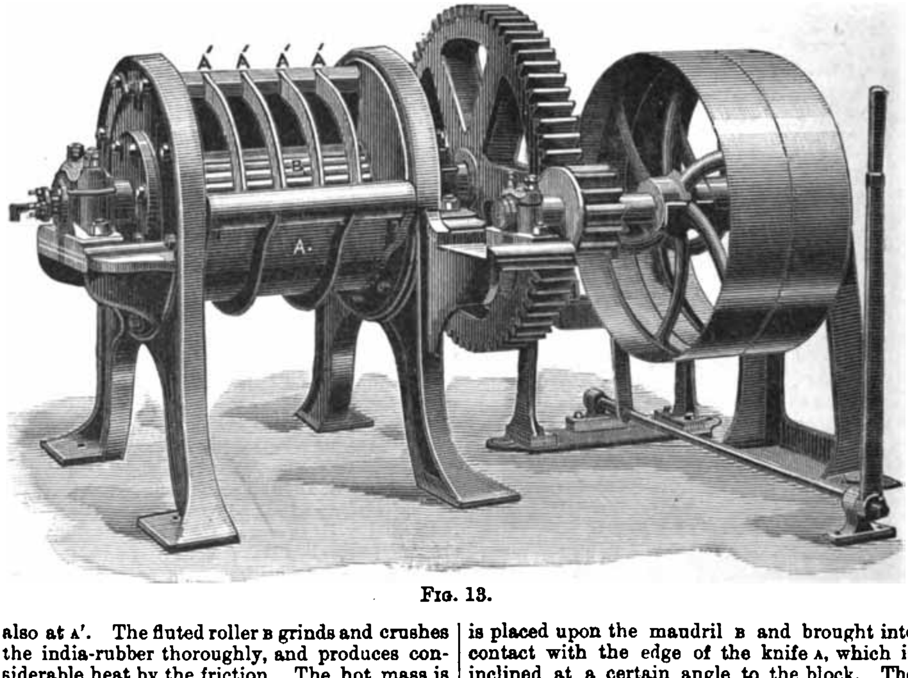

Fig. 13.

In fig. 13 the part of the machine marked A' throws back, thus enabling the workman to examine and handle the masticated india-rubber from time to time. This is shown in the diagram also at A'. The fluted roller B grinds and crushes the india-rubber thoroughly, and produces considerable heat by the friction. The hot mass is then taken at once to the block moulds (which may be either cylindrical or oblong), and pressed into the mould by hydraulic pressure, and out of the moulds again. The solid blocks thus obtained are then taken to an ice-cold chamber or frozen in some convenient manner until they have become exceedingly hard, when they are ready to be cut into sheets. This operation is carried out by means of the machine shown in fig. 15 for *cylindrical* blocks. The frozen block is placed upon the maundril B and brought into contact with the edge of the knife A, which is inclined at a certain angle to the block. The machine is then set in motion, water allowed to flow copiously over the block and knife-edge to facilitate the cutting operation and also to keep the india-rubber cool and the gauge adjusted to obtain a sheet of a certain thickness. The knife makes a great many horizontal oscillations in a minute, and as it presses continually against the block, which is slowly turned towards the knife-edge, the whole block is gradually cut into a sheet. Tobacco-pouches and similar articles are made from cut-sheet. They are vulcanised generally by the 'cold-cure process,' sometimes, however, the mass in the masticator has the requisite amount of sulphur or other vulcanising medium added to it thoroughly incorporated with it, when goods made from the sheet cut from this material are 'steam' or 'air' cured, and the excess of sulphur boiled out as in the manufacture of thread. In making tobacco-pouches, the workman cuts out the various parts and unites the edges or surfaces to be united, which being sticky, adhere afterwards together; the finished pouch is then immersed or sponged all over, inside and outside, with the cold-curing solution already described.

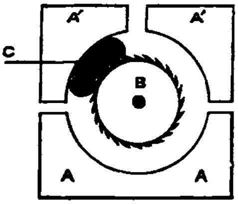

FIG. 14.

Ebonite and vulcanite. We have seen the effect of heating india-rubber with a small percentage of sulphur in the case of ordinary vulcanisation, greater elasticity of the india-rubber being the most characteristic result of such treatment. If the amount of added sulphur is largely increased, say to 25 p.c. on the weight of the india-rubber, on heating the mixture carefully to about 135°C. (275°F.) a hard black inelastic product (*ebonite*) is obtained, which resembles ebony in appearance. It can be turned into all kinds of objects, or it can be softened by heat and moulded to any required shape. If the mixture of sulphur and india-rubber has a certain amount of pigment added to it to impart a colour to it, the product is called *vulcanite* on being heated, as in the case of ebonite.

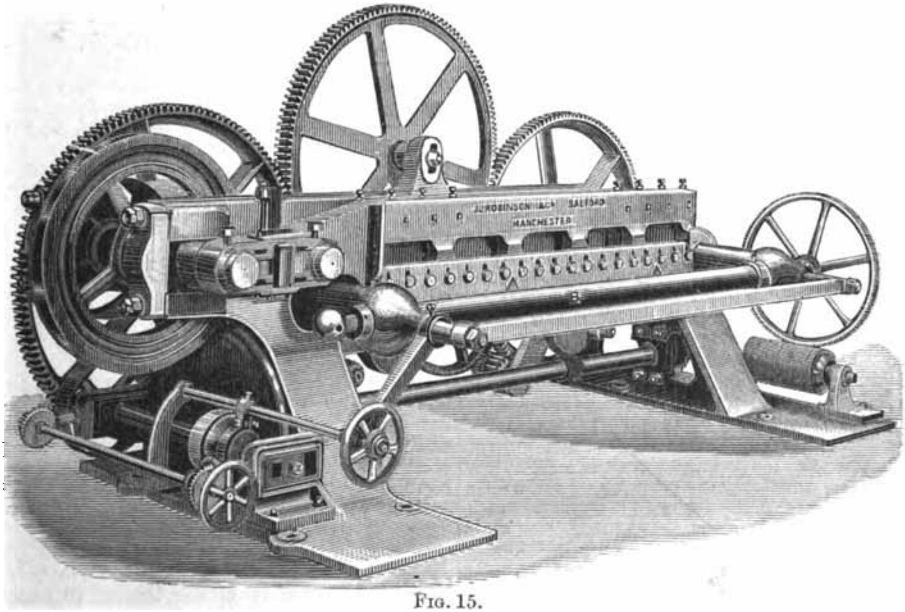

FIG. 15.

All varieties of caoutchouc are not suitable for the preparation of ebonite or vulcanite, the most suitable being those from India and Java. The raw caoutchouc is carefully washed and cleaned in the usual manner, dried, and mixed with the proper amount of sulphur by means of the mixing rollers described above. It is not desirable to add more than 30 p.c. of sulphur to the caoutchouc, as an increased amount renders the product harder and more brittle. The workman works up the caoutchouc to a soft plastic condition by means of the mixing-rollers before adding the sulphur to it; then he gradually adds to the mass pure flowers of sulphur, and works the mixture through the mixing-rollers as previously described. If he is going to make vulcanite, of course he also adds the necessary pigments to produce the required colour at this stage, and works them in. The plastic mixture now issues from the rollers in the form of a rough sheet, which is then passed through the calenders to form a smooth sheet of the required thickness, and generally cut into slabs of various sizes. These slabs, whilst still soft, are placed on a frame covered with wet canvas, and then plunged into tepid water in order to render them firmer and denser, wiped dry, and placed upon glass or pot trays which have been previously greased. They are allowed to rest in these trays for some hours, after which they are taken to the vulcanising chamber or vessel. The trays and their contents are placed upon shelves or frames constructed on a car, which runs on rails, and can be thus pushed on them into the vulcanising vessel and completely inclosed by it. The shelves upon which the trays rest are inclined at an angle of about 45°, in order to prevent the mixture from running when soft and also the accumulation of condensed water upon it. When everything is ready the vulcanising vessel is tightly closed, and steam admitted, and the proper temperature maintained until the articles are judged to be finished. Much skill is required in this part of the process, because a few degrees too much heat will seriously damage the articles, whilst a few degrees below the proper temperature will necessitate the work having to be done again.

The time required to produce ebonite in the vulcanisation or change is also dependent upon the class of articles which are to be made from it, experience alone telling the workman when to stop the process. Goods which are not properly converted, *i.e.* underdone, are soft, whereas goods which are overdone are porous, brittle, and worthless. Underdone ebonite can be converted into a good manufacture on being heated further in the vulcanising vessel. All kinds of articles can be moulded or turned out of ebonite; it is largely used in surgical instruments and also for electrical apparatus.

Note. — The machinery described in the various processes is that generally used throughout, but certain manufacturers make their own machinery in order to keep any improvements which they think they have discovered secret. One firm has a special secret machine for cutting elastic thread *in the sheet* and not in the roll by means of a lathe as described above. Some manufacturers again have secret processes and mixtures, which they consider superior to those usually adopted, but these so-called improvements generally prove to be imaginary. Unfortunately 'rule of thumb' principles are too frequently adopted in the manufacture of caoutchouc at the present time, the mechanical side being considered the most important, whilst the chemical and physical side is almost entirely neglected.

Deterioration of Manufactured India-rubber and its Causes.

Manufactured india-rubber is exceedingly susceptible to the action upon it of various damaging substances, but the final result of the action of all these bodies upon it is the same, namely *oxidation* of the india-rubber. Oxygen, therefore, is the great enemy of this substance, but it can only become really dangerous when brought into intimate contact with the india-rubber. This intimate contact can be brought about in various ways, viz.:—

(1) By the softening action upon the india-rubber surface of heavy coal-tar oils of higher boiling-point than the mixture of tolnol and xylol, which generally constitutes what is called solvent naphtha, these coal-tar oils remaining upon the spread cloth after the solvent naphtha has evaporated upon the spreading machine. Oxygen enters the material, is absorbed, and oxidises the india-rubber.

(2) A similar action is produced by various animal and vegetable oils, such as tallow oil, neats-foot oil, fish oil, palm oil, olive oil, cotton-seed oil, &c.

(3) By the action of copper oxide in conjunction with oil upon india-rubber. This destruction is common where india-rubber has been spread upon cloth which is greasy and contains oxide of copper in its fibre (derived from the dyeing process).

In all these cases of damage the india-rubber loses its elasticity more or less; when it is completely oxidised it is quite brittle. The products of this oxidation are two resinous bodies—one discovered by Spiller, and already referred to above, the other discovered by the author of this article. Spiller's resin is an acid body, forming soaps with alkalis, and soluble in alcohol, ether, chloroform, benzol, and carbon-bisulphide. The other resin is also an acid body, but it does not form soaps with alkalis, and is quite insoluble in the solvents which dissolve Spiller's resin. The following table of analyses made by the author will show conclusively *that the amount of oxygen taken up or combined with the caoutchouc is an index of the amount of deterioration which it has undergone.*

No. 1. Pure caoutchouc from Para.
No. 2. *Theoretical* vulcanised elastic thread.
No. 3. Vulcanised elastic thread, perfectly sound.
No. 4. Ditto damaged, but still elastic.
No. 5. Ditto damaged, brittle, and very hard.

——	No. 1	No. 2	No. 3	No. 4	No. 5
Carbon	87·27	87·50	77·91	72·53	64·00
Hydrogen	12·73	10·00	10·33	11·31	9·26
Sulphur	nil	2·50	5·15	1·97	2·28
Oxygen	nil	nil	6·61	14·19	24·46
	100·00	100·00	100·00	100·00	100·00

The samples Nos. 3, 4, and 5 were made at the same time, out of the same materials, and were placed under similar conditions. No. 5 closely resembles Spiller's resin in composition, but it contains both resins. Caoutchouc is supposed to combine with *not more* than 2·5 p.c. of sulphur, and this supposition appears to be confirmed by the analyses given in the table, for as the oxidation progresses the amount of sulphur decreases until only that which has actually combined with the caoutchouc remains. Most probably the uncombined sulphur has been eliminated in the form of sulphuretted hydrogen, whilst the carbon has combined with the oxygen of the air and been eliminated in the form of carbon-dioxide.

Much damage arises through the use of all kinds of substitutes for india-rubber, unless these are very skilfully prepared; but these substitutes cannot be further considered here, as they most certainly are not caoutchouc either in properties or composition.[1] C. A. B.

INDIAN FIRE is a light used in pyrotechnical displays and for purposes of signalling. It is usually composed of 7 parts of sulphur, 2 of realgar, and 24 of nitre.

INDIAN HEMP RESIN *v.* Resins.

INDIAN INK or **CHINESE INK.** This substance, used for writing or drawing, consists of lamp-black held together with animal or fish-glue and dried in the form of cakes or sticks of paint. According to Chinese writers, the invention of ink is due to one Tien-Tchen who lived between 2697 and 2597 B.C. It is said by them that at that time the ink used was a kind of lacquer; later some kind of black stone rubbed in water came into use; lastly, about 250 years B.C., balls of lamp-black from the burning of lacquer and firewood, afterwards mixed with size, became the customary material. It is probable, however, that the Chinese became acquainted with the substance from the Coreans, to whom they are indebted for other useful arts. The material used for producing the lamp-black is in most instances fir timber, although many other media, such as rice treated with a decoction of *Hibiscus mutabilis*, the bark of the pomegranate tree infused with vinegar, and rock-oil are employed. The glue or size appears at the present day to be always obtained either from oxen or fish; the points of difference between various makers being (1) the mode of its preparation; (2) the method of incorporation; and (3) the quantity relative to the amount of soot. Sometimes perfumed essences, as of musk or camphor, are added, especially in the choicest qualities. After baking, the sticks or other moulded forms are laid in a cool, dry place, and are said to improve with long keeping.

The manufacture of Indian ink is also carried on in Japan, the following description, from a native source, indicating the method followed in that country. 'The body of the ink is soot obtained from pine-wood or resin, and lamp-black from sesamum oil for the finest sort. This is mixed with liquid glue made of ox-skin. This operation is effected in a large, round, copper bowl formed of two spherical calottes placed one inch apart, so that the space between can be filled up with hot water to prevent the glue from hardening during the time it is being mixed by hand with the lamp-black. The cakes are formed in wooden moulds, and dried between paper and ashes. Camphor, or a peculiar mixture of scents which come from China, and a small quantity of carthamine (the red colouring substance of safflower) are added to the best kinds for improving the colour as well as for scenting the ink.'

M. Merimée (De la Peinture à l'Huile) asserted that the Chinese do not use an animal but a vegetable size; but apparently without warrant. For a curious monograph compiled from native Chinese sources *v.* L'Encre de Chine, son Histoire et sa Fabrication d'après documents chinois traduits par Maurice Jametel, Paris 1882.

INDIAN RED. A mineral pigment from the Persian Gulf. In appearance it is a coarse powder of a purplish-red colour.

Howe's analysis of (1) the entire mineral, and of (2) that portion soluble in hydrochloric acid, gave

	SiO_2,	Fe_2O_3,	Al_2O_3,	CaO,	MgO,	SO_3,	CO_2,	H_2O	
(1)	30·17	56·59	3·79	2·65	1·43	2·28	1·73	1·62	=100·26
(2)	—	3·19	2·22	2·65	0·87	2·28	1·73	—	=13·66

(Edin. New Phil. Jour. New Series, 2, 306.)

The portion insoluble in hydrochloric acid is a ferric silicate $Fe_2O_3.3SiO_2$. A pseudo-Indian red is composed principally of sesquioxide of iron.

INDIAN YELLOW, PIURI, PURREE, or **PIOURY,** is a pigment mainly used in India for colouring walls, doors, and lattice work, and by artists for water-colour work. On account of its disagreeable smell it is but rarely employed as a dye-stuff. It is made almost exclusively at Monghyr in Bengal, and is obtained from the urine of cows which have been fed upon mango leaves. On heating the urine, usually in an earthen pot, the colouring matter separates out; this is pressed into a ball and dried partly over a charcoal fire and finally in the sun. It sells on the spot at about 1 rupee per lb. and is mainly sent to Calcutta and Patna. One cow produces, on the average, 3·4 litres of urine per diem yielding 2 oz. (56 grams) of piuri. The yearly production is stated to be from 100 to 150 cwts., which is probably over-estimated (*v.* Journ. Soc. Arts, 1883 [5] 32, 16, and A. 254, 268).

Piuri occurs in commerce in the form of round balls, which internally are of a brilliant yellow colour, whereas the outer layers are either brown or of a dirty green colour. The substance has a characteristic urinous smell. The undecomposed part consists only of *euxanthic acid* ($C_{19}H_{18}O_{11}$) in the form of a magnesium or calcium salt; the outer and decomposed portion contains in addition *euxanthone* both free and combined. The composition of piuri seems to be variable: a fine sample, according to Graebe, contained

Euxanthic acid	51·0
Silicic acid and alumina . .	1·5
Magnesium	4·2
Calcium	3·4
Water and volatile matter . .	39·0
	99·1

MM. Lefranc et Cie. in Paris supply varying qualities of Indian yellow marked from A to G. That marked A is the best and is worth 300 frs. per kilo; C is 200 frs. and D 160 frs. whereas G is from 50 to 60 frs. The difference in the quality depends solely on the relative proportion of euxanthic acid and euxanthone:

Euxanthic acid	72·3	70·9	64·3	59·3	33–34
Euxanthone .	0·0	1·12	2·80	7·4	34
Mg . . .	5·35	4·88	4·85	4·60	3·70
Ca . . .	1·75	2·43	2·61	8·33	8·70

Euxanthic acid is easily obtained by digesting piuri of good quality with dilute hydrochloric acid and treating the residue with solution of ammonium carbonate. On the addition of

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[1] The writer is much indebted to Messrs. Joseph Robinson & Co., Manchester, Mr. Francis Shaw, Bradford, near Manchester, and Mr. Thomas Rowley, Manchester, for valuable information given in the technological portion of the above article.

hydrochloric acid to the filtered solution euxanthic acid of a pure yellow colour crystallises out. M.p. 156-158° with decomposition. It forms two series of salts $C_{19}H_{17}O_{11}M'$ and $C_{19}H_{16}O_{11}M'_2$. The magnesium salt, which is the main constituent of Indian yellow, is $C_{19}H_{16}O_{11}Mg.5H_2O$ (Graebe, A. 254, 268).

Euxanthic acid is, according to Spiegel, decomposed by hydrochloric acid into glycuronic acid and euxanthone:

$$C_{19}H_{18}O_{11} = C_{13}H_8O_4 + C_6H_{10}O_7.$$

Külz, in order to prove the animal origin of euxanthic acid, gave euxanthone to rabbits and dogs, and was able to detect euxanthic acid in the urine. Külz's experiments did not corroborate Schmid's statement that mangostin (obtained from *Garcinia mangostana*) is similarly converted into euxanthic acid by animals. (E. Külz, Zeit. für Biol. 33, 475-485; S. C. I. 6, 507.) *V.* EUXANTHONE.

Indian Yellow. Syn. for azo-yellow or azoflavin. A colouring matter obtained by Knecht by the action of nitric acid on diphenylamine orange.

INDICAN *v.* GLUCOSIDES.

INDIGO. This blue dyestuff has been known in the East Indies from the earliest times. The ancient Egyptians applied it in dyeing, but to the Romans it was only known as a pigment (*indicum*). Its employment in dyeing in Europe was very limited, until in 1516 it began to be imported from India by way of the Cape of Good Hope. The introduction and use of indigo met with great difficulties at first, in consequence of the opposition of those who cultivated its European rival the woad plant, and it was not until 1737 that its employment was legally permitted in France.

Indigo is obtainable from a large variety of plants chiefly tropical, and also in very small quantity from urine, especially that of the horse, and when it is in certain pathological conditions (Mem. Philos. Soc. Manch. 14, 239; Pr. 6, 327; P. M. [4] 14, 288). The chief indigo-yielding plants are various species of indigofera, *e.g. I. tinctoria*, *disperma*, *anil*, *argentea*, &c. which are cultivated chiefly in India, but also in China, Egypt, America, &c.

In Japan the indigo plant usually cultivated is the *Polygonum tinctorium* (Mem. Philos. Soc. Manch. [3] 6, 218). The European indigo plant, *Isatis tinctoria* or woad plant, employed from a remote period and at one time very largely cultivated, is now grown only in very limited quantity, being used as a ferment in the indigo dye-vat (woad vat).

Other indigo yielding plants are: *Nerium tinctorium*, *Asclepias tingens*, *Eupatorium tinctorium*, *Galega tinctoria*, *Marsdenia tinctoria*, *Spilanthus tinctorius*, several species of orchids *e.g. Bletia tankervillia*, *Calanthe veratrifolia*, &c.

The common indigo plant of India is *Indigofera tinctoria*, an herbaceous plant about three feet high, with pinnate leaves and purple papilionaceous flowers. Although perennial, the plant is reared from seed sown twice each year, in spring and during the rainy season, in order to obtain a larger yield of indigo. In early bloom the plant is cut down, and the colouring matter, which resides chiefly in the leaves is at once extracted. The plants are closely packed in large stone vats and well pressed down by means of heavy wooden bars. Water is run in till the plants are submerged, and they are then left to steep 9–15 hours according to the temperature of the air. Fermentation quickly ensues, and when, after the time indicated, it subsides, the yellow liquid which results is run off into vats situated at a lower level; into these men enter and agitate the liquid for 1½–3 hours by means of sticks or paddles. During this operation the colour of the liquid gradually changes; it becomes at first dark green and finally blue, the indigo being precipitated. After allowing the liquid to remain at rest for 2–3 hours, the clear supernatant water is drained off and the dark-blue pulpy sediment is run into a separate vessel. Here it is mixed with water and boiled during 4–5 hours in order to stop further fermentation, and also to remove certain useless yellow colouring matters. A second boiling for 3–4 hours with fresh water usually follows, to ensure a good product. Finally the semi-fluid mass is run on to canvas filters and there drained to the consistency of a stiff paste; this is pressed for about twelve hours in shallow wooden frames, and then cut by means of wire into the form of cubes, which are finally dried in open-air sheds, protected from direct sunlight.

So-called Madras indigo is prepared from the dried leaves instead of from those of the freshly gathered plant. After being dried in the sun the plant is thrashed to separate the leaves, and these are stored for a period of 3–4 weeks. When the leaf-powder has acquired a bluish-grey colour it is macerated with water, and the indigo is prepared according to the method described above. This difference in treatment is necessitated by reason of the large amount of certain extractive matters present in the plants grown on the Coromandel coast, which prevent the indigo from settling readily in the beating vats if the ordinary method is adopted. To facilitate the settling of the indigo precipitate it is not unusual to add lime to the vat. According to E. Alvarez the fermenting liquid obtained with the indigofera plants contains both micrococci and bacilli. The indigo fermentation, however, is really effected by a particular bacillus bearing a strong resemblance to the microbes of rhinoscleroma and pneumonia. It is noteworthy, also, that of all pathogenous microbes examined these alone are capable of producing the indigo fermentation, and further that the indigo bacillus possesses pathogenous properties.

In the so-called 'ammonia process' of indigo manufacture, recently introduced experimentally in Bhisai and Belsund, India (Journ. Soc. Chem. and Col. 2, 140), the fermented liquor is rapidly heated to 36°C., and a certain amount of ammonia and potassium nitrate is added previous to the beating process. It is even proposed to suppress the operation of fermenting and merely extract the fresh plants for a few minutes with boiling water, then add the ammonia, &c., and proceed as before. The process gives a larger yield of indigo, which, however, is only of medium quality.

There are numerous varieties of commercial indigo ranging in price from one to ten shillings per pound. From Asia come the indigos of Bengal, Oudh, Madras, Java, Manilla; from Africa those of Egypt and Senegal; and from America those of Guatemala, Caraccas, Mexico, Brazil, South Carolina, and the Antilles.

The best varieties are the Bengal, Java, and Guatemala indigos. Of these the reddish-coloured variety of Bengal indigo is preferred by dyers, while the Java indigos are esteemed for the manufacture of indigo-extract, chiefly because of their general purity, comparative freedom from extractive matter, and the absence of calcium carbonate.

A good quality of indigo has a deep violet-blue colour; it acquires a coppery lustre when rubbed with the finger-nail; it is light and porous, adhering to the tongue, and can be readily broken and ground. Low qualities which contain much extractive and mineral matter are dull and greyish in appearance, heavy, tough and hard, and do not become bronzy by rubbing with the finger-nail.

Valuation of indigos.—The chief indigo market of the world is London, where it is sold by auction at stated intervals. The buyers estimate the commercial value of the various samples by carefully observing and comparing their physical characteristics above referred to, and although by long practice and experience considerable skill in so doing is acquired, the method is very uncertain, and gives at most approximate values.

Of the numerous laboratory methods of valuation the following colorimetric, permanganate, hyposulphite, and gravimetric methods are worthy of note (Journ. Soc. Chem. and Col. 1, 74, 211).

Colorimetric method.—An intimate mixture of 1 gram of the finely ground indigo sample with 1 gram of ground glass is added with constant stirring to 20 c.c. H_2SO_4 (sp.gr. 1·845), and heated for one hour at 90°C. in an air bath. The solution thus obtained is diluted with water to 1 litre and filtered. A similar solution is made with another sample of indigo of known value. Equal measures of the two solutions are poured into the two tubes of a colorimeter, and water is then added to the deeper coloured solution until it equals the other in colour intensity. The value of the two indigos is directly proportionate to the volumes of their solutions thus obtained.

This simple method is useful when comparing indigos of similar character; if they are widely different in quality, and particularly in the amount of foreign organic matter present, it is difficult to determine exactly the point of equal colour-intensity of the solutions owing to their difference in hue, and the method becomes unreliable. It cannot be employed, therefore, to determine with accuracy the percentage of indigotin in a sample of indigo.

Permanganate method.—About 50 c.c. of the above-mentioned sulphuric acid solution of indigo diluted to 1 litre is added to about 250 c.c. water in a porcelain basin. A solution of permanganate of potash (0·5 gram per litre) is gradually added from a burette until the indigo solution acquires a pale-yellow colour free from any greenish tint.

The value of the permanganate solution should be ascertained by decolourising, in a similar manner, a solution of pure indigotin in sulphuric acid.

The results obtained by this and other oxidation methods are usually about 5 p.c. too high, owing to the presence of certain oxidisable foreign organic matters (indigo-gluten, &c.), and in low-class indigos, ferrous salts. This error is eliminated, according to C. Rawson, by purifying the indigo solution as follows. Previous to the titration with permanganate, the 50 c.c. indigo solution is mixed with 50 c.c. water and 32 grams common salt. After two hours' standing (or after half an hour if the solution is agitated, *e.g.* by a current of air), the indigotin is perfectly precipitated in the form of its sodium sulphonate compound. The precipitate is collected on a filter, washed with 50 c.c. of a strong solution of salt (sp.gr. 1·2). It is then dissolved in hot water, the solution is cooled, mixed with 1 c.c. sulphuric acid, diluted to 300 c.c., and titrated with permanganate as before. A slight correction should be made for the traces of indigotin sulphonate dissolved in the salt solution.

The permanganate method estimates the amount of indigotin and indigo-red combined.

Hyposulphite method (volumetric).—This method, proposed by A. Müller, is accurate, but it estimates only the indigotin. It consists in decolourising a sulphuric acid solution of indigo by reduction, by means of a standard solution of sodium hyposulphite (Na_2SO_2), the operation being performed in an atmosphere of coal-gas or other inert gas.

The hyposulphite solution is prepared by filling loosely a 100 c.c. flask with coils of sheet zinc, covering these with a solution of sodium bisulphite (sp.gr. 1·3), and allowing the mixture to stand for about one hour without access of air. When the liquid no longer smells of sulphur dioxide, it is decanted, mixed with 5 litres distilled water containing 50 grams slaked lime, and allowed to settle in a well-closed vessel. The clear liquid is syphoned off into a suitable store vessel and covered with a layer of petroleum oil; the vessel is so arranged that coal-gas can be admitted instead of air whenever the solution is drawn off to fill a burette, the upper portion of which must also be filled with an atmosphere of coal-gas.

The hyposulphite solution is standardised either by means of pure indigotin solution or by an ammoniacal solution of copper sulphate, to which a little indigo solution is added as an indicator. One molecule of copper sulphate is equivalent to 1 molecule of indigotin dissolved in sulphuric acid, since both are decolourised by an equal amount of hyposulphite solution. The standard copper solution is prepared by dissolving 1·904 gram $CuSO_4.5H_2O$ (equal to 1 mol. indigotin) in 1 litre water containing 100 c.c. ammonia solution (sp.gr. 0·880); of this solution 50 c.c. (*i.e.* equal to 0·05 gram indigotin) are run into a wide-mouthed flask of 200 c.c. capacity, then boiled to expel air, and cooled. The flask is fitted with a cork having four openings, one for the burette containing the indigo solution to serve as indicator, the other to receive the hyposulphite burette, and the others to allow coal-gas (previously washed with ferrous sulphate solution) to be passed through the flask during the titration. The hyposulphite is gradually run into the copper solution until the latter is nearly decolourised, a few drops of the indicator indigo solution are then added, and hyposulphite is again run in until the copper solution acquires a peculiar brownish-red colour. Previous to calculation, the amount of hyposulphite required to decolourise the few drops of indigo solution must be deducted from the total amount used.

The indigo to be estimated is dissolved in sulphuric acid as before, and the solution is decolourised with standard hyposulphite in a similar manner. When complete reduction has taken place the liquid assumes a pale-yellow or dirty brownish-yellow colour according to the quality of indigo under examination. The presence of ferric salts, which may occur in low-class indigos, is a possible source of error in this method.

Hyposulphite method (*gravimetric*).—This is a trustworthy method of valuation, introduced by C. Rawson. One gram of finely powdered indigo is ground into a paste with water, and introduced into a flask with 500-600 c.c. lime-water. The flask is furnished with a stopper having four perforations, one for the insertion of a syphon closed by a pinch-cock, another for a funnel with tap containing sodium hyposulphite, and the others for supplying a current of coal-gas. Having connected the flask with a supply of coal-gas, the mixture of indigo and lime-water is heated to 80°C., then 100-150 c.c. strong hyposulphite solution are added and the whole is maintained at 90-98°C. for half an hour. (The hyposulphite solution employed is about five times as concentrated as that described in the previous method.) After allowing insoluble matters to settle, 500 c.c. of the clear solution of reduced indigo are syphoned off and the remaining liquid is accurately measured. The reduced indigo solution withdrawn is thoroughly oxidised by a current of air, excess of hydrochloric acid is added, the precipitate is collected on a weighed filter, washed with hot water, dried, and weighed. The weight indicates indigotin and indigo-red. The latter may be estimated by dissolving it out with alcohol in an extraction apparatus, evaporating to dryness and weighing.

In addition to estimating the pure colouring matter in commercial indigo by one or other of the above methods, it is always advisable to determine the amount of moisture and mineral matter present. The former varies from 3-8 p.c., the latter (chiefly calcium and magnesium phosphates and carbonates, silica, &c.) varies from 2-50 p.c. The amount of indigotin may vary from 10-70 p.c. Indigo-red is usually present to the extent of 2-4 p.c., but in certain samples produced by the ammonia process, C. Rawson found it to amount to 20 p.c. of the total colouring matter present. Egyptian indigo is also said to be specially rich in indigo-red.

Chemical history of indigo.—By submitting commercial indigo to the successive action of boiling water, caustic alkali, and boiling alcohol, Berzelius obtained the following substances:—

Indigo-gluten, an amorphous brownish glue-like substance similar in its properties to ordinary vegetable gluten; *indigo-brown*, a brown amorphous gummy substance of a weak acid character; *indigo-red*, a body similar to indigotin in its general properties, but soluble in alcohol and ether with a purple colour. It forms with concentrated sulphuric acid a sulphonate which dyes wool and silk purple. It is capable of reduction in the same manner as indigotin, the solution dyeing cotton purple. It is less susceptible to oxidation than indigotin. In composition it is isomeric with indigotin, and it is very probably identical with indirubin and indigo-purpurin, although this is not definitely determined (A. 66, 5; Berzelius, Lehrb. 3, 385; Gmelin, 13, 48). The classic researches of Schunck have shown that the colour-giving principle which exists in the living woad plant and probably also in all indigo-yielding plants is a glucoside named *indican* ($C_{26}H_{31}NO_{17}$) (Trans. Ph. S. Manchester, 12, 177; 14, 181; P. M. (4) 10, 73; 15, 19; 117, 283). Schunck extracted dried woad leaves with ether, washed the ethereal solution with water, and by rapid evaporation of the aqueous solution at the ordinary temperature obtained the indican as a pale-brown syrup, soluble in alcohol, ether, and water, and possessing a bitter taste and an acid reaction.

If an aqueous solution of indican is boiled with dilute acids in contact with an oxidising agent, *e.g.* air, ferric chloride, &c., the indican is split up into indigotin and a peculiar sugar named *indiglucin*. At the same time there is produced a purple colouring matter (*indirubin*), also, in small quantity, leucin, and certain reddish-brown and orange coloured amorphous substances soluble in caustic alkali (*indifuscin* and *indifulvin*).

Under the influence of fermentation and oxidation, a similar decomposition of the indican takes place during the manufacture of indigo.

Indican is a very unstable substance; mere boiling or long heating of its aqueous solution suffices to alter it so that it becomes insoluble in ether, and yields, by treatment with acid, indiglucin but no indigotin, the latter being replaced by certain brown flocculent matters—viz. *indiretin* and *indihumin*. The latter is similar to and probably identical with indigo-brown. By the action of alkalis or alkaline earths at the ordinary temperature, indican yields indiglucin and *indicanin*. This substance is very similar to indican in its physical properties, but on treatment with acid it gives indiglucin and indirubin, but no indigotin. This action of alkalis on indican probably explains why indigo manufactured by the ammonia process is apt to contain more than the normal amount of indirubin or indigo-red.

Oxindicanin, is the name given to a brown gummy substance, insoluble in alcohol, obtained during the preparation of indican, and which yields, under the influence of acids, indiglucin and a brown substance similar to indifuscin.

The chief and most important products of the action of acids on indican are the colouring matters indigotin and indirubin.

Indirubin $C_{16}H_{10}N_2O_2$ is insoluble in water and alkalis, but readily soluble in alcohol with a purple colour. From alcohol and also by sublimation it may be obtained as purplish-brown lustrous needles, showing a bronze metallic lustre when rubbed. It begins to sublime at 140°C. In concentrated sulphuric acid it dissolves, giving a purple solution of indirubin-sulphonic-acid. Under the influence of reducing agents it gives a leuco- compound which dissolves in alkalis with a yellow colour. The solution is capable of dyeing cotton a purple colour fast to acids and soap. Indirubin dissolves in nitric acid with a purple colour which changes to yellow on boiling. It is not destroyed by boiling with a solution of chromic acid.

Indigotin, $C_{16}H_{10}N_2O_2$ (A. 195, 305) is the all-important colouring matter of indigo. It is obtained in the pure state by reducing commercial indigo in the manner to be subsequently described, and oxidising, by means of air, the clear decanted solution of the reduction product. The purified indigo precipitate thus obtained is crystallised from boiling aniline and washed with alcohol. Thus prepared it forms a dark-blue crystalline powder possessing a bronzy lustre. When heated it does not melt, but begins to sublime (eventually with partial decomposition) at a temperature of about 170°C., giving a purple vapour which condenses to form bronzy lustrous needles.

Indigotin is insoluble in water, ether, dilute acids, and alkalis. It dissolves slightly in boiling alcohol with a blue colour but separates out entirely on cooling. It is more soluble in phenol, chloroform, and carbon disulphide, but most readily in aniline, nitrobenzene, and high-boiling petroleum. In paraffin and certain fatty oils it dissolves with the same purple colour which it possesses in vapour form.

Submitted to dry distillation indigotin yields aniline, which was indeed first obtained in this manner by Unverdorben in 1826. Hot concentrated caustic alkalis dissolve indigotin with a yellow colour, possibly with the formation of indigo-white and isatinic acid. Melted with caustic alkali it yields orthoamidobenzoic acid (anthranilic acid) and salicylic acid (J. pr. 24, 11; 25, 434). Chlorine converts it at first into isatin chloride, but on further action it produces chloranil and chlorinated phenol. Bromine acts similarly.

Oxidising agents, *e.g.* chromic, permanganic, and nitric acids, convert indigotin into isatin (C_8H_5NO). This oxidation product only results when the action of nitric acid is sufficiently moderated; its further action yields nitrosalicylic acid (indigotic acid), and finally picric acid.

Under the influence of alkaline reducing agents indigotin takes up two atoms of hydrogen, and is thus changed into its leuco- compound *indigo-white*, which dissolves in the alkali present with a yellow colour. Such solutions at once oxidise on exposure to air with reproduction of indigotin, a fact which is utilised in the vat-method of indigo-dyeing, and also for the purpose of readily obtaining indigotin from commercial indigo. For the last-mentioned purpose one may suitably employ Fritsche's glucose-vat which is made up with 10 grams indigo, 10 grams glucose, 30 grams caustic soda, 600 c.c. alcohol (A. 44, 290). In this vat the indirubin and other matters are retained in solution by the alcohol and alkali used, so that on oxidation of the liquid fairly pure indigotin is obtained. As observed by Schunck this process may yield no indigotin, if small quantities of indigo and comparatively large quantities of alcohol, glucose, and caustic soda are employed, owing to the formation of peculiar compounds of indigotin with alcohol and acetic acid generated during the reaction. Loss of indigo may occur in a similar manner during its manufacture through over-fermentation, whereby the indican is decomposed with production of alcohol and acetic acid and the formation of similar compounds.

The hyposulphite method of reduction, already described, is also very suitable for preparing indigotin.

Indigo-white $C_{16}H_{12}N_2O_2$ is precipitated from its alkaline solutions by acids (A. 48, 257). When pure it forms a greyish-white lustrous precipitate, insoluble in water and dilute acids, but soluble in alcohol, ether, the alkalis, and alkaline earths. Its general chemical behaviour is that of a phenol.

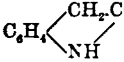
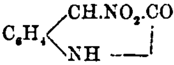
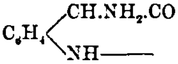
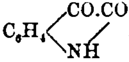
Indigotin monosulphonic acid
$C_{16}H_9(HSO_3)N_2O_2$
formerly called *sulphopurpuric acid*, is produced by the comparatively short action of sulphuric acid (sp.gr. 1·84) on indigotin at the ordinary temperature (B. J. 4, 189). On pouring the solution thus obtained into water, it is precipitated as a reddish-purple flocculent precipitate, insoluble in dilute acids but soluble in water. Its sodium salt under the name of *indigo-purple* serves for blueing bleached cotton-thread and silk in a soap bath.

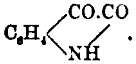
Indigotin disulphonic acid $C_{16}H_8(HSO_3)_2N_2O_2$, formerly called *sulphindigotic acid*, is produced by the action of fuming sulphuric acid on indigotin with the assistance of a gentle heat (B. J. 4, 190). The solution is diluted with water and the product is precipitated on the addition of common salt. In the form of a paste it is sold under the name of *indigo-extract*. The sodium salt is sold in a similar form as *indigo-carmine*. These products are used in large quantities in wool-dyeing. Under the influence of strong alkali these sulphonic acids give rise to yellow and red compounds which have been little studied.

Synthesis of indigotin.—In attempting to reconvert the oxidation product isatin into indigotin by reduction, Baeyer and Knop (1865–66) obtained successively dioxindol $C_8H_7NO_2$, oxindol C_8H_7NO, and, finally, indol C_8H_7N (A. 140, 29). This last product, which is to be regarded as the parent substance from which indigotin is derived, was prepared synthetically in 1869 by Baeyer and Emmerling by heating a mixture of nitrocinnamic acid, caustic potash, and iron filings (B. 2, 680). In 1870 these same chemists succeeded in producing indigotin from isatin by heating the latter with a mixture of phosphorus trichloride and acetyl chloride.

Already in 1869 (B. 2, 748) Kekulé suggested, but did not prove, that isatin might be an inner anhydride of ortho-amido-phenyl-glyoxylic acid $C_6H_4{<}\substack{CO.COOH\\NH_2}$. In 1878 Baeyer and Suida prepared oxindol synthetically from ortho-amidophenylacetic acid $C_6H_4{<}\substack{CH_2.COOH\\NH_2}$, of which they proved it to be an inner anhydride;

and in the same year Baeyer produced isatin from oxindol, thus completing the chain of transformations necessary to prepare indigotin artificially from coal-tar (B. 11, 582, 584, 1228).

Oxindol  was first changed by the action of nitrous acid into nitroso-oxindol , and this by reducing agents into amido-oxindol , and this finally, by oxidising agents or by nitrous acid, into isatin .

A further synthesis of isatin, and therefore also of indigotin, was effected by Claisen and Shadwell in 1879 (B. 12, 350). By the action of silver cyanide on ortho-nitrobenzoyl chloride $C_6H_4<\begin{smallmatrix}CO.Cl\\NO_2\end{smallmatrix}$ they obtained ortho-nitrobenzoyl cyanide $C_6H_4<\begin{smallmatrix}CO.CN\\NO_2\end{smallmatrix}$, which, by successive treatment with hydrochloric acid and caustic potash, yielded the potassium salt of ortho-nitrophenylglyoxylic acid $C_6H_4<\begin{smallmatrix}CO.COOK\\NO_2\end{smallmatrix}$; this, by reduction in alkaline solution, gave the potassium salt of ortho-amidophenylglyoxylic acid $C_6H_4<\begin{smallmatrix}CO.COOK\\NH_2\end{smallmatrix}$, which on the addition of acid yielded isatin . In this manner the original view of Kekulé concerning the constitution of isatin was verified.

In 1880 (B. 13, 2259) Baeyer obtained indigotin in various ways from cinnamic acid, which already in 1869, had been made to yield indol. By treating ortho-nitro-cinnamic acid

$$C_6H_4<\begin{smallmatrix}CH:CH.COOH\\NO_2\end{smallmatrix}$$

with bromine, there is produced ortho-nitro-dibromhydrocinnamic acid

$$C_6H_4<\begin{smallmatrix}CHBr.CHBr.COOH\\NO_2\end{smallmatrix},$$

which, on treatment with caustic alkali, yields ortho-nitro-phenyl-propiolic acid

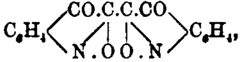
$$C_6H_4<\begin{smallmatrix}C:C.COOH\\NO_2\end{smallmatrix}.$$

On boiling this substance with caustic alkali, isatin is produced, but if reduced in alkaline solution—*e.g.* with glucose, or xanthates—it yields indigotin. This process was used industrially for some time for the production of ortho nitro-phenyl-propiolic acid (propiolic acid), its transformation into indigotin being effected on the fabric (calico).

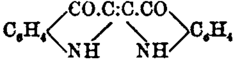
Another method of changing ortho-nitro-phenyl-propiolic acid into indigotin is as follows (Ann. 143, 325; 147, 78; 154, 137). It is first changed by boiling with water into ortho-nitro-phenyl-acetylene $C_6H_4<\begin{smallmatrix}C:CH\\NO_2\end{smallmatrix}$, the copper compound of which, by oxidation with potassium ferricyanide, yields dinitro-diphenyldiacetylene

$$C_6H_4<\begin{smallmatrix}C:C.C:C\\NO_2\quad NO_2\end{smallmatrix}>C_6H_4.$$

This body is changed by fuming sulphuric acid into its isomer diisatogen



which, by reduction, yields indigotin



(B. 15, 50, 746).

Another of Baeyer's indigotin syntheses (Germ. Pat. 11,857, 1880; Friedl. 127) is to treat ortho-nitro-cinnamic acid in alkaline solution with chlorine, whereby there is produced ortho-nitro-phenylchlorlactic acid

$$C_6H_4<\begin{smallmatrix}CH.OH.CHCl.COOH\\NO_2\end{smallmatrix},$$

which, by treatment with alkalis, changes into ortho-nitro-phenyloxacrylic acid

$$C_6H_4<\begin{smallmatrix}COH:CH.COOH\\NO_2\end{smallmatrix}.$$

On heating this body to 110°C. indigotin is produced.

In 1882 (B. 15, 2856) Baeyer and Drewsen prepared indigotin from ortho-nitro-benzaldehyde $C_6H_4<\begin{smallmatrix}CHO\\NO_2\end{smallmatrix}$. If this substance is treated with acetone, acetic-aldehyde, or pyro-racemic acid, products are formed which, under the influence of caustic alkali, readily yield indigotin. The reaction proceeds differently according to the reagent used. With the use of acetone the intermediate product is probably ortho-nitro-β-phenyl-lactic-methyl-ketone $C_6H_4<\begin{smallmatrix}CHOH.CH_2.COCH_3\\NO_2\end{smallmatrix}$, which, by the action of the alkali, yields indigotin and acetic acid. With acetic-aldehyde the intermediate body is ortho-nitro-phenyl-lactic-aldehyde $C_6H_4<\begin{smallmatrix}CHOH.CH_2.COH\\NO_2\end{smallmatrix}$, and this the alkali decomposes to form indigotin and formic acid. With pyro-racemic acid the intermediate substance is ortho-nitro-cinnamylformic acid

$$C_6H_4<\begin{smallmatrix}CH:CH.CO.COOH\\NO_2\end{smallmatrix},$$

which, under the influence of alkali, produces indigotin and oxalic acid.

Meister, Lucius, and Brüning (Germ. Pat. 20,255, 1882; Friedl. 142) patented a method similar to the first of the foregoing processes. Benzaldehyde and acetone are condensed according to Claisen's method (B. 350, 246, 2468) to form benzylidenacetone (cinnamylmethylketone) $C_6H_5.CH:CH.COCH_3$; this is nitrated, and of the para- and ortho-nitro-derivatives thus obtained the latter is treated with alkali, and thereby yields indigotin. The yield is small, and the process was soon abandoned. The same firm also patented the manufacture of *meta-methyl-indigotin* by the following method, nitrating meta-methylbenzaldehyde and treating the ortho-nitro-derivative produced, with alkali according to Baeyer and Drewsen's method given above. The methyl-indigotin obtained is very similar in appearance to indigotin, but is remarkable for its solubility in alcohol.

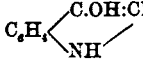
In 1883-84 (Germ. Pat. 30,329, 1883; 32,238, 1884; 33,064, 1884; Friedl. 143, 145, 146) H. Müller and the Baden Aniline & Soda Co. prepared *chlor-indigo* (and *brom-indigo*) by first preparing mono- or dichlor- or brom-benzaldehyde, changing these into the corresponding nitro- derivatives and treating with acetone and caustic alkali. The mono-chlor- and mono-brom-indigotin are very similar to indigotin in their physical and chemical properties; the tetra-chlor-indigo is also similar, but is distinguished by its greater resistance towards the action of reducing agents, and also of sulphuric acid.

In 1882 (Germ. Pat. 21,592, 1882; Friedl. 138; B. 17, 963) Baeyer and Bloem prepared indigotin for the first time from amido- compounds—viz. ortho-amido-aceto-phenone


$$C_6H_4\left\langle\begin{array}{l}CO.CH_3\\NH_2\end{array}\right.,$$

and from ortho-amido-phenyl-acetylene


$$C_6H_4\left\langle\begin{array}{l}C:CH\\NH_2\end{array}\right..$$

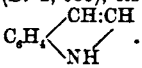
The acetyl derivatives of either of these bodies are dissolved in carbon disulphide and treated with bromine in the cold. On dissolving the bromine compound thus produced, in concentrated sulphuric acid, hydrobromic acid is evolved, and a colourless body is precipitated which, by the action of alkalis, decomposes to form indigotin. To ensure success the bromine must enter the methyl group of the acetyl-*o*-amidoaceto-phenone, and this takes place if the bromine acts in presence of conc. H_2SO_4 or in the dry condition. If the bromine enters only the benzene group (and this occurs when operating in aqueous or glacial acetic acid solutions), no indigotin is obtained; if the bromine enters both the methyl and the benzene groups—*e.g.* by working with chloroform solution—then brom-indigotin is ultimately obtained. During the formation of the indigotin in the subsequent process, indoxyl  $C_6H_4\left\langle\begin{array}{l}C.OH:CH\\NH\end{array}\right\rangle$ occurs as an intermediate product.

Gevekoht obtained indigotin by the prolonged action of an excess of ammonium sulphide on a cold alcoholic solution of ortho-nitro-brom-acetophenone containing the bromine in the methyl group, and finally evaporating the solution (A. 221, 330; Germ. Pat. 23,785, 1883; Friedl. 139). This method is probably essentially the same as that of Baeyer and Bloem, since the first action of the ammonium sulphide is no doubt to produce ortho-amido-brom-aceto-phenone.

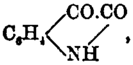
P. Meyer (B. 16, 2261, Germ. Pat. 25,136 and 27,979, 1883, Friedl. 148, 149) obtained indigotin or substituted-indigotin by first preparing isatin or substituted-isatin, according to a new method, and then reducing their chlorides by means of zinc or hydriodic acid in glacial acetic acid in the manner previously known. If 1 mol. dichlor-acetic acid is heated with 4 mols. aniline there is produced the intermediate substance phenyl-imesatin, which, by boiling with strong acids or bases, yields isatin, thus:

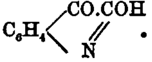
$$\underset{\text{Phenylimesatin}}{C_8H_5NO.N(C_6H_5)} + H_2O = \underset{\text{Isatin}}{C_8H_5NO_2} + C_6H_5.NH_2.$$

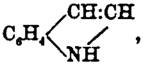
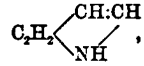
If in place of aniline in this reaction a para-monamine is employed, *e.g.* para-toluidine, the intermediate product obtained is *p*-toluyl-*p*-methylimesatin or *p*-methylisatin-*p*-toluylimid $C_8H_4(CH_3)NO.N(C_7H_7)$, and this yields by the action of acids or alkalis methylisatin $C_8H_4(CH_3)NO_2$ and toluidine.

In consequence of Baeyer's synthesis of *indol* from ortho-nitro-cinnamic acid (B. 2, 680), its constitution is regarded as being  $C_6H_4\left\langle\begin{array}{l}CH:CH\\NH\end{array}\right\rangle$.

Claisen and Shadwell's synthesis of *isatin*, already referred to, indicates its constitution as


$$C_6H_4\left\langle\begin{array}{l}CO.CO\\NH\end{array}\right\rangle,$$

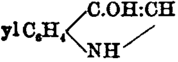
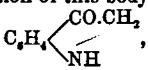
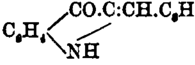
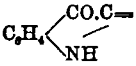
but numerous observations of Baeyer cause him to think that it contains a hydroxyl group, and that its formula is  $C_6H_4\left\langle\begin{array}{l}CO.COH\\N\end{array}\right\rangle$.

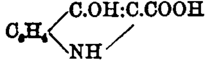
Indol  $C_6H_4\left\langle\begin{array}{l}CH:CH\\NH\end{array}\right\rangle$, the parent substance of indigotin, was first prepared from indigotin by reduction, as above stated, and first yielded this colouring matter in the hands of Nencki, by oxidation with ozone (B. 7, 1593; 8, 727; 9, 299). It forms colourless leafy crystals, having a peculiar, unpleasant odour. Its character is that of a weak base like pyrrol  $C_2H_2\left\langle\begin{array}{l}CH:CH\\NH\end{array}\right\rangle$, to which, indeed, it is chemically related.

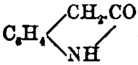
Indol occurs as a product of the pancreatic fermentation of albuminous matter, and may be also obtained by heating the latter with caustic potash (B. 7, 1593; 8, 336).

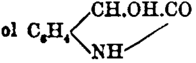
It has been synthesised in a variety of ways, *e.g.* by passing diethylorthotoluidine and other aromatic amines through red-hot tubes (B. 10, 692, 1262); melting carbostyril with caustic potash (Jahresb. 1877, 788); distilling nitropropenylbenzoic acid with lime (B. 15, 2547); passing tetrahydroquinolin through red-hot tubes (B. 16, 738); heating ortho-amido-styrol with sodium alcohol (B. 17, 1072); by heating ortho-nitro-phenyl acetaldehyde with zinc powder and ammonia (B. 17, 984).

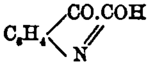
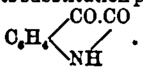
Of the numerous derivatives of indol the following are the most important:

Indoxyl  $C_6H_4\left\langle\begin{array}{l}C.OH:CH\\NH\end{array}\right\rangle$ (B. 12, 1192; 13, 415) occurs as salts of indoxyl sulphuric acid in the urine of herbivorous animals. It is an oily body which, by the action of oxidising agents, yields indigotin. Baeyer considers that there exists an isomeric modification of this body, which he terms pseudo-indoxyl  $C_6H_4\left\langle\begin{array}{l}CO.CH_2\\NH\end{array}\right\rangle$, of which, however, no derivatives are capable of existing in the free state, as for example, benzylidene-pseudoindoxyl  $C_6H_4\left\langle\begin{array}{l}CO.C:CH.C_6H_5\\NH\end{array}\right\rangle$. The diatomic residue of pseudo-indoxyl  $C_6H_4\left\langle\begin{array}{l}CO.C=\\NH\end{array}\right\rangle$ is termed the indogen group, which is considered as occurring in the indigotin molecule.

Indoxylic acid  $C_6H_4\left\langle\begin{array}{l}C.OH:C.COOH\\NH\end{array}\right\rangle$ (B. 14, 1741) is produced by decomposing with alkali its ethyl ether, a body obtained by reducing ortho-nitro-phenyl-propiolic-ether with ammonium sulphide. It is a white crystalline substance little soluble in water, and yields indigotin by oxidation.

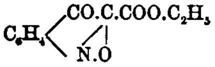
Oxindol

$C_6H_4\left\langle\begin{matrix}CH_2.CO\\NH\end{matrix}\right.$
(A. 140, 29; B. 11, 584) is produced by the reduction of isatin with sodium amalgam, or by boiling acetyl-ortho-amidophenylglycollic acid with hydriodic acid. In constitution it is to be regarded as an inner anhydride of ortho-amidophenylacetic acid. It forms colourless needles, m.p. 120°C.

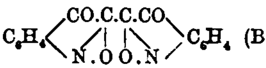
Dioxindol

$C_6H_4\left\langle\begin{matrix}CH.OH.CO\\NH\end{matrix}\right.$
(A. 140, 29) is the first product of the reduction of isatin with zinc powder. It is an inner anhydride of ortho-amido-phenyl-glycollic acid. It forms colourless needles, m.p. 180°C. When strongly heated it yields aniline.

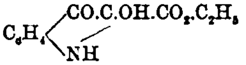
Isatin

$C_6H_4\left\langle\begin{matrix}CO.COH\\N\end{matrix}\right.$
may be obtained by oxidation of indigotin with chromic acid or nitric acid (J. pr. 24, 11; 25, 434), by the oxidation of amido-oxindol or of carbostyril (B. 11, 1228; 14, 1921), by boiling ortho-nitro-phenylpropiolic acid with caustic alkali (B. 13, 2259), and according to other methods already given. Its constitution is that of an inner anhydride of ortho-amido-phenylglyoxylic acid (B. 12, 350). It forms orange-red prisms, m.p. 200°C. With thiophene it forms a blue colouring matter called indophenin ($C_{12}H_7NOS$) (B. 18, 2637). By the action of dilute nitric acid it yields nitro-salicylic acid. Heated with caustic alkali it gives aniline. Reduced with ammonium sulphide, isatid ($C_{16}H_{12}N_2O_4$) is formed (J. pr. 24, 11; 25, 434). It combines with hydroxylamine to form nitroso-oxindol (B. 16, 518, 1714; A. 140, 29). According to Baeyer, an isomeric modification of isatin probably exists, which is only stable in the form of its substitution products; it is called pseudo-isatin

$C_6H_4\left\langle\begin{matrix}CO.CO\\NH\end{matrix}\right.$.

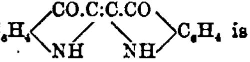
Isatinic acid

$C_6H_4\left\langle\begin{matrix}CO:COOH\\NH_2\end{matrix}\right.$
, in the form of its salts, is obtained by heating isatin with strong caustic alkali or by reduction of ortho-nitro-phenyl-glyoxylic acid. Only its salts are stable, the free acid decomposing into isatin and water by merely boiling its aqueous solution. Its constitution is that of ortho-amido-phenyl-glyoxylic acid (B. 12, 350).

Isatogenic acid ether

$C_6H_4\left\langle\begin{matrix}CO.C.COO.C_2H_5\\N.O\end{matrix}\right.$
(B. 14, 1741; 15, 50, 746) is produced by the action of concentrated sulphuric acid on ortho-nitro-phenylpropiolic-acid-ether, with which it is indeed isomeric. It forms yellow needles, m.p. 115°C.

Diisatogen

$C_6H_4\left\langle\begin{matrix}CO.C.C.CO\\N.O\ O.N\end{matrix}\right\rangle C_6H_4$
(B. 15, 50, 746) is obtained by the action of concentrated sulphuric acid on dinitro-diphenyldiacetylene. It forms red needles, soluble only in chloroform, nitrobenzene, and concentrated sulphuric acid.

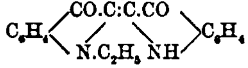
Indoxanthinic acid ether

$C_6H_4\left\langle\begin{matrix}CO.C.OH.CO_2.C_2H_5\\NH\end{matrix}\right.$
(B. 15, 775) is a product of the oxidation of indoxylic-acid-ether by means of ferric chloride. It forms yellow needles, m.p. 107°C. Under the influence of alkalis it yields ortho-amido-benzoïc acid (anthranilic acid).

Indigotin

$C_6H_4\left\langle\begin{matrix}CO.C:C.CO\\NH\quad NH\end{matrix}\right\rangle C_6H_4$
is to be regarded, in accordance with Baeyer's researches, as composed of two indogen groups, or as the indogenide of pseudo-isatin, *i.e.* pseudo-isatin in which an oxygen atom is replaced by the indogen group. It contains the imid group, and is only obtainable from compounds containing a benzene residue with which a carbon atom linked to oxygen, *i.e.* the group (:CO), is connected.

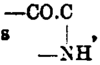
Since it is a derivative of diphenyldiacetylene the carbon atoms must be arranged thus:

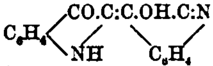
$$C_6H_5.C.C.C.C.C_6H_5.$$

The mode of its production and its properties show that it is closely related to indirubin and to the indogenide of ethyl-pseudo-isatin



$$C_6H_4\left\langle\begin{matrix}CO.C:C.CO\\N.C_2H_5\ NH\end{matrix}\right\rangle C_6H_4$$

The chromophoric group of indigotin is

$\begin{matrix}—CO.C\\|\\—NH\end{matrix}$,
which forms a closed ring with the benzene residue.

Indirubin

$C_6H_4\left\langle\begin{matrix}CO.C:C.OH.C:N\\NH\qquad C_6H_4\end{matrix}\right.$
(B. 14, 1741; 17, 975) is obtained by mixing aqueous solutions of indoxyl and isatin with the addition of sodium carbonate. It is isomeric with indigotin, and in constitution must be considered as the indogenide of isatin. It forms a brownish-red powder, soluble in alcohol with a violet colour and in cold concentrated sulphuric acid with a dark-grey colour. When heated with sulphuric acid it gives a violet sulphuric acid solution. It is not considered identical with the indirubin of Schunck. Further comparison is desirable.

Indigopurpurin $C_{16}H_{10}N_2O_2$ (B. 12, 456; 3, 514) is isomeric with indigotin, and occurs as a by-product during the formation of indigotin from isatin chloride. It is similar in appearance to indigotin, but sublimes at a lower temperature, giving reddish-coloured needles. It dissolves in alcohol with a red colour, and its diluted sulphuric acid solution is also red.

The identity of indigopurpurin and the indirubin of Baeyer above referred to, though possible, is not properly established.

The indirubin, however, obtained by Schunck as a decomposition product of indican is (according to Schunck) identical with Baeyer's indigopurpurin, and very probably also with the indigo-red of Berzelius.

Indoïn $C_{20}H_{20}N_4O_5$ (B. 14, 1741) is obtained by the reduction with ferrous sulphate of ortho-nitro-phenylpropiolic acid in sulphuric acid solution. It is very similar to indigotin, but differs from it by its ready solubility in cold aniline and in aqueous sulphurous acid, and the difficulty with which it yields sulphonic derivatives.

Application of indigo (Hummel, Dyeing of Textile Fabrics, 295).—The most important method of dyeing silk, wool, and cotton with indigo is the *vat-method*. In this method the indigotin is reduced in the presence of alkalis or alkaline earths to indigo-white, the material is impregnated with the indigo-white solution obtained, and, after removing excess, exposed to air. The indigo-white is thus oxidised and converted into indigo-blue (indigotin), which being precipitated in direct contact with the fibre remains indelibly attached to it. The colour thus obtained is a dull blue of great fastness to light, acids, alkalis, &c.

The usual indigo-vat for *cotton* is the *lime and copperas vat*, composed of the following ingredients: 4,000 litres water, 40 kilos. finely ground indigo, 60-80 kilos. ferrous sulphate, 50-100 kilos. slaked lime. It is customary to employ a range of vats containing gradually increasing amounts of indigo. Calico is hooked in a stretched condition on a wooden frame, and thus dipped in each vat in succession for twenty minutes (beginning with the weakest), and exposing to the air between each immersion. When the requisite depth of colour is obtained, the cloth is washed in dilute acid to remove calcium carbonate, and finally washed in water and dried. For pale shades of blue, or 'skying' as it is termed, the calico is passed through the vat in the open width, by means of a series of rollers fixed on a frame immersed in the vat. After squeezing out excess of liquid by means of rollers, the cloth is passed up and down over rollers outside the vat, in order to oxidise the vat liquor and precipitate the indigo-blue on the fibre.

In dyeing cotton, the depth of blue depends upon the number of immersions and the concentration of the vat, and not upon the duration of the immersion; hence it appears that cotton does not attract indigo-white, and is merely dyed by reason of the indigo-white solution absorbed.

The *zinc powder vat* is made up with 4,000 litres water, 40 kilos. indigo, 20 kilos. zinc powder, 20 kilos. slaked lime. Excess of zinc must be avoided, otherwise the vat is apt to be muddy through continuous disengagement of hydrogen. To obtain a clear vat more readily, by facilitating the liberation of the hydrogen, a rough bottom is given to the vat by adding 10-20 kilos. iron borings.

For dyeing *wool* the so-called fermentation vats are employed, of which the most important is the *woad vat*. The ingredients of a woad vat are: 15 kilos. indigo, 300 kilos. woad, 10 kilos. bran, 2-15 kilos. madder, 12 kilos. slaked lime. A steady and healthy fermentation is promoted by keeping the temperature at 45-50°C. Excessive fermentation is prevented by making suitable additions of lime. The dyeing power is maintained by adding from day to day about 8 kilos. indigo with suitable quantities of lime. A woad vat continues to be used for several months until the sediment becomes too bulky to obtain the necessary clear-liquor space for dyeing.

The *soda and potash vats* are similar to the woad vat, the difference being that the lime is replaced by carbonate of soda or potash, and the woad is omitted; the fermentation is induced and maintained by means of bran, sometimes with the addition of madder, molasses, &c. The soda vat is much used in Germany. Collin and Benoist (Germ. Pat. 30,449, 1884) have in recent years proposed to avoid detrimental fermentations in the indigo vat, by employing a completely fermentescible food material and a pure ferment. For a vat of 8,000 litres, 16 kilos. flour or starch are boiled for a few minutes with a solution of 1·6 kilos. sodium carbonate. The starch paste thus obtained is transferred to the vat, and 8 kilos. glucose, 5·38 kilos. sodium carbonate, and 1 kilo. magnesia are added. During the working of the vat the lactic, butyric, and other acids formed are neutralised, also the indigo-white is dissolved, by suitable additions of soda. The pure ferment required, *Desmobacterium hydrogeniferum*, is obtained by first digesting 100 grams potato cuttings in 500 c.c. water at 40-44°C. Another flask is filled with 1 litre water containing 1·5 gram sodium phosphate, 3 grams ammonium tartrate, 5 grams glucose, 5 grams soluble starch, 3 grams sodium carbonate, 0·5 grams lime. This solution is sterilised by boiling; 50-60 c.c. of the potato liquor, containing the desmobacterium and other organisms, are afterwards introduced and the whole is maintained for 4-5 days at 38-40°C. The liquid, which is then full of desmobacteria, is absorbed by wood-flour, and this is dried at a low temperature. Of this ferment 50 grams suffice for a vat of 12 cubic metres.

In the *urine vat*, which is of minor importance and only suitable for a small trade, the ingredients are: 500 litres stale urine, 4 kilos. common salt, 1 kilo. madder, 1 kilo. indigo.

The *hyposulphite vat* of Schützenberger and De Lalande, though of comparatively recent introduction, is finding favour because of its simplicity in working. The active reducing agent is hyposulphurous acid (hydrosulphurous acid) H_2SO_2. In a closed vessel provided with an agitator, a strong solution of bisulphite of soda (sp.gr. 1·3) is allowed to act upon zinc foil for about one hour, with occasional stirring. Zinc powder may also be used, if care is taken to keep the mixture cool during the reaction. The acid sodium hyposulphite thus produced, being unstable, is drawn off into another closed vessel and there neutralised with milk of lime. Zinc oxide and calcium sulphite are allowed to settle, and the clear solution is used as soon as possible for reducing the indigo. If not required at once, it should be mixed with milk of lime to render it more stable.

It is customary to make a strong stock-solution of reduced-indigo by mixing together the following ingredients: 1 kilo. ground indigo, 1-1·3 kilos. milk of lime (200 grams quicklime per litre), 10-12 litres concentrated sodium hyposulphite solution (sp.gr. 1·18). The mixture is heated to 70°-75°C. to effect reduction rapidly. Care must be taken to use a sufficiency of lime to dissolve the indigo-white.

In setting the hyposulphite vat, the vat is filled with water at 50°C.; a little sodium hyposulphite is added to deprive it of any oxidising power due to air, and a sufficiency of the concentrated solution of reduced-indigo is added. The vat may be used at once. Its dyeing power is maintained by making further additions of reduced-indigo solution, care being taken always to have a slight excess of hyposulphite. When dyeing with this vat the liquor becomes more and more alkaline, and it is necessary to add occasionally dilute hydrochloric acid (Bull. Soc. Rouen, 2, 17).

In dyeing wool in the indigo vat the depth of colour is regulated, not only by the concentration of the indigo-white solution, but also by the duration of the immersions, and it seems evident, therefore, that the wool really attracts indigo-white, and is not merely dyed by reason of the amount of indigo-white in the solution absorbed, as is the case with cotton.

Silk is now seldom dyed in the indigo vat, a satisfactory dark blue being obtained from induline by simpler methods. When desired, the woad or hyposulphite vat may be employed.

Another method of dyeing with indigo, quite different from the vat-method, but only applicable in the case of the animal fibres, is based upon the fact that these attract the so-called indigotin-sulphonic-acids. Wool and silk are dyed in a solution of indigo-carmine, or indigo-extract, acidulated with sulphuric acid. The colours thus obtained (formerly called *Saxony blues*) are much brighter than those produced by the vat method, but they are not fast to the action of light or alkalis. By the latter they are decolourised through the formation of the alkali salts of the sulphonic acid; the colour is restored on passing through acidulated water.

In calico-printing, indigo-blue prints are obtained in various ways, of which the following are the most important (Persoz, Traité de l'impression, 3, 15; O'Neil, Calico-Printing, 2, 221).

Resist method (O'Neill, Text. Col. 1, 65, 134, 206).—Previous to dyeing in the vat, the calico is printed with a *reserve* or *resist*, *i.e.* starch or gum thickening containing certain substances which prevent the fixing of the indigotin upon the fibre. Such substances may act mechanically, *e.g.* china clay, or chemically, *e.g.* copper salts, or, as is usually the case, mixtures of the two may be employed. In a chemical resist the copper salts, or other oxidising agents, oxidise the indigo-white and precipitate the indigotin before the vat solution can penetrate the fibre in the printed parts. In the Java prints, known as 'Baticks,' melted wax is printed as a mechanical resist.

After dyeing in the vat and washing off the resist, a white pattern on a blue ground is the result. If a pale indigo-blue is dyed before printing the resist, and a dark blue is dyed afterwards, the resultant pattern is pale blue on a dark-blue ground. By mixing lead salts with the resist colour and passing the dyed cloth through bichromate of potash solution, a yellow pattern is obtained, and by suitably combining these several methods one may obtain a variegated pattern containing white, pale blue, yellow, green, and dark blue.

Discharge method (O'Neill, Text. Col. 3, 217). This method is based upon the fact that indigo-blue is readily destroyed or discharged by oxidising agents. The calico is first dyed blue in the vat, washed and dried. It is then printed with a thickened solution of sodium bichromate, dried, and passed through a strongly acid solution of oxalic and sulphuric acids. The chromic acid thus liberated in the printed parts of the cloth oxidises and destroys the blue, leaving a white pattern. The sodium bichromate may also be thickened with albumen, and such pigments added as are not readily affected by acids, *e.g.* chrome green, vermilion, chromate of lead, &c. By steaming, to coagulate the albumen and fix the pigments, and then passing through acid, the most variegated patterns on an indigo-blue ground are obtained.

Indigo-blue is readily discharged by an alkaline solution of potassium ferricyanide, and this fact has also been applied by the calico printer to obtain both white and coloured discharge patterns (Mercer, Mem. Chem. Soc. 3, 320).

Other discharging agents employed are metallic chlorates; these, under suitable conditions, *e.g.* printed and steamed, discharge the blue and leave metallic oxides upon the fibre, which may afterwards be dyed with various colouring matters.

Dark and light indigo-blue patterns may be printed upon calico by the so-called 'glucose method.' The calico is impregnated with a solution of glucose, dried, and printed with a mixture of ground indigo and strong caustic soda thickened with British-gum. The printed fabric is steamed and washed. During the steaming process the indigotin is reduced, the indigo-white solution thoroughly penetrates the fibre, and this is oxidised during the subsequent washing.

This method is now largely employed; if the above-mentioned discharge methods are subsequently applied, one obtains variegated patterns.

An interesting method of printing indigo-blue upon calico, but which has been almost entirely supplanted by the 'glucose method,' is that in which ortho-nitrophenyl propiolic acid (propiolic acid) is employed (Germ. Pat. 11,858, 1880; 15,516, 1881; Friedl. 131, 133). This substance, in the form of a paste, mixed with starch paste, alkali (borax), and xanthate of soda $CS\Big<{}^{O.C_2H_5}_{S.Na}$, is printed on the calico, which is then merely hung up for twelve to twenty-four hours at the ordinary temperature to develop the blue. Indigotin is produced in this case from the propiolic acid by the reducing action of the xanthate of soda in the presence of alkali. The fabric is subsequently passed through carbonate of soda solution and washed with soap.[1] J. J. H.

INDIGO COPPER. *Cupric sulphide v.* COPPER.

INDIUM. Symbol In. At. w. 113·4 (Winkler, Bunsen).

Indium occurs in minute quantities in zinc blende, notably in that from Freiberg, from which it is usually obtained, and in which it was discovered by Reich and Richter by means

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[1] The most recent synthesis of indigotin (May 1890) and one which may probably become of commercial value, is that of Heumann, in which 1 part phenylglycocoll $C_6H_5.NH.CH_2.CO.OH$ is heated with 2 parts NaOH to 260°C. in a closed retort. On oxidising an aqueous solution of the melt by means of a current of air indigotin is precipitated. It seems possible that during the melting with alkali the phenylglycocoll loses 1 mol. H_2O, and yields pseudo-indoxyl $C_6H_4\left\{\begin{matrix}CO\\NH\end{matrix}\right\}CH_2$, the CH_2 groups of which, during the subsequent oxidation, lose hydrogen, the residues of 2 mols. then uniting to form indigotin $C_6H_4\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C{:}C\left\{\begin{matrix}CO\\NH\end{matrix}\right\}C_6H_4$.

of the spectroscope. The calamine from Onela, in the province of Bergamo, is said to be rich in indium (A. and G. de Negri).

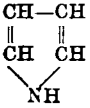
Indium is a white, non-crystallisable, easily-malleable metal, softer than lead, and of sp.gr. 7·42, and melting-point 176°. It retains its lustre in air or boiling water, but oxidises before the blow-pipe, imparting a blue colour to the flame. It dissolves slowly in hydrochloric or sulphuric acid, readily in nitric acid.

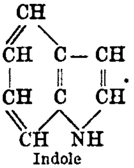
Indium, like gallium, belongs to the aluminium group of metals. It forms a pale-yellow oxide In_2O_3, and the corresponding hydroxide, three chlorides $InCl$, $InCl_2$, and $InCl_3$, and a bromide, iodide, sulphide, and other salts. Like gallium, it forms an alum

$$In_2(SO_4)_3(NH_4)_2SO_4 24H_2O$$

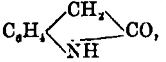
with ammonium, but not with sodium or potassium.

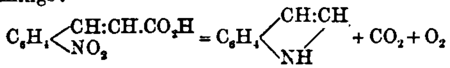
INDOLES. Indole C_8H_7N was first obtained from indigo derivatives. It may be regarded as made up of a benzene nucleus and a pyrrhole nucleus, which are conjugated so as to have two carbon atoms in the ortho- position in common. It is thus related to pyrrhole in the same way as naphthalene to benzene:


Pyrrhole


Indole

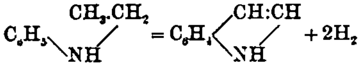
In like manner, a pyrrhole nucleus may be conjugated with naphthalene so as to yield a naphthindole. Numerous homologues have also been prepared.

Indole C_8H_7N was first obtained by Baeyer by distilling either oxindole  $C_6H_4\langle{}^{CH_2}_{NH}\rangle CO$, or the product obtained from indigo by reduction with tin and hydrochloric acid, with zinc-dust (A. Suppl. 7, 56). Formed when *o*-nitro-cinnamic acid is distilled with caustic potash and iron filings:



$$C_6H_4\langle{}^{CH:CH.CO_2H}_{NO_2} = C_6H_4\langle{}^{CH:CH}_{NH}\rangle + CO_2 + O_2$$

(Baeyer and Emmerling, B. 2, 680). By passing the vapour of ethylaniline and other alkyl-anilines through a red-hot tube:



$$C_6H_5\langle{}^{CH_3.CH_2}_{NH}\rangle = C_6H_4\langle{}^{CH:CH}_{NH}\rangle + 2H_2$$

(Baeyer and Caro, B. 10, 692 and 1262). By the pancreatic fermentation of albumen (Nencki, B. 7, 1593; 8, 336). Best prepared by the action of dichlorether $CH_2Cl.CHCl.O.C_2H_5$ on aniline. A mixture of 50 grams of aniline with an equal bulk of water is heated with a reflux condenser, and to the boiling liquid 25 grams of dichlorether are gradually added. The boiling is continued for an hour, after which the water and excess of aniline are distilled off and the residue is heated for about four hours at 210–230°. On distilling the product with steam, indole passes over and may be purified by means of its picrate. In this reaction ethylidene-dianiline is formed, which, on heating to a higher temperature, breaks up into indole and aniline $C_6H_5.N:CH.CH_2.NH.C_6H_5 = C_8H_7N + C_6H_5.NH_2$ (Nencki and Berlinerblau, Germ. Pat. 40,889, Nov. 7, 1886; Berlinerblau, M. 8, 181).—Colourless laminæ, with a satiny lustre. Melts at 52°, and boils with partial decomposition at 245°; readily volatile with steam. Moderately soluble in boiling water, easily soluble in alcohol, ether, and hydrocarbons. Nitrous acid precipitates from the aqueous solution in presence of nitric acid *nitrosoindole nitrate* in the form of minute red needles. An aqueous solution, or the vapour of indole, colours a pine chip moistened with hydrochloric acid and alcohol cherry-red, the colour afterwards changing to reddish-brown. Indole suspended in water and oxidised with ozone yields traces of indigotin (Nencki, B. 8, 727). Heated with acetic anhydride it gives *acetyl-indole*

$$C_8H_6N(C_2H_3O),$$

melting at 182–183°. From a solution of indole in light petroleum picric acid precipitates the picrate $C_8H_7N,C_6H_2(NO_2)_3(OH)$ in long dark-red needles. Indole is a weak base: it forms with concentrated hydrochloric acid a sparingly soluble salt which is decomposed by boiling with water.

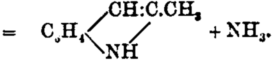
The *homologues of indole* are most readily obtained by heating the phenylhydrazones of ketones of the formulæ $R'.CO.CH_3$ or

$$R'.CO.CH_2.R',$$

or the phenylhydrazones of aldehydes of the formula $R'.CH_2.CHO$, with zinc chloride to 180°. The zinc chloride abstracts the elements of ammonia from the hydrazone:

$$C_6H_5.NH.N:C(CH_3)_2$$

Acetone-phenylhydrazone

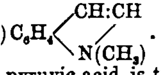


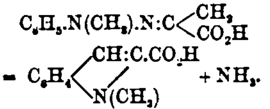
$$= C_6H_4\langle{}^{CH:C.CH_3}_{NH}\rangle + NH_3.$$

β-Methylindole
(Methylketole)

Indole itself cannot be prepared by this reaction, apparently because the compound formed from aldehyde and phenylhydrazine is destroyed by the violence of the action which occurs when it is heated with zinc chloride. By employing homologues of phenylhydrazine, indoles may be obtained in which the alkyl replaces hydrogen of the benzene nucleus; whilst secondary hydrazines give secondary indoles in which the hydrogen of the imido- group is replaced by an alkyl. Ketonic acids may be substituted for ketones in the reaction, yielding indole-carboxylic acids. If naphthylhydrazines are employed in place of phenylhydrazine, naphthindoles are formed (E. Fischer, Eng. Pat., No. 7,137 of 1886; A. 236, 116).

For an account of E. Fischer's nomenclature of the indole derivatives *v.* A. 236, 121.

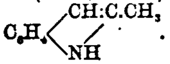
Methylindole (*tertiary*)  $C_6H_4\langle{}^{CH:CH}_{N(CH_3)}\rangle$. When methyl-phenylhydrazone-pyruvic acid is treated with hydrochloric acid it parts with the elements of ammonia (a reaction which, in the case of primary hydrazones, only occurs when zinc chloride is used, *v. supra*) yielding methyl-indole-carboxylic acid:



$$C_6H_5.N(CH_3).N:C\begin{array}{l}\diagup CH_3\\ \diagdown CO_2H\end{array} = C_6H_4\begin{array}{l}\diagup CH:C.CO_2H\\ \diagdown N(CH_3)\end{array} + NH_3.$$

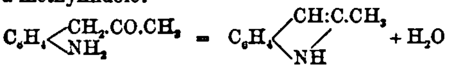
On heating the latter compound to 205° it parts with carbon dioxide, forming tertiary methylindole (E. Fischer and Hess, B. 17, 562).—Yellowish oil, of sp.gr. 1·0707 at 0°. Does not solidify at −20°. Boils at 240-241° (cor.) under 720 mm. pressure. Colours a pine-chip moistened with hydrochloric acid reddish violet.

α-Methylindole (*Methylketole*)



$$C_6H_4\begin{array}{l}\diagup CH:C.CH_3\\ \diagdown NH\end{array}.$$

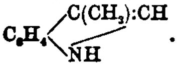
By reducing *o*-nitro-phenylacetone with ammonia and zinc-dust. The *o*-amido-phenylacetone which is formed parts with water yielding α-methylindole:



$$C_6H_4\begin{array}{l}\diagup CH_2.CO.CH_3\\ \diagdown NH_2\end{array} = C_6H_4\begin{array}{l}\diagup CH:C.CH_3\\ \diagdown NH\end{array} + H_2O$$

(Baeyer and Jackson, B. 13, 187). By heating acetone-phenylhydrazone with five times its weight of zinc chloride for half-an-hour on the water-bath, and then for a few minutes to 180° (E. Fischer, A. 236, 126; *v. supra*).—Needles or laminæ. Melts at 59-60° and boils at 272° (cor.) under 750 mm. pressure. Smells like indole. Sparingly soluble in boiling water, readily soluble in alcohol and ether. Colours a pine-chip moistened with hydrochloric acid red.

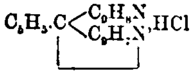
β-Methylindole (*Skatole*)



$$C_6H_4\begin{array}{l}\diagup C(CH_3):CH\\ \diagdown NH\end{array}.$$

First discovered in human fæces, of which it forms the chief volatile constituent (Brieger, B. 12, 1,986). Occurs in the wood of *Celtis reticulosa*, Java (Dunstan, Pr. 46, 211). Formed by fusing albumen with caustic potash, or by the putrefaction of albumen under water (Nencki, J. pr. [2] 17, 98). Obtained along with indole in distilling with zinc-dust the product of the reduction of indigo by means of stannous chloride (Baeyer, B. 13, 2339). Prepared by heating propionaldehydrazone $CH_3.CH_2.CH:N_2H.C_6H_5$ with an equal weight of zinc chloride and distilling the product with steam. Lustrous laminæ, melting at 95°. Boils at 265-266° (cor.) under 755 mm. pressure. Has a strong odour of fæces; that obtained from indigo is stated to have no fæcal smell. Dissolves in concentrated hydrochloric acid with a violet colour.

Rosindoles. By heating methylketole with benzoyl-chloride on the water bath with the addition of zinc chloride, a red colouring-matter, closely resembling magenta, is obtained. This colouring-matter is the hydrochloride of a base of the formula $C_{23}H_{20}N_2:2C_9H_9N + C_7H_5OCl = C_{24}H_{20}N_2, HCl + H_2O$. It has possibly the constitution



$$C_6H_5.C\begin{array}{l}\diagup C_9H_8N\\ \diagdown C_9H_7N\end{array},HCl$$

and would thus be closely allied to the triphenylmethane colouring matters (*q. v.*). The hydrochloride forms small crystals with a green metallic lustre, and closely resembles in appearance rosaniline hydrochloride. Similar compounds may be obtained from other indole derivatives (E. Fischer and Wagner, B. 20, 815).

Neither the indoles themselves, nor the foregoing colouring matters derived from them appear as yet to have met with any industrial application. F. R. J.

INDOPHENOLS *v.* INDAMINES AND INDOPHENOLS.

INDULINES. A very numerous class of blue colouring matters belonging or closely related to the saffranine group of colours is known under the general title of 'Indulines.' They are prepared by heating an amidoazo-compound with an amine in the presence of the chloride of the amine. As might be expected, such a process allows of an almost infinite series of variations, and a great number of the colours have at various times been made and used.

By far the most important is also the earliest known; the details of its preparation, described below, are practically those of all the others.

100 lbs. amidoazobenzene, 130 lbs. aniline hydrochloride, and 300 lbs. aniline are introduced into a cast-iron still capable of holding 70–80 gallons, or twice the volume of the melt made in it. The still is provided with an agitator, swan neck, charging hole, thermometer tube, and discharge valve.

The whole is heated for about six hours to about 140–150°; the melt is then run out into water, caustic soda added, and the unaltered aniline recovered. The yield of induline base should equal or slightly exceed the weight of amido-azobenzene used.

The induline base is dried, ground, and heated with sulphuric acid, when a sulphonic acid corresponding in properties to the soluble blue acid is produced. This is purified in the usual manner and converted into a sodium salt, in which state it is sent into the market. The corresponding 'Nicholson' acid is unknown.

If the induline 3B, as the above is called, instead of being precipitated, is further heated for some hours with more aniline or aniline chloride, it undergoes phenylation, and on treatment with alcohol and crystallisation splendid bronze-coloured needles of a very much greener shade of induline, known as induline 6B, separate.

Thomas and Witt give two methods of production—viz. 100 parts of induline 3B are heated with 45 parts aniline hydrochloride and 200 parts of aniline. Since, however, it is quite unnecessary to separate the 3B colour and separately treat it, they point out that the whole of the operations can be made continuous. Thus, 100 parts diazoamidobenzene, 300 parts aniline, and 130 parts aniline hydrochloride are gently warmed to 40–50°C., and in this way the diazoamido- changes into the isomeric amido-azobenzene. The heat is then raised to 110° for four or five hours, whereby the 3B induline is produced. 65 parts aniline hydrochloride are then added, and the heat increased to 160–170° for twenty-four hours, when the melt is cooled, mixed with alcohol, and the 6B induline separates as a crystalline magma, which is washed and dried and converted into sulphonic acid by heating 100 parts with 300 of H_2SO_4 of sp.gr. 1·840 to 110°.

Up to November, 1889, patents have been obtained for many variations in the process, such as for the preparation of indulines by the action of amidoazo- compounds on phenols and quinones, with or without the presence of a dehydrating agent; for the action of amidoazo- compounds or of azophenine and its homologues on diamines in the presence of benzoic acid; for obtaining red basic dyes of the same series by the action of various quinones, oxyquinones, quinonimides, and conjugated azo-dye-stuffs on aniline and aniline hydrochloride; for producing soluble indulines of green shade by the action of paradiamines on ordinary induline in the presence of benzoic acid, and for the production of soluble red shades by a similar treatment with metadiamines; and, lastly, for colours obtained by the action of amidoazo-compounds on secondary and tertiary amines.

Nigrosine, *Coupier's blue.* Another series of blue to blue-grey dyes is produced by heating various proportions of nitrobenzene, aniline, and aniline hydrochloride in the presence of ferric chloride to 180-200°. The product consists of mixed blue to bluish-grey colouring matters of the induline class, those generally known as nigrosines being thus produced. The process is a purely empirical one, and admits of great variation in every detail according to the shade desired. R. J. F.

INK. A coloured fluid used in writing, printing, &c. (Gr. *engkauston—engkaio*, to burn in; Lat. *encaustum*, the purple-red ink used only in the signature of the emperors; It. *inchiostro*; Fr. *encre*; Dutch *inkt.*)

It may be a convenient although not rigidly accurate division of the subject to recognise a distinction between ink prepared for writing and that prepared for printing.

Writing ink.—Black writing ink, as commonly prepared, is a ferroso-ferric gallate suspended in water, and obtained by adding a decoction of substances containing tannin (usually nut-galls) to a solution of copperas.

Galls contain gallotannic and gallic acids, which, with ferric salts, form a black precipitate; with ferrous salts the precipitate is white, which, however, becomes black when oxidised by exposure to air. A proportion of gum is added for the purpose of suspending the precipitate equally throughout the solution and of preventing its deposit.

Although other materials may be used, it has been found that the best properties of writing ink—viz. fluidity, penetration, and permanence—are obtained by the use of the ingredients abovenamed. Either with the object of reducing the cost of production or of introducing an agent which at the moment of use may impart a deeper black to the paper, in preference to the blue-black tinge which requires time to intensify it, logwood and indigo extracts have been used by some makers. When logwood is employed, a smaller quantity of galls is required, since logwood contains a large percentage of tannin. Ink made from indigo extract (irregularly named alizarin ink) is prepared by dissolving indigo in strong sulphuric acid, the ferrous sulphate being supplied by scraps of iron immersed in the extract. Excess of uncombined acid in the solution is removed by the addition of chalk, which unites with the free acid to form a precipitate of calcium sulphate. Vicat, of Brunswick, gives the following table as the composition of the three varieties of ink above described:—

——	Galls ink	Galls-logwood ink	Galls-indigo ink
Tannic extract 5 p.c.	1 litre	¾ litre	1 litre
Ferrous sulphate .	45 grams	45 grams	—
Gum senegal .	20–30 „	20–30 „	—
Logwood solution 3 p.c.	—	¼ litre	—
Metallic iron .	—	—	9 grams
Indigo . . .	—	—	6¼ „
Concentrated sulphuric acid	—	—	25 „
Chalk . . .	—	—	1 „

Runge prepared a writing fluid, under the name of 'chrome ink,' which was cheap, intensely coloured, non-corrosive to steel pens, and extremely permanent on paper. The drawback to its use consisted in the fact that on exposure to the air the colouring separated from the medium in broad flakes. Böttger and Viedt both assert that this fault may be obviated by the use of soda. The manner of preparing chrome ink is as follows: 1 part of chromate (not bichromate) of potassium is added to 1,000 parts of a saturated solution of logwood made by boiling 22 lbs. of logwood in a sufficient quantity of water to give 14 gallons of decoction. The chromate of potassium is introduced gradually when the solution is cold, the mixture being constantly stirred during the addition. Gum is injurious to the mixture.

The following receipts for making black writing ink are taken from the sources named:

No. 1 (Cooley's Cyclopædia).—Aleppo galls, well bruised, 4 oz.; clean soft water 1 quart; macerate in a clean corked bottle for ten days or a fortnight, or even longer, with frequent agitation; then add of gum arabic dissolved in a wineglassful of water 1½ oz.; lump sugar ½ oz.; mix well, and afterwards further add of sulphate of iron (green copperas), crushed small, 1½ oz.; agitate occasionally for two or three days, when the ink may be decanted for use, but is better if the whole is left to digest together for two or three weeks. *Product:* 1 quart of excellent ink, writing pale at first, but soon turning intensely black.

No. 2 (Ure).—12 lbs. of nut-galls, 5 lbs. green sulphate of iron, 5 lbs. Senegal gum, 12 gallons of water. The bruised nut-galls are to be put into a cylindrical copper of a depth equal to the diameter, and boiled during three hours with three-fourths of the above quantity of water, taking care to add fresh water to replace what is lost by evaporation. The decoction is to be emptied into a tub, allowed to settle, and, the clear liquid being drawn off, the lees are to be drained. The gum is to be dissolved in a small quantity of hot water, and the mucilage thus formed, being filtered, is added to the clear decoction. The sulphate of iron must likewise be separately dissolved and well mixed with the above. The colour darkens by degrees in consequence of the peroxidation of the iron on exposing the ink to the action of the air. *Product:* 12 gallons.

Copying ink. Any ink which retains enough solubility to give off an impression from the written sheet on to a sheet of damp paper may be used for copying. Runge's chrome ink described above may be so used. Other logwood inks and ferrous gallate inks being soluble only until oxidised by exposure to the air, which occurs almost as soon as the words are written, require the addition of some substance which forms a glaze, arresting the action of the air. This glaze must be soluble when brought into contact with the damped copying paper; the pigment is then freed so as to produce the impress. Such substances are gum arabic, gum Senegal, dextrin, and glycerine. Where several copies are required, the ink employed should contain more staining matter in proportion.

Indelible ink, or **Incorrodible ink.** Compositions passing under these names consist of finely divided carbonaceous substances, such as Indian ink or lampblack, held in suspension in a glutinous or resinous liquor. They are devised so as to resist the action of strong acid or alkaline solutions. An ink having these properties may be made of Indian ink rubbed into ordinary writing ink.

Red ink is usually prepared from Brazil wood by adding stannous chloride to a decoction of the dyestuff and thickening with gum arabic. Cochineal and carmine produce a more brilliant colour, but they are less permanent. The red ink of a well-known maker is compounded as follows:—Add to a quantity of common carbonate of potassium, sodium, or ammonium, twice its weight of crude argol (bitartrate of potash as deposited by wine) in powder. When the effervescence has ceased, decant or filter the solution from the insoluble matter, and add by measure half its quantity of oxalate of aluminium prepared by dissolving damp newly precipitated alumina in as small a quantity as possible of a concentrated solution of oxalic acid. The mixture is next coloured when cold with bruised or powdered cochineal, and, after standing for forty-eight hours, is strained, when it is fit for use.

Blue ink. Prussian blue is the colouring matter employed. The pigment is placed in an earthen vessel, and either strong hydrochloric acid, nitric acid, or sulphuric acid is added to it. After the mixture has remained two or three days, much water is added; and after settling the supernatant liquor is drawn off from the sediment. This sediment is well washed until all traces of iron and free acid disappear from the water, after which it is dried and mixed with oxalic acid in the proportion of 8 parts of Prussian blue to 1 part of acid. The pigment being now soluble in water, so much of this latter is added as will bring it to the required intensity.

Inks of other colours can be made from decoctions of dyestuffs mixed with alum used as a mordant and gum senegal or gum arabic; as, *e.g.*, brown ink from catechu or logwood, to which a little bichromate of potash is added; violet and purple inks from logwood with a small admixture of chloride of tin or of alum; yellow ink from gamboge, &c. &c. Aniline colours also offer a selection of tints for this purpose.

Gold and silver inks are prepared from gold and silver, or from cheaper substances such as bronze powder and Dutch leaf. The leaf metal mixed with honey is carefully ground down to the finest possible condition; it is then well washed and dried. A medium is furnished by a preparation consisting of 1 part of pure gum arabic and 1 part of soluble potash glass in 4 parts of distilled water. As a rule 1 part of the powder is sufficient for 3 or 4 parts of the medium.

Sympathetic, Diplomatic, or **Secret inks.** These preparations are devised to trace words or figures which are invisible when written but which become visible when subjected to heat or appropriate chemical reagents. Examples:—A weak infusion of galls is colourless on paper, but becomes black when moistened with a solution of copperas; and if a weak solution of copperas be used, the writing will be invisible, till the paper is moistened with a weak solution of galls. Equal parts of sulphate of copper and sal ammoniac dissolved in water form a colourless ink, the writing of which turns yellow on the application of heat. Weak solutions of nitrate of silver and terchloride of gold when exposed to the sunlight become dark brown and purple respectively. Solutions of chloride or nitro-muriate of cobalt give tracings which become green or blue when heated and disappear again as the paper cools.

Marking ink. The ink thus named is chiefly used for marking letters, stamping patterns, &c., upon linen. It is usually made from a salt of silver, generally the nitrate, dissolved in water and ammonia with a little gum. It is customary to add a little Indian ink or sap green as an aid to the person writing, although it is the decomposition of the salt and not the temporary colouring matter which produces the permanent stain. The marks made by nitrate of silver can be discharged by a solution of cyanide of potassium with or without iodine; but they are sufficiently enduring under ordinary conditions. It is recommended that the linen to be written upon should be moistened with a solution of carbonate of soda and gum, which is dried by passing a smoothing iron over it.

The following receipts for marking ink are taken from the sources indicated:—

No. 1 (Ency. Brit.).—Equal parts of nitrate of silver and dry tartaric acid are triturated in a mortar and treated with water, when a reaction takes place resulting in the formation of tartrate of silver and the liberation of nitric acid. The acid is neutralised, and at the same time the silver tartrate is dissolved by the addition of ammonia, and this solution, with colouring matter and gum, forms an ink which may be used with an ordinary steel pen.

No. 2 (Redwood's ink).—Dissolve 1 oz. nitrate of silver and 1½ oz. of crystallised carbonate of soda in separate portions of distilled water, and mix the solutions; collect the resulting precipitate on a filter, wash it well with distilled water, and introduce it while still moist into a Wedgwood-ware mortar; add 8 scruples of tartaric acid, and triturate the whole until effervescence has ceased; next add a sufficient quantity of ammonia to dissolve the tartrate of silver; mix in 4 fluid drachms of archil, 4 drachms of white sugar, and 12 of finely powdered gum arabic, and pour in as much distilled water as will make 6 ounces of mixture.

A cheap marking ink used by bleachers for distinguishing the pieces of cloth passing through their hands, and capable of resisting chlorine, is made by dissolving coal-tar in naphtha.

Printing ink. Ink prepared for use with type, copper-plate, &c. &c., is composed of an oil or varnish mixed with a pigment of the required colour.

The qualifications of good printing ink are well described by Mr. Underwood in a communication made by him to the Society of Arts:—

(1) It must distribute freely and easily, and work sharp and clean.

(2) It must not have too much tenacity for the type, but have a much greater affinity for the paper and so come off freely upon it.

(3) It must dry almost immediately on the paper, and not dry at all on the type or rollers.

(4) It should be literally proof against the effects of time and chemical reagents, and never change colour.

The oil most commonly used is a fine quality of linseed oil; the pigment for black ink is usually lampblack previously calcined in order to remove empyreumatic oils and resins. (For inks of other colours, *v. infra.*) To these in the process next described are added resin and soap for the purpose of giving body to the ink and of furnishing it with a medium which will be readily taken up by the damped sheet of paper.

The linseed oil is boiled and continuously stirred meanwhile; if, when a smoke begins to arise from it, it does not of itself take fire, a light is applied to it and the flame permitted to burn some half hour, at the end of which time it is extinguished. This is done to communicate a sufficient drying property to the oil. It is still allowed to boil gently until of a proper consistency; that is, until a sample of the varnish cooled upon a palette knife may be drawn out into strings of half an inch in length. A small quantity of resin and of soap is now added, and the whole is slowly boiled together. It is the usual course to be provided with varnishes of two or more degrees of coherence, so as to be adapted to various temperatures and to different classes of work. Neither water nor alcohol dissolves a varnish so prepared, but it mingles readily enough with fresh oil and unites with mucilages into a mass diffusible in water in an emulsive form. The oil loses from one-tenth to one-eighth of its weight by boiling into the thick varnish (Watts). Black colouring matter is added in the form of lampblack, with which a little indigo or Prussian blue is mixed in order to correct the brown tinge of lampblack alone. It is said that so marvellously thin is the layer of ink on small type that one pound weight even of cheap newspaper ink will cover no less than 7,000 feet of type matter.

Ink prepared for lithography ought to conform to the following requirements. It should be flowing in the pen, not spreading on the stone; capable of forming delicate traces, and very black to show its delineations. The most essential quality of the ink is to sink well into the stone, so as to reproduce the most delicate outlines of the drawing and to afford a great many impressions. It must therefore be able to resist the acid with which the stone is moistened in the preparation without letting any of its greasy matter escape.

Lithographic ink may be prepared as follows:—Mastic (in tears) 8 oz., shellac 12 oz., Venice turpentine, 1 oz.: melt together; add of wax 1 lb., tallow 6 oz.; when dissolved, add further of hard tallow soap in shavings 6 oz.; and when the whole is perfectly combined, add of lampblack 4 oz.; lastly, mix well, cut in moulds, and when cold cut it into square pieces. This is used for writing on stones.

Autography is the operation by which a writing or a drawing is transferred from paper to stone. For autographic ink:—White wax 8 oz., white soap 2 oz. to 3 oz.; melt, and when combined add lampblack 1 oz.; mix well, heat strongly, and add shellac 2 oz.; again heat strongly and stir well together. On the mixture cooling pour it out as before. With this ink lines may be drawn of the finest and fullest class, without danger of its spreading; and the copy may be kept for years before being transferred. These inks are rubbed down with a little water in the same way as Indian ink.

Coloured printing inks. These inks are made from the varnish above described by the addition of dry colours; taking great care that the colours are thoroughly well ground and assimilated with the varnish, since lumps of any kind not only clog the type but alter the tint. Some tints which are exceedingly light will require an admixture of white powder to give the necessary body to the ink.

The following pigments are enumerated by Southward (Practical Printing) as eligible for coloured printing inks:

Red.—Orange lead, vermilion, burnt sienna, Venetian red, Indian red, lake vermilion, orange mineral, rose pink, and rose lead.

Yellow.—Yellow ochre, gamboge, and chromate of lead.

Blue.—Cobalt, Prussian blue, indigo, Antwerp blue, Chinese blue, French ultramarine, and German ultramarine.

Green.—Verdigris, green verditer, and mixtures of yellow and blue.

Purple.—A mixture of those used for red and blue.

Deep brown.—Burnt umber with a little scarlet lake.

Pale brown.—Burnt sienna: a rich shade is obtained by using a little scarlet lake.

Lilac.—Cobalt blue with a little carmine added.

Pale lilac.—Carmine with a little cobalt blue.

Amber.—Pale chrome with a little carmine.

Pink.—Carmine or crimson lake.

Shades and tints.—A bright red is best got from pale vermilion with a little carmine added; dark vermilion when mixed with the varnish produces a dull colour. Orange red and vermilion ground together also produce a very bright tint, and one that is more permanent than an entire vermilion colour. Cheaper substitutes are orange mineral, rose pink, and red lead. Chromate of lead makes the brightest colour. For dull yellow, use yellow ochre. Indigo is excessively dark, and requires a good deal of trouble to lighten it. It makes a fine showy colour when brightness is not required. Prussian blue is useful, but it dries very quickly, hence the roller must be frequently cleaned. There is this objection to Prussian, Antwerp, and Chinese blues, that they are hard to grind and likely to turn greenish with the varnish when used thin. For green any of the yellows and blues may be mixed. The varnish itself having a yellow tinge will produce a decidedly greenish tint with a small quantity of Antwerp blue. Emerald green is got by mixing pale chrome with a little Chinese blue, and then adding the emerald green until the tint is satisfactory.

In using painter's colours it is advisable to avoid as much as possible the heavy ones. Some colours require less oil in the varnish than others. For the comparative permanence of colouring matters, *v.* PIGMENTS.

A bronze of changeable hue may be given to inks with the following mixture (Southward):—Gum shellac 1½ lbs. dissolved in one gallon of 0·95 p.c. alcohol or Cologne spirits for twenty-four hours. Then add 14 oz. aniline red. Let the mixture stand for a few hours longer, when it will be ready for use. When added to good blue, black, or other dark ink, it gives a rich hue to it. The quantity must be carefully apportioned.

Ticket-writers' ink is made of good black ink, with liquid gum added to produce a gloss.

Ink for writing on glass is a solution of gum arabic in strong hydrofluoric acid coloured with some matter which can withstand the acid: cudbear is used for this purpose.

For enamelled cards ordinary printing ink is mixed with a few drops of equal parts of copal varnish and mastic varnish.

Ink for indiarubber stamps. The following preparation produces ink adapted for this purpose. It does not easily dry upon the pad, and is readily taken up by the paper:—Aniline colour in solid form (blue, red, &c.), 16 parts; boiling distilled water, 80 parts; glycerine, 7 parts. The colour is dissolved in the water, and the other ingredients are added whilst agitating.

See Watts' Dict. of Chemistry (1st edit.), Ure's Dict. of Arts, Manufactures, &c., Cooley's Cyclop. of Practical Receipts, Southward's Practical Printing, Noble's Principles and Practice of Colour Printing.

INSECT WAX *v.* WAX.

INULA CAMPHOR *v.* CAMPHORS.

IODINE. Symbol I. At. wt. 127. This element was discovered in 1812 by Courtois in the mother liquor of kelp. The discovery was first announced to the French Institute in 1813. The properties of the new element were further investigated by Clement and Desormes, Gay-Lussac, and Davy.

Iodine is a crystalline solid of greyish-black colour and bright metallic lustre resembling plumbago. Its sp.gr. is 4·948. It is obtained by sublimation in brilliant rhomboidal plates, or in elongated octahedrons belonging to the trimetric system. In very thin plates it transmits light of a red colour. It melts at 114·15°, and boils at 184·35° (Ramsay). It volatilises at ordinary temperatures spontaneously in the air, diffusing an odour resembling chlorine. It is sometimes employed in this way in hospitals as a disinfectant. The vapour has an intense rich violet colour, and is one of the heaviest of all known gases having a sp.gr. of 8·801. A stratum 4 inches thick presents a black mass quite impervious to light. It is very slightly soluble in water, requiring about 7,000 parts for solution. It is soluble in chloroform, bromoform, carbon disulphide, petroleum spirit, and benzene, forming violet solutions, also in ethylic, methylic, and amylic alcohols, and in ether and glycerine, forming brown solutions. It is very soluble in potassium iodide, of which 1 part in 2 parts of water will dissolve 2 parts of iodine. In reactions it resembles chlorine and bromine, but is less energetic, and is displaced from its compounds by these elements. It has a strong affinity for most of the metals, and in the presence of water attacks and dissolves gold. The most characteristic reaction of free iodine is the dark-blue compound formed with starch; this test is extremely sensitive, and will reveal the presence of one-millionth part in any liquid containing it. Another characteristic reaction is to liberate the iodine from a solution by nitrosulphuric acid, and dissolve it out by carbon disulphide; this affords an accurate and easy method of estimating it by the depth of the crimson colour of the solvent; it is also extremely sensitive, and well adapted to estimate minute traces of the element.

Iodine in minute quantities is very largely distributed throughout the animal, vegetable, and mineral kingdoms. As a mineral it occurs in combination with silver, mercury, and lead, in ores from Mexico, Chili, and Spain, with zinc in Silesia, and with lead in South America. It is also found in dolomite from Saxony, in limestone from Montpellier, in shale from Sweden, and in phosphate of lime from France. It exists also in the 'caliche' of Chili in the form of sodium iodate. This is the only mineral source from which it is manufactured, and it is rapidly becoming the most important of all the commercial sources.

Many mineral waters contain iodine, notably those of Carlsbad in Bavaria, Hall in Austria, Marienbad in Bohemia, Holberg in Pomerania, Halle in Saxony, Sales in Piedmont, Nix in Savoy, Kreuznach in Galicia, Halse in Java, and Jallien in France. It is also found in the waters of Friedrichshall, Castellamare, Heilbrun, Homburg, Seidchutz, and Vichy; and in this country those of Leamington, Bonington, Bath, Cheltenham, and Woodhall. The water of the Woodhall spa, near Lincoln, is exceptionally rich in iodine and bromine, and is remarkable for containing iodine in the free state (Wanklyn). It is a valuable remedy in skin diseases. The sea is an abundant source of it. Iodine is always present in sea-water, but in such a very minute proportion that it is difficult of detection except by operating on large quantities. It has been estimated in the Atlantic at 1 part in 280,000,000 (Stanford); all fishes and all animal products from the sea appear to contain iodine, but in very minute quantity. The following table shows a few of the marine products in which it has been estimated:—

Cod-liver oil . .	·000322 p.c. iodine.
Cod-liver . . .	·000817 „
Codfish . . .	·000160 „
Herring, salt . .	·000650 „
Whale oil . . .	·000100 „

Seal oil . . .	·000050 p.c. iodine.
Oysters (Portuguese) .	·000040 ,,
Prawns . . .	·000440 ,,
Limpets . . .	·003200 ,,
Cockles . . .	·002140 ,,
Whelks . . .	·008920 ,,
Mussels . . .	·035720 ,,
Sponge (Turkey) . .	·200000 ,,
Sponge (Honeycomb) .	·054000 ,,

Nearly all seaweeds or marine algæ contain it. It is present even in the *Zostera marina* or grass wrack, natural order Naiadaceæ, a flowering plant growing only in the sea; but there are some remarkable exceptions. These are the gelatinous species of algæ, the *Chondrus crispus* (or Irish moss), and *Gelidem corneum* of British species, and the *Euchemia spinosa*, or *Agar agar* of foreign species, do not contain iodine. The *Enteromorpha compressa*, or common sea grass, which when dry has a strong odour of the sea, but does not contain iodine. The salsola or salt wort, *Salsola kali*, natural order Chenopodiaceæ, growing on the sea shore, and from which barilla was made, contains no iodine. Some of the algæ are comparatively rich in iodine, and the ash of these plants, known as kelp, for many years formed the only commercial source of this important element.

Manufacture. — Courtois, a saltpetre maker in Paris, who discovered iodine, obtained it from the kelp liquors which were used to furnish the salts of potash required in his manufacture, and this was for many years the only commercial source of iodine. The manufacture was unsuccessful commercially in the hands of the discoverer, and he died in poverty. It was afterwards successfully carried out by MM. Cournerie of Cherbourg, and has continued to be an important manufacture on the Normandy coasts. In this country it was first made on the small scale by Dr. Ure of Glasgow, and the manufacture has since been almost exclusively confined to this city, where it has assumed considerable importance. It was first made there in quantity in 1841, and the imports of kelp into Clyde in that year amounted to 2,565 tons. In 1845 there were four small works engaged in the manufacture of iodine. Kelp was then used for soap making on account of the sodium carbonate it contained, and the iodine was extracted from the leys of the soapboilers. In 1846 there were twenty makers of iodine in Glasgow, who then treated the kelp directly, extracting also the potash salts which had a high value in the market. The fall in the price of potash salts owing to the discovery of the Stassfurt mineral, which reduced the price to one third, the very variable character of the kelp used, and the extreme fluctuations in the price of iodine, ranging from 4*s.* to 34*s.* per lb., soon reduced the number of makers, and now there are only two British works, both near Glasgow. The produce of iodine in this manufacture from kelp was so limited that it offered unusual temptations to speculators, who derived most of the benefit from the high prices, the manufacturers suffering the losses during the low prices.

The following table shows the imports of kelp into Clyde and the price of iodine for a period of forty-five years. For the last seven years the kelp is estimated, as since 1878 very little has come into the Clyde, the works not being now situated in Glasgow.

Kelp Imports into Clyde, years ending June 30.

Year	Tons of kelp	Price of Iodine per lb.		Year	Tons of kelp	Price of Iodine per lb.	
		s.	*d.*			*s.*	*d.*
1885	5,000	11	3	1862	9,414	5	8
1884	5,000	5	2	1861	9,722	7	0
1883	6,000	5	0	1860	7,754	8	6
1882	7,000	7	3	1859	8,190	9	8
1881	7,000	7	8	1858	8,123	10	6
1880	7,000	11	3	1857	8,641	12	4
1879	7,000	15	6	1856	6,849	13	8
1878	7,951	12	9	1855	5,826	13	4
1877	7,959	11	9	1854	4,679	12	0
1876	8,964	7	8	1853	6,491	15	4
1875	8,643	10	8	1852	5,418	15	0
1874	10,923	15	8	1851	7,320	8	8
1873	9,449	24	8	1850	11,421	10	8
1872	10,049	34	0	1849	4,731	11	0
1871	9,384	14	4	1848	4,400	11	0
1870	9,257	12	8	1847	4,000	11	0
1869	8,978	13	0	1846	3,627	21	3
1868	8,116	12	8	1845	6,086	31	1
1867	8,174	12	0	1844	3,263	12	0
1866	8,858	10	0	1843	1,965	6	0
1865	13,741	7	8	1842	1,887	4	8
1864	11,349	8	4	1841	2,565	5	0
1863	14,018	5	0				

Fluctuations.

Average	Ten Years, 1876 to 1885
6,887	5,000 in 1885 to 8,964 in 1876.
9/6	5/ in 1883 to 15/6 in 1879.
Average	Ten Years, 1866 to 1875
9,187	8,116 in 1868 to 10,923 in 1874.
15/11¼	10/ in 1866 to 34/ in 1872.
Average	Ten Years, 1856 to 1865
9,730	6,349 in 1859 to 14,018 in 1863.
8/10	5/ in 1863 to 13/8 in 1856.
Average	Ten Years, 1846 to 1855
5,811	3,627 in 1846 to 11,421 in 1850.
12/11	8/8 in 1851 to 21/3 in 1846.
Average	Five Years, 1841 to 1845
3,133	1,887 in 1842 to 6,086 in 1845.
11/9	4/8 in 1842 to 31/1 in 1845.

The general average of 45 years from 1841 to 1885 gives 7,373 tons of kelp as the average annual amount worked, and the average price of iodine is 11*s.* 9½*d.* or about the present price.

The history of kelp, or *varec* as it is called in France, is extremely interesting. It is a crude rough slag made by burning seaweed in long shallow pits. For many years it was a large and valuable article of commerce, and greatly enriched the proprietors of the West Highland estates where it was principally made. It was then the only source of soda. At the beginning of this century it realised 20*l.* to 22*l.* per ton, and the Hebrides alone yielded 20,000 tons per annum, worth upwards of 400,000*l.* per annum; and as the burners only received 35*s.* to 40*s.* per ton for their share, the profit to the Highland lairds was enormous, and it induced an amount of extravagance which ruined most of them. It was largely used in soap making and in glass making, and within the memory of some few men still living there were glass works at Dumbarton using this material, which were celebrated for the quality of their glass. At a glass work in Drontheim in Norway, it was still used for this purpose up to about twenty years ago. The importation of barilla gave the first blow to kelp. and it fell in price, and for the twenty-two years ending 1822 the average price was 10*l.* 10*s.* The duty was then taken off barilla, and the price of kelp again fell to 8*l.* 10*s.*; in 1823 the salt duty was repealed and kelp fell again to 3*l.*, and in 1831 to 2*l.*, at which price there was no further profit on the manufacture. In the meantime soda was being largely made by the Le Blanc process, and kelp was superseded altogether as a source of soda. It must have been a most expensive source, as it yielded only about 4 p.c. of alkali and often less than 1 p.c.; it must at one time have cost the soap makers what would have been equal to 100*l.* per ton for soda ash, worth now about 5*l.*

The manufacture of iodine and potash salts then began to assume some importance, but the kelp required was not the same, that which contained the most soda containing the least potash and iodine. Moreover the kelpers had been taught to burn at a high temperature, which improves the yield of sodium carbonate but which volatilises much of the potash and 50 p.c. of the iodine. The seaweed employed by the kelpers was of a kind containing little iodine, and not very rich in potash. They used almost exclusively the black wrack, cut in large quantities in the Highland lochs, and consisting of the three fuci, *Fucus vesiculosus*, *F. nodosus*, and *F. serratus*, which are all uncovered at low tide. This is now entirely unutilised: the kelp made from it is known as cut weed kelp. The following is the average analysis from numerous cargoes of the kelp:

Potassium sulphate	23·08
Potassium chloride	1·45
Sodium chloride	19·13
Sodium carbonate	6·48
Insoluble	43·71
Water	6·22
	100·07
Total potash	13·40
Iodine, lbs. per ton	4·18
	=0·18 p.c.

These seaweeds form a certain crop of kelp, as the quantity required can always be obtained by cutting in the summer, and the plants alter very little by exposure to rain. Drift kelp is the only variety now employed. It is made from the red wracks, the *Laminaria digitata*, or tangle, and the *L. stenophylla*. These are always submerged by the tide, and contain about ten times as much iodine as the fuci. These seaweeds are torn up by the storms from the rocks on which they grow, and cast ashore; unlike the black wrack these plants suffer much from rain, the more valuable salts being completely washed away, and are often after drying quite valueless, the kelper losing all his labour. At first the iodine was not the most important product, as the potash salts were so remunerative. Potassium chloride, or 'muriate' as it is technically called, was worth 25*l.* per ton. The discovery of the Stassfurt mineral reduced its value to about one third, and the further discovery of bromine in the same mineral reduced the price of that element from 38*s.* to 1*s.* 3*d.* per lb., the present value. The amount of bromine in kelp is small, only about one tenth of the iodine, and it is not now extracted from this source. It is remarkable that the algæ should select iodine, as bromine is a much larger constituent of sea-water, which usually contains about 6 parts in 100,000, and according to Dittmar appears to bear the constant relation to the chlorine of ·34 to 100, whereas iodine exists only as a minute trace, difficult even of detection, although the aggregate amount in the ocean must be enormous.

The algæ differ considerably in the proportion of iodine which they take up from the sea-water, and only two species, the *Laminaria digitata*, and the *L. stenophylla* are worth burning for kelp.

It is remarkable that the giant algæ of the Falkland Islands contain very little iodine, although these are the largest sea-plants in the world. The *D'Urvillæa utilis*, a marine tree with a stem a foot in diameter, and the *Macrocystis pyrifera* which grows to the length of 1,500 feet, contain only traces of iodine; in some samples it can scarcely be detected.

The following table shows the average yield of the most important varieties. The kelp plant figures are taken from a large number of analyses, from seaweed gathered all around the shores of Great Britain and Ireland; also Denmark, Norway, and Iceland.

Dry weeds	Per cent.	lbs. per ton
Drift Kelp:		
Laminaria digitata, Tangle, stem	0·4535	10·158
„ „ „ frond	0·2946	6·599
„ *stenophylla*	0·4777	10·702
„ *saccharina*, Sugar Wrack	0·2794	6·258
Cut Kelp:		
Fucus serratus, Black Wrack	0·0856	1·807
„ *nodosus*, Knobbed Wrack	0·0572	1·281
„ *vesiculosus*, Bladder Wrack	0·0297	·665
Various:		
Halidrys siliquosa, Sea Oak	0·2131	4·773
Japanese Seaweed, edible	0·3171	7·102
Hymanthalia lorea, Sea Laces	0·0892	1·998
Rhodomema palmata, Dulse, edible	0·0712	1·594
Chorda filum, Sea Twine	0·1200	2·688
Zostera marina, Grass Wrack	0·0457	1·023
D'Urvillæa utilis, Falkland Islands	0·0075	·179
Macrocystis pyrifera „ „	0·0308	·690

It will be seen that even in the drift weeds the quantity of iodine is inconsiderable, but if the plants are properly burnt to a loose ash at a low temperature, they ought to yield a kelp containing 25 to 30 lbs. of iodine to the ton. 12 lbs. per ton is, however, above the average yield from ordinary drift kelp. It is impossible to prevent the kelpers from burning it into a hard slag by working it up, when molten, with iron clauts. Sand and stones are thus mixed up with it, and the great heat employed drives off more than half the iodine. The result is a hard slag of great density, and this density forms one of the difficulties in inducing the kelpers to burn the weed to a loose ash, which they imagine, from the lightness, will not give them the weight they expect. As an actual fact, of course, the total weight of the ash so produced is considerably more, from the same quantity of weed used; but old fallacies die hard, especially amongst the poor and ignorant people who do this work. There is the further disadvantage that the sulphates are reduced to sulphides or oxysulphides, and entail a considerable extra expenditure of oil of vitriol to decompose these; sulphur is thus obtained as one of the by-products of the lixiviation of kelp, in which it ought not to exist at all. The presence of silica as sand greatly assists the volatilisation of the iodine.

The following table shows the analyses of very good samples of Irish and Scotch kelp, and also of the latter burnt into loose ash, and the comparison of these indicates clearly the effect of the heat of burning:—

—	Kelp		Ash
	Irish	Scotch	Scotch
Potassium sulphate .	11·14	13·95	12·71
,, chloride .	27·17	17·79	18·09
Sodium ,, . .	9·00	14·00	6·80
,, carbonate . .	5·82	3·92	3·43
,, sulphide .	Heavy trace	Heavy trace	Slight trace
,, thiosulphate .	1·22	·75	·17
,, iodide . .	·82	·76	1·48
,, sulphocyanide	Heavy trace	Heavy trace	Slight trace
Soluble organic matter .	Nil	Nil	·42
Insoluble . . .	41·41	44·80	49·75
Water	3·10	4·05	7·00
	99·68	100·02	99·85
Total potash . . .	23·17	18·77	18·32
Iodine, lbs. per ton . .	15¼	14½	28
Carbon in insoluble part	Nil	Nil	9·00

The first improvement in this manufacture was introduced by Stanford in 1863, when works were erected in the outer Hebrides for the carbonisation of the seaweed in closed retorts, thus converting the tangle into charcoal and collecting the products of destructive distillation, consisting principally of tar and ammoniacal liquor, in suitable condensers. A very porous charcoal is thus produced which contains all the iodine present in the seaweed employed; it is quickly and easily lixiviated, and gives very white salts containing no sulphides. The residual charcoal, after lixiviation, does not resemble that from wood, which is principally carbon with a small percentage of ash, but in its composition and general character approaches animal charcoal obtained from bone. The following table shows the comparison:—

—	Seaweed	Bone
*Carbon	52·54	11·77
Calcium phosphate . . .	10·92	77·70
,, carbonate . . .	15·56	1·43
,, sulphate . . .	—	·35
Magnesium carbonate . .	11·34	—
Alkaline salts	5·70	1·09
Silica, &c.	3·94	·66
	100·00	100·00
*Containing nitrogen = ammonia	1·75	1·50

The presence of magnesium carbonate is a peculiar characteristic of this charcoal, as all seaweeds are rich in magnesian salts. Seaweed charcoal, as might be expected from its composition, is an excellent decolouriser and deodoriser. As compared with animal charcoal it is much lighter and more bulky, and therefore has not replaced it as a decolouriser, although from its high percentage of carbon it would well stand the constant re-burning required in sugar works, and be improved by this treatment. It has been a good deal used in sewage filtration, and in the 'carbon closets' employed in some of the Clyde ship-yards; it is eminently adapted for these purposes, and forms a cheap and efficient deodoriser. It is also largely used as a basis for 'carbon cement,' a patented material extensively employed for the covering of boilers to prevent the radiation of heat, and consisting mainly of this charcoal agglutinated with algin. Charcoal is well known as the best solid non-conductor of heat, and the lightness of this variety makes it specially applicable to this purpose. The ss. 'City of Paris' and several other of the new Atlantic liners have their boilers covered with this material.

This process by carbonisation, which has been in use in the islands of Tyree and North and South Uist for twenty-five years, with great benefit to the crofters and cottars of these islands, is remunerative and efficient as far as it goes. It requires, however, the erection of separate carbonising works in each island, and, as the winter tangle only is used, it is difficult to secure sufficient supplies except from a large area. Moreover, it burns away a large portion of the plant which might be turned to account, and may be compared to the destructive distillation of oak or mahogany and the conversion of these valuable woods into charcoal, acetic acid, and tar, instead of making them into chairs and tables. Some process which would utilise the entire plant, yielding sufficiently valuable products to pay for the collecting and shipping of the weed from the wild and distant shores where it is cast up, and exporting it to a central factory, was still the desideratum. This has now been realised. It had been noticed by Stanford that the whole of the alkaline salts present in the seaweed, and a considerable quantity of extractive matter containing dextrine and mannite, could be extracted from the *Laminaria* or red seaweeds by simple maceration in cold water, which removes about 33 p.c. of the weight of the air-dry weed; and of this, 20 to 22 p.c. consists of the salts of potash and soda, with some of the salts of magnesia, and it contains also the whole of the iodine.

The residue, which is the plant apparently unaltered, consists of a nitrogenous substance resembling albumen, and to which the name of 'algin' has been given, and the algic cellulose or algulose, which represents the cellular fabric of the plant. The algin or alginic acid is removed by digesting it with solution of sodium carbonate, which dissolves it as sodium alginate, leaving the algulose. The solution can be effected in the cold, but it is necessary to employ heat, otherwise it is impossible to filter off the algulose. A Taylor filter is the only one that can be employed, the filtration being extremely difficult on account of the great viscosity of the algin or sodium alginate and the extreme fineness of the cellular algulose. The process adopted is to boil the seaweed with sodium carbonate, and filter; the algulose is separated by filtration, and the filtrate is mixed with hydrochloric acid, and the alginic acid is then easily filtered off; the solution is neutralised with caustic soda, evaporated to dryness, and carbonised, the residue forming the 'kelp substitute.' The alginic acid, which has a slight amber colour, is washed, bleached, and redissolved in sodium carbonate; the resulting liquor, evaporated in a vacuum pan, forms the commercial alginate of soda or 'soluble algin.' By evaporation on glass plates or porcelain slabs, the algin is obtained in the form of a transparent flexible sheet, and by immersing this in a very dilute solution of hydrochloric acid it is converted into alginic acid or 'insoluble algin,' which, without altering its appearance, renders the sheet perfectly insoluble in water. The soluble algin is a definite salt of soda, having the composition, when pure, $C_{76}H_{77}Na_3N_2O_{22}$. The seaweed is thus split up into three constituents:

Water extract	*Soda extract*	*Residue*
Alkaline salts and iodine	Sodium alginate or algin	Algic cellulose or algulose

The following are the comparative yields of the three processes on 100 tons of air-dry *Laminaria* containing about 33 p.c. of moisture. It will be seen that the wet process utilises all.

Kelp process.

Per cent. utilised, 18.

Kelp. 18 tons	Salts, 9 tons. Iodine, 270 lbs.	Residuals: kelp waste 18 tons, valueless

Char process.

Per cent. utilised, 36.

Char. 36 tons	Salts, 15 tons. Iodine, 600 lbs.	Residuals: charcoal, 36 tons; tar and ammonia

Wet process.

Per cent. utilised, 68.

Water extract. 33 tons	Salts, 20 tons. Iodine, 600 lbs.	Residuals: algin, 20 tons; algulose, 15 tons

Commercial algin or sodium alginate resembles gum arabic, and in the sheet form can scarcely be distinguished from gelatine, from which it differs by the solution not gelatinising, and by giving no reaction with tannin. It is distinguished from albumen by not coagulating on heating; from starch by giving no colour with iodine; from dextrine and gum arabic by its insolubility in dilute acids. All mineral acids, and citric, tartaric, lactic, oxalic, and picric amongst the organic acids, precipitate alginic acid in a gelatinous form.

It precipitates all the alkaline earths as alginates, with the exception of magnesium, the alginate of which is soluble. It precipitates nearly all the metals as alginates, but gives no precipitate with mercuric chloride, nor with potassium silicate. The following analyses show the usual composition of the commercial algin:

—	No. 1		No. 2		Average	
Water	17·13		19·30		18·22	
Organic matter	59·97		58·13		59·05	
Sodium carbonate	18·32	per cent.	17·78	per cent.	18·05	per cent.
Neutral salts	2·98	ash	2·77	ash	2·87	ash
Insoluble ash	1·60	22·90	2·02	22·57	1·81	22·73
	100·00		100·00		100·00	
Soda Na_2O	10·71		10·40		10·55	

This substance, known as soluble algin, is sodium alginate, but potassium, ammonium, lithium, or magnesium alginate are all soluble algins, and scarcely distinguishable in appearance. These all present the form of thin flexible sheets, resembling gelatine, and having the same colour, but none are gelatinous. The solution of algin resembles that of gum arabic, which in many of its applications it may be expected to replace; it is quite soluble in cold water, but the solution takes about twelve hours to complete. It is so extremely viscous that a 2 p.c. solution is as thick as a 50 p.c. solution of gum arabic, and a 5 p.c. solution with difficulty is poured out of a wide-mouthed bottle. Nearly all the mineral acids precipitate alginic acid ($C_{76}H_{80}N_2O_{22}$) from the solution as a very gelatinous precipitate; a 2 p.c. solution becomes semi-solid when thus treated. In this respect it resembles a strong solution of egg albumen, and it can be employed for thickening colours in printing, or as a mordant in the same manner. Alginic acid is insoluble in water, so that in dressing fabrics the soluble algin forms a flexible varnish, which can be converted into a lustrous hard glaze by passing it through a weak mineral acid. This process, which would destroy the ordinary starch and gum dressings, renders it also permanent and insoluble in water, the fabric becoming waterproof. As the alginates of calcium, aluminium, iron, &c., are all insoluble, the same effect is obtained by the use of solutions of these metals for the final wash. Alginic acid when dry resembles albumen, but it can be obtained also in thin transparent sheets, and readily coloured like gelatine, from which, however, it differs in being insoluble in hot water. It forms an excellent substitute for bladder skins in tying over bottles and pots, as it softens in water, is very pliable, and dialyses well. It can also be obtained in blocks, which are easily turned and polished, and have a sp.gr. of 1·534. That of the ivory nut, so largely employed in turning for studs and buttons, is only 1·376. Calcium alginate ($C_{76}H_{77}Ca_3N_2O_{22}$) resembles it, but is whiter, like bone; it also takes a good polish, and has a sp.gr. of 1·609, near that of ivory, which is 1·820.

Aluminium alginate $Al_7(C_{76}H_{77}N_2O_{22})_2$ is very soluble in ammonia, and the aluminium ammonio-alginate is insoluble when dry, so that it makes a cheap waterproof varnish. It forms a good mordant or dung substitute in dyeing. Copper alginate ($C_{76}H_{77}Cu_3N_2O_{22}$) is soluble in ammonia, forming a beautiful blue copper ammonio-alginate, which is also insoluble when dry, and makes a varnish useful for waterproofing fabrics which are liable to decomposition or to attacks of insects.

Ferric alginate ($C_{76}H_{77}Fe_3N_2O_{22}$) is also soluble in ammonia, forming a bright red ferro-ammonio-alginate; insoluble when dry, and proposed as a styptic, and for administering iron internally. These metals are most completely precipitated from solution by sodium alginate.

Nickel, cobalt, zinc, cadmium, manganese, chromium, uranium, silver, platinum, tin, arsenic, and antimony all form soluble ammonio-alginates, some of which are beautiful salts. Sodium alginate, mixed with a bichromate, is sensitive to light in the same way as gelatine, the mixture becoming insoluble in water after exposure to light.

Alginic acid is a moderately strong acid, evolving carbonic acid in the cold from the alkaline carbonates and from the magnesium carbonate; in the latter case the two insoluble substances in the presence of water form soluble magnesium alginate. The use of algin requires a thorough knowledge of its properties, on account of the numerous metallic salts which precipitate it, and with which it is therefore incompatible; these reactions limit to a great extent the application of the substance in solution as a substitute for gum and other bodies used for thickening purposes.

Algulose or algic cellulose contains no fibre, but consists of fine cellular tissue, which makes a transparent and very tough paper. It dries to a hard mass resembling ebony, but denser. It can be turned and polished, and makes good buttons, knobs, door handles, &c. Ordinary algulose has a sp.gr. of 1·181; that from tangle is much denser, having a sp.gr. of 1·486. Ebony is only 1·187, and boxwood 1·28, lignum vitæ 1·333, so that none of the harder woods are so dense or so tough, since the algulose has considerable elasticity.

The kelp substitute in this wet process is obtained by evaporating and carbonising the acid liquor from which the alginic acid has been precipitated, after neutralising it with caustic soda. It contains all the iodine and potash salts of the weed, and should yield about 30 lbs. of iodine to the ton. It contains no sulphides, and is easily lixiviated.

Lixiviation of kelp.—Little improvement has taken place in this process; the same simple method which has been in use for many years is still adopted in the Scotch works, principally because it furnishes at once good dry iodine ready for the market without further drying or resublimation.

The kelp reaches the factory in large masses; these are first broken up in pieces about the size of road metal. With seaweed charcoal and kelp substitute this is unnecessary, but with this exception the same process is followed. The lixiviation is effected in rectangular iron vats with false bottoms; the vats are coupled together and heated by steam, and treated exhaustively. The whole arrangement is similar in every respect to that adopted in the lixiviation of black ash in the Leblanc process of soda manufacture. The solution is run off at about 40° to 45°Tw. This is evaporated in open hemispherical cast-iron boiling pans, about 9 feet in diameter, and the salts which deposit are fished out. In some works this boiling down is effected in cylindrical wrought-iron closed pans, heated by a coil of steam pipes round the inside of the pan, and provided with mechanical stirrers to keep the deposited salts in suspension. When the liquor is reduced to 62°Tw. the whole is run out into a settler to allow the salts to deposit, and the supernatant liquor is run off hot into the crystallisers. In both cases the salt fished out or deposited is a crude sulphate of potash, which adheres a good deal to the pan and contains 50 to 60 p.c. of potassium sulphate, combined with sodium sulphate and chloride. The liquid is run into cylindrical iron coolers, and a crop of potassium chloride crystallises out in two or three days. The mother liquor is again boiled down, and the salt deposited is fished out; this salt is known as 'kelp salt,' and consists of sodium chloride, containing sodium carbonate equal to 8 to 10 p.c. of alkali (Na_2O). The hot liquor is again run into the cooler, and another crop of potassium chloride is obtained. This process is repeated several times, kelp salt being fished out in the boiling pan, and potassium chloride crystallised out in the cooler. These successive crops of 'muriate,' as it is technically called, range in strength from 80 to 95 p.c. of potassium chloride.

The mother liquor, which has a density of 85° to 95°Tw., is now rich in iodine, and is treated for its extraction. The several salts all contain iodine, and require careful washing to obtain it. These salts are known as 'Kelp salt,' which was formerly used for reducing the strength of soda ash, but is now unsaleable. 'Sulphate,' which is sold at a low price for manurial purposes, and the 'Muriate,' is largely used for the manufacture of saltpetre, potassium carbonate, and chlorate, bichromate and the prussiates. The residual kelp waste formerly realised about 5*s.* per ton, and was employed in the common bottle glass manufacture; it consists principally of the carbonates of lime and magnesia, and some phosphates. It is all used as a manure in France, but in this country the farmers have always rejected it.

The following is the analysis of an average sample:

Salts of soda and potash . .	1·50
Carbon	3·09
Calcium sulphate	3·06
,, sulphide	1·70
,, carbonate . . .	20·50
*Calcium and magnesium phosphates	6·72
Magnesium carbonate . . .	6·89
Magnesia	2·22
Silicic acid and sand . . .	20·82
Water	33·50
Total	100·00
*Containing phosphoric acid . .	2·70

The mother liquor, containing the iodides and bromides, also contains considerable quantities of sulphides, sulphites, and hyposulphites of sodium; it is mixed with about one-seventh of its volume of sulphuric acid, free from arsenic, about 145°Tw. (sp.gr. 1·725), and allowed to settle for 24 hours. This is effected in a closed lead-lined wooden vessel, provided with means to collect any sulphuretted hydrogen which may be given off. The sulphur compounds are decomposed, and a considerable deposit of sulphur takes place. This is known as 'Sulphur waste'; when dry it contains about 70 p.c. of sulphur, and is used in vitriol making. It also obstinately retains iodine, and requires long steaming to extract it. The liquor is strained off from the sulphur and run into the iodine still. This was formerly made of lead, but it now assumes the form of a deep hemispherical iron pot, heated by an open fire, and covered with a strong leaden lid, to which are luted two earthenware arms; these are connected with two series of stoneware udells, about ten in each set. These udells have stone stoppers beneath to allow any water containing chlorine, bromine, and iodine to drain off. The apparatus is shown in the drawing, fig. 16. Manganese dioxide is added at intervals to the contents of the still, and the iodine is carried over with the steam. The reaction is as follows: $2NaI + 3H_2SO_4 + MnO_2 = I_2 + 2NaHSO_4 + MnSO_4 + 2H_2O$. Repeated distillations go on, without changing the udells, until these are full of iodine, the bulk of which, and the best, is found in the udells forming the centre of the series. The deposition of the iodine in successive layers squeezes the moisture out, and it is obtained in a firm, well crystalline form ready for market. On this account, this old-fashioned process is the only one adopted in this country; many others have been proposed and tried, but have not been commercially successful. Commercial iodine is always sent out in 1 cwt. kegs; the consumption is usually reckoned in kegs, which means 1 cwt. It improves by keeping, becoming perfectly dry; and as it can be stored in a small compass, and often represents considerable value, it has been a favourite commodity for small speculative buyers. Bromine does not now pay for the collection, but when it is required the arms are changed and a simple worm-condensing arrangement of lead or earthenware, or a series of stoneware Woulff bottles is attached: a further quantity of manganese dioxide is added to the still, and the bromine distilled over. The liquor remaining in the still, and known as 'waste still liquor,' is a dense acid liquid of sp.gr. 1·235 to 1·500, containing sulphates of iron, manganese, potassium, and sodium; it is very troublesome to deal with and is run away as useless.

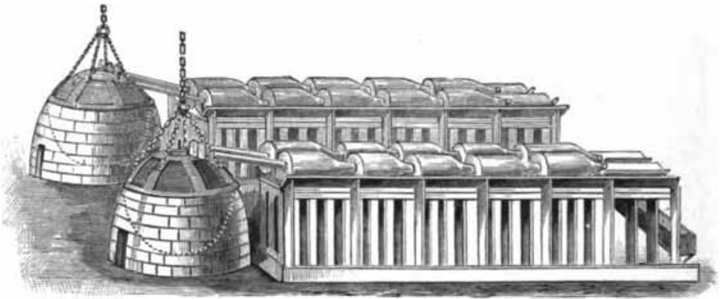


Fig. 16.

The following is the analysis of an ordinary average sample. One gallon contained 3·327 lbs. of dry salts:—

—	Liquor per cent.	Dry salts per cent.
Potassium sulphate .	5·13	15·42
Sodium „ .	9·10	27·36
Sodium chloride . .	6·80	20·43
Manganese sulphate .	3·75	11·27
Iron persulphate . .	3·00	9·02
Calcium sulphate . .	·19	·57
Magnesium sulphate .	·04	·12
Sulphuric acid, free .	5·26	15·81
	33·27	100·00

The iodine used for medicine is resublimed in small earthen or porcelain covered pans, and is then known as 'resublimed iodine'; it is obtained in large brilliant plates, and is anhydrous. The pans employed must be shallow, as the vapour is very dense.

When iodine is badly made it may contain white needles, which consist of iodine cyanide; it is now a rare impurity, but a very poisonous one.

In France a different method is adopted. After the precipitation of the sulphur in the mother liquor by sulphuric acid in slight excess, and boiling for some time, the clear liquor, after standing to settle, is drawn off and diluted with water to 40°Tw. Chlorine is then passed into the solution, until saturated, and the iodine is precipitated in a pulverulent form. Great care must be taken that too much chlorine is not added, as chloride of iodine may be formed, and go off as vapour. The clear liquor is then drawn off, and the iodine repeatedly washed by decantation to remove the salts. It is then drained in earthen vessels with perforated bottoms, and finally dried on porous tiles. It is then resublimed. This is effected in ordinary earthenware retorts with short necks, and heated in a sand-bath in which they are completely immersed, the iodine being sublimed into earthen receivers. To recover the bromine from the liquor after extraction of the iodine, it is evaporated to dryness, and the residue is distilled in a leaden retort with sulphuric acid and manganese dioxide; it is collected in a receiver under strong sulphuric acid. The iodine made in France is not exported; it is all used locally, and made into potassium or other iodide, or resublimed so that a precipitated damp iodine answers all the purposes. The production of iodine in France has fallen off considerably during the last ten years, and but a small part of the produce is now made there, only sufficient for their own consumption.

Iodine from caliche. This mineral, the crude nitrate of soda of Peru and Chili, now forms by far the most important source of iodine. It contains iodine in the form of sodium iodate, which accumulates in the mother liquors from which the sodium nitrate has been crystallised. The proportion of iodine in the caliche varies considerably in the different deposits; in some it is absent altogether, in others it runs as high as 0·17 p.c. or 3·8 lbs. per ton. It may be taken at 0·1 to 0·34 p.c. on the nitrate produced, or an average of about 0·2 p.c. or 4·58 lbs. per ton. As the quantity of nitrate exported from Peru and Chili is about 700,000 tons, at this average it would represent 28,000 kegs or cwts. of iodine, which would be about five times the present consumption of the world. For various reasons, however, only a portion of these nitrate mother liquors is worked for iodine; some are not rich enough to make the extraction pay. There are forty-three works engaged in the manufacture of sodium nitrate, employing 9,048 men, but on account of the inaccessible position of many of these, and the difficulty of transport and fuel (coal costs 70*s*. per ton), and of obtaining water, only a few of these find it worth while to extract the iodine. It first came over in quantity in 1874, about 497 kegs. In the following year 900 kegs were exported, and since then the export has continually increased. It was at first a very crude article, containing little over 50 p.c. of iodine, and a good deal was exported in the form of copper iodide. It is now, however, sent over in a pure state.

The following is the analysis of one of the samples of iodine sent from Peru in 1874:

Iodine	52·53
Sodium iodate	1·26
„ nitrate	11·62
Potassium nitrate	2·49
„ sulphate	1·78
Iodine chloride	3·34
Magnesium chloride	·36
Insoluble matter	1·52
Water	25·20
	100·10

In 1877 the total production of iodine in Scotland was estimated at 1,200 kegs, in France at 800 kegs, and the probable future production of Chili was estimated at 6,000 kegs (*v.* Brit. Assoc.; Stanford, C. N. April 27, 1877), an estimate which is now rapidly becoming closely realised.

In 1882 the export of iodine from Iquique was 205,800 kilos. or 4,116 cwt., divided as follows:

To London	120,900 kilos.
Hamburg	62,100 „
New York	22,800 „
	205,800 „

In 1885 the production had risen to 256,796 kilos., or 5,120 cwt., and the present output is estimated at 300,000 kilos. or 6,000 cwt. This is about five times the present total production of Great Britain and France, and more than the world can at present consume; large stocks have accumulated and become unsaleable, and the Chilian makers have reduced their production, and in some cases stopped it altogether for three years. In 1887 only 73,600 kilos. or 1,472 cwt. were exported from Iquique.

The quantity sold throughout the world in 1887 was 6,375 cwt., of which about 1,000 kegs were used in colour making. In 1888 the total sales amounted to 5,659 cwt. The present average annual consumption may be taken at something over 6,000 cwt.

The final mother liquor, or 'aqua vieja,' from the caliche, contains the following ingredients, and runs about 95°T.:

Sodium nitrate	28
„ chloride	11
„ sulphate	3
Magnesium sulphate	3
Sodium iodate	22
Water	33
	100

It is run into wooden vats lined with lead, and the iodine is precipitated; the agent employed is sodium bisulphite in solution. The exact amount of iodine in the mother liquor is estimated, and a definite quantity of the solution is added to completely precipitate the iodine. The supernatant liquid is drawn off and used over again with the nitrate liquors.

The iodine is washed with water, and pressed into thick cakes. It then contains 80 to 85 p.c. of iodine and 6 to 10 p.c. of mineral matter, and requires to be purified by resublimation. This is effected in a cast-iron retort, to which eight earthenware condensers or udells are attached. The retort is heated by a slow fire, and when the operation is completed the retort is allowed to cool, and the iodine removed from the udells. It is thus obtained pure. The complete plant is shown in the descriptive plans, figs. 17 and 18.

The sodium bisulphite is prepared by passing the fumes of burning native sulphur into a solution of 'sal natron' or sodium carbonate. The sulphur, which is one of the many minerals found in this interesting region, is burned in a brick chamber, and the fumes drawn by a steam injector into perforated pipes in the solution of sal natron. The manufacture of this substance is also peculiar to the district. It is obtained by burning together 85 parts of sodium nitrate and 15 parts of coal. The mixture is made in the form of a cone 5 feet high, with a space of 2 feet dug out round the base. It is saturated with water and ignited; the sodium carbonate thus formed fuses and runs out into the pit. It is dissolved in water, and the solution is pure enough for use in this process, the impurities consisting of sodium sulphate and chloride, the unburnt coal being left in the residue undissolved.

Uses of iodine.—About one-fifth of the total consumption of iodine is employed in the manufacture of aniline colours; a good deal of this is recovered and used again. It is principally used in the manufacture of Hofmann violet, and aniline green in the form of iodide of methyl;

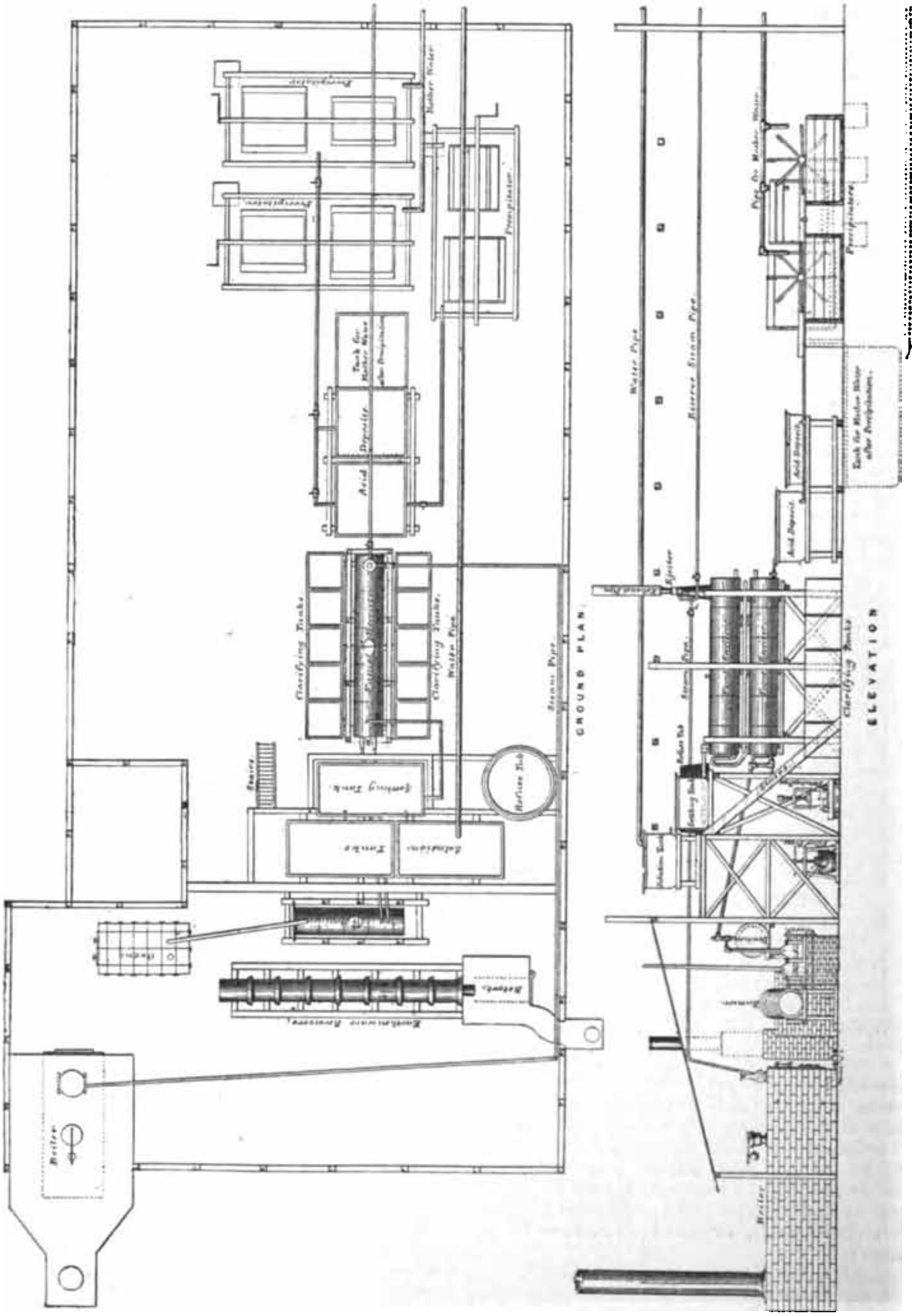
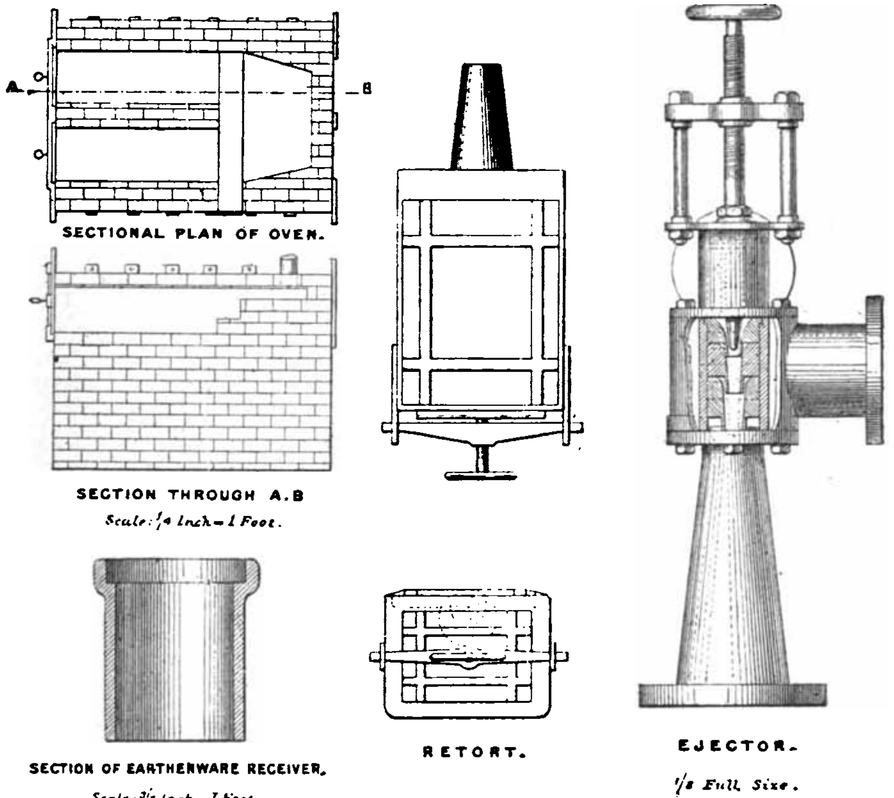


FIG. 17.

also for making erythrosin and the blue shade eosins, in which iodine is made to react upon fluoresceïn. Some substitution products are occasionally made, such as the ethylated chrysaniline. A small quantity is used in photography, but the bulk of the iodine of commerce is employed in medicine. Iodine, iodoform, and the iodides of arsenic, iron, lead, mercury (red iodide), potassium, sodium, and sulphur are all officinal in the British Pharmacopœia; the preparations employed will be referred to under their respective names. Hydriodic acid, ethyl iodide, and iodides of ammonium, cadmium, mercury (green iodide), starch, and iodol are also used in medicine, and each will therefore be noticed. Iodine, if pure, should sublime without residue, and the portion subliming first should not include any slender colourless prisms emitting a pungent odour (cyanide). The British Pharmacopœia directs that 12·7 grains dissolved in an ounce of water, containing 15 grains of potassium iodide, should require for complete decolouration 1,000 grain measures of the volumetric solution of sodium hyposulphite, which contains 24·8 grains of the salt.



SECTIONAL PLAN OF OVEN.

SECTION THROUGH A.B

Scale: 1/4 Inch = 1 Foot.

SECTION OF EARTHENWARE RECEIVER.

Scale 3/8 Inch = 1 Foot.

RETORT.

EJECTOR.

1/8 Full Size.

Fig. 18.

It is employed in the B. P. in the form of *Tinctura iodi*, 1 in 40, *Liquor iodi*, 1 in 24, *Linimentum iodi*, 1 in 8, *Unguentum iodi*, 1 in 31, and *Vapor iodi.* In the tincture and the liquor, it is dissolved with potassium iodide in rectified spirit and water respectively. The liniment contains the same ingredients dissolved in rectified spirit, with the addition of glycerin. In the ointment the same ingredients are employed, substituting lard for the spirit. The vapour is for the inhalation of iodine, the tincture with water is placed in a suitable inhaler and gently heated.

A volumetric solution of iodine dissolved in potassium iodide is used in the laboratory for titrating solutions of arsenious acid, of sulphurous acid, and sodium hyposulphite. It contains 12·7 grams of iodine in 1,000 c.c., and corresponds to 1·7 gram of sulphuretted hydrogen, 3·2 grams of sulphurous anhydride, and 4·95 grams of arsenious anhydride. Iodine is also used for testing oils which differ as to the amount absorbed, and some can be distinguished from others by this means.

Other unofficial preparations of iodine are also employed in medicine. *Glycerium* iodi is iodine dissolved in glycerine, used for external application. *Pigmentum iodi*, Coster's paste, is iodine dissolved in light oil of wood tar, and used for ringworm. *Tinctura iodi decolorata* is a tincture made with rectified spirit, and in which the iodine is decolourised by ammonia. It is used for chilblains. *Collodium iodi* is flexible collodion containing 30 grains of iodine to the ounce, and is very useful for painting on wounds. Carbolised iodine solution is a colourless mixture of tincture of iodine, phenol, and glycerine in hot water; it is used as a gargle or pigment in diphtheria, and internally for Asiatic cholera.

Medicinal properties of iodine.—Iodine was first employed in medicine in the form of burnt sponge, a remedy long used in treating goitre. When administered internally it is usually in combination with an alkali; taken alone it is an irritant poison. It is a most powerful alterative, impoverishing the blood and stimulating the absorbents. It is antisyphilitic and antiscrofulic. In syphilis, scrofula, and chronic rheumatism it is largely used, and especially in swellings of the joints and enlarged glands, which are also treated by painting externally with tincture of iodine, in which it acts as a counter-irritant. It has a remarkable power in expelling both mercury and lead from the system. The vapour mixed with steam from hot water is useful in inhalation for many affections of the air passages. Long-continued use may give rise to the depressing nervous train of symptoms known as iodism, and for which belladonna is employed as an antidote. Copious drinks of solution of starch form the antidote in cases of poisoning. Used alone, iodine is a powerful disinfectant and decolouriser, acting in the same way as chlorine. It may be allowed to evaporate spontaneously, but is very apt to colour the sheets, blinds, or anything dressed with starch; it is also used in candles, the burning of which volatilises it.

Hydriodic acid or *Iodhydric acid*, HI, is a colourless gas, very soluble in water and resembling hydrochloric acid; it forms dense white fumes in the air; its sp.gr. is 4·429. It liquefies under pressure, and solidifies at −51°. It is composed of equal volumes of iodine and hydrogen, and contains 99·2 p.c. of its weight of iodine. The aqueous acid is colourless, but on exposure to air it becomes coloured by the deposition of iodine from oxidation. It is decomposed by sulphuric and nitric acids, and by chlorine and bromine which set the iodine free.

The following table shows the relative percentage of hydriodic acid at different specific gravities:

Sp.gr. at 15°	Per cent. of acid
1·708	51·9
1·551	47·2
1·442	39·2
1·297	30·3
1·175	18·5
1·083	5·9

It is usually prepared in the liquid form by passing sulphydric acid into water in the presence of iodine $H_2S + I = 2HI + S$. At first the action is slow on account of the deposition of sulphur covering up the iodine and preventing its solution; the hydriodic acid when formed, however, dissolves an increasing proportion of iodine, and by the gradual addition of iodine and water as the action progresses, large quantities of hydriodic acid may thus be obtained up to a sp.gr. of 1·56.

A modification of this process for very pure acid has been proposed by Winkler. The iodine is dissolved in carbon bisulphide, and the solution covered with a stratum of water; when the sulphydric acid is passed into the mixture, the hydriodic acid dissolves in the water, and the sulphur in the carbon bisulphide. The aqueous solution only requires boiling for a few minutes to expel the sulphydric acid, and to obtain the hydriodic acid quite pure. Hydriodic acid is employed in the manufacture of some of the iodides, and used in medicine in the form of syrup.

Another method was suggested by Kolbe. One part of amorphous phosphorus is added to 15 parts of water in a tubulated retort filled with carbonic acid gas, and 20 parts of iodine gradually added. The resulting liquid is allowed to stand and then heated for a short time, cooled, mixed with four parts of water and distilled. It yields a colourless acid free from uncombined iodine: $P + 5I + 4H_2O = 5HI + H_3PO_4$.

Iodic acid, HIO_3. This acid is usually prepared by boiling iodine in strong nitric acid, free from nitrous acid. Iodic acid is deposited in crystals. When heated it gives off water, and iodic anhydride, I_2O_5 is obtained in small white crystals. It is very soluble in water, and easily decomposed by reducing agents forming hydriodic acid and free iodine.

The iodates have the general formula MIO_3.

Potassium iodate, KIO_3, forms small white cubic crystals. Sodium iodate, $NaIO_3$, crystallises in small eight-sided prisms. Both salts are poisonous. Both are obtained in considerable quantity in the manufacture of the respective iodides by No. 2 process as described below. The iodates can easily be separated by taking out the first salts deposited on evaporation, as these are less soluble than the iodides. If iodic acid were required on the large scale it could be easily made as a by-product of the iodide manufacture by crystallising out the iodate before fusion, and precipitating it with barium chloride as barium iodate. This is then decomposed by sulphuric acid. It has, however, no commercial application.

Iodine trichloride, ICl_3, is obtained in orange-yellow crystals by passing chlorine into a flask containing iodine vapour sublimed from a small retort. It is a very active disinfectant and germicide in solution of 1 to 1,000. It has been used in medicine internally. In contact with organic matter, chlorine and iodine are liberated in a nascent state.

Iodine cyanide, or *Iodide of cyanogen*, CNI. This very poisonous substance is interesting as forming an occasional impurity in commercial iodine; it is very seldom met with now, and ought never to be present if the manufacture is properly carried out. Its occurrence is probably due to an insufficient addition of oil of vitriol to the saturating vat or to the iodine still. It is usually prepared in the laboratory by the distillation of iodine with mercuric cyanide. When present in iodine it presents the appearance of exceedingly fine silky needles, colourless, and very volatile, even at ordinary temperatures, and with a penetrating pungent odour which excites tears. It sublimes without change. It is soluble in water and alcohol, also in ether and fixed and volatile oils. The aqueous solution does not give the starch reaction of iodine, nor does it precipitate silver nitrate.

Sulphur iodide, SI_2, is a dark crystalline body, obtained by gently heating in a glass flask 1 part of sulphur with 4 parts of iodine until the mixture liquefies; the flask is then broken, and the crystalline mass removed. It is insoluble in water, but soluble in glycerine. It has the odour and staining properties of iodine. It is used in medicine externally in skin diseases applied in an ointment. The official preparation is *Unguentum sulphuris iodidi*, containing 30 grains to 1 ounce.

Arsenious iodide, or *Iodide of arsenic*, AsI_3. This salt forms small orange-coloured crystals, soluble in water and in alcohol; it has a neutral reaction, and gives a yellow precipitate with sulphuretted hydrogen. Heated in a test-tube it almost entirely volatilises, violet vapours of iodine being set free.

It is prepared by direct combination of metallic arsenic and iodine, or by evaporating together to dryness solutions of arsenious and hydriodic acids. The dose is $\frac{1}{30}$ of a grain; and the Pharmacopœia preparation is *Liquor arsenii et hydrargyri iodidi*, about 1 grain in 100.

Iodide of nitrogen, *Iodamide*, NHI_2, or *Diamine di-iodide*, $N_2H_4I_2$ (A. Guyard, A. Ch. [6] 1, 368), is a dark-brown powder, obtained by adding iodine to excess of solution of ammonia. It is a most violent explosive, but its action is uncontrollable, and it is impossible to keep it in safety. It has therefore found no commercial application, but has been proposed as a chemical photometer on account of the ease with which it is decomposed by light in presence of excess of ammonia (*v.* Guyard, *loc. cit.*).

Ammonium iodide, NH_4I. This is a white crystalline salt, very deliquescent and becoming yellow on exposure to air. It is prepared by saturating hydriodic acid with ammonia, or by decomposing iodide of iron with ammonium carbonate and filtering off the iron precipitate. The solution in either case is evaporated and set aside to crystallise. It is used in photography, and also in medicine instead of potassium iodide, especially in rheumatism, as causing less depression than the potassium salt. It must be kept from the access of light and air, as iodine is freely given off. It is soluble in alcohol.

Potassium iodide or '*Hydriodate of potash,*' KI. This is the most important of the iodides, and forms a considerable article of manufacture, as the greater portion of the iodine of commerce goes into consumption in this form. It is a white, colourless, and odourless salt crystallising in large cubes, and permanent in the air. It contains no water of crystallisation, and is very soluble in water, dissolving in two-thirds of its weight. It is also soluble in alcohol. There are three methods employed in the manufacture.

1st. Solution of hydriodic acid is saturated with potassium carbonate, and the solution evaporated and crystallised. This is the most direct method, and there is no loss; it gives a pure product, but it is expensive and tedious.

2nd. Iodine is dissolved in solution of caustic potash. This produces a mixture of potassium iodide and potassium iodate; the reaction is $6I + 6KHO = 5KI + KIO_3 + 3H_2O$. The solution is evaporated to dryness, a little charcoal is added, and the product fused in an iron pot at a red heat until all the iodate is decomposed, and potassium iodide alone remains. The mass is dissolved in water, the solution filtered and crystallised.

3rd. Iodide of iron is first prepared by the addition of iron borings, and iodine to water; the latter must be added gradually to keep down the temperature; the solution is filtered, mixed with potassium carbonate and the iron precipitate washed and filter-pressed. The solution is then evaporated to dryness and redissolved, and the solution crystallised.

This process is that most commonly adopted by manufacturers. The crystallisation is performed in enamelled iron pans, surrounded by a steam jacket in brickwork, and very gradually cooled. The best crystals are obtained on fluted glass rods suspended in the liquid.

The second process is that directed by the British Pharmacopœia.

Potassium iodide or '*Hydriodate,*' as it is often called, is used in photography, but medicine is the principal outlet, and requires a large consumption. It is a powerful alterative, diuretic, and absorbent; and is much administered internally, especially in rheumatism and syphilis; the dose is 5 to 10 grains, but doses of 100 grains have been given in some cases. Its properties are similar to those of iodine. As iodine is freely soluble in potassium iodide solution, it presents an excellent form for its internal administration.

It must contain no iodate; this is easily detected by the addition of tartaric acid and starch solution, which sets free hydriodic acid, and if there be any trace of iodate present free iodine is liberated, as shown by the blue colour of the iodide of starch. Potassium iodide should not contain water, and therefore should not lose weight when heated; it should contain no sulphate, and therefore give no precipitate with barium chloride insoluble in nitric acid. A feeble alkaline reaction from the presence of a slight trace of carbonate, indicated by cloudiness with lime or baryta water, soluble in nitric acid is allowed by the London Pharmacopœia (but not by the German) as tending to retain the colour of the iodide when long kept. Chlorides of potassium or sodium are a common impurity; the presence of a chloride is shown by precipitating with silver nitrate, and agitating the precipitate with ammonia. The ammonia solution should give no precipitate with nitric acid. Ten grains require for complete precipitation 602 grain measures of a volumetric solution of silver nitrate containing 17 grains of the salt in 1,000 grain measures. It is almost impossible to obtain this salt, when made on the large scale, quite free from chloride (the B. P. allows a 'very little') as potassium carbonate cannot be prepared in quantity without it; a good iodide contains:

Potassium iodide	99·4
„ chloride	·2
Water	·4
	100·0

This salt is officinal in the following preparations; the number of grains in one fluid ounce is given in each case. *Linimentum iodi* 22 grains; *Linimentum potassii iodidi cum Sapone* 54½ grains; *Liquor iodi* 33 grains; *Tinctura iodii* 11 grains; *Unguentum iodi* 16 grains; *Unguentum potassii iodi* 54 grains. Potassium iodide is sometimes administered in large doses, and it is important medicinally that it should contain no iodate, as this salt is poisonous; it must not be prescribed in mixtures containing potassium chlorate, for this salt decomposes it, forming iodate.

Sodium iodide, NaI. This salt is obtained as a deliquescent white crystalline powder, soluble in two-thirds of its weight of water. It may be prepared by the same method as the corresponding potassium salt; that from iodide of iron is usually employed, and the solution is simply evaporated to dryness. It crystallises in anhydrous cubes and also in hexagonal plates, having the formula $NaI,2H_2O$. It is used in medicine for the same purposes, but the principal application is as a precipitant of silver and gold from the weak copper ores of the Tharsis and other copper-extracting companies. The same tests as in the potassium salt may be used for its purity; 1 gram requires 66 c.c. of the volumetric solution of silver nitrate for complete precipitation.

Ferrous iodide, or *Iodide of iron*, FeI_2. This is a crystalline green deliquescent mass. It has been already referred to in the third method of manufacture of potassium iodide. The green solution is evaporated in an iron dish until a drop taken out solidifies on cooling; it is then poured out on a porcelain slab, and when solidified is broken up and put in a well-stoppered bottle. It is only employed in medicine, and more particularly in the form of syrup of iodide of iron, in which it can be better preserved. The official preparations are *Pilula ferri iodidi*, and *Syrupus ferri iodidi*, containing 34·4 grains of the salt in one fluid ounce. It is a tonic alterative useful in anæmia of scrofulous patients, especially children.

A similar syrup of manganese iodide is also sometimes used in medicine.

Zinc iodide, ZnI_2. An easily fusible compound which sublimes in needles. It is prepared in the same way as the iron salt, and obtained by evaporation as a white crystalline deliquescent salt. It is sometimes used in photography.

Plumbic iodide, or *Iodide of lead*, PbI_2. This is a brilliant yellow powder, made by precipitating solutions of lead nitrate and potassium iodide, and washing and drying the precipitate. By boiling the powder in water, and allowing the solution to cool, it is obtained in bright yellow crystalline scales. It is employed in medicine externally in the form of ointment and plaster. The official preparations are *Emplastrum plumbi iodidi*, 1 part in 9; and *Unguentum plumbi iodidi*, 1 part in 8.

Mercurous iodide, HgI, or *Green iodide of mercury*, is a green insoluble powder, which darkens on exposure to light. It is prepared by rubbing together in a porcelain mortar the equivalent proportion of mercury and iodine, and moistening the mixture with alcohol until the metallic globules cease to appear and a green powder is obtained. This must be dried in the air in a dark room, and preserved in a bottle put away from the light. It can be obtained in yellow crystals by sublimation. It is insoluble in water and alcohol. It is employed in medicine in doses of 1 to 3 grains. It is an irritant poison and is used in syphilis.

Mercuric iodide, or *Red iodide of mercury*, HgI_2. This is a brilliant scarlet powder, known as Chinese vermilion. It may be prepared in the same manner as the green iodide, using double the equivalent of iodine; but a better product is obtained by precipitation. Solution of mercuric chloride, or corrosive sublimate, is precipitated with potassium iodide, both salts being dissolved in boiling water; the precipitate is washed and dried over the water bath. By sublimation it may be obtained in large and beautiful crystals, which when hot are yellow, but reassume their scarlet colour on cooling. It is insoluble in water, but very soluble in solution of potassium iodide. This solution contains a double iodide of mercury and potassium and is used in analysis as a precipitant for alkaloids. It forms a pigment more brilliant than vermilion, but it is not much used for this purpose, as it is easily altered by exposure. It is employed in medicine, especially in syphilis, in doses of a thirty-second to an eighth of a grain, and also externally as an ointment. The official preparations are *Liquor arsenii et hydrargyri iodidi*, containing 1 grain in 100 grain measures, and *Unguentum hydrargyri iodidi rubri*, containing 1 part in 28. It is an irritant poison employed in syphilitic cases. It has been recently introduced as a germicide for washing wounds, instead of corrosive sublimate, which is not so effective and is more poisonous. It has also been used as an antifermentive in tanning.

Bismuth iodide, BI_3, is a red powder obtained by precipitation from bismuth nitrate by potassium iodide. It has recently been introduced into medicine as a substitute for iodoform in treating wounds. It has no odour. This iodide is soluble in potassium iodide, forming a double iodide employed in analysis as a precipitant for alkaloids.

Silver iodide, AgI. This salt occurs native, in hexagonal crystals, as *iodargyrite* or *iodyrite*. It is obtained by precipitation from a solution of argentic nitrate and any soluble iodide. This salt is not employed commercially in this form. It is the active salt of iodine which is used in photography, but it is always produced in silver on the plate or the paper. It is the form in which iodine is often precipitated and weighed. It is insoluble in ammonia, but soluble in potassium iodide and cyanide, and in sodium hyposulphite.

Palladium iodide, PdI_2. This is a dark-brown powder, interesting as the most insoluble salt of iodine, and as a form in which it is estimated in analysis.

Cuprous iodide, or *Iodide of copper*, Cu_2I. This is a drab-coloured powder obtained by precipitation from the mixed solutions of potassium iodide and cupric sulphate. It was proposed by Soubeiran as a method of obtaining iodine from kelp liquors, but it has not been much used. Only half the iodine is precipitated, the other half being set free, according to the following reaction:

$$Cu_2.SO_4 + 2KI = K_2SO_4 + Cu_2I + I.$$

It is necessary, therefore, to add a reducing agent as sulphurous acid or sodium hyposulphite, but ferrous sulphate is usually employed; the whole of the iodine is then thrown down as cuprous iodide,

$$\begin{gathered}2Cu_2SO_4 + 2Fe_2SO_4 + 2KI \\ = K_2SO_4 + (Fe_2)_2(SO_4)_3 + 2Cu_2I.\end{gathered}$$

It is insoluble in water; on exposure to a red heat it fuses to a brown mass. The iodine can be separated from it by heating it with manganese peroxide or strong sulphuric acid. Or it may be decomposed by boiling with water and zinc, which yields zinc iodide and metallic copper. Or it may be treated with potassium or sodium hydrates or carbonates, which decompose it, forming cuprous oxide and potassium or sodium iodide. With ammonia it combines, forming ammonio-cuprous iodide $Cu_2I, 2NH_3$; a white crystalline powder.

Iodide of starch, or *Iodised starch*, is a dark-blue powder obtained by triturating iodine with a little water and adding gradually starch in powder until it assumes a deep and uniform colour, and drying at a low temperature. It is decolourised at 100°. It is used in medicine as a mild form of administering iodine internally, in doses of half a drachm to four drachms. In the form of a paste it is employed to cleanse and heal foul sores and ulcers.

Iodal, $C_4HI_3O_2$. This body is a colourless oily liquid resembling chloral in odour. It begins to boil at 25° with decomposition, and is decomposed by alkalis into iodoform and formic acid. It is prepared by the action of a mixture of concentrated nitric acid and absolute alcohol on iodine. It has been recommended as an anæsthetic, in doses of 1 to 2 grains.

Estimation of iodine.—The violet vapour of free iodine is characteristic, and there are also four very sensitive tests for iodine and iodides, for the former the blue colour test with starch, and the crimson solution in chloroform, benzine, or carbon disulphide; for the latter the precipitation as silver or palladium iodide. All these can be employed in estimating iodine, the colour tests by comparison with standard solutions, and the gravimetric tests by weighing the iodine as silver iodide or palladium iodide. Insoluble iodides must be converted into alkaline iodides before precipitation by silver nitrate or palladium chloride. This may be effected by fusing with sodium carbonate, or preferably by a mixture of this and potassium carbonate. Another method for a metallic iodide is to suspend it in water and pass sulphuretted hydrogen through the mixture; the metal is precipitated as a sulphide, and hydriodic acid formed. Silver iodide is generally heated with zinc and dilute sulphuric acid, the silver is reduced to the metallic state, and zinc iodide remains in solution.

If the iodine exists in the form of a soluble iodate it must be reduced to an iodide by sulphurous acid. With organic iodides it is usual to ignite with pure caustic soda.

In the colour tests the iodine must be set free by bromine, chlorine, or, preferably, nitro-sulphuric acid. The starch method, owing to the easy decomposition of the iodide of starch, is not generally available, but the separation of the iodine from solution by a solvent forms a process of great accuracy, of easy and rapid execution, and of general application. In estimating the iodine in kelp or seaweed ash, or kelp substitute, the following process is adopted. Kelp is not an easy cargo to sample. There is often great difference in the value of the large masses forming the cargo. Stones and sand are a frequent cause of annoyance; stones are often found fused into the centre of a block of kelp, and forming most of the block. These can only be detected by breaking up all the large pieces. With seaweed ash, or charcoal, or kelp substitute there is no difficulty. Where there is much sand the kelp is more friable. The sand is generally composed of shells, and is mostly carbonate of lime; but it is sometimes quartz, flint, or other form of silica. To insure an accurate sample, about 100 lbs. are carefully picked from a cargo of say 100 tons, and ground up. A portion of this is finely powdered and kept as a sample for reference. Of this 100 grains are taken to estimate the moisture, another 100 grains are taken to estimate the soluble matter, the carbon, and the ash, also the potash and the iodine in the soluble matter. The kelp is treated with about 4 ounces of hot water, which dissolves little or none of the oxysulphides. This operation is repeated and the residue washed, and the solution made up to 5,000 grains measure. In a portion of this the potash is estimated by platinum tetrachloride. For estimating the iodine one-tenth part or 500 grains measure, equal to 10 grains of kelp, is taken. This will not contain more than one-tenth of a grain of iodine, generally about one-twentieth of a grain, often only one hundredth of a grain. If the amount exceeds one-tenth of a grain, it is advisable to dilute the solution with an equal bulk of water. One hundred grains measure of carbon disulphide are then added, and a few drops (one to three) of nitro-sulphuric acid dropped in. This reagent is prepared by treating starch with nitric acid, and passing the nitrous fumes into sulphuric acid of 1·843 sp.gr. to saturation. The mixture keeps perfectly well. The testings are performed in large even test tubes, and compared with graduated standard solutions of potassium iodide treated in precisely the same manner. By this method $\frac{1}{250,000}$th part of iodine is easily detected and measured, and up to $\frac{1}{100,000}$th part the estimation is very accurate. It has several advantages over the use of starch, as besides the introduction of an organic substance liable to change, the blue colour of the iodide of starch is distributed over the whole liquid, and when dilute can only be seen by looking down the length of the tube. Moreover, the solution is not transparent, and the indications are not sharp enough for accurate quantitative work, though useful often in testing. The carbon disulphide method is quite as sensitive, and the iodine is removed from the solution and concentrated in a sixth of the volume at the bottom of the tube. The maximum effect, which takes time with the starch, is immediate in this case. The carbon disulphide solution of iodine can be removed, and the iodine recovered from it by an alkali for further experiment if desired, but it is quite unnecessary for accurate results. It is usual to remove it from the disulphide by zinc in the presence of water, so that the reagent can be used over and over again. Many years of experience of this and other processes have shown that this is the only one to be relied on where many such estimations have to be performed daily, especially in kelp and its products, which contain such a small proportion of iodine. If the iodine is to be determined in a seaweed or other organic material, the sample must always be carbonised in a small iron retort or close crucible, and not burnt to ash in an open crucible. The salts are washed out from the charcoal, and the carbon and ash estimated by burning the residue. If this be not done, it is almost impossible to completely burn away the carbon in the presence of so much alkaline salts which at a high temperature fuse and cover it over. If, moreover, a long time is taken, as it must be, over an ordinary Bunsen burner, a large portion of the potash and all the iodine may be easily burnt off. If the salts contain magnesium, as all those from seaweeds do, it is necessary to make sure that there is an excess of alkali present, or it will be rapidly burnt off.

In kelp and seaweed there always is sufficient alkali, and this precaution is unnecessary, but where the object is to estimate iodine in organic substances containing it in minute traces, more caustic soda should always be added before carbonising. As all seaweeds also contain soluble sulphates which become reduced to sulphides and oxysulphides when burnt to ash, carbonisation presents another advantage, as it prevents this change.

Palladium chloride is the only reagent which can be relied on for the direct gravimetric estimation of iodine in mixed liquors containing chlorides and bromides. The kelp liquor must be mixed with hydrochloric acid and set aside in a warm place till the sulphur compounds are decomposed, it is then filtered off and precipitated with palladium chloride, and allowed to stand for some time. The black precipitate of palladium iodide may be washed with hot water, and lastly with a little alcohol, dried at a gentle heat, and weighed on a tared filter; 100 parts contain 70·45 parts of iodine. Or it may be ignited in a platinum crucible, and the iodine calculated from the weight of the palladium left; 100 parts of palladium are equal to 238·5 parts of iodine. If chlorine is also to be estimated in the same liquid, palladium nitrate must be substituted for the chloride. If bromine is also present the chloride must be used, or a soluble chloride must be added, or the bromine will be precipitated with the palladium iodide. This method gives discordant results with kelp, on account of the cyanides often present. Free alkalis, chlorine, and bromine also prevent the precipitation.

In the caliche of Peru the iodine exists as an iodate, and this must first be reduced to an iodide by sulphurous acid or sodium bisulphite. There are several methods of estimating iodine, bromine, and chlorine, directly and indirectly, when present together. A very simple method of separating these elements directly is to distil over the iodine first by boiling with ferric sulphate; it may be condensed in solution of potassium iodide and titrated with sodium hyposulphite. The bromine is then separated from the residue in the retort, which has been allowed to cool, by gently warming the solution after addition of potassium permanganate, and distilling it into solution of ammonia in excess, in which it is titrated with an acid; or estimated gravimetrically by precipitation as silver bromide. The chlorine can be estimated in the residue or by difference from a determination of the total quantity of chlorine, bromine, and iodine in the original substance by precipitation as silver salts. Another method is to distil over the iodine with a concentrated solution of potassium bichromate; after the iodine is removed the addition of a little sulphuric acid to the retort will set free the bromine, the chlorine can then be determined as in the last process.

Field's method of separating these three halogens is to divide a solution into three equal parts; each portion is precipitated by silver nitrate. No. 1 is washed, dried, and weighed. No. 2 is digested with potassium bromide, then washed, dried, and weighed. No. 3 is digested with potassium iodide, then washed, dried, and weighed. No. 1 contains the silver chloride, bromide, and iodide. No. 2 contains only silver bromide and iodide, the chloride having been by this process converted into bromide. No. 3 contains silver iodide only, the chloride and bromide having been both converted into iodide. The exact quantities of each in the solution can therefore be easily calculated. The valuation of commercial iodine has been before alluded to; the sodium hyposulphite is usually standardised by titrating it with a potassium iodide solution of pure iodine. It has been given in grains; in grams it is 100 c.c. = 2·48 grams ($\frac{1}{100}$th of $Na_2I_2O_3,5H_2O$) and is equal to 1·27 grams of iodine ($\frac{1}{100}$th of atomic weight in grams). Another method of volumetrically estimating the strength of an iodine solution is to pass sulphuretted hydrogen into it until decolourised; the hydriodic acid formed is then titrated with decinormal-soda, using methyl orange as an indicator.

Commercial iodine seldom contains any impurity but moisture; it is almost impossible to estimate the water by drying in the ordinary way. An easy method is to rub it up with five times its weight of pure dry mercury, adding a little alcohol. It is then dried for twelve hours, or until it ceases to lose weight, over sulphuric acid in a desiccator. This process is accurate to about 0·1 p.c., but most suitable for very damp iodine. Another method is to add a weighed quantity (about double the weight of the iodine) of zinc sheet in small pieces in a tared capsule, and adding a little water, when the iodine is all converted into zinc iodide; the contents of the capsule are gradually evaporated to dryness and weighed, the weight then includes that of the dry iodine. It is better, however, in all cases to estimate the iodine by titration. The same may be said of the valuation of potassium iodide; but in this case it is often also necessary to estimate a small quantity of chloride which is always present; and silver nitrate is the best reagent for this purpose, as the chloride ought to represent so small a percentage as to be difficult of detection. Bromine as a rule need not be looked for. Should it be present, however, some other process must be employed. It is necessary to take at least 50 grains of the potassium iodide, and add to it not less than 51 grains of pure silver nitrate, the precipitate is digested in strong ammonia, then filtered off, washed, dried, and fused with the usual precautions. The solution is concentrated by evaporation, and the silver chloride precipitated by nitric acid. This gives accurate results, even when the potassium chloride is under one half per cent. E. C. C. S.

IODINE SCARLET *v.* PIGMENTS.

IODOFORM *Triiodomethane* CHI_3. Iodoform was discovered in 1822 by Serullas (A. Ch. [2] 20, 165; 22, 172; 25, 311; 29, 225; 39, 230), and Dumas in 1834 (A. Ch. [2] 56, 122) determined its exact composition. Serullas obtained it by acting on alcohol with iodine in presence of caustic or carbonated alkalis. The reaction may be stated thus: $CH_3.CH_2.OH + 4I_2 + 6KOH = CHI_3 + HCOOK + 5KI + 5H_2O$. Numerous other compounds have been suggested as substitutes for alcohol in this reaction, by Serullas, Bouchardat (J. Ph. [2] 23, 1; [3] 3, 18), Lefort (C. R. 23, 229), Millon (C. R. 21, 828), and others; but Lieben (A. Suppl. 7, 218 a. 377) has shown that many of these, such as ether, chloroform, methyl alcohol, formic and acetic acids, phenol and probably the carbohydrates, when properly purified, do not yield iodoform. The reaction, however, takes place with ethylic ethers, which first break up by the action of water into alcohol and acid; with aldehyde, acetone, and generally with the higher normal alcohols of the fatty series and their corresponding aldehydes; also with ethylidene lactic acid, turpentine, methyl benzene, and some other compounds. This reaction serves in many instances as a very delicate and reliable test for the presence of alcohol. It may be obtained in dilute solutions (Lieben, A. Suppl. 7, 236). In the reaction with turpentine, Guyot (J. Ph. [4] 13, 318) and Chautaud (J. Ph. [4] 14, 19) employ iodated lime. When iodine is made to act on sodium ethoxide, instead of on alcohol and alkali, methylene iodide is formed together with only small proportions of iodoform (Butlerow, A. 107, 110; Mulder, R. T. C. 7, 310). Iodoform was observed by Erlenmeyer (J. 1861, 668) among the products of the action of hydriodic acid on glycerin, and Rice (Ph. [3] 6, 765) notes that a mixture of 'white precipitate' alcohol and iodine does not explode from the formation of iodide of nitrogen when phenol is present, but that nitrogen and iodoform are formed. Iodoform may also be extracted from the product of the action of coal gas on iodine (Johnston, P. M. 17, 1).

To prepare iodoform Filhol (J. Ph. [3] 7, 267) adds 1 part of alcohol to a solution of 2 parts of crystallised sodium carbonate in 10 parts of water and raises the temperature to 60-80°. 1 part of iodine is then gradually added, and when the liquid has become colourless, iodoform slowly forms and sinks to the bottom and may be removed by filtration. The filtrate is heated as before, another portion of sodium carbonate and alcohol added, and chlorine is led into the mixture to liberate iodine which has combined with the alkali. Another deposit of iodoform occurs, and the process may be repeated until the product represents nearly half the iodine employed. Another plan, suggested by Rother (Ph. [3] 4, 594), is to warm the following mixture till it becomes colourless: iodine 32 parts, potassium carbonate 32 parts, 95 p.c. alcohol 16 parts, water 80 parts. The iodoform which deposits is removed, and to the clear solution a mixture of potassium dichromate 2 to 3 parts, and hydrochloric acid 16 to 24 parts, is added to liberate iodine. After neutralising the solution with carbonate of potassium, 32 parts more of that salt are added, together with 6 parts of iodine and 16 parts of alcohol, and the heat being maintained a second quantity of iodoform precipitates. This may be removed and the operation repeated several times (*cf.* Cornelius a. Gille, J. Ph. [3] 22, 196; Smith, Ph. [3] 5, 211; Bell, Ph. [3] 12, 786; Günther, Ar. Ph. [3] 25, 373; Curtman, Bn. 1, 209). A method has been suggested in which free iodine is separated from its salts, in presence of alcohol, aldehyde or acetone, by electrolysis (D. P. J. 255, 88; S. C. I. 1885, 243). According to Suilliot and Raynaud (Bl. [3] 1, 3) almost the whole of the iodine employed is obtained as iodoform when acetone is acted upon by what is possibly nascent potassium hypoiodite produced by treating potassium iodide with sodium hypochlorite. A slight excess of dilute solution of sodium hypochlorite is added to a mixture of potassium iodide 50 parts, acetone 6 parts, and sodium hydroxide 2 parts, dissolved in 1 to 2 litres of water. The reaction probably takes place thus:

$$(1)\ KI + NaClO = KIO + NaCl.$$

$$(2)\ CH_3.CO.CH_3 + 3KIO$$
$$= CHI_3 + CH_3COOK + 2KHO.$$

This process has been applied to the working of kelp, and is said to produce iodoform of a very high degree of purity (Ph. [3] 20, 423).

Iodoform crystallises in lemon-yellow hexagonal plates (Rammelsberg a. Kokscharow, J. 1857, 431) which melt at 119°, volatilise when heated (*cf.* Dott, Ph. [3] 16, 299; 17, 282), or better in a current of steam. It has a persistent and disagreeable odour. It is nearly insoluble in water, benzene, or petroleum ether, but dissolves in ether, alcohol, and volatile oils (*cf.* Vulpius, Ar. Ph. [3] 20, 44). Lowering of the freezing-point in benzene solution (Paterno, B. 22, 465). In the dry state iodoform is not acted on by sunlight; but in solution, with access of oxygen, it rapidly liberates free iodine (Humbert, J. Ph. [3] 29, 352; Hebeler, Ph. [3] 16, 1088; Daccomo, G. 16, 247; Neuss a. Schmidt, Ph. [3] 19, 247; Fischer, Ph. Z, 34, 31). Iodoform has been much used in medicine and surgery as an antiseptic, but its value in this respect has often been questioned. It would appear, however, that while outside the system it exerts no antiseptic power, it acts differently in presence of pus at the temperature of the body. Iodine is, in this case, liberated which combines with ptomaïnes to render them innocuous (De Ruyter, Med. Press Cir. 1887, 403; *cf.* Riedlin, Ar. f. Hygiene, 7, 309, and references B. 22, 66*R*). Numerous attempts have been made to mask the odour of iodoform in its pharmaceutical preparations (Ph. [3] 8, 439; 11, 111 a. 895; 12, 439 a. 703; 16, 288; 17, 556; 18, 249). Iodoform gauze (Daux, J. Ph. [5] 16, 201).

When iodoform is heated in closed tubes to 150° methylene iodide is formed (Hofmann, C. J. 13, 65). The zinc-copper couple reduces it to acetylene (Gladstone a. Tribe, C. J. 28, 512). Bromine converts it into bromoform (Löscher, B. 21, 410), and phosphorus pentachloride into chloroform (Bn. 1, 209). Finely divided silver, even in the cold, reduces iodoform, acetylene and silver iodide being formed. Other metals act in the same way, but in the case of iron in the presence of water the products are methyl and methylene iodides (Cazeneuve, C. R. 97, 1371; 98, 369). With sodium ethoxide, methylene iodide, acrylic acid, and ethyllactic acid are produced (Butlerow, A. 107, 110; 114, 204; 118, 325). Methylene iodide is also formed by the action of potassium hydroxide on a solution of iodoform in acetone (Willgerodt a. Muller, C. C.

1884, 808). Iodoform reacts with certain mercury and silver salts. Mercuric acetate is reduced to mercurous acetate with evolution of carbon dioxide (Cotton, J. Ph. [5] 16, 481); mercurous chloride is converted into mercurous iodide and chloroform (Drescher, Ph. [3] 17, 882), the reaction being similar to that between iodoform and phosphorus pentachloride; and dry silver nitrate is decomposed with explosive violence, silver iodide, nitrogen peroxide, nitric acid, and carbonic acid being probably formed (Ph. [3] 20, 62). The last-mentioned reaction has been made the basis of a method for the volumetric estimation of iodoform (Greshoff, R. T. C. 7, 342). A crystalline but unstable compound of iodoform with strychnine is described by Lextrait (C. R. 92, 1057). A reaction, which has been employed as a test, is obtained when a few drops of an alcoholic solution of iodoform are added to a small quantity of a mixture of phenol and solution of caustic potash, and the mixture gently warmed. A red precipitate falls which, dissolved in a small quantity of alcohol, exhibits a carmine red colour (Lustgarten, M. 3, 717). Detection of adulteration (Kremel, Ph. Post, 21, 213). A. S.

IODOL *Tetraiodopyrrole* C_4I_4NH. Iodol is a recently introduced antiseptic, similar in its action to iodoform. It is less energetic, but is free from the disagreeable odour which characterises that compound. References to communications on the physiological action of iodol and its application in therapeutics are given by Ciamician (G. 16, 543). *Cf.* Trousseau (Ph. [3] 17, 265); and Robinson (Ch. Z. 1887, 222).

Ciamician and Dennstedt, who first prepared iodol, obtained it by acting on potassium pyrrole, C_4H_4NK, with iodine in ethereal solution (B. 15, 2582). It is formed, even in the cold, when iodine is brought in contact with pyrrole, in presence of such indifferent solvents as alcohol, wood spirit, chloroform, acetone, carbon disulphide, or acetic ether. The reaction may be explained thus: $C_4H_4NH + 8I = C_4I_4NH + 4HI$. It is, however, better to add some agent to remove the hydriodic acid as it is formed, such as alkalis or their carbonates; or to oxidise it and thereby utilise the whole of the iodine, such as ferric chloride, cupric sulphate, chlorine or bromine, oxide of manganese, &c. (Ciamician a. Silber, B. 18, 1766; 19, 327 *R*). Iodol may also be obtained from the corresponding chlorine or bromine derivatives of pyrrole by the action of metallic iodides (Patent, B. 20, 123 *R*).

Iodol crystallises from alcohol in light-yellow microscopic needles. Heated to 140-150° it decomposes without melting. It is insoluble in water but easily dissolves in ether, in hot alcohol or glacial acetic acid, or in alcoholic potash. The alcoholic solution with nitric acid gives an intense red colour, and a green colour is obtained when the crystals are heated with sulphuric acid. Acted upon by zinc-dust and potassium hydroxide, iodol is converted into pyrrole (C. a. S., B. 19, 3027). A. S.

IPECACUANHA. *Ipecacuanha Root*, *Racine d'Ipécacuanha*, Fr.; *Brechwurzel*, Ger. Ipecacuanha occurs in commerce as a dusky grey root, with a thick bark, transversely corrugated or ringed, the corrugations often penetrating to the woody interior, and minutely wrinkled longitudinally. The root attains a diameter in some cases of $\frac{2}{10}$ to $\frac{3}{10}$ of an inch, and as many as twenty rings may be counted to the inch in length. It has a short friable, not fibrous, fracture, and the bark, which constitutes some three-fourths of the root, separates easily from the wood. (*Cf.* Fl. a. H. 373; Tschirch a. Lüdtke, Ar. Ph. 1888, 432.)

The drug was first introduced into Europe from Brazil about the close of the seventeenth century as a remedy for dysentery, and since that period it has always retained a place among articles of materia medica. Its employment has, however, been mainly as an expectorant and emetic, but it has frequently been used in the treatment of intestinal diseases, and recently its historic reputation as a remedy for dysentery has been revived in India. Applied locally the powdered root is an irritant, and in large doses it is poisonous. (*Cf.* Pereira, Mat. Med. 1853, 2, 1591; Fl. a. H. 370.) It is administered either in the state of powder—for instance, admixed with opium and potassium sulphate in the well-known Dover's Powder—or made into pills, or in vinous solution. The mode of preparation of the drug for use in medicine has been much studied by pharmacists (*v.* indexes Ph. and Year-Bk. Ph.).

The root is derived from the *Cephaëlis Ipecacuanha* (Richard), a low shrub found for the most part between 8° and 22° S. latitude, in Brazil and also to some extent in the adjoining portions of New Granada and Bolivia. The plant grows in shady forests, in valleys, but not actually in swamps. Attempts have been made to cultivate it in India which have been materially assisted by the work of Edinburgh botanists, but so far with only moderate success (*cf.* Ph. [3] 1, 5 a. 170; 2, 227, 672 a. 775; 3, 328; 4, 221, 241 a. 261; 7, 433; 8, 30 a. 366; 18, 359, 400, 405 a. 534; 19, 468). According to Balfour (T. E. 26, 781) the plant exists in two varieties, one having a woody and the other an herbaceous stem (*cf.* plate, Bentl. a. T. 145; Fl. a. H. 374; Pocklington, Ph. [3] 2, 841 a. 921).

The most important constituent of ipecacuanha is the alkaloid *emetine* $C_{30}H_{40}N_2O_5$ first obtained in an impure state by Pelletier a. Magendie in 1817 (A. Ch. [2] 4, 172), and further studied by Pelletier (J. Ph. [2] 3, 145; 14, 200), P. a. Dumas (A. Ch. [2] 24, 180), Merck (N. J. T. 20, 1 a. 134), Buchner (R. P. 7, 289), Landerer (R. P. 52, 211), Reich (Ar. Ph. [2] 113, 193), and more recently by Lefort (J. Ph. [4] 9, 241), Pander (J. 1871, 373), Glénard (J. Ph. 22, 178; C. R. 81, 100), Lefort a. F. Würtz (C. R. 84, 1299), Power (Ph. [3] 8, 344), Kunz (Ar. Ph. [3] 25, 461) and Podwyssotzky (Ph. [3] 10, 642); Kremel (Ar. Ph. [3] 26, 419). To obtain emetine Glénard extracts the root with cold water acidulated with sulphuric acid, and treats the solution with an excess of lime. A precipitate forms which contains the alkaloid and yields it to ether. On evaporating the ethereal solution to dryness and extracting the residue with water acidulated with hydrochloric acid, a solution is obtained which on concentration gives crystals of emetine hydrochloride. This salt may be purified by recrystallisation and the alkaloid set free by means of ammonia. Lefort and F. Würtz take advantage of the comparative insolubility of emetine nitrate. These chemists extract the root with alcohol, remove the alcohol from the solution by distillation, dissolve the residue in water and add a concentrated solution of potassium nitrate. A thick crystalline mass results, containing emetine nitrate. It is washed with water and then dissolved in alcohol, and the solution poured into milk of lime. The mixture is evaporated to dryness and extracted with ether, which on evaporation leaves the alkaloid as a yellow powder. It is converted into sulphate, regenerated by ammonia, and crystallised from alcohol. Podwyssotzky removes the oil and colouring matter from the root in the first instance by treatment with ether and petroleum ether, and from the dried residue obtains the alkaloid in the following manner. It is exhausted with warm 85 p.c. alcohol. The solution is evaporated to a syrup and enough concentrated solution of ferric chloride added to combine with all the tannin. An excess of sodium carbonate is then added, which leaves the tannate undecomposed and the mass is extracted several times with hot petroleum ether which removes the emetine, and after concentration yields it, on cooling or on blowing air through it, as a white precipitate. Another plan suggested by the same chemist is to treat the powder with enough hydrochloric acid to form a paste, then to add ferric chloride and sodium carbonate, and after allowing the mixture to rest, to extract it with ether. The ethereal solution, shaken with acidulated water, gives up the alkaloid, and from the aqueous solution treated with soda, petroleum ether, extracts it and on evaporation yields it in a pulverulent form (*cf.* Lyons, Ph. [3] 16, 627; extraction of emetine from pharmaceutical residues, Brownen, Ph. [3] 9, 216).

Emetine is a white powder which changes to yellow and brown when exposed to sunlight. According to Flückiger it does not exist in the root in greater proportion than about 1 p.c., though many observers have obtained apparently higher results. It melts at 62-65° (Podw.), or 65-74° (Kunz). It has a bitter, somewhat astringent taste, and is poisonous (*cf.* D'Ornellas, Ph. [3] 4, 575). It dissolves in chloroform, methyl and ethyl alcohol, and in fixed and volatile oils, is sparingly soluble in ether and petroleum ether, and is almost insoluble in water (*cf.* Julliard, L'Union Ph. 1888, 515). A solution of molybdic acid in sulphuric acid gives a red colour changing to green in presence of even $\frac{1}{100}$ milligram of emetine (Pander). When a minute portion of emetine is treated with chlorinated lime, preferably acidulated, an orange or lemon colour is obtained. This, like the foregoing reaction, may be employed as a test (Power). Of the salts of emetine the *hydrochloride* was analysed by Glénard and the *nitrate* by Lefort and Würtz. The *platinochloride*, $C_{30}H_{40}N_2O_5,H_2PtCl_6$, was analysed by Kunz; also the *chromate*, $C_{30}H_{40}N_2O_5,H_2Cr_2O_7$, the *methiodide*, $C_{30}H_{40}N_2O_5,MeI$; and *methylemetonium hydroxide*, $C_{30}H_{40}N_2O_5Me.OH$.

To determine the value of ipecacuanha or its pharmaceutical preparations, an estimation of the emetine they contain is made. This is done either by a process similar to one of those given for the extraction of the alkaloid (*v.* Kremel, Ph. Post, 21, 151) or, having obtained a suitable solution, by titration with Mayer's reagent (*cf.* Zinoffsky, Ph. [3] 3, 342; Dragendorff, Werthbestimmung einiger starkwirkender Droguen, 1874, 37; Stewart, Am. J. Pharm. 1876, 359; Naylor, Ph. [3] 16, 507; Lyons, Ph. [3] 16, 627; Fr. 28, 258; Flückiger, Ph. [3] 16, 643; Jones, Ph. [3] 17, 277; Alcock, Ph. [3] 16, 680; Ransom, Ph. [3] 18, 241 a. 400; Cripps a. Whitby, Ph. [3] 19, 721; Braithwaite a. J. C. Umney, Ph. [3] 20, 252 a. 253; Blunt, Ph. [3] 20, 254 a. 380; Arndt, Ph. Z. 1889, 585).

Besides emetine, ipecacuanha contains a compound *ipecacuanhic acid* $C_{14}H_{18}O_7$ (Willigt, Sitz. B. 5, 192) which was thought by Pelletier (A. Ch. [2] 4, 172) to be gallic acid. It is a reddish-brown amorphous mass, with a bitter taste and very hygroscopic. It is soluble in water and alcohol, but less so in ether. With ferric chloride it gives a green colour. It reduces salts of silver and mercury, and is not precipitated by neutral acetate of lead. Kunz found the root to contain *choline*. The colouring matter of ipecacuanha was examined by Podwyssotzky. It forms purple-red compounds with alkalis. From its combination with barium an acid was obtained, *erythrocephaleïn* which crystallises from chloroform in straw-coloured needles. When the root is distilled with sodium carbonate and a little ferric chloride, a distillate is obtained from which a crystalline fluorescent *volatile alkaloid* may be isolated (Arndt, C. C. 1889, 433; Ph. Z. 1889, 585). It is present to the extent of 0·3 p.c. It forms compounds with most alkaloidal reagents, and gives a *hydrochloride* which crystallises in fluorescent octahedrons. Ipecacuanha also contains *gum* (Willigt), *starch*, 30 p.c. in the cortical and 7 p.c. in the woody portion (Fl. a. H.), and other constituents usually found in plants. It yields about 3 p.c. of ash (Mumms, Ph. [3] 17, 898).

For characters of allied plants, such as striated ipecacuanha, *Psycotria emetica* (Mutis), and undulated ipecacuanha, *Richardia scabra* (Linn.) and others sometimes substituted for *Cephaëlis*, *cf.* Fl. a H. 375; Attfield (Ph. [2] 11, 140); Planchon (J. Ph. [4] 16, 404; 17, 19); Power; Kirkby (Ph. [3] 16, 126); Hooper (Ph. [3] 18, 317); and Ransom (Ph. [3] 18, 787).

A. S.

IRIDIUM *v.* Platinum metals.

IRIDOSMINE *v.* Platinum metals.

IRIDOSMIUM *v.* Platinum metals.

IRIS GREEN. *Sap Green v.* Pigments.

IRISH MOSS GUM *v.* Gums.

IRON. Fe. At.wt. 55·88. *History.*—Iron has been known and prized from the very earliest historical period, articles of the metal having been found among the contents of the Great Pyramid of Egypt, where they are believed to have remained for 5,000 years. Iron was also used in Nineveh in considerable quantities, and in the British Museum are picks, hammers, and saws made of iron, found by Layard in the ruins of Nineveh, and which are believed to be of a date not later than 880 B.C. Iron is frequently mentioned in the earlier books of the Bible; it was much prized by the Greeks, and was discovered by Schliemann in the ruins of Mycenæ, which was destroyed B.C. 561. The Chinese were acquainted with the use of iron at a very early period, and it was also highly valued and much worked by the Romans. The metal employed in all the above instances was obtained by direct reduction from the ore, by methods very closely resembling those still in use by semi-barbarous peoples in various parts of the world. In England iron was largely worked by the Romans, and in the Forest of Dean there are still to be seen remains of these old Roman workings, while the partly reduced slags left by the Romans have in more modern times been employed for many years in the blast furnaces of that district as a source of iron. At the Norman invasion Gloucester possessed a considerable trade in iron, but until the introduction of coal Sussex was the chief seat of the manufacture in this country. The exact date at which the blast furnace was introduced is not known, and it was probably the result of a gradual development of the more primitive hearths formerly in use. Cast iron was, however, known to Agricola, who died in 1555, and was employed for cannon in this country in the year 1543. At this period small blast furnaces were employed which were capable of producing about 7 to 10 tons of metal per week, while the fuel used was charcoal. The resulting pig-iron was afterwards converted into wrought iron in a finery, or small hearth, not unlike the smith's fire. The large quantities of wood employed for the production of charcoal for this manufacture led to the introduction of various Acts of Parliament during the sixteenth century, which had for their object the restriction of the industry to certain districts, and a diminution of the waste of valuable timber. In the early part of the seventeenth century Dud Dudley succeeded in 'charring coal' or producing a coke suitable for use in the blast furnace, but the use of coal did not become general until after Abraham Darby had again introduced the manufacture of coke at Colebrook Dale about 1730. The introduction of the steam engine by Watt led to the use of more powerful blowing machinery, and gave increased yields, which have again been much improved upon by the application of hot blast in 1829, by subsequent alteration in the shape of the interior, and by the recent considerable increase in the size and the capacity of the furnaces. Various other improvements have from time to time been adopted, such as the utilisation of the gases from the furnace, the use of regenerative hot blast stoves, and the introduction of improved methods of calcining the ore, so that the present output of the best furnaces is about one hundred times that of the blast furnaces of two hundred years ago, while the consumption of fuel has been reduced to about one-fifth of that formerly employed. In connection with the manufacture of steel, the cementation process is in various forms of very great antiquity, but a notable improvement was effected by Huntsman, about 1740, by the introduction of cast steel, while a further advance was made in 1839, when Heath introduced the use of manganese in steel melting. As before mentioned, wrought iron was originally prepared directly from the ore, and at a subsequent date was obtained from cast iron by the use of the open-hearth finery. In 1784 Cort patented the puddling process, and in so doing laid the foundation of much of the prosperity of England during the century which followed. But in recent years the whole system of the manufacture of wrought iron has been revolutionised by the magnificent inventions of Bessemer and Siemens, by which the decarburised iron is obtained in the fluid condition. The metal then is commonly known as 'mild steel,' and has met with such a variety of applications that for rails, girders, guns, shipbuilding, bridge construction, and many other uses, it has gradually replaced the iron obtained by the puddling process.

Chief iron ores. Iron is occasionally found native, either in the form of meteorites also containing nickel, or as metal which, by the action of heat and reducing agents, has been naturally separated from the ore. These sources are, however, unimportant, except for savage tribes, who are in some instances largely dependent upon such methods of supply. Iron is very widely distributed throughout the crust of the earth in various forms, but on account of its cheapness, and the readiness with which it combines with various elements, such as sulphur, phosphorus, or arsenic, which, if present in the metal, would injuriously affect its mechanical properties, comparatively few ferruginous compounds are practically available as sources of iron. It is necessary if an iron ore is to be profitably employed that the working expenses and carriage should be small, that the ore should be rich and readily reduced, and that it should be free from sulphur, phosphorus, arsenic, or other impurities which seriously deteriorate the quality of the iron. Such ores are practically either oxides or carbonates.

Oxides of iron. These may be divided into three classes.

1. *Magnetites.* Magnetic oxide of iron (Fe_3O_4) is the richest oxide of iron which occurs in nature; if pure, it would contain 72·4 p.c. of metallic iron. Its colour varies from brownish-grey to iron black; it is brittle, magnetic, and produces a black streak. It crystallises in the cubic system, but is generally found massive. It occurs in immense quantities of remarkable purity in Sweden, also in the eastern portions of the United States and on the shores of Lake Superior. The Swedish iron which has so long been famed, is made from this ore. *Ilmenite* is an impure magnetite containing titanium. *Franklinite* may be regarded as a magnetite in which the ferrous oxide is more or less replaced by oxide of zinc, and *Chrome Iron Ore* is a magnetite in which the ferric oxide is replaced by oxide of chromium.

2. *Red hæmatites.* Ferric oxide (Fe_2O_3) occurs in a number of forms which possess different physical characters, such as *Micaceous iron ore*, *Specular iron ore*, *Kidney iron stone*, &c. These forms differ in hardness, density, and colour, but each gives a red streak. Red hæmatite is generally very free from phosphorus, and is found in large quantities in Cumberland, where it is employed in the preparation of a pig-iron low in phosphorus, suitable for the ordinary, or acid, Bessemer process. In the United States an immense deposit of red fossil (hæmatite) ore runs from Clinton in the State of New York to Birmingham in Alabama.

3. *Brown hæmatites.* Ferric oxide occurs associated with a variable amount of combined water in the different varieties of brown hæmatites. In colour these vary from light to dark brown, and they give a brown streak. A specially rich, pure, and easily reducible variety is now imported in large quantities from Spain, while a pure variety is also found in the Forest of Dean. In Northamptonshire, Lincolnshire, &c., a brown hæmatite is employed which contains about 10 p.c. of silica and over 0·5 p.c. of phosphorus. Brown ores are also met with in considerable quantities in the United States. *Limonite*, *Bog iron ores*, and *Lake ores* are other examples of hydrated oxides of iron occurring in various localities.

Carbonates. These consist essentially of ferrous carbonate ($FeCO_3$), the important differences in character observed in various ores depending chiefly upon the amount and character of the impurities present. These ores are widely distributed and of great importance.

Spathic iron ore is the purest form in which ferrous carbonate occurs; it has a pearly lustre and is generally light brown in colour. There are very extensive deposits of this ore in various parts of Europe, notably at Erzberg in Styria; the ore is usually free from phosphorus, but contains much manganese.

Clay iron stone.—Is a less pure variety of ferrous carbonate which contains clayey matter, and has long been one of the most important ores of this country; it usually occurs in the coal measures. The ore is generally dark in colour, and contains from 35 to 40 p.c. of metallic iron, associated with less manganese and more phosphorus than in the purer spathic ores.

Cleveland iron stone is a variety of clay iron stone met with in the North Riding of Yorkshire. It is generally uniform in character and contains about 33 p.c. of metallic iron: it contains little manganese, but the percentage of phosphorus is higher than in either of the ores previously mentioned, except perhaps in the case of the impure brown hæmatites.

Black band iron stone is an ore which occurs chiefly in Scotland and North Staffordshire. It contains a variable amount of bituminous matter which imparts a characteristic black colour, and which frequently enables the ore to be calcined without the addition of any extra fuel. In other respects black band very closely resembles clay iron stone.

In addition to the ores previously enumerated, several other materials are employed for the production of iron, such as 'tap-cinder,' which is essentially ferrous silicate, and is produced in the puddling process. In this case the product obtained is a common variety of iron known as cinder pig. Tap-cinder is only met with in quantities suitable for the requirements of blast furnaces in those districts where puddling has been conducted for a considerable period. The residue from Spanish pyrites, after the extraction of sulphur and copper, is commonly known as 'purple ore,' and has been made into bricks and used in the blast-furnace. It is, however, more often used as a fettling in the puddling process.

The following table will illustrate the approximate composition of the various ores of iron. It will be understood, of course, that such materials are subject to considerable variations in character, and it has been thought better to give approximate values deduced from a number of analyses, than to introduce a mass of figures detailing actual results obtained.

Approximate composition of iron ores.

—	Magnetite	Red Hæmatite	Brown Hæmatite		Carbonate ores			
			Forest of Dean	Northampton	Spathic	Clay band	Cleveland	Black band
Ferric oxide (Fe_2O_3)	65	90	90	65	—	0·5	3	3
Ferrous oxide (FeO)	25	—	—	—	50	47	40	41
Manganous oxide (MnO)	—	—	—	0·5	10	2	1	1
Carbon dioxide (CO_2)	—	—	—	—	38	30	25	26
Silica (SiO_2)	10	6	1	13	2	10	8	7
Alumina (Al_2O_3)	—	1	—	3	—	5	7	3
Lime (CaO)	—	1	—	variable	—	2	7	2
Magnesia (MgO)	—	—	—	—	—	2	4	1
Phosphoric anhydride (P_2O_5)	trace	trace	trace	1·3	trace	0·6	1·5	0·6
Water	—	—	9	14	—	1	2	1
Organic matter	—	—	—	—	—	trace	trace	15

Preparation of iron ores.—The mechanical preparation of iron ores is very simple, and consists of a rough assortment of the size of the materials to be employed. In some cases the larger pieces are broken by hand or suitable crushing machinery, while in other instances the very fine ore is separated by riddles and used for other purposes, as it would be apt to choke up the blast furnace. Poor ores, such as those of Cleveland, are charged in larger pieces than the richer hæmatites or magnetites. Non-calcareous ores which contain iron pyrites are frequently weathered for a few months, and the sulphur becoming oxidised passes away in solution as ferrous sulphate. Shale is also removed by weathering.

Calcination.—Many iron ores are calcined before being used in the blast furnace, the object being to remove volatile substances such as sulphur, water, carbon dioxide, arsenic, &c., and to concentrate the iron in the residue. Two other important objects are also gained by calcination; in the first place the iron is oxidised from the ferrous to the ferric condition, which prevents the formation of scouring slags, rich in ferrous silicate, during reduction in the blast furnace; and further, the material is rendered much more porous so that it is more readily acted upon by the gases of the furnace. From the above remarks it will be evident that some ores, such as red hæmatites, do not require calcination. When calcining, it is necessary to regulate the temperature as carefully as possible; with low temperatures the ore is insufficiently calcined, while if the heat be too great, or too much fuel is employed, the materials clot together and much of the benefit otherwise obtained is thus lost. Calcination is often conducted in open heaps, or between rectangular walls, exactly as is the case with many ores of other metals; but these methods are costly in fuel, space, and labour, and are apt to give irregular results, so are chiefly used for roasting tap-cinder in Staffordshire, or the black bands of North Staffordshire and Scotland, in which latter case the ore itself contains the necessary fuel. Kilns are now very generally employed for calcining, and in the Cleveland district the use of large circular kilns, constructed of iron lined with firebrick, is almost universal. In such kilns the ore and fuel are charged in at the top, and the calcined material removed from the bottom, the operation being continuous; in such kilns calcination is well under control, fuel is economised, and labour is saved.

Production of pig-iron.—The ore having, if necessary, been prepared as before described, is now *smelted* in the *blast furnace* to produce pig-iron. For this purpose it is introduced at the top of the furnace together with the *flux* necessary to form a fluid slag (or 'cinder') with the gangue of the ore; *fuel* is also added in sufficient quantity to melt the materials and to reduce the iron. The air necessary for combustion is introduced near the bottom of the furnace, having been blown, and usually also heated, by suitable appliances. The operation is continuous, a furnace frequently working without any important stoppage for a number of years. The whole of the materials introduced into the furnace have either to be melted and flow off from the bottom as iron and cinder, or to be converted into vapour and pass off as 'waste gases' from the top.

The blast furnace.—The earliest form of blast furnace is shown in fig. 1, which represents a form employed on the Continent for the production of wrought iron about 500 years ago. After the furnace had been heated, ore and fuel were introduced at the top, and blast from below; the result was the production of a bloom of wrought iron, which owing to the low temperatures of such furnaces was never melted, but was removed by taking down the brickwork at the front of the furnace. Doubtless in some of the larger furnaces of this description cast iron would sometimes be accidentally obtained, and as the value of this material for castings, and for the direct production of wrought iron by means of the finery came to be recognised, cast iron would be regularly made. This change was probably introduced early in the sixteenth century, and the furnaces gradually increased in size until they were capable of producing about twenty tons of pig-iron per week, using charcoal for fuel. About 150 years ago coke was introduced as fuel in the blast furnace, and the size and production was slightly increased. Fig. 2 shows a representative Welsh blast furnace of about the year 1825. This was built of solid masonry, with a cubical hearth about 30 inches long, and yielded about 25 tons of pig-iron per week. Since this period enormous changes have been introduced, commencing with the use of hot blast in Scotland in 1829; the adoption of round and larger hearths in S. Staffordshire about 1835; the utilisation of the waste gases; the largely increased height and capacity adopted in the Cleveland district shortly after 1860, and the use of hot blast stoves on the regenerative principle at a still later date. Fig. 3 represents a modern Cleveland blast furnace, the height of which would be about 80 feet, its capacity about 25,500 cubic feet, and the weekly production of pig-iron varying from 300 to about 1,000 tons, according to the character of the ore used, the temperature and pressure of the blast, and other circumstances. Such a furnace is closed at the top by means of the 'cup and cone' arrangement, into which the materials are

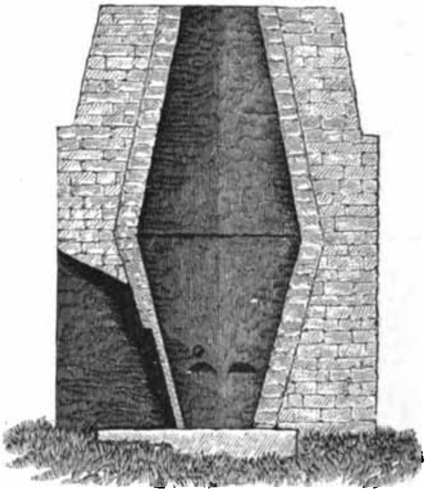


Fig. 1.

Fig. 2.

charged, and delivered into the furnace at suitable intervals by lowering the moveable cone. The combustible gases are conducted by means of suitable pipes to the regenerative stoves employed for heating the blast, or to the boilers required for raising steam for the works. The furnace itself is very light in construction for so large an erection, which is intended to contain a great weight and to resist a very high temperature. The outer casing is of iron plates riveted together, while the furnace is lined with refractory firebrick. The blast is delivered into the furnace by about six twyers, which are connected with the hot blast main, and which are water-jacketed where they enter the furnace to prevent them being rapidly destroyed by the high temperature. The following summary will illustrate the nature of the products, and the approximate weight of the charges employed for the production of one ton of No. 3 Ormesby (Cleveland) hot blast pig-iron:

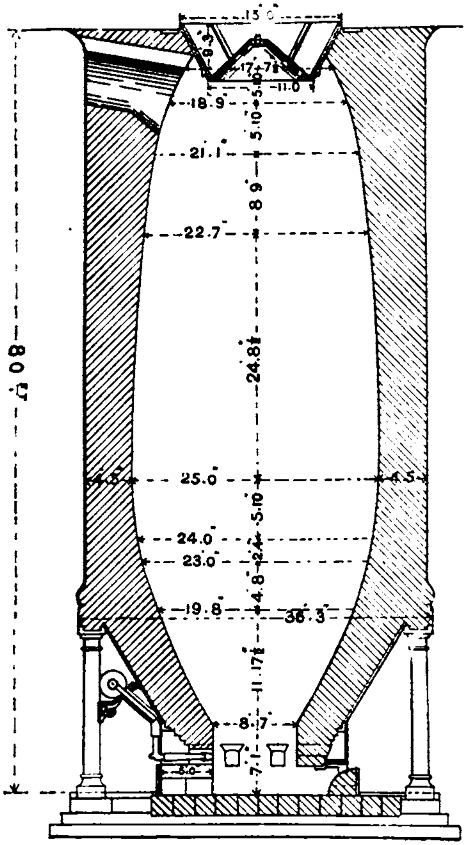


Fig. 3.

Charge	cwt.	Products	cwt.
Calcined iron stone	48	Iron . . .	20
Limestone . .	12	Slag . . .	30
Hard Durham coke	20		
Blast . . .	100	Waste gases .	130
	9 tons		9 tons

In working richer ores, such as hæmatites, the amount of limestone and ore employed would be less than the quantities required in the Cleveland district, and the weight of slag would be proportionately diminished. To prepare a No. 1 pig-iron the quantity of fuel used would be somewhat greater, while with a No. 4, or a white iron, rather less fuel would be required; the weight of the blast and of the waste gases would vary in a corresponding manner. Usually the only material added as a flux is limestone, which is sometimes burnt before being charged into the furnace. Other fluxes are often indirectly added in the form of iron ores rich in argillaceous or aluminous matter, as mixtures of ore are frequently made to obtain a more fusible cinder. The fuel most generally used is hard coke, free from sulphur, and with as little ash as possible. Raw bituminous coal is used in Scotland and North Staffordshire and in parts of the United States, though lower furnaces are necessary as the fuel is more friable. Mixtures of coal and coke are not uncommon, while anthracite is employed in this country at Brynamman, and largely in America, particularly in Eastern Pennsylvania. Charcoal is still used on the Continent in Styria, and more largely in some parts of America (particularly Michigan) for the production of a superior class of iron where coal is scarce.

The chief changes which take place in the blast furnace may be briefly summarised as follows. The ore in the first part of its descent is rapidly heated to low redness, at which temperature the carbonic oxide, which at this point forms about 36 p.c. of the furnace gases, reduces the ferric oxide to metallic iron; thus

$$Fe_2O_3 + 3CO = Fe_2 + 3CO_2.$$

The iron is not melted at this low temperature, but remains as a metallic sponge, which if brought in contact with the air would rapidly burn, and so reproduce ferric oxide. At a part of the furnace slightly lower than that at which reduction is chiefly accomplished the limestone is decomposed, carbon dioxide being evolved and lime produced; thus $CaCO_3 = CaO + CO_2$. During the next stage of the process, which occupies more time than either of the others, the materials gradually descend to the boshes of the furnace, and in so doing absorb heat from the ascending gases. Carbon in a state of minute subdivision, produced by the reduction of carbonic oxide, is also deposited in the pores of the spongy iron, which becomes more and more carburised as it descends to the hotter parts of the furnace where fusion takes place. In passing from the boshes to the hearth the temperature is sufficiently high to cause the combination of the silica in the gangue with the lime, alumina, and other bases in the charge, and thus to form a fluid cinder, which separates from the now molten iron, the latter sinking to the bottom of the hearth, while the slag on account of its relative lightness floats on the top. The cinder is either tapped off at intervals, or is allowed to flow regularly off through what is known as the 'slagging hole.' The iron is allowed to accumulate, and is then tapped off from a lower point, usually at intervals of about twelve hours, into moulds roughly made in sand. The product is cast iron, but on account of its being cast in long pieces of D section, which are called 'pigs,' and which generally weigh about 1 cwt. each, this variety of cast iron is commercially known as pig-iron.

CHEMICAL PROPERTIES OF CAST IRON.

The metal obtained as just described is by no means pure metallic iron, but usually contains at least 5 p.c. of other materials, such as carbon, silicon, sulphur, phosphorus, manganese, chromium, &c., &c. The element which imparts the characteristic properties to cast iron is *carbon*, which is present to the extent of at least 1·5 p.c. Under ordinary conditions the maximum amount of carbon found in pig-iron is 4·75 p.c., but in the presence of much manganese this amount may be considerably exceeded. The carbon is present in cast iron in two distinct conditions, known respectively as 'graphitic' and 'combined.' Graphitic carbon renders the iron *grey* in fracture, soft to the tool, and capable of taking a sharp impression of a mould. Combined carbon gives a *white* fracture, the metal is very hard, it melts at a lower temperature, but is never so fluid as in the case of grey iron. Graphitic carbon may be separated from the metal either by mechanical or chemical processes, and may be obtained in either of these ways in a state of great purity. Combined carbon on the other hand cannot be mechanically separated from cast iron; while if white iron be treated with an acid, such as hydrochloric or sulphuric, the carbon passes off in the gaseous condition, with the hydrogen evolved, in the form of badly smelling hydrocarbons. The graphitic carbon, on the other hand, would in a similar case be left behind in the insoluble residue. Though in this way the practical distinction between graphitic and combined carbon is very plainly marked, still chemists are not yet decided as to the exact nature of the combination which takes place between carbon and iron at high temperatures. Probably a mixture of several carbides of iron is produced, and this mixture in the case of white iron remains dissolved in the excess of iron present; in the case of grey iron, however, the carbon is separated from solution before the metal solidifies. Iron which contains combined and graphitic carbon in nearly equal proportions has a characteristic fracture, and on this account is called 'mottled' iron. Slow cooling produces grey iron, while rapid cooling, or 'chilling,' produces white iron.

Silicon is always present in cast iron, the amount varying from about 0·2 p.c. in specially pure Swedish iron, to upwards of 18 p.c. in some varieties of 'silicon pig' which are specially prepared for certain purposes. The average is probably from 1 to 4 p.c. When present in large proportions silicon renders the pig hard, weak, and brittle; it is also quite unsuitable for use in the puddling furnace on account of the waste of time and the injury to the lining of the furnace. Silicon, however, renders cast iron soft, strong, and grey when present in suitable proportions; and silicious irons have recently been largely used in the foundry on this account, as they allow of the use of larger quantities of foundry scrap, which is white and hard. They also allow in many cases of the employment of cheaper irons in foundry mixtures (Turner, C. J. 1885-86). For such purposes the amount of silicon should vary from about 0·8 to 3·5 p.c., according to the size and character of the work; the lower value would be employed for chilled rolls or other purposes where crushing strength is desired, while the higher value would be preferred where fluidity and softness are necessary. In the blast furnace high temperatures and silicious slags favour the absorption of silicon.

Sulphur is generally present only in very small quantities in good cast iron. With much sulphur the metal is white, hard, and unsound in the foundry; and if converted into wrought iron or steel the product is red short, and useless. In the blast furnace hot working, a slag rich in lime, and the presence of either silicon or manganese in the metal, prevents the absorption of sulphur.

Manganese is always present in pig-iron; its reduction is favoured by hot working and basic slags. *Spiegel-eisen* is a white iron, containing upwards of 5 p.c. of manganese. With 20 p.c. of manganese or upwards, the metal is known as *ferro-manganese*, which occasionally contains as much as 86 p.c. of metallic manganese. Both spiegel-eisen and ferro-manganese are used in steel-making, as additions at the end of the operation, the object being to add a little manganese to the bath of metal to prevent red-shortness.

Pig-iron which contains manganese is generally low in sulphur; this fact has been applied to the production of a special pig for use in the basic process, where both sulphur and silicon are required to be present in small quantity.

Phosphorus varies from 0·02 in best Swedish or hæmatite iron to upwards of 5 p.c. in common cinder pig. In the case of each of the elements previously considered only a portion of that which is present in the blast furnace charge passes into the metal, but with phosphorus practically the whole of that which is present in the materials used passes into the pig-iron. For foundry and forge purposes probably a little phosphorus is actually beneficial in cast iron, but in the case of wrought iron or steel its presence is highly prejudicial, as it produces remarkable brittleness in the metal when cold. Hence in the manufacture of steel by the ordinary or 'acid' process, either Bessemer or Siemens, only such pig-iron as is free from phosphorus may be employed, since by the acid process no phosphorus is removed. For irons containing phosphorus the 'basic' process must be employed if they are to be converted into steel (*v. infra*, p. 362). A representative selection of analyses of cast-iron will be found in tables at the end of this article.

Grades of pig-iron.—For a great number of uses pig iron is sold by the appearance on fracture. A pig which is very grey, with large crystals, is called No. 1; if the fracture shows smaller crystals it is called No. 2; with still closer grain it would be sold as No. 3 or 4. If white and grey are mixed it is called mottled; when graphitic carbon almost entirely disappears it is called white. On account of their softness and fluidity Nos. 1, 2, and 3 are chiefly employed for foundry purposes, and usually command a somewhat higher price. No. 4 is largely used in the puddling process, and would be called a forge or 'strong' iron. No. 4 is also employed in mixtures in the foundry when heavy castings are required, or when the metal is to be chilled —*i.e.*, when the surface is to be rendered white and hard by cooling in contact with a mass of metal, technically known as a 'chill.' Mottled and white irons are chiefly used in mixtures of pig-iron to give hardness, strength, or density.

Foundry practice.—The ironfounder commonly employs a mixture of irons, and it is the custom to mix not merely different grades of iron, but also metal from different localities. This originated at first from the results of practical experience, but it has since been shown in many cases to be in accordance with scientific knowledge, as the best foundry iron for any particular purpose contains a certain proportion of combined and graphitic carbon, silicon, phosphorus, &c. (Turner, Journ. Iron and Steel Inst. 1886), and these constituents can usually be best regulated by mixing together the irons obtained from different localities. If special strength is required the silicon should not exceed about 2 p.c., and the phosphorus should be somewhat less than half that quantity. But if softness and fluidity are specially desired these amounts may frequently be nearly doubled without serious injury. The metal is melted in a small blast furnace called a cupola, which is constructed of iron plates, lined with fire-brick or ganister; it is circular in section, and is driven with a low pressure cold blast, introduced through twyers near the bottom. The metal is charged from the top, the fuel used being hard coke free from sulphur; the weight of coke varies from about 5 to 15 p.c. of the metal used, being higher with smaller outputs. A small quantity of limestone is added to act as a flux. The metal on melting runs down, accumulating in the bottom of the cupola below the twyers, and is then tapped off at intervals into suitable ladles. For special qualities of castings, melting is sometimes performed in a reverberatory furnace; this is more expensive, but gives a cleaner and more uniform metal, which can, if necessary, be tested before using. For the majority of purposes 'green sand moulding' is adopted, a pattern being first prepared and an impression obtained in fine sand, which has been previously mixed with a small proportion of carbonaceous matter, such as coke-dust. For special work, or intricate forms, other varieties of moulds are prepared, which are often of loam; this is supported by masonry, and braced with tie rods, &c., as may be found necessary. Such moulds are carefully dried before being used; in some cases drying is performed in stoves at a low red heat, in other instances by means of a fire which is placed inside the mould. In the latter case gaseous fuel is commonly employed. Green sand moulds are not dried before using; where they can be used they have the advantages of rapidity and economy.

Iron, when remelted in the foundry, becomes harder, owing to the elimination of silicon and the absorption of sulphur. Hence in some cases, when the metal is originally too soft, a great improvement is noticed on remelting several times; but in other cases no improvement is observed, and frequently deterioration results. Many observers, among whom was Sir W. Fairbairn (B. A. Report, 1853, p. 87), have stated that iron is improved by remelting a certain number of times, and that afterwards by further melting it again deteriorates. But the experiments of various observers gave very conflicting results in this direction, some recommending very few meltings, others a larger number. It has been shown by Turner (C. J. 1886, p. 493) that the effect formerly attributed to the operation of remelting is really due to the chemical changes which take place during that operation, and that the chemical composition of the product, when rightly understood, gives an indication of its mechanical properties.

Production of wrought iron.—It has already been mentioned that by the earlier processes wrought iron was produced directly from the ore. Similar processes are still carried on by semi-civilised races in various parts of the world, and in an improved form direct reduction is largely practised in parts of America where charcoal is cheap and where no ready means of transit exist. During recent years many attempts in the same direction have also been made in various parts of Europe. In several instances great expectations have been raised in connection with these suggested improvements, but few of them have met with much commercial success. In these methods of reducing the iron ore the temperature employed is usually not sufficiently high to melt the metal obtained; the phosphorus present in the ore remains in a great measure in the slag, which is rich in oxide of iron, and the wrought iron obtained even from moderately phosphoric ores, is still sufficiently pure to be useful. The direct method is usually extravagant both in fuel and labour, while the slags produced frequently contain sufficient iron to make them valuable for use in the blast furnace.

Wrought iron is now generally prepared by an indirect process, cast iron being produced as an intermediate product between the ore and the finished metal. The impurities of the crude pig-iron are then removed by oxidation, and pass away either in the form of gas, as with carbon, or, like phosphorus, silicon, and manganese, remain in the slag. This purification was originally performed in small hearths called 'fineries,' and for the production of specially selected metal these have survived in isolated places to the present day. But a most important change was introduced in 1784, when Cort patented the puddling process, in which the operation of purification is conducted in a reverberatory furnace. In Cort's original furnace the working bottom was made of sand, and white pig-iron was employed; the iron never became perfectly fluid, and from the pasty character of the metal the 'puddling' process derived its name. This original form of the process, though once largely used, has now almost entirely given way to what is known as 'pig boiling,' in distinction from the earlier 'dry process.' Pig boiling was introduced by Joseph Hall, of Tipton, Staffordshire, about 1820. In principle the operation is exactly the same in either case, while in practice the chief differences are in the construction of the furnace, the materials forming the bottom, and the kind of cast iron employed. In the more modern process (which, however, is gradually being replaced for many purposes by the use of 'mild steel') the furnace bottom is constructed of cast-iron plates, and the bridge is internally cooled either by air or water; the cast iron bottom plates are covered with a layer of oxide of iron about 3 inches thick, which forms the working bottom of the furnace; the sides are formed of fettling, also consisting essentially of oxide of iron; while the metal used is a grey iron, usually what is known as a No. 4 forge quality. The result of these changes is that the furnace works with fewer repairs; that, owing to the use of oxidising fettling, the operation is conducted more rapidly, and larger charges can be employed; while, as grey iron is used, the metal is perfectly fluid when melted, and 'boils' vigorously during the elimination of the carbon. A sketch of the furnace used is given in fig. 4.

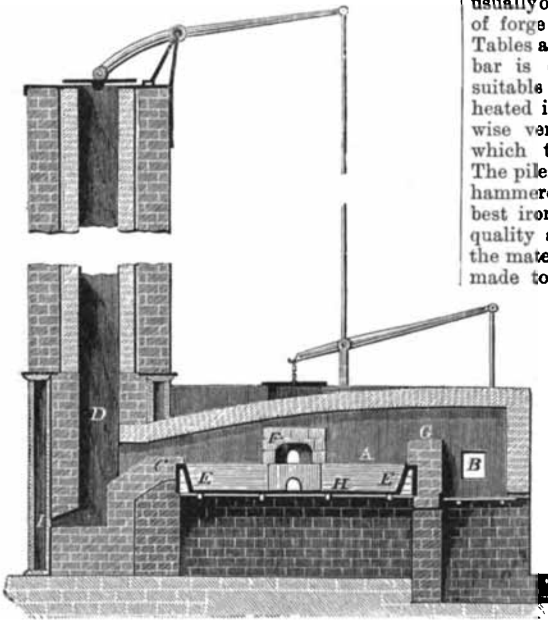


Fig. 4.

A, Furnace bed; B, Firing hole; C, Flue; D, Chimney; E, Fettling; F, Working door; G, Fire bridge; H, Cast-iron bottom plate.

The operation is conducted as follows. The furnace being at a red heat from the previous charge, the fettling is repaired, as necessary, by the addition of bull-dog, pottery mine, hæmatite, or other forms of oxide of iron. About 4 or 4½ cwts. of pig iron are then charged on to the bed of the furnace, the door being closed and the temperature raised while melting proceeds. After about thirty minutes the iron is generally melted, and is then kept fluid and well rabbled for about ten minutes, the length of time depending very much on the composition of the metal employed. By this time practically the whole of the silicon has been removed, and much of the manganese. The temperature is then lowered somewhat, by regulating the damper, and a violent reaction ensues between the oxygen of the fettling and the carbon in the metal. The iron boils vigorously owing to the escape of carbonic oxide, which burns in jets at the surface, and a quantity of slag, called tap-cinder, is removed, part of this being allowed to boil over the fore plate of the furnace, and the remainder being tapped out at the end of the operation. The phosphorus gradually passes out during the process, being eliminated most rapidly at this stage, and passing into the tap-cinder. After the boiling stage is over the metal 'drops' and 'comes to nature'—i.e. granules of malleable iron gradually separate, and the whole becomes quite pasty. In this condition it is 'balled up' by the puddler into blooms, each of which is somewhat under 100 lbs. in weight. These are then hammered and rolled, forming 'puddled bar,' which is not yet fit to be sent into commerce. The whole operation of puddling usually occupies about seventy minutes. Analyses of forge irons, puddled bar, &c., are given in Tables at the end of this article. The puddled bar is cut up into lengths and made into suitable bundles called 'piles,' which are re-heated in a furnace which is larger but otherwise very similar in construction to that in which the puddling operation is conducted. The piles are withdrawn at a welding heat, and hammered or rolled to produce merchant iron, best iron, best best iron, &c., according to the quality and the amount of work expended on the material. A number of attempts have been made to introduce mechanical contrivances to replace the laborious process of puddling; but, after numerous trials, these have been almost entirely abandoned in this country, though a revolving furnace invented by Danks is successfully used in America. Until some few years ago, wrought iron was used for ship building, bridge construction, rails, armour plates, and similar purposes, for which it has since been largely replaced by steel. Wrought iron is now chiefly employed for purposes which require a reliable metal which can be easily welded or otherwise worked by the smith.

Steel. Steel was formerly defined as a variety of iron which contained from 0·15 to 1·5 p.c. of carbon, and which was capable of being hardened and tempered. This definition, however, has now to be extended so as to include various forms of 'mild steel' which contain under 0·15 p.c. of carbon, and which cannot be hardened. We therefore include under the designation of 'steel' all metal which, though containing under 0·15 p.c. of carbon, has been produced in the molten condition. In such a classification wrought iron is obviously excluded, as it is produced in a pasty form. The characters of steel depend largely on the proportion of carbon and other elements which enter into its composition. With low percentages of carbon the metal possesses great ductility, moderate tenacity, and very slight power of hardening. With 0·45 p.c. of carbon the ductility is somewhat less, the tenacity greater, while its hardening power is quite appreciable. Such a metal would be employed in the manufacture of rails and for similar purposes. With from 0·6 to

1 p.c. of carbon the ductility is still lower, while the tenacity reaches upwards of 40 tons per square inch of section, and a metal is obtained which can be readily hardened and tempered. This class of steel is largely used for cutting tools, drills, dies, &c., and for best purposes is still usually produced in crucibles. With carbon from 1 to 1·5 p.c. a steel is obtained which is suitable for the hardest tools, and which requires to be very skilfully hardened and tempered. As the proportion of carbon increases also, the steel requires to be worked at a somewhat lower temperature. With upwards of 1·5 p.c. of carbon the metal is brittle, is no longer capable of being hardened, it is more fusible, and thus gradually passes into cast iron. Hardening increases the tenacity of steel, but diminishes its ductility. The tenacity of steel, like that of wrought iron, is also increased by the amount of work done in rolling or in drawing out the metal into wire, and certain varieties of steel wire are prepared which have a tensile strength of upwards of 100 tons per square inch. The presence of manganese in steel increases its tenacity; in suitable proportions it also very materially improves the working properties of the metal, and on this account is employed both in crucible steel making and in the Bessemer and Siemens processes. In large quantities manganese renders steel permanently harder, and also causes it to be unmagnetisable (Hadfield). Phosphorus renders steel cold short, and should on this account not exceed 0·1 p.c., while crucible steel of special quality usually contains not more than 0·04 p.c. of phosphorus. Sulphur renders steel red short, and should never exceed a few hundredths per cent. Silicon renders mild steel red short and brittle, though the presence of manganese very much modifies these effects, so that with about 0·5 p.c. of manganese several tenths per cent. of silicon may sometimes be present without injury. In steel castings about 0·3 p.c. of silicon is frequently added to promote soundness. Arsenic renders steel both hot and cold short; practically the whole of the arsenic present in the blast furnace charge passes into the pig iron, and is not removed during conversion into steel (*v.* Stead, also Harbord & Tucker, Jour. Iron & Steel Inst. 1888, part 1). Chromium in small quantities gives increased tenacity, and on this account is frequently added to basic or other very mild steel so as to impart greater strength. With considerable proportions of chromium the welding power of steel is much reduced. Tungsten, titanium, aluminium, nickel and other metals have also been added to steel, though only on a comparatively limited scale.

Production of steel.—A variety of steel, or more correctly steely iron, was obtained by the earlier processes used for the production of wrought iron directly from the ore, when the process was modified by altering the amount of blast used, and the angle at which it was introduced, together with a slight increase in the quantity of fuel employed. By these means the metal prepared contained sufficient carbon to impart steely properties, though when obtained by such methods the steel is never of uniform quality. A steely iron was also frequently prepared in the puddling furnace when the process was carried on in such a manner as to remove the metal before the carbon was completely eliminated. But for some centuries at least the best varieties of steel have been prepared by what is known as the 'cementation' process. For this purpose, bar iron of the best quality is cut up in suitable lengths and placed in charcoal in the cementation furnace. This furnace consists essentially of two rectangular chambers which are constructed of fire-brick, and are arranged to contain the iron and charcoal. The charge of iron used in one operation is generally about 15 tons. A fireplace under the chambers supplies the necessary heat, while the whole is contained in the base of a large conical chimney stack. The iron is carefully arranged and surrounded with charcoal, while the rectangular chests, which are open at the top, are covered with 'swarf' to protect the contents as far as possible from oxidation. The heat is continued for a period of about seven days, though the time will vary somewhat with the temper required and other circumstances. The progress of the operation is judged by the appearance of the fracture of trial bars, which can be removed and examined from time to time. The product is known as 'blister' steel, the name being derived from the characteristic hollow protuberances occurring on the surface. Dr. Percy has shown that these are probably due to carbonic oxide evolved at a high temperature by the action of carbon on the oxygen of the intermingled slag. In good blister steel they should be as evenly distributed as possible. When fractured, the blister steel is generally found to consist of an outer crystalline layer of steel surrounding an inner core of slightly altered iron. The exact theory of cementation has not been made out with certainty, though carbonic oxide is known to play an important part in the process; but the result is that the metal, when heated in contact with solid carbon, becomes gradually carburised on the outside, and if the heating be continued for a sufficient length of time, carburisation gradually extends throughout the whole of the mass. Blister steel, when piled and reheated, is known as 'shear' steel, and gains considerably in uniformity by the treatment. The name is derived from the fact that shears used for cutting woollen cloth were formerly made of this variety of steel. But for best steel for tools and other purposes it is usual to employ 'cast steel,' the best qualities of which are prepared by melting blister steel in clay or plumbago crucibles. The charges usually weigh somewhat less than 100 lbs., a little glass or other flux is employed, and the crucible is kept covered while melting proceeds. Heating is conducted usually in wind furnaces, using coke as fuel, though gaseous fuel has been somewhat largely introduced. This has the advantage of being more under control; it is also economical in working, and enables the process to be carried on continuously, while the wind furnace 'clinkers' up and has to be stopped for cleaning. Cast steel is also prepared in crucibles from materials other than blister steel, but the product is usually of an inferior character. It is found advantageous (especially with cheaper mixtures) to introduce a little manganese in the production of crucible steel, as the metal then possesses better working qualities. The 'body,' which is so characteristic of good steel, appears to be closely connected with its chemical composition, and is associated with special freedom from phosphorus and similar impurities. Crucible steel contains a few hundredths per cent. of silicon, which is reduced from the silicious material of the crucible during the melting, and which appears to play an important part in producing solid castings. For special purposes, in recent years, considerable quantities of manganese have been introduced into crucible steel; while smaller quantities of chromium, silicon, tungsten, and titanium have also been used for tool steels, though in the case of these elements the proportion employed seldom exceeds a few per cent. of the steel made, and they are often present in very much smaller quantities.

Bessemer steel. The magnificent method of producing steel with which the name of Bessemer will always be connected, and which has done so much to revolutionise the iron trade of the world, was described and patented in 1856. At first great incredulity was manifested by ironmasters, and the product was inferior; but when it came to be recognised that only iron free from phosphorus could be employed in this process, and that the red shortness which at first had been so difficult to overcome could be removed by the addition of manganese before tapping the metal, the success of the process was assured. The iron now used in the ordinary, or as it has come to be called the 'acid' Bessemer process, is of special quality, and is made from hæmatite ores. It should contain only a few hundredths p.c. of phosphorus, and about 2 to 3 p.c. of silicon. The metal is either remelted in a cupola or is run directly from the blast furnace according to circumstances, but in either case is introduced in the molten condition into an egg-shaped vessel known as a 'converter,' and which has been heated either by a previous charge or by lighting a fire inside. The converter is constructed externally of iron plates, and is arranged so as to rotate on trunnions which are fixed on either side a little below the middle of the vessel. By this arrangement the converter can be readily manipulated as required during the process. At the lower part of the vessel is a moveable bottom, fitted with a blast box into which air is admitted during the 'blow' at a pressure of about 20 lbs. to the square inch. From the blast box the air enters the vessel through a number of holes passing through a fireclay or ganister bottom lining. The sides of the converter are generally lined by means of ganister (a silicious or 'acid' material) which is generally rammed into position. At the top of the converter, a little on one side, is an opening which serves for the introduction of the metal in the first place, then for the escape of waste gases during the blow, and lastly for the tapping of the metal and slag when the operation is concluded. The charge of pig-iron, which weighs from about 5 to 12 tons, is introduced while the vessel is in a horizontal position, in order to avoid closing the twyers at the bottom; the blast is then turned on and the vessel rotated so as to cause the blast to rise through the bath of metal. The silicon present is rapidly oxidised and passes into the slag, at the same time producing sufficient heat not merely to maintain the fluidity of the metal, but actually to very much increase its temperature. After the silicon has in this manner been removed, which generally occupies about 10 minutes, the carbon is attacked, and this is evidenced by a marked increase in the size and luminosity of the flame produced. This flame continues for rather more than 10 minutes, and then, when the carbon has been burned out, suddenly 'drops,' *i.e.* becomes much smaller and less luminous, showing that the operation is concluded. During the whole of the blow the metal remains molten, and the temperature produced by the combustion of the carbon and silicon is so great that the resulting decarburised metal can be readily poured into suitable ingot moulds. But if used in this form, when it is almost perfectly freed from carbon and manganese, the metal would be red short, and would also be too soft for many purposes. It is usual, therefore, after the flame has dropped, to add a quantity of spiegeleisen or ferro-manganese in order to counteract this red shortness and to introduce the required amount of carbon. After the requisite addition has been made the metal is allowed to stand a few minutes so as to some extent to mix the constituents; it is then 'teemed' into the ladle and thence cast into ingots.

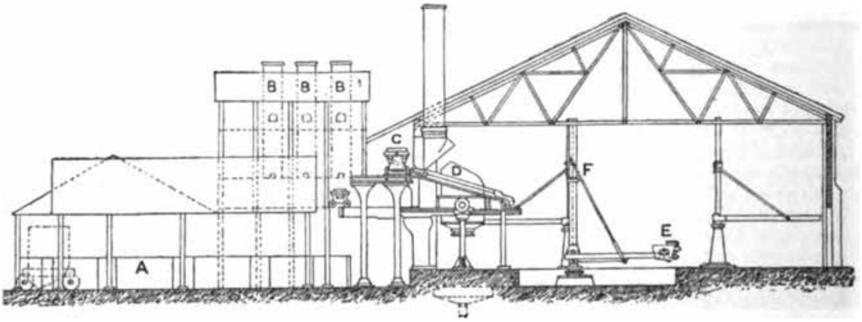


Fig. 5.

A, Shop for preparing Basic Lining; B, Cupolas for calcining Dolomite and remelting iron; C, Ladle for Cast Iron; D, Bessemer Converter; E, Steel Ladle; F, Ladle Crane.

The basic Bessemer process.—It will be noticed that in the original Bessemer process the vessel is lined with silicious or acid materials, and only cast iron free from phosphorus can be employed, as practically none of this element is removed during the blow. But a modification of the process has been introduced by Messrs. Thomas and Gilchrist which has most successfully solved the problem of the treatment of phosphoric iron. Fig. 5 (after A. Holley) shows the general arrangement of a basic Bessemer works. The mechanical arrangements of the plant and general principles involved in the two processes are exactly alike with the exception that the lining used in the basic process is a mixture of lime and magnesia, obtained by calcining dolomite. This is mixed with dry tar in suitable proportions so as to make it bind, and is then either rammed into shape with hot tools, or pressed into bricks and baked as may be most convenient. The cast iron used should be as low in silicon as possible, on account of the injurious action of a silicious slag on the basic material of which the lining is composed. The phosphorus, on the other hand, may be as high as 3 p.c. or even upwards without exerting any injurious effect on the finished product. The 'blow' is conducted in the early stages just as in the acid Bessemer process, silicon being removed first, while carbon afterwards passes out, and the flame 'drops' as before. Lime is then added and an after blow is given which lasts some 5 minutes, depending on the amount of phosphorus present; during this stage the phosphorus is almost completely removed and passes into the slag. The progress of the operation is judged by means of small samples which are withdrawn and examined at intervals during the after blow. When ready, the metal is tapped as usual, and the product is a specially mild and soft metal. The slag has already found several useful applications, the chief being, when ground in fine powder, as a phosphoric manure; it has also come into extensive use recently as a material for the construction of the bottoms of reheating furnaces (Harbord and Tucker's patent). The basic Bessemer process has been successfully applied on a large scale for some years in this country, but is used still more extensively on the Continent.

In Bessemer's earlier experiments small converters were employed; some of which were moveable, while others were fixed. Both of these forms have been recently reintroduced and small converters have met with considerable favour for special purposes.

Siemens steel. Numerous attempts have been made to prepare steel by decarburising cast iron by some method other than that previously described; but the only really successful rival to the Bessemer process was originated by the late Sir William Siemens. The invention of the Siemens furnace, with the accompanying gas producers and regenerators, placed in the hands of the practical man the successful application of a beautiful scientific principle which has been largely used in many branches of manufacture, such as the production of glass, porcelain, and pottery; for the reheating of iron and steel, and for numerous other purposes. Space will not here allow of the description of the apparatus, and it will only be necessary to mention that by this means a temperature can be easily and economically obtained which is amply sufficient to melt wrought iron, and to enable it to be readily poured when melted. Apart from the method used in heating the furnace, the Siemens-Martin process (which was invented by Siemens, and rendered commercially successful by M. Martin) closely resembles in principle the original puddling process. The furnace is of the same general shape as the puddling furnace, but is capable of working a charge of from 5 to about 15 tons. The external portions are of cast iron lined with very refractory silicious firebrick, while the working bottom is of refractory sand. The pig-iron to be used is charged first, and the malleable iron and iron ores which are added to decarburise the pig-iron are introduced at suitable intervals during the operation, which generally lasts about 8 to 10 hours. Several modifications of the process have been introduced, it being convenient sometimes to omit either the malleable iron or the ore, while in some cases malleable iron or steel scrap only has been used (Martin's process). In any case, so long as a silicious lining is employed, all the materials used must be as free as possible from phosphorus. The *basic process* has been adapted to the Siemens furnace, though all the difficulties due to a new departure have scarcely been surmounted in this direction at present, but there is every prospect of an extensive application of the Siemens furnace to phosphoric materials. For basic working the chief modification introduced is the substitution of a working bottom of basic material, similar to that used in the basic Bessemer process for the ordinary silicious bed (*v.* Wailes, J. Iron and Steel Inst., 1887, part 2. Also Harbord, *ibid.*, 1886). If the acid Siemens furnace may be regarded as a large puddling furnace with gaseous fuel, working on Cort's original lines, except that the temperature used is sufficiently high to melt the resulting malleable iron and so produce mild steel, then we may consider the basic Siemens process as closely resembling the 'pig boiling' of more recent times, except that, as in the previous case, the operation is on a much larger scale and the product is in a molten condition.

As compared with the Bessemer process the Siemens, or as it is frequently called, the 'open hearth' process, possesses the advantage that it is more under control, and for this reason is frequently preferred when work of a specially uniform character is required; it is also more in favour for steel castings. The Bessemer plant, on the other hand, gives more rapid working, and hence is preferred for large outputs. There is little doubt that equally good steel may be produced by either of the processes, though the pneumatic method requires very careful attention when special uniformity is desired.

Malleable cast iron. For many purposes where a complex form is necessary, and only moderate strength is required, the articles are cast in green sand in the ordinary way, but using a special variety of pig-iron low in silicon, phosphorus, and manganese. The castings so prepared are white, hard, and brittle; but when heated, in contact with oxide of iron, in covered cast-iron boxes, to a cherry-red heat for about forty-eight hours, they become grey and soft. The softness so developed is accompanied with

Analysis of pig-iron.

Ore	Red hæmatite		Forest of Dean Brown hæmatite		Northamptonshire Brown hæmatite		South Staffordshire All Mine (clay iron stone, cold blast)							Clay, iron stone (Dowlais)
Analyst	Greenwood		Woolwich Arsenal		Henry	Turner	Tucker							Riley
Variety	No. 1	No. 2	No. 1	Grey forge	Grey	Grey	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	White	No. 3 Cold blast
Graphitic carbon . .	3·045	2·579	3·26	3·08	1·150	2·65	3·30	2·68	2·55	2·14	1·90	0·55	0·20	3·10
Combined carbon . .	0·704	1·175	—	—	0·554	·08	0·40	0·45	0·40	0.50	0·56	1·70	2·00	0·04
Silicon	2·003	1·758	2·34	2·18	1·900	2·95	1·88	1·72	1·92	1·33	0·97	0·89	0·71	2·16
Manganese . . .	0·309	0·130	0·23	0·14	0·414	0·40	0·40	0·54	0·40	0·25	0·52	0·46	0·50	0·50
Phosphorus . . .	0·037	0·038	0·14	0·14	1·807	1·84	0·71	0·68	0·52	0·56	0·51	0·48	0·47	0·63
Sulphur	0·008	0·014	0·04	0·06	0·395	·06	0·02	0·04	0·07	0·09	0·12	0·16	0·19	0·11
Metallic iron . . .	93·800	94·304	—	—	93·780	92·02	93·29	93·89	94·13	95·13	95·42	95·76	95·93	93·46

Ore	Carron Black band	Cleveland iron stone			Cinder	Dannemora magnetite	—	Mixed	Spanish	Cleveland	Carbonaceous
Analyst	M'Alley	Stead			Tucker	Henry	Tookey	Turner	Turner	Stead	Fleming
Variety	No. 1	No. 3	Forge	Mottled	Soft grey	White	Spiegeleisen	Silicon spiegel	Silicon pig	Silicon pig	Ohio softener
Graphitic carbon . .	3·00	3·70	3·40	2·90	2·90	—	5·04	1·71	1·12	3·15	2·85
Combined carbon . .	0·50	0·30	0·25	0·75	0·25	4·20			0·69	0·01	·30
Silicon	1·96	2·50	2·10	1·00	2·84	0·08	0·41	8·72	9·80	4·48	5·90
Manganese . . .	1·71	0·72	0·50	0·47	0·44	0·10	7·57	16·92	1·95	0·72	1·00
Phosphorus . . .	0·69	1·50	1·60	1·60	2·80	0·05	0·16	—	0·21	1·97	1·10
Sulphur	0·04	0·04	0·06	0·15	0·05	trace	0·08	—	0·04	0·01	0·02
Metallic iron . . .	92·10	92·00	92·28	92·75	90·72	95·57	86·74	71·87	86·19	89·66	88·83

Analyses of wrought iron, steel, &c.

Description	Special strong foundry iron	Refined iron	Puddled bar	Wrought iron	Basic Bessemer metal, end of blow	Bessemer soft steel
Locality	—	Bromford	S. Stafford	S. Stafford	S. Stafford	Neuberg
Authority . . .	Turner	Dick	Turner	Turner	Walton	Greenwood
Carbon	0·47 (combined)	3·07	0·10	0·06	0·02	0·126
Silicon	1·43	0·63	0·13	0·04	0·01	0·135
Manganese	1·04	trace	0·08	0·08	0·06	0·158
Phosphorus	0·58	0·73	0·35	0·20	0·04	0·060
Sulphur	0·07	0·16	0·05	0·05	0·04	0·014
Iron	—	95·14	99·29	99·57	99·83	—

Description	Siemens soft steel	Bessemer steel rails	Siemens steel tyres	Silicon cast steel	Crucible steel for forgings	Hard tool steel
Locality	—	—	Sheffield	Terre Noire	—	—
Authority . . .	Greenwood	Greenwood	Turner	Pourcel	Greenwood	Greenwood
Carbon	0·167	0·21	0·58	0·61	0·36	1·144
Silicon	0·023	0·047	0·23	0·23	0·02	0·166
Manganese	0·044	0·36	0·64	0·70	0·30	0·104
Phosphorus	0·062	0·035	0·03	0·12	0·03	—
Sulphur	0·013	0·052	0·03	0·05	0·02	—
Iron	—	—	98·49	—	—	—

Analyses of various slags.

Material	Blast furnace cinders			Refinery slag	Tap cinder	Mill cinder	Bessemer slag, end of blow
	With white iron	Grey iron	Cold blast grey iron				
Locality	Dowlais	Cleve-land	South Stafford	Dowlais	Dowlais	Dowlais	—
Authority	Riley	Bell	Percy	Riley	Riley	Riley	Snelus
Silica	43·07	29·92	39·52	25·77	7·71	28·71	46·75
Alumina	14·85	21·70	15·11	3·60	1·63	2·47	2·80
Ferrous oxide . . .	2·53	0·32	2·02	65·52	66·32	66·01	16·86
Ferric oxide.	—	—	—	—	8·27	—	—
Manganous oxide . .	1·37	0·80	2·89	1·57	1·29	0·19	32·23
Lime	28·92	38·72	32·52	0·45	3·91	0·81	1·19
Magnesia	5·87	6·10	3·49	1·28	0·34	0·27	0·52
Potash.	1·84	—	1·06	—	—	—	—
Calcium sulphide. . .	1·90	—	2·15	—	—	—	—
Phosphoric anhydride . .	—	0·07	—	1·37	8·07	1·22	0·01
Sulphur	—	1·61	—	0·23	1·78	0·11	trace

considerable malleability, so that the articles can be readily worked under the tool and punched, planed, &c., as required. Malleable cast iron, however, will not weld like ordinary malleable iron. This process is chiefly conducted in this country in the Midlands, particularly at Walsall and Birmingham, and the heating in contact with oxide of iron is known technically as 'annealing.' This is really an incorrect use of the term, and 'inverse cementation' has been sometimes substituted for the word annealing, but this is not very suitable either, as the change appears to be more in the state of the carbon than in the total quantity of this element which is actually present.

Tin plates. In order to protect iron from oxidation it is frequently covered with a thin layer of metallic tin. This is chiefly applied to the protection of thin plates of iron, which are first rolled in the ordinary way, and, after a preparation (including 'pickling' in dilute sulphuric acid, annealing, and cold rolling) in order to obtain a suitable surface, are immersed in a bath of molten tin which is kept covered with grease. In this way a thin coating of tin adheres to the surface of the iron and protects it from oxidation so long as the iron is completely covered. In case the tin is removed from any part of the surface, however, oxidation takes place more readily than in the original metal. For this reason galvanised iron is to be preferred for purposes where iron has to be exposed to atmospheric action, and where there is no chance of articles of food coming in contact with the zinc. Tin plates are largely manufactured in South Wales, and were formerly made from an iron possessing special malleability, and which was prepared in the old-fashioned open hearth. At present most of the tin plates sold are prepared from mild steel, chiefly that produced by the Siemens process. (For details of preparation *v.* TIN PLATES.)

Galvanised iron. Iron which has to be exposed to the weather or other oxidising agencies is frequently galvanised, *i.e.* covered with a thin coating of metallic zinc. In this case the metal is previously cleaned from scale &c. by being 'pickled' in hydrochloric acid, and after cleansing the article is immersed for a few moments in a bath of molten zinc, which is kept covered with a little ammonium chloride. By this means a uniform covering of zinc is obtained, which protects the iron underneath, not merely so long as the coating is perfect, but also when the zinc has been partly removed. Galvanised iron, however, cannot be used in contact with either mineral or vegetable acids, and hence is not employed for cooking utensils, nor for the cans in which food is preserved. In this country the galvanised iron trade has largely increased during the last twenty years, and is now chiefly conducted in the Midlands around Wolverhampton. (For further details *v.* ZINC.)

Literature.

Bell, Sir Lowthian. Principles of the Manufacture of Iron and Steel. London, 1884.

Bruno-Kerl. Handbuch der Metallurgischen Hüttenkunde. Band iii. Leipzig, 1864.

Deshayes, V. Classement et Emploi des Aciers. Paris, about 1880.

Gruner, M. L. De l'Acier et de sa fabrication. Paris, 1867.

Jeans, J. S. Steel, its history, manufacture, and Uses. London, 1880.

Ledebur, A. Handbuch der Eisenhüttenkunde. Leipzig, 1884.

Overman. Manufacture of Iron. London, 1854.

Percy, J. Metallurgy, Iron and Steel. London, 1864.

Wedding, H. Darstellung des Schmiedbaren Eisens. Braunschweig, 1875.

Also—

Journals of the Iron and Steel Institute, the Institute of Civil Engineers, and the Institute of Mechanical Engineers.

T. T.

COMPOUNDS OF IRON.

Oxides. Three oxides of iron are known:—The ferrous or monoxide FeO; the ferric or sesquioxide Fe_2O_3; and the ferrosoferric or magnetic oxide $FeOFe_2O_3$, or Fe_3O_4. The trioxide FeO_3 which may be considered to exist in ferrates has not been isolated.

Iron monoxide, *Ferrous oxide* FeO, is a powerful base. It may be prepared by the reduction of the sesquioxide by heating to 300°C. in a current of hydrogen. On exposure to air, especially when freshly prepared, it oxidises with incandescence.

The hydrated oxide is precipitated on addition of caustic soda to a ferrous salt in absence of air. When absolutely pure the precipitate is white, but it rapidly absorbs oxygen, acquiring a greenish hue and becoming ultimately converted into the red sesquioxide.

Iron monoxide absorbs carbonic acid with avidity. It dissolves in about 150,000 parts of water. It is used to impart a green colour to glass.

Ferroso-ferric oxide, *Magnetic oxide, Black oxide* $FeOFe_2O_3$, or Fe_3O_4, occurs in nature as *magnetite* (*magnetic iron ore* or *lodestone*) in most parts of the world, and constitutes one of the most important ores of iron. It is always attracted by the magnet, but does not always possess the property of attracting iron. It may be prepared by passing steam or carbonic acid gas over red-hot iron. It is probable a coating of this oxide which renders iron 'passive,' or unacted upon by concentrated nitric acid or water. This property is taken advantage of in the Bower-Barff process for preventing the rusting of iron, in which the metal is heated to redness and subjected to the action of steam. The oxide is soluble in strong acids, the solutions containing a mixture of ferrous and ferric salts.

Iron sesquioxide, or **ferric oxide,** Fe_2O_3, occurs anhydrous as *hæmatite, specular iron ore, kidney ore,* and *micaceous iron ore,* and, in the hydrated condition, as the yellow or brownish *limonite* $2Fe_2O_3, 3H_2O$, of which *bog iron ore, pea iron ore,* and certain *clay iron stones* are earthy varieties. *Göthite* $Fe_2O_3H_2O$, and *Targite* $2Fe_2O_3H_2O$, are other forms in which the hydrated oxide occurs. The earthy varieties of hæmatite are known as *reddle* or *raddle,* and as *red ochre,* and are used as pigments; the earthy varieties of limonite being similarly used under the names *yellow* and *brown ochre.*

The anhydrous oxide may be obtained as a steel-grey crystalline powder by heating the hydrated oxide or a ferrous or ferric salt containing a volatile acid. It may also be prepared in small crystals by passing the vapour of ferric chloride over heated lime. The ignited or native oxide is slowly soluble in acids, the best solvent being a mixture of 8 parts sulphuric acid and 3 parts water.

The residue obtained in the manufacture of Nordhausen sulphuric acid by distillation of ferrous sulphate consists of this oxide, and is known as *colcothar,* and is largely used as a pigment. On account of the absence of grit it is used as polishing *rouge*; the parts which are of a scarlet colour—*i.e.,* which have not been strongly heated—being preferred for glass polishing and for jewellery, &c., while the more strongly heated parts, which possess a bluish tint, are employed under the term *crocus* for polishing metals.

Iron oxide is invariably present in considerable quantities in *copper paint* (*v.* COPPER OXIDES).

This oxide may be combined with the monoxides of calcium, magnesium, zinc, copper, and other metals. The resultant oxides, which are prepared usually by fusing the mixed oxides, are always magnetic, and correspond in composition with the magnetic iron oxide. The oxide containing magnesium, Fe_2O_3MgO, occurs as *magnoferrite*, and that containing zinc and manganese is found as *Franklinite*.

The hydrated oxide is best prepared by precipitating a solution of ferric chloride with excess of ammonia. It forms a bulky, brown, slimy precipitate, which shrinks considerably in drying. It slowly gives up its water at 320°C., and if heated to dull redness when anhydrous, suddenly contracts and glows brightly, becoming much less soluble in acids.

The freshly precipitated oxide is readily soluble in acids and in concentrated solutions of ferric salts. The solution in ferric chloride, when containing excess of oxide, may be slowly dialysed with separation of a dark-red liquid containing 98·5 parts of the oxide to 1·5 parts of hydrochloric acid. A similar solution containing a small amount of acetate is prepared by dialysing ferric acetate, and is used medicinally as *dialysed iron*.

When the hydrated oxide is allowed to remain for some months under water, a crystalline powder containing $Fe_2O_3(HO)_6$ is obtained which corresponds to the native limonite. This hydrate is the colouring ingredient of yellow clays, &c., and constitutes the rust on iron and the precipitate from chalybeate streams. It may also be obtained by precipitation from a cold solution of a ferric salt and drying without the aid of heat, over sulphuric acid.

The hydrated oxide combines with sugar, forming a soluble compound, thus lowering the percentage of crystalline sugar obtained from the pans and raising the proportion of molasses. On this account raw sugar is soon injured by contact with iron vessels, and even the clearing 'char' should be as free as possible from iron.

The hydrated oxide is largely used for removing sulphuretted hydrogen from coal gas. A hydrated sulphide is thus produced with evolution of water. When the oxide ceases to absorb the gas, it is exposed to a current of air, care being taken to prevent great rise of temperature, and the oxide is reproduced with separation of free sulphur. The large quantity of Prussian blue contained in the 'spent oxide' is now separated by some continental manufacturers.

A yellowish-brown hydrated sesquioxide, precipitated on calico by the action of caustic soda on ferrous sulphate, is known as *chamois* or *rouille*.

Ferric acid H_2FeO_4 is only known in combination. The potassium salt is produced with evolution of considerable heat by heating the sesquioxide with potassium nitrate or hydrate, or with a mixture of the two substances.

Ferrous sulphide FeS is found in certain meteorites. It may be considered to exist in combination with the sesquisulphide in *pyrrhotine* or *magnetic pyrites*, and in combination with other sulphides in other minerals. It is found in considerable quantities in the black deposit in cesspools, &c., being produced by the action of organic matter on ferruginous bodies or iron oxide in presence of sulphates.

It may be prepared by heating a mixture of iron filings and sulphur, or of ferrous sulphate and charcoal; by stirring a white-hot rod of wrought iron in melted sulphur; by heating other iron sulphides to bright redness in hydrogen, or by precipitating ferrous salts with alkaline sulphides or sulphuretted hydrogen. In the compact state, ferrous sulphide is a very hard, metallic-looking black, or nearly black, solid, permanent in air, and fusible at a full red heat. The precipitated sulphide, however, is readily oxidised to sulphate in air, especially when moist.

It is decomposed by acids with evolution of sulphuretted hydrogen, and is usually employed for the preparation of that gas.

Ferrous sulphide forms the main constituent of *iron lute* (*v.* LUTES).

Ferroso-ferric sulphide $FeS.Fe_2S_3$ forms one of the varieties of *pyrrhotine*; it is obtained when iron pyrites is heated out of contact with air for the production of sulphur. A *sesquisulphide* Fe_2S_3 is obtained by gently heating a mixture of iron and sulphur or by the action of sulphuretted hydrogen on the sesquioxide below 100° C. It combines with other sulphides of iron, and with the sulphides of silver, potassium, and sodium.

Ferric sulphide FeS_2 occurs in immense quantities as *iron pyrites* or *mundic* in hard yellow, brassy cubes or other forms in the cubic system, and in masses of various shapes. The ovoid masses of this mineral are frequently known as 'thunderbolts.'

This mineral, as well as *marcasite* or *white iron pyrites*, and other minerals of the same composition, but crystallising in the rhombic system, is produced in nature by the reduction of ferrous sulphate by organic matter, and is therefore often found forming fossils in peat, chalk, &c., and in clay, containing much organic matter.

Pyrites is quite permanent in air, but marcasite becomes slowly oxidised and disintegrated on exposure. Iron pyrites is largely employed as a source of sulphur in the manufacture of sulphuric acid, ferrous sulphate, &c. (*v.* SULPHURIC ACID; SULPHUR; FERROUS SULPHATE).

Ferric arsenide occurs in nature as *Lölingite* $FeAs_2$, and with sulphur as *mispickel* or *arsenical pyrites* Fe_2AsS, from which the greater part of the arsenical compounds in commerce are obtained (*v.* ARSENIC). Arsenic combines directly with iron.

Compounds of carbon phosphorus, silicon, and nitrogen with iron are also known. The effects produced on the properties of iron and steel by the three first-named elements are described under the manufacture of iron.

Ferrous salts. Anhydrous ferrous salts are usually colourless; the hydrated salts are greenish or blue. The solutions are sweet and astringent and ink-like in taste, and form powerful reducing agents.

Ferrous chloride $FeCl_2$ may be prepared in the anhydrous condition by passing dry hydrochloric acid gas over red-hot iron or by reducing ferric chloride in a current of hydrogen. In solution it is obtained by dissolving iron in hydrochloric acid. It crystallises in very deliquescent green crystals containing $FeCl_2 4H_2O$, soluble in alcohol, and very soluble in water. The solution is used medicinally.

Ferrous bromide, iodide, and fluoride are also known.

Ferrous sulphate, green vitriol or **copperas,** $FeSO_4 7H_2O$, occurs as *melanterite*, being derived from the decomposition of the native sulphide, especially of marcasite.

The pure salt is prepared by heating an excess of iron wire or 1½ parts of precipitated ferrous sulphide in 1½ parts of sulphuric acid diluted with four times its weight of water. The solution is acidulated if necessary, and is filtered quickly. Bluish-green monoclinic crystals containing $FeSO_4 7H_2O$, and having a sp.gr. of 1·889 at 4° (Joule and Playfair), are thus produced.

Ferrous sulphate may be obtained in rhombic prisms containing 4 molecules of water, isomorphous with zinc sulphate, and in triclinic crystals containing 5 molecules of water. Crystals may also be produced containing 3 and 2 molecules of water.

Large quantities of this sulphate are obtained as a by-product in the preparation of alum by the oxidation of pyritic shale in S. Lancashire (*v.* ALUMINIUM); in the manufacture of copper sulphate (*v.* COPPER), and in small quantities in the preparation of sulphuretted hydrogen for precipitating arsenic from sulphuric acid. It is prepared on the large scale by dissolving scrap iron in warm sulphuric acid of 1·150 sp.gr., and concentrating the nearly neutral solution. The liquid is settled, quickly drawn off, allowed to clear for twenty-four hours, and run into crystallising tanks, in which strings, straws, or wooden laths are suspended to induce crystallisation. The crystals are washed with a minimum quantity of water and dried.

When sulphur is distilled from iron pyrites, the residue, known as *sulphur waste*, is laid upon inclined shelves in contact with air to oxidise. The weathered mass is levigated, and the ferrous sulphate is crystallised out.

Ferrous sulphate is obtained at Fahlun during the extraction of copper sulphate from mine water, and also from the runnings of other mines.

The *Salzburg vitriol* prepared at Buxweiler contains ferrous and copper sulphates (*v.* COPPER).

Crude ferrous sulphate always contains ferric sulphate, which gives the crystals a more decided green colour; they are frequently coated with a yellow deposit due to oxidation. By washing with absolute alcohol, this deposit, being soluble, is removed, and the crystals are rendered more permanent.

The pure salt may be obtained in the most permanent condition by precipitating a concentrated aqueous solution by addition of excess of alcohol and washing the precipitated crystals with nearly absolute alcohol. The presence of even a trace of ferric salt increases the liability of the crystals to oxidation.

Ferrous sulphate is insoluble in absolute alcohol. Its solubility in 100 parts of water is:

10°C.	15°	25°	32·5°	46°	60°	90°	100°
61	70	115	151	227	263	370	333

The reduced solubility at 100° may be attributed to partial dehydration or dissociation.

The aqueous solution slowly oxidises on exposure to air, and deposits a yellowish, highly basic ferric sulphate, leaving the normal ferric sulphate in solution. The acid finally becomes divided between the precipitated salt and that in solution, rendering the former less basic but still insoluble, and converting the normal salt into a soluble basic sulphate.

On account of its reducing power, it precipitates gold and palladium from solution, and reduces indigo to the soluble condition.

When gradually heated to 140°C. it loses six molecules of water and becomes colourless, but the remaining molecule is not removed at 260°, and, except when heated in small quantities, it is impossible to render the salt anhydrous without loss of acid. At a red heat a basic sulphate is produced, with evolution of sulphuric anhydride, and, at higher temperatures, the oxide alone is left.

Ferrous sulphate is largely used in dyeing and tanning, and in the manufacture of inks (*v.* INKS), Prussian blue, and other pigments, Nordhausen sulphuric acid, red oxide of iron, &c. In weak solution it is said to promote the growth of certain plants, especially of roots. When added to excremental matters it absorbs ammonia and other volatile substances, and renders the matter almost odourless.

In dyeing textiles, leather, wood, &c., it is largely used for the production of various shades of black, grey, lilac, and brown. It is used as a mordant for the production of Prussian blue in calico-printing, and is the raw material from which acetates, nitrosulphates, and other iron mordants are prepared. A fine yellowish-brown colour precipitated on calico by the action of caustic soda on ferrous sulphate is known as *chamois* or *rouille*.

Ferrous disulphate FeS_2O_7 is separated as a white powder on addition of excess of concentrated sulphuric acid to a concentrated aqueous solution of the normal sulphate. On addition of water, it is decomposed into the normal salt and free acid.

With ammonium and potassium sulphates, ferrous sulphate produces double salts containing 6 molecules of water and of great stability and fine crystalline form.

Ferrous ammonium sulphate

$$FeSO_4,NH_4SO_4,6H_2O$$

is prepared by dissolving molecular proportions of the two sulphates in the minimum quantity of hot water filtering hot and crystallising. It forms fine bluish-green monoclinic crystals of sp.gr. 1·813, of which 100 parts of water dissolves 21·6 parts at 20°C. and 56·7 parts at 75°.

The double salt is permanent in air, particularly when precipitated by addition of alcohol to the concentrated aqueous solution and washed with absolute alcohol, and is used by chemists in place of ferrous sulphate, especially for standardising solutions.

Ferrous phosphate $Fe_3(PO_4)_2 8H_2O$ occurs as *Vivianite* or *blue iron earth*, sometimes mixed with clay and peat or associated with bog iron ore. It may be produced by addition of sodium phosphate to ferrous sulphate. The fresh precipitate is used medicinally. When quite pure it is white, but it rapidly becomes bluish or green from oxidation.

Ferrous carbonate $FeCO_3$ occurs as *spathose iron ore*, together with the carbonates of lime, magnesia, and manganese. *Clay iron stone* is an argillaceous ferrous carbonate.

Ferrous carbonate dissolves in water containing free carbonic acid, the acid salt so produced being the essential constituent of chalybeate waters. The solution is decomposed rapidly on boiling and slowly on exposure to air, with precipitation of an ochreous deposit of the hydrated oxide, which, in the case of mineral waters, frequently contains organic matter and ferric arsenate and is occasionally found to contain antimony.

Ferrous nitrate $Fe(NO_3)_2 6H_2O$ is prepared by dissolving ferrous sulphide in dilute nitric acid, or, preferably, by addition of barium nitrate to ferrous sulphate solution.

Ferrous ferricyanide *v.* CYANIDES.

Ferrous acetate *v.* ACETATES.

Ferric salts are usually of yellowish or reddish brown colour. In solution they are reduced to the ferrous condition by zinc, or, with precipitation of sulphur, by sulphuretted hydrogen. Potassium or other soluble thiocyanate imparts an intense blood-red colour to a neutral or acid solution of a ferric salt.

Ferric chloride, $FeCl_3$ or Fe_2Cl_6, mây be obtained in the anhydrous condition by passing chlorine gas over red-hot iron or by passing hydrochloric acid gas over the heated sesquioxide. Thus prepared, it forms iridescent iron-black scales which are dichroic, appearing red by transmitted and green by reflected light.

In solution it may be prepared by dissolving the precipitated sesquioxide in hydrochloric acid, and driving off the excess of acid by heat; or, preferably, by dissolving iron in hydrochloric acid and passing chlorine through the liquid until saturated with that gas, finally entirely removing the chlorine by passage of a current of carbonic acid gas through the warm liquid.

Ferric chloride is volatile at a red heat. It is very deliquescent and dissolves in alcohol and ether. The concentrated aqueous solution is dark brown and oily; if diluted it becomes of a pale-yellow colour.

Hydrous crystals may be obtained containing 6, 10, or 12 molecules of water.

Ferric chloride is sometimes used as a disinfectant. It deodorises sewage with partial reduction to ferrous chloride.

With potassium chloride it produces a finely crystallised garnet-coloured double chloride $Fe_2Cl_6.4KCl.2H_2O$ decomposed by water. A similar garnet-coloured salt crystallising in cubes is formed with ammonium chloride and is used medicinally as *ammonio-chloride of iron.* The salt used, however, does not correspond to the potassium salt, but usually contains less than 2 p.c. of iron. It is very deliquescent and may be considered as formed by the combination of the normal salt $FeCl_6 4NH_4Cl.2H_2O$ with variable proportions of ammonium chloride.

Soluble and insoluble *oxychlorides* of iron are known, but are unimportant.

Ferric sulphate $Fe_2(SO_4)_3$ occurs as *coquimbite* in Chili in white silky pyramids containing $Fe_2(SO_4)_3 9H_2O$. It is usually prepared by mixing one equivalent of concentrated sulphuric acid with a solution of two equivalents of ferrous sulphate, concentrated nitric acid being added in portions to the hot solution until red fumes cease to be evolved. On concentrating the solution to a syrup colourless crystals are obtained.

Several hydrated basic sulphates are prepared artificially, or occur in nature.

Ferric sulphate is used to a slight extent in dyeing cotton, but not in printing. The basic sulphates are used for dyeing cotton, for the production of buffs, or, in combination with logwood and sumach, for blacks. The iron mordant prepared by treating ferrous sulphate with nitric acid is sold as *nitrosulphate* or *nitrate of iron*, and is used in dyeing, but not in printing cotton.

With alkaline sulphates ferric sulphate forms double salts, resembling and corresponding in composition to alum.

The potassium-salt, *potassium iron alum* $Fe_2(SO_4)_3K_2SO_4 24H_2O$, is prepared by mixing molecular proportions of ferric and potassium sulphates and concentrating the solution spontaneously. It forms fine violet octahedra very liable to decompose spontaneously into a brown, gummy, deliquescent mass. This alum is used to a limited extent in dyeing and calico printing.

The corresponding ammonia alum is more permanent.

Ferric nitrate $Fe_2(NO_3)_6$ may be obtained in several states of hydration by crystallising the solution obtained by the action of concentrated nitric acid on scrap iron or iron oxide. It is usually prepared by the first method for use as a mordant for producing buffs and blacks in dyeing. An alkaline mordant is prepared for dyeing and calico printing by treating a ferric salt with caustic soda, with addition preferably of glycerin, or sometimes of glucose, to prevent precipitation of the oxide.

Ferric phosphates are of no commercial importance. A ferric phosphate formed by the oxidation of *vivianite* occurs as *Beraunite* $Fe_2(PO_4)_2 4Fe_2PO_4(HO)_3 8H_2O$, and another occurs as *Dufrenite* $Fe_2(HO)_3PO_4$.

Ferric arsenite $Fe_2(AsO_3)_2$ is of interest as being the salt produced when freshly precipitated hydrated oxide of iron is taken as an antidote in cases of arsenical poisoning. It may be obtained as a brown precipitate by addition of arsenious acid or an arsenite to a solution of ferric acetate.

Ferric acetate *v.* ACETATES.

Ferric ferrocyanide *v.* CYANIDES.

Ferric tannate or *gallo-tannate* forms the basis of black inks (*v.* INK). The sponges, sand, pumice-stone, &c., of Gerson's filters are impregnated with the tannate, which is said to completely remove all organic matter from water (*v.* Steiger, S. C. I., 1886, 416).

Ferric citrate $Fe(C_6H_5O_7)$ is prepared by dissolving the hydrated oxide in citric acid, and evaporating the solution in thin layers. It forms permanent, transparent, garnet-coloured scales, which dissolve slowly in water, but are insoluble in alcohol.

Ferric ammonium citrate is prepared as above, with addition of ammonia. It forms thin, transparent, deep-red scales, which dissolve readily in water, but not in absolute alcohol.

It is constantly used in medicine, as is also the double *citrate of iron and quinine*.

IRON CEMENT *v.* Lutes.

IRON LIQUOR. *Ferrous acetate v.* Acetic acid.

IRON PYRITES. *Ferric sulphide v.* Iron.

ISATIN *v.* Indigo.

ISATIN YELLOW *v.* Hydrazone colouring matters.

ISATROPYL COCAÏNE *v.* Vegeto-alkaloids.

ISINGLASS (Fr. *Colle de poisson*; Ger. *Hausenblase*) consists of the dried swimming-bladders of various fishes. These bladders differ in shape and size, according to their origin, and are prepared either by simply drying them whilst slightly distended, which process forms 'pipe isinglass,' or by slitting them open, pressing, and drying them in the form of 'leaf isinglass.' That form, again, which is known as 'purse isinglass,' consists of such bladders as contain a natural opening.

The chief supply of isinglass is derived from Russia and Hudson's Bay; some portion also being obtained from Brazil, West Indies, Penang, Bombay, and Manilla; the finest kind, the 'Beluga leaf,' coming from the first-named of these countries, and being the produce of a species of sturgeon. Other Russian or Siberian varieties are 'Astrakhan leaf,' 'Saliansky leaf,' and 'Samovy leaf.'

The following are the principal species of fish from which Russian isinglass is obtained: *Acipenser huso*, or the Hausen; *A. Güldenstædtii*, or the Osseter; *A. ruthenus*, or the Sterlet; *A. stellatus*, or the Sewruga; *Silurus glanis* and *Cyprinus carpio*. The isinglass of New York is derived from *Labrus squeteague*; that of New England—the 'ribbon isinglass'—from the common Cod, *Gadus Morrhua*. In Brazil it is taken from a species of *Silurus*; and in Iceland, from *Gadus* and *Molva vulgaris*, or the Ling.

The chief emporium for Russian isinglass is the great fair of Nijni-Novgorod, whence the largest part of the merchandise finds its way to London, through the agency of St. Petersburg traders. It arrives here about the end of June. Those supplies which reach us from Brazil and other countries are received at all seasons.

The fish being taken, the bladders are immediately removed, sufficient care in the cleansing of them from mucus and blood-stains being often purposely neglected, since a loss of weight results in the process when properly performed. In consequence of this neglect, the value of the material is diminished in proportion to the impurities which it contains.

On its arrival here isinglass is a hard, tough substance, and for many purposes it is necessary to 'cut' it. The operations of 'cutting' consist, first, in soaking the flakes until somewhat pliable, trimming the edges, and scraping off the dark spots; next, in putting them through two sets of rollers, under great pressure, by which they are flattened to the thickness of writing-paper; and, finally, in cutting them into fibres of extreme fineness, a process now almost always effected by a machine constructed for that purpose.

The uses for which isinglass is employed are the 'fining' or clarifying of fermented beverages, as ale and wine, and various culinary preparations. For the former purpose the properties of isinglass are remarkable; for, whilst possessing the exact chemical composition of gelatin, it has the power, which is wanting in gelatin, of entangling in the film or web which it forms as it dissolves, all the physical impurities contained in the liquids which it is sought to clarify. The lower grades of isinglass are used either in the natural or the manufactured condition by brewers and the manufacturers of cider, and the better classes of the Russian material by wine merchants. For the purpose of the brewer it is usual to dissolve the isinglass in sulphurous acid, since this has a tendency to preserve the ale.

The choicest descriptions are used by the cook and the confectioner for the thickening of soups, jellies, &c., but as for these purposes the fining properties of isinglass are not of any account, gelatin serves equally well, and has, under the name of patent isinglass, been so employed.

ISOAMYLACETIC ACID *v.* Fatty acids.

ISOAMYL PHENOL *v.* Phenol and its homologues.

ISOANTHRAFLAVIC ACID *v.* Alizarin and allied colouring matters.

ISOBUTYLACETIC ACID *v.* Fatty acids.

ISOBUTYL PHENOL *v.* Phenol and its homologues.

ISOBUTYRIC ACID *v.* Fatty acids.

ISOCAPRIC ACID *v.* Fatty acids.

ISOCINCHOMERONIC ACID *v.* Bone oil.

ISOHEPTOIC ACID or **METHYLBUTYLACETIC ACID** *v.* Fatty acids.

ISOHEPTYLACETIC ACID *v.* Fatty acids.

ISOLICHENIN *v.* Gums.

ISOMESIDIC ACID *v.* Gum resins.

ISOMORIN *v.* Fustic.

ISONARCEÏNE *v.* Vegeto-alkaloids.

ISONARCOTINE *v.* Vegeto-alkaloids.

ISONICOTINIC ACID *v.* Bone oil.

ISONONOIC ACID *v.* Fatty acids.

ISOOCTOIC ACID *v.* Fatty acids.

ISOŒNANTHIC ACID *v.* Fatty acids.

ISOPURPURIC ACID *Picrocyanic acid* $C_8H_5N_5O_6$. This acid does not exist in the free state. Its *potassium* salt, $C_8H_4N_5O_6K$, is obtained by gradually adding a solution of 2 parts of potassium cyanide dissolved in 4 parts of water at 60° to a hot solution of 1 part of picric acid in 9 parts of water, and separates on cooling as a crystalline magma, which is filtered off, pressed, washed with cold water, and recrystallised from boiling water. It crystallises in brown scales, which appear green by reflected light, dissolve sparingly in cold water, and explode when heated at about 215° (Hlasiwetz, A. 110, 289; Baeyer, J. 1859, 458; Kopp, B. 5, 644). Potassium isopurpurate dyes silk and wool in shades of brown from an acetic or tartaric acid bath, and was formerly employed as a dye under the name *garnet brown* (Zulkowsky, M. J. 1868, 661) (*v. Picric acid*, art. Phenol and its homologues).

ISOQUINOLINE *v.* Quinoline.

ISOQUINOLINE RED *v.* Quinoline.

α-ISORCINOL *v.* *Cresorcinol*, art. Phenol and its homologues.

ISOSCOPARIN *v.* Broom tops.

ISOSTEARIC ACID *v.* Fatty acids.

ISOUVITIC ACID *v.* Gum resins.

ISOVALERIC ACID or **ISOPROPYLACETIC ACID** *v.* Fatty acids.

ISOVITINIC ACID *v.* Gum resins.

ITACOLUMITE. An altered sandstone or quartzite, usually micaceous and sometimes felspathic, remarkable for displaying more or less flexibility, whence it is commonly known as *flexible sandstone.* The name itacolumite was given to it by v. Eschwege more than a century ago, in consequence of its occurrence at Itacolumi, a mountain in the province of Minas Geraes, in Brazil. O. A. Derby, in describing the geology of the district, points out that the rock is flexible only in those parts which have been affected by atmospheric agencies (Am. J. Sc. 28, 1884, 205). Flexible sandstone is also found in India—at Kaliana, in the Jheend State, and at Charli, in Berar—in North Carolina, and in Georgia. Its occasional association with diamonds has led to the belief that in some localities it represents the matrix of the gem. The flexibility of itacolumite has often been attributed to the presence of mica, but this mineral is by no means a necessary constituent of the rock, and the peculiar mobility is more probably due to the state of aggregation of the component grains of quartz (*v.* G. Spezia, Atti d. R. Ac. d. Sc. Torino, 1886, 21). Klaproth long ago ascribed the flexibility to the manner in which the grains are hinged together; and Wetherill, on a microscopic examination, found the articulated structure so manifest that he proposed to name the rock *articulite* (Am. J. Sc. 44, 1867, 61; C. N. 22, 1870, 111, 266). O. Mügge has referred the flexibility of the Indian slabs to a similar cause (N. Jahrb. 1, 1887, 195). R. D. Oldham, after a careful examination of the Indian itacolumite, in the field and under the microscope, concludes that the flexibility is connected with the incipient decomposition of the rock, whereby a peculiar structure has been developed; the grains of quartz being grouped in irregular-shaped aggregates which interlock, but yet enjoy a certain freedom of motion in consequence of the presence of free spaces due to the removal of part of the original rock (Rec. Geol. Surv. India, 22, 1889, 51). F. W. R.

IVY GUM RESIN *v.* Gum Resins.

J

JABORANDI. *Pilocarpus.* The natives of the eastern parts of South America employ the word 'jaborandi' to designate a group of plants having similar diaphoretic and sialagogue properties. The most important of these, the official jaborandi, was introduced into European medicine by Coutinho and Gubler in 1874 (Rép. de Pharm. 2, 171). The plant, of which the leaves were used, was identified by Baillon as the *Pilocarpus pennatifolius* (Lemaire) (*cf.* Holmes, Ph. [3] 5, 581 a. 641; Planchon, J. Ph. [4] 21, 295; Bentl. a. T., plate 48; Stiles, Ph. [3] 7, 629).

Three alkaloids have been separated from jaborandi. Rabuteau (Ph. [3] 4, 911) and Byasson (Ph. [3] 5, 826) investigated the leaves chemically, but the first definite compound, *pilocarpine* $C_{11}H_{16}N_2O_2$, was discovered by Hardy (C. R. Soc. Biol. 1875, 109; Bl. 24, 497; J. Ph. [4] 23, 95; Ph. [3] 6, 887; 7, 496) and independently just afterwards by Gerrard (Ph. [3] [5] 865 a. 965; 6, 227; 7, 255; 10, 214; 11, 608). To obtain it, Hardy prepares a soft aqueous extract which is treated with alcohol, the alcoholic solution evaporated to a thick syrup, and this dissolved in a little water and precipitated with ammoniacal acetate of lead. The mixture is filtered and the lead removed from the filtrate by sulphuretted hydrogen which then contains the alkaloid as acetate. Mercuric chloride is added, which forms an insoluble double chloride. This is separated, washed with water, and decomposed by sulphuretted hydrogen. The solution contains hydrochloride of pilocarpine, and treated with ammonia and chloroform it yields to the latter the free alkaloid. Gerrard suggests the following process. The leaves are exhausted with 84 p.c. alcohol, containing 1 p.c. of strong solution of ammonia. The solution is neutralised with tartaric acid, the alcohol removed by distillation, and the residue treated with excess of ammonia and alcohol and the alcohol again distilled off. From the residue chloroform extracts crude pilocarpine which is best purified by conversion into the nitrate, which admits of easy recrystallisation from alcohol, and from this salt the free alkaloid may be readily obtained. Poehl (Bl. [2] 34, 340) uses phosphomolybdic acid as a precipitant for pilocarpine, both in valuing the drug and in the preparation of the alkaloid; and Christensen (Ph. [3] 12, 400) for the former purpose weighs the alkaloid in the form of a gold salt. Another process is proposed by Petit (Ph. [3] 8, 46).

Analyses of pilocarpine and its salts have been made by Kingzett (C. J. 30, 367; Ph. [3] 8, 255; 11, 587), Poehl, Harnack a. Meyer (A. 204, 67), and others. The last-named chemists determined the formula now adopted (*cf.* Chastaing, J. Ph. [5] 4, 336). The free base is crystalline, dextrorotatory, and soluble in alcohol, ether, and chloroform, but only sparingly soluble in water (Petit). It is poisonous, and, like nicotine, the physiological action of which it resembles, it contracts the pupil of the eye. Its more important derivatives are: *salts*—$C_{11}H_{16}N_2O_2,HCl$, needles soluble in alcohol (Poehl); $C_{11}H_{16}N_2O_2,HNO_3$, rhombic lamellæ soluble in water, sparingly in alcohol (Hardy a. Calmels, C. R. 102, 1116); $(C_{11}H_{16}N_2O_2,HCl)_2PtCl_4$, soluble prisms, and $(C_{11}H_{16}N_2O_2)_2PtCl_4$, very soluble crystalline powder (H. a. C.);

$C_{11}H_{16}N_2O_2,AuCl_3$,

needles, $C_{11}H_{16}N_2O_2(AuCl_3)_2$, slender needles, also the acid salts $C_{11}H_{16}N_2O_2,HCl,AuCl_3$, a crystalline precipitate, and

$C_{11}H_{16}N_2O_2(HClAuCl_3)_2$ (H. a. C.);

halogen derivatives—$C_{11}H_{14}Cl_2N_2O_2$ (Chastaing, C. R. 100, 1593); $C_{11}H_{14}Br_2N_2O_2$ (Chastaing, C. R. 97, 1435); $C_{11}H_{15}IN_2O_2$ (Chastaing); *alkyle derivatives*—$C_{11}H_{16}N_2O_2,MeI$ (H. a. M.); $C_{11}H_{16}N_2O_2,EtI$ (Chastaing, C. R. 101, 507).

The second alkaloid found in jaborandi was *jaborine*, $C_{22}H_{32}N_4O_4$ (Harnack a. Meyer). They separated it as an amorphous compound from commercial pilocarpine by taking advantage of the difference of solubility of the two alkaloids and their platinic salts, and also the fact that jaborine does not crystallise. It forms platinum and gold salts. It is poisonous and antagonistic to pilocarpine, belonging to the group of mydriatic alkaloids. The remaining base *pilocarpidine* $C_{10}H_{14}N_2O_2$, was obtained by Merck (Ph. [3] 16, 106) and Harnack (A. 238, 230). It is syrupy, but forms a crystalline nitrate and platinum and salts. In its physiological action it resembles pilocarpine but is not so energetic. It is moderately soluble in water, easily in alcohol and chloroform, difficultly in ether and benzene, and insoluble in petroleum ether (*cf.* H. a. C., C. R. 102, 1116).

The chemical relations of these compounds and others derived from them are interesting. Pilocarpine is shown to be methyl-pilocarpidine by the action of hydrochloric or nitric acid, which converts it into *methyl alcohol*, and an artificial *pilocarpidine* which has not, however, yet been identified with the pilocarpidine derived directly from jaborandi (Hardy a. C., C. R. 102, 1116). Again, by the action of water pilocarpine may be made to break up into *trimethylamine* and *β-pyridine-α-lactic acid*, $C_5H_4N.C.OH.Me.COOH$ (H. a. C.). Now the same chemists have shown that, commencing with this acid, both pilocarpidine and pilocarpine can be obtained synthetically (C. R. 105, 68). β-pyridine-α-lactic acid is converted by phosphorus bromide into β-pyridine-α-bromopropionic acid, and this, by the action of trimethylamine, into β-pyridine-α-dimethylamidopropionic acid, $C_5H_4N.C.NMe_2.Me.COOH$, or *pilocarpidine*. Pilocarpidine easily combines with methyl iodide, and methyliodopilocarpidine by the action of potassium manganate yields *pilocarpine* $C_5H_4N.C.\underline{N^{v}Me_2Me.CO.O}$. Probably intramolecular change in the position of a methyl group takes place together with condensation. When pilocarpine is heated by itself it splits into *jaborine*, identical with the natural jaborine of jaborandi (Harnack a. M.), *jaboric acid*, $C_{19}H_{25}N_3O_5$, a new compound, and *pilocarpidine*. Both jaborine and jaboric acid are condensation products of pilocarpine, and both yield pilocarpidine when treated with dilute acids or alkali (Hardy a. C., C. R. 102, 1251). Distilled with potash, pilocarpine is said to yield traces of coniine (Poehl, B. 12, 2185; Harnack a. Meyer; Chastaing, C. R. 94, 233), but the chief products are *methylamine*, carbonic anhydride, and butyric and acetic acids. When a solution of natural pilocarpidine is submitted to repeated evaporation an alkaloid *jaboridine*, $C_{10}H_{12}N_2O_3$, is formed, which is probably identical with the *jaborandine* of Paraguay jaborandi described by Parodi (Revist. Farm. 1875, 3; Harnack, A. 238, 234). This base is also produced by the action of concentrated nitric acid on pilocarpine (Chastaing, C. R. 94, 968). It is a mydriatic alkaloid resembling jaborine in its action. Finally, another basic compound, *jabonine* $C_9H_{14}N_2$, is obtained by distilling either pilocarpine or pilocarpidine with baryta. It is an oil boiling at 235-240° (Hardy a. C., C. R. 103, 277).

Of the constituents of jaborandi which have been examined, there only remains to be mentioned the volatile oil, which exists to the extent of about ½ p.c. in the leaves. This consists of a dextrorotatory terpene which boils at 178°, *pilocarpene* $C_{10}H_{16}$, and some higher boiling liquid and solid compounds. Pilocarpene has the sp. gr. 0·852, and forms a crystalline hydrochloride $C_{10}H_{16}2HCl$ which melts at 49·5°. A. S.

JADE. This name has been applied to several hard stones, of green or grey colour, used for ornamental purposes, but differing greatly from each other in chemical composition, and to a less extent in physical characters. True jade, or *Nephrite*, sometimes distinguished as 'Oriental jade,' is a mineral of the hornblende group, apparently compact, but shown by microscopic examination to consist of a felted mass of very fine fibres. It is to this fibrous structure that the characteristic toughness of jade is due. Its hardness is about 5·75, but it is said to be softer when first extracted from its matrix, and therefore more easily worked. Its sp.gr. is about 3 in the green variety, and rather less in the cream-coloured jade. Analysis shows it to be a silicate of magnesium and calcium, the green jade being generally placed with actinolite, and the white with tremolite.

Jadeite is Damour's name for a similar mineral, denser and slightly harder than jade. Sp.gr. 3·1–3·4; H = 6·5–7. Its structure is usually granular rather than fibrous, and the prismatic cleavages occasionally seen in microscopic sections suggest a pyroxene rather than a hornblende. Krenner regards it as monoclinic, while Arzruni holds it to be triclinic. Jadeite is a silicate of sodium and aluminium, and may perhaps be regarded as a variety of acmite in which Fe_2O_3 is replaced by Al_2O_3. The following are typical analyses of jade and jadeite:

	I.	II.	III.	IV.
Silica . . .	59·50	52·25	58·11	58·28
Magnesia . .	24·24	18·07	21·97	1·99
Lime . . .	11·60	19·27	12·01	2·53
Ferrous oxide .	1·35	6·80	0·38	2·42
Manganous oxide	0·79	—	—	0·22
Ferric oxide .	—	—	5·44	—
Chromic oxide .	—	0·26	—	—
Alumina . .	0·75	0·58	0·24	21·86
Potash . .	1·57	—	—	—
Soda . .	—	0·68	—	12·97
Water &c. .	0·85	1·50	1·78	—
	100·65	99·41	99·93	100·27

I. Jade from Turkestan, by v. Fellenberg. II. Jade from New Zealand, by Damour. III. Jade from Alaska, by F. W. Clarke. IV. Jadeite implement from Swiss lake-dwelling, by v. Fellenberg.

Jade and jadeite are minerals of very limited occurrence, but probably more widely diffused than formerly supposed. New Zealand is a well-known locality for typical jade, and the Maoris prized it, under the name of *punamu*, as the material for their choicest weapons and amulets. It is found exclusively on the western coast of the South Island, generally as pebbles in the beds of streams, but it also occurs *in situ*. (For description and analyses v. v. Hochstetter, Sitz. W. 49, 1865, 466; also F. Berwerth, do., 80, 1880, 102, 116.) Jade is also found in New Caledonia, and weapons of jadeite are used in New Guinea, suggesting its occurrence in that island.

By the Chinese jade is very highly esteemed, and carved with great labour in most elaborate forms. It is known in China as *yu*, a name which is applied, however, to many other hard stones used for ornamental purposes. Most of the jade used in China now comes from Upper Burma, where it is quarried over a large tract of country, chiefly on the west bank of the Uyu river, the head-quarters of the trade being at Mogaung. It is worked by the Kachins, who regard themselves as the owners, and by Shans and Burmese (Rep. Chief Commr., Rangoon, 1888). Formerly the Chinese derived their jade from the Kuen-Lun Mountains in Turkestan, and their old quarries in the Karakash Valley have been visited and described by H. von Schlagintweit, Dr. Cayley, and Stoliczka (*v.* Sitz. Wiss. 2, 1873, 227; Q. J. Geol. Soc. 30, 1874, 568). Jade is also found in Siberia. chiefly as boulders in the River Anote, near Alibert's graphite mines, Mount Batougol, Province of Irkutsk.

Implements worked in jade and jadeite occur among the remains of the prehistoric lake-dwellings of Switzerland, and in ancient burial-places in France and Western Germany; they were also found by Schliemann at Hissarlik. The absence of native jade in such localities led to the suggestion that the material had been obtained by barter in prehistoric times, or that the implements had been brought by immigrants from Central Asia. This view has, however, been vigorously opposed, especially by Dr. Meyer, of Dresden (Die Nephritfrage kein ethnologisches Problem, 1883). The European implements may have been made of indigenous jade, as the mineral has been found *in situ* at Jordansmühl, and near Reichenstein, in Silesia, while jadeite is recorded from Monte Viso, in Piedmont. Certain hornblende rocks are hardly distinguishable from jade.

Numerous implements and amulets of jade and jadeite have been found in Mexico and Central America, especially in Costa Rica, while they also occur along the coast of British Columbia and Alaska. It has been suggested that such objects were obtained by early intercourse with Asia, but most authorities now regard them as autochthonous. In fact, jade has been found by G. M. Stoney in the Jade Mountains, north of the river Kowak, in Alaska. The subject has been discussed by Dr. G. W. Dawson, and the Alaskan jade has been analysed by Prof. F. W. Clarke, and studied microscopically by G. W. Merrill (Proc. U.S. Nat. Mus. 1888, 115; also G. F. Kunz's Gems of N. America, N. York, 1890).

Various green and grey minerals, used for implements and ornaments, have frequently been mistaken for jade; the commonest of these jade-like substances being fibrolite, saussurite, chloromelanite, pectolite, and serpentine. (For Jadeite *v.* Damour, C. R. [41] 1863, 161; and for the subject generally, with collected analyses, *v.* H. Fischer, Nephrit und Jadeit, 2nd ed. Stuttgart, 1880.) F. W. R.

JALAP *v.* Resins.

JALAPIN *v.* Glucosides.

JAMESONITE. *Lead sulphantimonite v.* Antimony.

JAPACONITINE *v.* Vegetable alkaloids.

JAPAN BLACK *v.* Brunswick black.

JAPAN EARTH. *Terra japonica v.* Catechu.

JAPAN LACQUER. A black varnish prepared from *Stagmaria verniciflua*.

JAPAN SAGO. Starch obtained from the stem of *Cycas revoluta*.

JAPAN WAX. This vegetable wax is obtained from *Rhus succedanea* and *Rhus vernicifera* indigenous to China and Japan, and from *Rhus sylvestris* indigenous to Japan only. The fruits are ground by means of millstones and the flour boiled in water from which the floating wax is skimmed: or, by another process, the fruits having been broken are dried and roasted, after which they are ground and the flour is exposed to the action of water vapour to melt the fat in the cells, from which it is then pressed out. Japan wax is whiter and more brittle than beeswax, and breaks with a conchoidal fracture. Its odour is resinous and tallowy.

In Japan the wax is used for the manufacture of candles and for producing a lustre on wood-ware. In England it is employed in candles and matches and in polishing materials. It is also made use of by perfumers in preparing pomades with the admixture of castor oil.

It is frequently adulterated with water and tallow to the extent, it is said, of 30 p.c. Japan wax forms the most important article of import among vegetable waxes in this country, the importation of the article in 1881 being over 11,000 boxes of about 132 lbs. each.

Japan wax melts at 54·5°F. and congeals at 40·5°F. In heating it becomes transparent at 10° to 12°F. below its melting-point. If remelted a short time after congealing, it melts at 41° to 42°F. and acquires the original melting-point only after long storing. The crude wax has a specific gravity of 1·000 to 1·006; the bleached wax 0·970 to 0·980.

It is insoluble in cold alcohol, but soluble in boiling alcohol of 97 p.c. The solution upon cooling appears as a white crystalline mass. It is soluble in benzene, petroleum, and warm ether. It saponifies with readiness.

JAPANESE SARDINE, OIL OF. This oil, which was introduced into Europe in 1885, but which found little acceptance on account of its most unpleasant smell, due to the crude manner of its extraction, is considered by Villon to be capable of profitable application in dyeing, and in the stearine and soap manufactures. The oil is chiefly obtained from the Island of Yesso, and from the peninsula of Ava, near Yokohama, and is extracted from the fish, either by boiling with water or by allowing them to rot in heaps, when the greater part of the oil flows out, the residue being obtained by pressure. This oil contains about 30 p.c. of solid fat, and begins to run at

20-22°C. It is refined in Yokohama by being heated for an hour at 50-60°C. in iron boilers of 100 litres capacity, and then run off into wooden vessels, where it soon separates into three layers. The upper layer is liquid and clear oil, the middle layer consists of solid fat, and the lower is water, with albuminous substances and portions of the fish. The liquid oil, when light, costs in Hamburg 40 marks per 100 kilos., and about 37·5 marks when brown. The solid fat is remelted, filtered and run into boxes, in which it solidifies. This fat is yellow, and is sold in Rotterdam as fish-stearin or fish-wax at 43 marks per 100 kilos. In the Indo-Chinese colonies, and especially in Cambodia, the production of this fish fat might be very considerable; about 400,000 kilos. a month could readily be exported. Experiments as to the application of this new product would be of great value (Villon, Corps Gras. Ind. 1887, 178; S. C. I. 6, 372).

JAPANNING. In Japan, whence this art takes its name, and where it has attained an excellence not reached by the Chinese, from whom it was borrowed by the Japanese, nor by subsequent imitators in other parts of the world, the process is performed in the following manner. The lacquer employed contains as its principal ingredient the sap of *Rhus vernicifera*, the lacquer tree of Japan, which is cultivated all over the main island of Niphon and in several districts of the islands Kiusiu and Sikok. The sap is drawn from wounds made in the trees. Mr. John L. Quin, Her Majesty's Acting Consul at Hakodate (1882) stated the quantity so extracted to be at the rate of a yearly average of 30,000 to 40,000 tubs, each tub being of about 4 gallons capacity, and of about 12*l.* value. The first process in preparing the crude lacquer is to evaporate the water which is contained in the sap as it flows from the tree by exposing it in shallow vessels to the heat of the sun: during this time about 1 p.c. of fresh water is added to the sap three times a day for two or three days according to the power of the sun. The reason of this is explained by Mr. Quin:—'If crude liquor, which is originally of the colour and consistency of cream, is exposed to the sun for a few days without adding water, it loses its creamy colour, and becomes quite black or nearly so; it also becomes thinner and transparent, or rather translucent, as can be seen when it is smeared on a white board. It will not now dry if applied to an article even if kept a month or more in the damp press. But if water is mixed with the lacquer which has thus been exposed and become black, it at once loses the black colour and its transparency, and becomes again of a creamy colour though slightly darker than at first.' 'It is a remarkable fact,' says Audsley, 'that lacquer, however prepared, will not dry perfectly on any material in the open air, but requires a damp close atmosphere to perfect the operation.' The next process therefore is to introduce the coated article into the 'damp press,' which is a cupboard or box having its interior brushed over at intervals with water, or in larger works a damp cellar or cave serves this purpose. From six to fifty hours is taken up in drying the lacquer at this stage.

For producing lacquers of different colours and for various purposes, processes more or less secret to individual manufacturers are followed; thus *Nakanuri-urushi*, or middle-coating lacquer, used for under-coat in best work is crude sap exposed until its colour is a deep transparent brown; *Rō-urushi*, or black lacquer, is prepared from crude or branch lacquer, *Seshime-urushi*, by the addition of a liquid made by boiling iron-filings in strong rice vinegar and subjecting the mixture to the sun's rays for several days, frequently stirring until it becomes a dense black. *Moritate-urushi*, or finishing lacquer, is a compound of *Ki-urushi* with a small quantity of turpentine and some water collected from whetstones on which steel tools have been sharpened. This lacquer is employed for the final coating of common ware and receives no polishing by hand. Other lacquers, such as vermilion, gold, silver, tin, &c., are produced by the admixture of the colouring matters required with crude lacquer. Oil or camphor may be added as a thinning medium. The work of laying the lacquer upon wood or metal is a process involving many successive coatings, after each of which the work is returned to the damp press. Calculated roughly, the time occupied in drying in the damp press amounts to 532 hours, or upwards of twenty-two days; for the highest class work this may reach a much higher figure.

A series of examples illustrating the operations of Japanese lacquering is preserved in the Museum of Economic Botany, Kew.

In Europe japanning is taken to mean the art of coating surfaces with varnishes which are then hardened by subjecting them to a high temperature, an art which holds an intermediate position between painting and enamelling. The varnishes are transparent and durable bodies, in black or other colours, black being the hue which is most extensively used. Black varnish is composed of pure natural asphaltum mixed into a preparation of gum anime dissolved in linseed oil and turpentine. This in thin coatings appears brown, and requires several courses to acquire the requisite blackness; the article treated being placed in a stove of about 150° after each coating. For colours, the necessary mineral pigments or metallic powders are mixed with a transparent copal varnish of less body than ordinary painters' varnish.

European japanning, although very far behind the work produced by the process described as in use among the Japanese, produces a very brilliant and durable coating to small articles of metal work and papier mâché. It is also applied as a facing for stone to imitate marble.

JARGON or **JARGOON.** A name applied to those varieties of zircon which may be cut and polished as gem stones. The adamantine lustre and high dispersive power of this mineral give it some resemblance to the diamond; and colourless jargoons, cut as brilliants and roses, are sometimes known as 'Matura diamonds;' Matura, in Ceylon, being the chief locality for such stones. From the diamond, however, the jargoon is immediately distinguished by its high density. The sp.gr. varies from 4 to 4·8, and in many cases is increased on heating the mineral, but Professor Church has shown that this is not so with all zircons. The jargoon differs again from diamond by crystallising in the tetragonal system and by possessing strong double

refraction, while it is greatly inferior in hardness (H = 7·5), though sufficiently hard to resist the knife or even a piece of quartz. Jargoons exhibit a great range of colour, the variety most prized being of a reddish-orange tint, and distinguished under the name of *jacinth*, *hyacinth*, or *noble zircon*. In 1789 Klaproth proved the identity of zircon and hyacinth. Both consist of zirconium silicate, but the cause of the beautiful hyacinthine colour is not well understood; it disappears when the stone is strongly heated. According to F. Sandberger, the colour of the dark-red zircons may be referred to the presence of cuprous oxide, while G. Spezia ascribes it, in most cases, to iron oxide. Church discovered a system of dark absorption bands in the spectrum of jargoon, which have been regarded as due to some compound of uranium. It has been shown by the same authority that many gem-stones believed to be hyacinth are merely essonite, or cinnamon stone, a variety of garnet. The higher density and superior lustre of the true hyacinth are sufficient to separate it at once from garnet. The hyacinthine zircon is a somewhat rare mineral. It is found of good colour in the basalts and volcanic sand of Expailly in Auvergne, but usually too small to be of commercial value. The finest known specimens occur as rolled pebbles in the gold-bearing river sands and drifts of New South Wales, especially in the Abercrombie River. The smoky, blue and green jargoons, used in jewellery, are mostly brought from Ceylon.
F. W. R.

JASPER. A compact and opaque variety of quartz, usually coloured red, yellow, or brown, by means of ferric oxide or its hydrate. It is cut and polished as an ornamental stone, and was much prized by the ancients, but their *jaspis* included other minerals than those now designated as jasper. The well-known *Egyptian jasper* is found as nodules and pebbles in the Nile Valley, and resembles a brown flint, with dark zones and cloudings. *Banded jasper* is a striped variety well illustrated by the beautiful red and green 'riband jaspers' of Siberia. Some banded jaspers appear to be metamorphic sedimentary rocks, while others are striated felsitic tuffs. The so-called *porcelain jasper* is merely a shale highly indurated by exposure to a high temperature. F. W. R.

JAUNE ACIDE. *Acid yellow v.* Azo-colouring matters.

JAUNE ANGLAIS. *Victoria yellow v.* Cresol.

JAUNE BRILLANT. *Cadmium sulphide v.* Cadmium.

JAUNE DE FER, JAUNE DE MARS. *Mars yellow v.* Pigments.

JAUNE D'OR. *Martius's yellow.*

JAUNE N. *Curcumeïn; Orange N. v.* Azo-colouring matters.

JAUNE SOLIDE. *Fast yellow r.* Azo-colouring matters.

JAVA WAX *v.* Wax.

JET. (Fr. *Jaïet*; Ger. *Gagat.*) A variety of the class of anthracites and lignites similar in appearance to cannel; being hard and capable of taking a lustrous surface by polishing, it is used for making small ornamental articles. It is found on the Yorkshire coast near Whitby, in Spain, Bohemia, and Styria, occurring in the trap and limestone formations. The name is supposed to be a corruption of the *Gagates* of Pliny and Dioscorides, who described the mineral as found near the mouth of the river Gagas in Lycia.

The jet of Whitby is evidently coniferous wood, thin sections of it showing under the microscope resin masses of oval figure, enveloping larger tissue than occurs elsewhere. On its surface impressions of fossils, especially ammonites, frequently appear, which seem to show that the material must at some time have passed through a plastic condition.

Whitby jet is divided into 'hard' and 'soft,' of which the former is the most esteemed; it is found near the base of the Upper Lias and, sparingly, in other parts of that formation. Soft jet occurs in the sandstones and oolitic shales. The hard variety is obtained in compressed layers varying from an inch or two in length and ⅛th in thickness, to 6 feet long, 30 inches wide, and 4 inches thick. The largest piece ever found was 6 feet 4 inches long, 4½ to 5½ inches wide, and 1 and 1½ inches thick; it weighed 11 lbs. 8 oz.

The collection of jet was formerly effected by cutting down the cliffs until the jet-veins showed themselves; to-day the cliffs are almost abandoned and the works are carried on inland to a distance of twenty miles. The operation is described by J. A. Bower (Jour. Soc. of Arts, 22) in these words: 'The process of obtaining jet here is simple; the faces of the hills are turned down bodily, and by then tunnelling for some distance, and after carrying several passages parallel from the face of the hill, transverse shafts are cut. When the rock becomes too hard the miners retire, pulling down the roofs on their return; in these falls the bulk of the jet is found.' The rough jet obtained from the inland mines is encased in a brown skin; that from the cliffs is covered with a blue skin. This is chipped off, the pieces of jet are sawn into suitable sizes and handed over to the carver or turner (*v.* Whitby Jet and its Manufacture, Jour. Soc. of Arts, 22, 80; Illustrations of the Geology of Yorkshire, Part I. The Yorkshire Coast, by John Phillips).

JOHNSON'S POWDER *v.* Explosives.

JUDSON POWDER *v.* Explosives.

JUGLONE *v.* Naphthalene.

JUNIPER, OIL OF, *v.* Oils, essential.

JUNIPER. (*Genièvre*, Fr.; *Wachholder*, Ger.) The fruit, or so-called berries, of juniper have been employed in medicine from very early times. It is a reputed diuretic. Sometimes it has been used as an article of food, and the large proportion of sugar which it contains has rendered it available for fermentation and the distillation of spirit. Such a product was in France called *Genièvre* and hence the contracted form *gin* employed in this country for a spirit which now is merely flavoured with juniper. The juniper of modern medicine is the *Juniperus communis* (Linn.; Bentl. a. T. 255) a well-known evergreen shrub which inhabits the northern regions of both hemispheres. The fruits are gathered chiefly in Hungary, Austria, and the south of France (Fl. a. H. 624; Morel, Ph. [3] 8, 886).

The most important constituent of juniper is the *volatile oil*, which though it occurs in all parts of the plant, is found chiefly in and is always distilled from the fruit. Both the quantity and quality of the oil varies with the age of the fruit. That obtained from the green fruit is larger in proportion, and is a lighter oil, than that distilled from the ripe fruit. The former is the more highly esteemed. The yield varies from 0·4 to 1·2 or perhaps 2·0 p.c. It is a colourless liquid, having a strong odour of juniper and a hot aromatic taste. It boils at 155° to 200° or 205° and its specific gravity varies from 0·86 to 0·88 (Morel). It consists of a *terpene* boiling at 155°, sp.gr. 0·839 at 25° (Blanchet, A. 7, 165), together with *polymeric terpenes*, chiefly $(C_{10}H_{16})_2$(?), which boil above 180°, mostly about 200°. Wallach (A. 227, 228) has examined the terpene (*pinene*). The oil is lævogyrate. According to Blanchet, it forms a crystalline *hydrate*, and Soubeiran and Capitaine (J. Ph. 26, 78) describe a liquid *hydrochloride*. Tilden (Ph. [3] 8, 189) prepared from it a *nitrosyl chloride compound* $C_{10}H_{16}NOCl$. On long standing it deposits a *camphor* (Gm. 14, 295). Generally its reactions are similar to those of turpentine oil (Gm. 14, 292; Dragendorff, Ph. [3] 6, 581; Barth, Z. 1867, 509; Morel).

The other constituents of juniper fruits may be seen from the analyses of Donath (D. P. J. 208, 300) and Ritthausen (Landw. Versuchs-Stat. 20, 423). The chief of these is *glucose*, of which Donath finds 29·65 and Ritthausen 14·36 p.c. The bitter substance *juniperin*, which occurs only to the extent of 0·37 p.c., was first studied by Steer (Sitz. B. 21, 383). *Resins*, *cf.* Trommsdorff (Gm. 17, 449). A. S.

JUTE is the bast fibre of two plants of the natural order Tiliaceæ, viz. *Corchorus capsularis* and *Corchorus olitorius*, cultivated for the most part in Bengal, where they are indigenous. Although differing in size and in the form of their seed-pods, the plants are not greatly dissimilar in appearance and are not commercially distinguished from each other. The seed is sown annually, in April or May, and the plants after flowering, which takes place from August to September, and having now attained a height of five or six feet in the case of *C. olitorius*, and of five to ten feet in that of *C. capsularis*, are cut down and thrown into pits of water to soak, after the manner of steeping flax. From a few days to a month is required to bring the stalks into a condition for stripping the bast from the wood and freeing it from cortex, these operations being purely manual. After being washed and dried the jute is made up into bales for sale.

Jute is very largely used for the manufacture of sacking and wrapping cloths (Hessians), as a paper-making fibre, and as a substitute for hair in making theatrical wigs. It is also employed for carpet-making and inferior cordage and, in India, for making small domestic articles such as nets and muzzles for oxen. In these islands the principal seat of the jute industry is Dundee.

The fibre occurs in strands of considerable length, 6–12 feet; the spinning unit or filament is of various lengths, according to the degree of subdivision practised. The filament is a complex of the ultimate fibres, of which from 5 to 12 are usually seen in the section at any point. They are polygonal in section and much thickened (lignified); their length does not exceed 2–3 mm., whereas those of flax and hemp—also bast fibres—are from 25–40 mm. long. This structural inferiority, together with the fact that the fibre substance yields somewhat readily to the action of oxidants (air and light) in presence of water, characterises jute as a 'weak fibre.'

Treated by the 'line spinning' process it may be spun into yarns of considerable fineness, but, owing to the large proportion of waste ('tow'), at relatively large cost. These yarns when bleached—preferably by 'soda bleach' (sodium hypochlorite)—have considerable lustre; they are soft and of a cream shade, and take up the majority of colouring matters—wood and aniline dyes—directly from the dye-bath. Jute fabrics are also successfully printed in steam styles, the presence of sodium sulphite being necessary to preserve the fibre substance from the action of the steaming process (Développement de l'Industrie de Jute, Cross and Witt, Bull. Mulh. 1881).

According to the investigations of Cross and Bevan, jute does not contain cellulose as such, but in the form of bastose or lignocellulose, which is a link between the carbohydrates and the aromatic compounds. Treated with chlorine it gives a yellow chlorinated derivative which when hydrolised yields substances belonging to the tannic acid group. Hence it may be said that jute possesses a mordant which makes it receptive of aniline colours in a degree possessed by none of those fibrous materials which require the intervention of a mordant. When quantities of the fibre are kept in a damp situation, more especially when exposed to sea-water, it is decomposed into substances analogous to tannin and to acids of the group of pectic acid. Under treatment by acids, jute is disintegrated, yielding xylose and furfural (*v.* also Tollens, An. 254, 325). It is easily bleached by permanganate of potash after cleansing with soap or alkali, with a loss in weight of 3 to 4 p.c. In practice this is generally too expensive a process, and the substances usually employed are hypochlorites, in which great care is necessary, as chlorinated compounds may be formed and the fibre destroyed (*supra*).

In an early paper by Cross and Bevan (C. N. 42, 77) the chemical constituents of jute are thus described:—

'The inorganic constituents of the normal fibre are:

'(*a*) *Water of hydration*, varying from 10 to 12 p.c. of its weight with the temperature and hygrometric state of the air. It is to be regarded as dependent both on the chemical nature and structure of the fibre (chemical adhesion), although scarcely upon its external structure (capillarity), as conjectured by Sir W. Thomson.

'(*b*) *Ash.*—The general features of the inorganic skeleton of the fibre may be expressed by the following average percentage numbers: SiO_2, 30–35; Fe_2O_3, 5–8; Al_2O_3, 5–6; Mn_2O_3, 0·5–0·9; CaO, 13–16; $K_2O + Na_2O$, 5–10; P_2O_5, 8–13; SO_3, 1–5.

'(*c*) Organic (considered with exclusion of *a* and *b*). Combustions of the fibre (purified by boiling in dilute ammonia; the fibre thereby sustains a loss of 1 p.c. of its weight, losing a resinous constituent which causes the adhesion of portions of cortical parenchyma and the matting together of the fibres in the raw state) showed it to have the following aggregate (average) composition: C 46·5, H 5·80. Nitrogen is present only in minute quantity; *e.g.* in a fair specimen (previously boiled in dilute sodium carbonate) the quantity determined was 0·053 p.c. The proximate constituents of the fibre are *cellulose* 70–80 p.c., as isolated by the ordinary methods, and "*intercellular and encrusting substance*," or lignone, 20–30 p.c.' For a further account of the chemistry of jute and its derivatives *v.* Cross and Bevan, C. J. and S. C. I. 1882, 90; Cross, Bevan and King, Report on Indian Fibres, Col. Ind. Exh., London, 1887; WATTS' DICTIONARY OF CHEMISTRY, art. CELLULOSE; *v.* also vol. i., art. CELLULOSE.

The Crimean War of 1854–56, and the American Civil War of 1861–63, which restricted in turn the supply of flax and of cotton, gave an impetus to the importation of raw jute, which independently of those influences has rapidly grown since 1867, when the quantity taken by this country was 79,000 tons. In 1877 it was 187,500 tons, and rose to 286,368, 267,724, and 328,626 tons in the years 1885, 1886, and 1887 respectively.

K

KAINITE (from καινός, new). A salt of variable composition found in the Stassfurt saltworks and in other places, consisting mainly of potassium magnesium sulphate combined with magnesium chloride $K_2Mg(SO_4)_2.MgCl_2.6H_2O$ (Frank, J. 1868, 1019). On treatment with water it is decomposed, and its solution deposits in the first place $K_2Mg(SO_4)_2.6H_2O$, afterwards $MgSO_4.7H_2O$, whilst the chlorides of magnesium and potassium remain dissolved. It forms a fine-grained non-deliquescent mass of a grey or yellowish colour, which effloresces in a dry atmosphere. According to v. Hauer the kainite of Galicia, which occurs in two horizontal beds from 70 to 80 feet thick, without any intervening layer, and mixed with only small quantities of sylvin and rock salt, consists mainly of $MgSO_4.KCl.3H_2O$ (*v.* POTASSIUM).

KAIRINE *v.* QUINOLINE.

KAIROCOLL *v.* QUINOLINE.

KAIROLINE *v.* QUINOLINE.

KAISERGELB *v.* AURANTIA.

KAISERROTH. The sodium salt of dinitrodibromfluoresceïn. Called also Eosin Scarlet, Safrosine, and Lutétienne (*v.* PHTHALEÏN COLOURING MATTERS).

KALIBORITE. A mineral resembling *kieserite*, found by Feit in the salt deposits at Schmidtmannshall. Is a hydrated borate of potassium and magnesium,

$$2K_2B_6O_{10}.9MgB_4O_7.39H_2O.$$

Water disintegrates the mineral, but is otherwise without action on it. Easily soluble in warm mineral acids. Sp.gr. 2·05 (C. Z. 13, 1188).

KAMALA RESINS *v.* RESINS.

KAOLIN. A name frequently applied to china clay (*q. v.*).

KAOLINITE *v.* CLAY.

KAPNAMOR *v.* WOOD, DESTRUCTIVE DISTILLATION OF.

KARELINITE. An oxysulphide of bismuth $Bi_2S.Bi_2O_3$ found in the Sawodinsk mine in the Altaï; of a lead-grey colour, sp.gr. 6·6 (Hermann, J. pr. 75, 448).

KELP *v.* IODINE.

KEPHIR *v.* MILK.

KERASITE, CERASINE, or **HORN-LEAD.** A naturally occurring compound of lead chloride and lead carbonate.

KERMES, GRAINS OF KERMES, ALKERMES. The dried body of an insect (*Coccus ilicis*) found in the south of Europe and in many parts of Asia. Formerly much used for dyeing scarlet.

KERMES MINERAL. Amorphous antimony sulphide *v.* ANTIMONY.

KERMESITE. *Red antimony. Antimony blende. Pyrantimonite. Pyrostibite.* An oxysulphide of antimony formed by the oxidation of antimony sulphide, and occurring associated with grey and white antimony in Hungary, Saxony, Dauphiné, &c. Found in monoclinic crystals or in capillary tufts of six-sided prisms, of a cherry-red colour and adamantine lustre. Composition $Sb_2O_3.2Sb_2S_3$.

KEROSENE or **KEROSINE** *v.* PETROLEUM.

KETONES. The ketones are a class of organic compounds containing one or more carbonyl or CO groups united with hydrocarbon radicles, and are divided into ketones, diketones, triketones, &c., according to the number of carbonyl groups in the molecule. They are further classed as fatty, mixed, or aromatic ketones according as the radicles associated with the carbonyl group or groups are derived wholly from paraffinoid, partly from paraffinoid and partly from benzenoid, or wholly from benzenoid hydrocarbons. It is usual to describe these compounds by reference to the hydrocarbon radicles present in the molecule, thus the substance $CH_3.CO.C_2H_5$ is termed methylethylketone, and with few exceptions, *e.g.* acetone (dimethylketone), acetophenone (methylphenylketone), and benzophenone (diphenylketone), where trivial names were given before the constitution of the respective compounds was known, this nomenclature is adhered to in the case of the ketones.

The diketones are divided into several classes: thus, when the two carbonyl groups are directly united, as in diacetyl $CH_3.CO.CO.CH_3$, the compound is an α-diketone, when they are separated by a carbon atom; as in acetylacetone $CH_3.CO.CH_2.CO.CH_3$, it is a β-diketone; when by a chain of two carbon atoms, as in acetonylacetone $CH_3.CO.CH_2.CH_2.CO.CH_3$, it is a γ-diketone. No uniform system of nomenclature obtains in the case of the diketones; α-diketones are frequently described by reference to the acid radicles present in the molecule; thus the compound $CH_3.CO.CO.C_6H_5$ is termed acetylbenzoyl; it is, however, known also as methylphenyl-α-diketone, also as ω-phenyl-α-ω-diketopropane in accordance with the systematic nomenclature proposed by Baeyer (B. 19, 160), and equal confusion prevails in the case of the other classes of diketones.

Ketones. *Preparation.*—The one general method for the preparation of fatty, mixed, and aromatic ketones consists in distilling a salt, preferably the calcium salt, of the corresponding acid. Acetone is obtained by distilling dry calcium acetate:

$$\underset{\text{(calcium acetate)}}{(CH_3.CO.O)_2Ca} = \underset{\text{(acetone)}}{(CH_3)_2CO} + CaCO_3;$$

benzophenone by distilling calcium benzoate, and acetophenone by distilling a mixture in equimolecular proportions of calcium acetate and benzoate. In no case, however, is the distillate so obtained pure, and in particular the preparation of mixed ketones by this method leads to a very impure product, since it contains in addition each of the ketones and the impurities which would result were each organic salt submitted to destructive distillation; thus, in the case of acetophenone, benzene, acetone, benzophenone, and the impurities which are formed in the preparation of the two latter from calcium acetate and benzoate respectively, are also present in the distillate. Those fatty ketones which contain a methyl group directly attached to the carbonyl radicle, *e.g.* acetone, methylethylketone, &c., can be purified by converting them into their crystalline compounds with sodium hydrogen sulphite (bisulphite), and subsequently decomposing these by distillation with an aqueous solution of an alkaline carbonate. In all other cases (except that of methylbenzylketone), however, combination with alkaline bisulphites does not take place, and fractional distillation is the only method which can be adopted for purifying the great majority of these substances. Many synthetical methods for the preparation of ketones have been described, but reference can only be made here to a few of the more general of these.

Fatty and mixed ketones may be obtained: (1) By the action of the chlorides of acid radicles on zinc methyl or ethyl:

$$\underset{\text{(acetic chloride)}}{2CH_3COCl} + Zn(CH_3)_2 = \underset{\text{(acetone)}}{2CH_3.CO.CH_3} + ZnCl_2$$

(Freund, A. 118, 1; Pawlow, A. 188, 104; Popow, B. 4, 720; 5, 501).

(2) By boiling the ethereal salts of β-ketonic acids with dilute aqueous potash, baryta, or sulphuric acid:

$$\underset{\text{(ethylic acetoacetate)}}{CH_3.CO.CH_2.CO.OC_2H_5} + H_2O$$
$$= \underset{\text{(acetone)}}{CH_3.CO.CH_3} + CO_2 + \underset{\text{(alcohol)}}{C_2H_5.OH}$$

(Frankland and Duppa, A. 138, 216, 332; 145, 82; Wislicenus, A. 190, 276; Baeyer and Perkin, B. 16, 2131; Perkin and Calman, C. J. 49, 154).

Mixed ketones can further be prepared on the large scale by a method which cannot be employed for the production of fatty ketones, viz. by heating the chloride of a fatty acid with a benzenoid hydrocarbon in the presence of aluminium chloride:

$$\underset{\text{(acetic chloride)}}{CH_3.COCl} + C_6H_6 = \underset{\text{(acetophenone)}}{CH_3.CO.C_6H_5} + HCl$$

(Friedel and Crafts, A. Ch. [6] 1, 507).

Aromatic ketones can be obtained—(1) By oxidising the corresponding hydrocarbons by means of chromic acid:

$$\underset{\text{(diphenylmethane)}}{C_6H_5.CH_2.C_6H_5} + O_2 = \underset{\text{(benzophenone)}}{C_6H_5.CO.C_6H_5} + H_2O$$

(Zincke, A. 159, 377).

(2) By heating the chloride of an aromatic acid with a benzenoid hydrocarbon and aluminium chloride:

$$\underset{\text{(benzoic chloride)}}{C_6H_5COCl} + C_6H_6 = C_6H_5.CO.C_6H_5 + HCl$$

(Friedel and Crafts, *l.c.*; Ador and Rilliet, B. 12, 2298; Elbs, J. pr. [2] 33, 181; 35, 465).

(3) By the action of phosgene on a benzenoid hydrocarbon in the presence of aluminium chloride:

$$COCl_2 + 2C_6H_6 = CO(C_6H_5)_2 + 2HCl$$

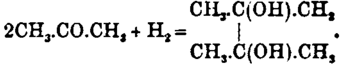
(Friedel and Crafts, A. Ch. [6] 1, 518).

General properties and reactions.—(1) The ketones are for the most part colourless liquids having ethereal or aromatic odours, and with few exceptions are insoluble in water, but readily soluble in alcohol, ether, &c.

(2) On reduction with sodium amalgam, ketones are converted into secondary alcohols:

$$CH_3.CO.CH_3 + H_2 = \underset{\text{(isopropyl alcohol)}}{CH_3.CH(OH).CH_3};$$

at the same time condensation of the ketone molecule also occurs with the formation of dihydric alcohols known as *pinacones*:



$$2CH_3.CO.CH_3 + H_2 = \begin{array}{c} CH_3.C(OH).CH_3 \\ | \\ CH_3.C(OH).CH_3 \end{array}.$$

(3) When treated with hydroxylamine, ketones are converted into *oximes*, which for the most part are crystalline solids:

$$(CH_3)_2CO + NH_2.OH = \underset{\text{(acetoxime)}}{(CH_3)_2C:N.OH} + H_2O$$

(V. Meyer and Janny, B. 15, 1324; Janny, B. 15, 2778; Spiegler, M. 5, 203; Auwers, B. 22, 604).

(4) Ketones react with phenylhydrazine yielding crystalline *hydrazones*:

$$(CH_3)_2CO + NH_2.NHC_6H_5$$
$$= (CH_3)_2C:N.NHC_6H_5 + H_2O$$

(Reisenegger, B. 16, 661; E. Fischer, B. 17, 572).

(5) On oxidation with a mixture of potassium bichromate and dilute sulphuric acid, fatty ketones break up with the formation of acids of the acetic series. If the hydrocarbon radicles are both primary, the carbonyl group remains attached to the less complex radicle, and the more complex is separately oxidised:

$$\underset{\text{(methylpropylketone)}}{CH_3.CO.CH_2.CH_2.CH_3} + 3O$$
$$= \underset{\text{(acetic acid)}}{CH_3.CO.OH} + \underset{\text{(propionic acid)}}{CH_3.CH_2.CO.OH};$$

but if the more complex radicle belongs to the secondary series, it is first oxidised to a ketone, which is subsequently further oxidised to acids of the acetic series:

$$\underset{\text{(methylisopropylketone)}}{CH_3.CO.CH(CH_3)_2} + 2O$$
$$= CH_3.CO.OH + \underset{\text{(acetone)}}{CO(CH_3)_2}$$

(Wagner, B. 15, 1194; B. 18, 2266; 18, *Referate*, 178).

Mixed ketones under these conditions yield a mixture of benzoic acid and an acid of the acetic series, the carbonyl group remaining attached to the benzenoid hydrocarbon radicle:

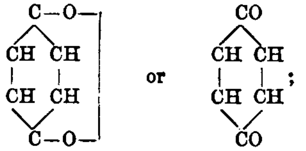
$$\underset{\text{(acetophenone)}}{C_6H_5.CO.CH_3} + 3O = \underset{\text{(benzoic acid)}}{C_6H_5.CO.OH} + \underset{\text{(formic acid)}}{H.CO.OH},$$

the formic acid being at once further oxidised to carbon dioxide and water. A mixed ketone such as methylbenzylketone $C_6H_5.CH_2.CO.CH_3$, which may be regarded as a phenyl derivative of acetone, follows the rule for fatty ketones and yields benzoic and acetic acids on oxidation (Popow, *l.c.*).

Diketones.—The chief methods of preparation and the more noteworthy properties and reactions of the diketones have been already described (*v.* DIKETONES).

Classed together under the general term 'quinones' is a group of coloured diketones, which may be regarded as derived from benzenoid hydrocarbons by the displacement of two hydrogen by two oxygen-atoms in ortho- or para-positions. Quinones can in some cases be obtained by the direct oxidation of hydrocarbons (*e.g.* naphthalene, anthracene, phenanthrene, and chrysene), or, when this method fails, by oxidation of amido- derivatives of the hydrocarbons (*e.g.* aniline, α-naphthylamine, α-amido-β-naphthol) by means of chromic acid. They most nearly resemble the α-diketones in properties (*e.g.* they are yellowish in colour, and in some cases have a similar odour), but differ, however, from these in not forming osazones[1] on treatment with phenylhydrazine and from all diketones in not yielding compounds of the type of secondary alcohols on reduction. Comparison of the properties of the quinones shows that these differences are most marked, as would be expected, in the paraquinones, such as quinone and α-naphthaquinone, and become much less so in the orthoquinones, such as phenanthraquinone, in which the carbonyl groups are in contiguous positions in the 'rings.'[2]

The constitution of quinone has been represented by one of two formulæ

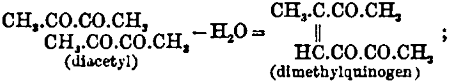


in other words, it has been regarded either as a peroxide or a diketone, and the same may be said of quinones generally. The peroxide formula was formerly assigned by Graebe to quinone, on the assumption that the two oxygen atoms became most probably attached to contiguous carbon atoms, since only one of the dihydroxy-benzenes (hydroquinone) can be oxidised to quinone. Hydroquinone has been proved beyond question to be a para- derivative, and Fittig's diketone formula (A. 166, 381; B. 6, 168; *cf.* Zincke, B. 6, 137) is now very widely accepted for both para- and ortho-quinones.

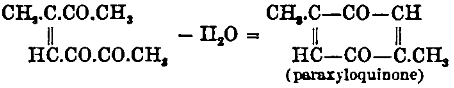
The diketonic constitution of quinone, which of all quinones shows the least resemblance in its reactions to open-chain diketones, is placed beyond doubt by the following considerations:

(1) Quinone reacts with an equimolecular proportion of hydroxylamine hydrochloride, forming quinonoxime or paranitrosophenol $O:C_6H_4:N.OH$ (Goldschmidt, B. 17, 213; Goldschmidt and Schmid, B. 17, 2060), and with two molecular proportions yielding quinonedioxime $OH.N:C_6H_4:N.OH$ (Nietzki and Kehrmann, B. 20, 616).

(2) Paraxyloquinone can be prepared synthetically by warming a solution of diacetyl in aqueous alkali, a reaction which clearly seems to point to the presence of two carbonyl-radicles in quinone:



$$\underset{\text{(diacetyl)}}{\begin{array}{l} CH_3.CO.CO.CH_3 \\ \quad CH_3.CO.CO.CH_3 \end{array}} - H_2O = \underset{\text{(dimethylquinogen)}}{\begin{array}{c} CH_3.C.CO.CH_3 \\ \| \\ HC.CO.CO.CH_3 \end{array}};$$



$$\begin{array}{c} CH_3.C.CO.CH_3 \\ \| \\ HC.CO.CO.CH_3 \end{array} - H_2O = \underset{\text{(paraxyloquinone)}}{\begin{array}{ccccc} CH_3.C & - & CO & - & CH \\ \| & & & & \| \\ HC & - & CO & - & C.CH_3 \end{array}}$$

(Pechmann, B. 21, 1417). The fact that the carbonyl groups in the quinones form part of a closed chain, no doubt, accounts for the fact that they differ in many of their reactions from open-chain diketones; how profoundly the nature of the radicles associated with the carbonyl groups modifies some of the reactions of an α-diketone, for example, can be seen by comparing the action of aqueous alkalis on diacetyl, acetylbenzoyl, and their homologues, whereby quinones are generated (Pechmann, *l.c.*; B. 22, 2130), with that on benzil, which results in the formation of diphenylglycollic acid:

$$C_6H_5.CO.CO.C_6H_5 + KHO$$
$$= (C_6H_5)_2.CH(OH).CO.OK$$

(Liebig, A. 25, 25; Zinin, A. 31, 329; Fischer, B. 14, 326).

When the ketones are compared one very striking fact comes out. Fatty ketones containing one carbonyl radicle are destitute of colour in the ordinary sense of the term—that is, they form colourless liquids or solids; and the same is true of mixed ketones and the aromatic

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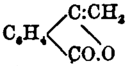
[1] Dihydrazones, in which the phenylhydrazine residues, $(N.NHC_6H_5)_2$ are attached to contiguous carbon atoms (Fischer, B. 21, 985).

[2] Quinone is yellow in colour, has a pungent odour, is readily volatile with steam, and in many of its reactions exhibits the character of an oxidising agent. It does not yield a hydrazone, but is reduced to hydroquinone (quinol) on treatment with phenylhydrazine. α-Naphthaquinone resembles quinone in most of its properties, but is not reduced by sulphurous anhydride in the cold, and yields benzeneazo-α-naphthol when treated with phenylhydrazine (Zincke and Bindewald, B. 17, 3026). Anthraquinone, a true para-diketone, exhibits none of the characteristic reactions of an open-chain diketone. It is yellow in colour, but destitute of odour and non-volatile with steam, is not reduced by sulphurous acid, and does not react with phenylhydrazine. β-Naphthaquinone, phenanthraquinone, chrysoquinone, and retenequinone differ from the paraquinones by being orange in colour, destitute of odour, and non-volatile with steam. Moreover they closely resemble α-diketones such as benzil in their reactions; thus they yield azines by condensation with orthodiamines (Witt, B. 19, 2795; Hinsberg, A. 237, 340; Liebermann and Witt, B. 20, 2443; *v.* AZINES); combine with phenylhydrazine, yielding hydrazones in the case of phenanthraquinone and chrysoquinone (Zincke, B. 16, 1563; 18, 786 footnote); are reduced to the corresponding quinols by warming with sulphurous acid, and form crystalline compounds with alkaline bisulphites; and the last three, together with the homonucleal dichloro-β-naphthaquinone, are converted into derivatives of glycollic acid when boiled with concentrated aqueous alkalis (Baeyer, B. 10, 125; Bamberger and Kranzfeld, B. 18, 1933; Bamberger and Hooker, A. 229, 132; Zincke and Frölich, B. 20, 1266), whilst phenanthraquinone resembles benzil and diacetyl in forming condensation products with aldehydes and ammonia (Japp and Streatfeild, C. J. 41, 417; *cf.* Japp and Wynne, C. J. 49, 464; Wadsworth, C. J. 57, 8).

ketones, with apparently the two exceptions of diphenyleneketone $\left\langle\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\right\rangle CO$ and pyreneketone $C_{10}H_8\left\langle\begin{matrix}CH\\CH\end{matrix}\right\rangle CO$ (Bamberger and Philip, A. 240, 178). Certain diketones, however, are invariably found to be coloured in various shades of yellow, and this appearance of colour is evidently associated with a particular arrangement of the carbonyl radicles in the molecule, since in the case of open-chain diketones only α-diketones—compounds containing the carbonyl groups in *contiguous* positions in the molecule, such as homologues of diacetyl $CH_3.CO.CO.CH_3$ (Freund, A. 118, 35; Brühl, B. 12, 318; Fittig and Daimler, B. 20, 203; Fittig, B. 20, 3183; Pechmann, B. 20, 3162; 21, 1412; Brömme and Claisen, B. 21, 1134; Otte and Pechmann, B. 22, 2115), of benzoylacetyl $C_6H_5.CO.CO.CH_3$ (Toennies, B. 20, 2983; Müller and Pechmann, B. 22, 2127), of benzil $C_6H_5.CO.CO.C_6H_5$ (Boesler, B. 14, 325), and of benzfuril $C_6H_5.CO.CO.C_4H_3O$ (E. Fischer, A. 211, 229)—are yellow liquids or solids, whilst homologues of acetylacetone $CH_3.CO.CH_2.CO.CH_3$ (Combes, C. R. 103, 814; Claisen and Ehrhardt, B. 22, 1009); of benzoylacetone (Fischer and Bülow, B. 18, 2131, 2136; Claisen, B. 20, 655; Beyer and Claisen, B. 20, 2180; Stylos, B. 20, 2181; Claisen and Lowman, B. 21, 1150), and of acetonylacetone $CH_3.CO.CH_2.CH_2.CO.CH_3$ (Paal, B. 18, 58) are colourless. It is true that a γ-diketone, acetophenoneacetone, is described by Paal as a yellow oil (B. 16, 2868; 17, 914), but it may well be that the colour was due to impurity, since the ketone is prepared from an unstable acid and is an oil which cannot be purified by distillation owing to decomposition.

All closed-chain diketones—quinones—are coloured, and the shade varies from the yellow of quinone to the orange-red of phenanthraquinone. It should be noted in this connection that W. Wislicenus has prepared diketohydrindene $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CH_2$ and its methyl and dimethyl derivatives (A. 246, 351; Wislicenus and Kötzle, A. 252, 72), and finds them to be colourless substances; whilst, on the other hand, Gabriel has described a compound, methylenphthalyl  $C_6H_4\left\langle\begin{matrix}C{:}CH_2\\CO.O\end{matrix}\right.$, obtained by the condensation of phthalic anhydride and ethyl malonate (B. 14, 926), and Gabriel and Michael a compound formulated as $C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CMe_2$, by heating phthalic anhydride with isobutyric acid, and both substances crystallise in yellow needles. The lactonic constitution assigned by Gabriel to methylenphthalyl seems in no way to account for the colour, and it is possible that further investigation will show that these compounds have the constitution now assigned by Wislicenus to the diketohydrindenes.

The occurrence of colour in quinone $O{:}C_6H_4{:}O$ and quinones generally is of considerable theoretical importance in connection with the origin of colour in dye-stuffs, inasmuch as it seems probable that the great majority of organic dyes may be formulated on the quinone type (Armstrong, C. J. Proc. 1888, 29; Nietzki, Chemie der organischen Farbstoffe, edition 1889, pp. 6 and others; compare also Nietzki, Dietze, and Mackler, B. 22, 3026).

Of the triketones, one only—diphenyltriketone $C_6H_5.CO.CO.CO.C_6H_5$ (Pechmann, B. 22, 852)—is known to be coloured, and in this case the carbonyl groups are present in contiguous positions. It is worthy of note that this triketone crystallises in colourless prisms with three molecular proportions of water—a fact pointing to formation of a hydroxy- derivative by combination with the elements of water.

Acetone, acetophenone, butyrone, and the diketones have already been described under the respective headings (*q. v.*), and quinone (*v.* QUINONES), the naphthaquinones (*v.* NAPHTHALENE), anthraquinone (*v.* ALIZARIN AND ALLIED COLOURING MATTERS), and phenanthraquinone (*v.* PHENANTHRENE), will form the subjects of separate articles. The remainder of the present article will, therefore, be confined to a description of benzophenone and benzil, both of which yield derivatives employed in the manufacture of dye-stuffs.

BENZOPHENONE, *Diphenylketone*, *Benzone*, $C_6H_5.CO.C_6H_5$.

Formation.—Benzophenone is obtained by the dry distillation of calcium benzoate (Péligot, A. 12, 41; Chancel, A. 72, 279; 80, 285), by distilling benzil over heated litharge (Wittenberg and V. Meyer, B. 16, 501), and together with benzene by heating benzil with soda-lime (Jena, A. 155, 87). It can also be prepared by heating benzoic chloride and eight to ten times its weight of benzene with aluminium chloride (Friedel and Crafts, A. Ch. [6] 1, 510); by heating benzoic acid, benzene, and either phosphoric anhydride or metaphosphoric acid in sealed tubes at 180°–200° (Kollarits and Merz, B. 5, 447; 6, 538); by heating benzene saturated with phosgene (carbonyl dichloride) with aluminium chloride (Friedel and Crafts, A. Ch. [6] 1, 518); and in small quantity by heating benzoic chloride and benzene with zinc at 180°–200° (Grucarevic and Merz, B. 6, 1243). It is further formed when diphenylmethane is oxidised by means of a mixture of potassium bichromate and sulphuric acid (Zincke, A. 159, 377).

Preparation.—(1) Dry calcium benzoate is mixed with one-tenth its weight of caustic lime and distilled in an iron retort: a mercury bottle answers the purpose very well. The red liquid which passes over is fractionated, and the fraction boiling at 290°–310° is collected separately. On cooling it solidifies, and the crystallised benzophenone is freed from liquid impurities by pressure, and finally purified by crystallisation from a mixture of alcohol and ether. The yield amounts to about one-fourth the weight of the calcium benzoate employed (Chancel). Benzene, diphenyl, and other hydrocarbons, and also anthraquinone, if caustic lime is not mixed with the benzoate before distillation, are present in the distillate; but fractionation is sufficient to separate the ketone from these impurities, since all, with the exception of benzene, boil well above 310° (Kekulé and Franchimont, B. 5, 909; Behr, B. 5, 971).

(2) Benzene, cooled to its crystallising point, is saturated with phosgene, and aluminium chloride is added in small portions at a time

to the solution contained in a reflux apparatus. The reaction sets in at ordinary temperatures with the evolution of hydrogen chloride, and is continued until the addition of aluminium chloride to the product causes no further evolution of the gas. The product is then carefully treated with water, washed with dilute potash, and fractionated. 100 grams of benzene require about 55 grams of phosgene and 36 grams of aluminium chloride, and the product amounts to about 33 grams; much of the phosgene is mechanically carried away by the escaping hydrogen chloride during the reaction (Friedel, Crafts and Ador, A. Ch. [6] 1, 520; B. 10, 1856; *cf.* Elbs, J. pr. [2] 35, 465).

(3) A mixture of equivalent amounts of benzene and benzoic chloride is dissolved in carbon bisulphide, and the solution gradually run into a reflux apparatus containing an equal volume of carbon bisulphide, and a weight of aluminium chloride equal to that of the benzoic chloride. The product is then heated on a water bath until the evolution of hydrogen chloride ceases, and, when cold, is carefully treated with water until no further reaction ensues, and steam-distilled; carbon bisulphide, unattacked benzene, and benzoic acid pass over, whilst the impure benzophenone remains in the distilling vessel as a heavy oil, which may be purified by careful washing, first with very dilute hydrochloric acid, then with very dilute caustic soda, and finally with water. It is then dried at 110° and fractionated. The yield of crystallised ketone amounts to 70 to 75 p.c. It is necessary that the substances and apparatus employed should be perfectly dry, and atmospheric moisture must be excluded by placing a calcium chloride tube at the top of the reflux condenser (Elbs, J. pr. [2] 33, 181; 35, 465).

Properties.—Benzophenone is dimorphous, crystallising usually in large rhombic prisms (Wickel, C. J. 50, 234), which melt at 48–49° (Linnemann, A. 133, 4), but occasionally in well-formed, apparently monoclinic forms, which melt at 26–26·5°, and, when kept for some time, become opaque and pass into the rhombic form (Zincke, A. 159, 381; B. 4, 577). It boils at 170° under 15 mm. pressure (Angelbis and Anschütz, B. 17, 165), at—

303·7°	at 723·05 mm.	305·3°	at 747·79 mm.
303·9°	,, 726·29 ,,	305·5°	,, 750·91 ,,
304·1°	,, 729·33 ,,	305·7°	,, 754·03 ,,
304·3°	,, 732·38 ,,	305·9°	,, 757·17 ,,
304·5°	,, 735·45 ,,	306·1°	,, 760·32 ,,
304·7°	,, 738·52 ,,	306·3°	,, 763·48 ,,
304·9°	,, 741·60 ,,	306·4°	,, 765·06 ,,
305·1°	,, 744·69 ,,		

(Crafts, Bl. 39, 282). It is insoluble in water, but readily soluble in alcohol and ether, and combines neither with alkaline bisulphites nor with ammonia.

Reactions.—Benzophenone reacts with hydroxylamine forming an oxime which crystallises in slender needles melting at 139·5–140° (Beckmann, B. 19, 989; 20, 1508, 2581), and with phenylhydrazine forming a hydrazone which crystallises in colourless slender needles melting at 137° (E. Fischer, B. 17, 576; Pickel, A. 232, 228). Phosphorus pentachloride converts it into the extremely reactive chloride $(C_6H_5)_2CCl_2$ (Behr, B. 3, 752; Kekulé and Franchimont, B. 5, 909). On reduction with sodium amalgam (Linnemann, A. 133, 6), or preferably by warming in alcoholic solution with 5–10 times its weight of zinc-dust, and a few c.c. of concentrated aqueous potash (Elbs, J. pr. [2] 33, 184), it is converted into benzhydrol (diphenylcarbinol) $(C_6H_5)_2CH.OH$, whilst when reduced in alcoholic solution with zinc and sulphuric acid it yields benzpinacone, α-benzpinacoline and finally β-benzpinacoline (Thörner and Zincke, B. 11, 65, 1396). When heated with hydriodic acid it forms diphenylmethane (Graebe, B. 7, 1624), and diphenylmethane together with tetraphenylethane and tetraphenylethylene are produced when it is heated with zinc-dust (Städel, B. 6, 1401; 9, 562). When its vapour is led through a tube heated to bright redness, it yields benzene, diphenyl, paradiphenylbenzene, carbon monoxide and hydrogen (Barbier and Roux, Bl. 46, 270), and when heated with potash- or soda-lime at 260° it decomposes into benzene and a benzoate (Chancel). Concentrated nitric acid converts it into two isomeric dinitrobenzophenones (Städel, A. 194, 349), and when heated with fuming sulphuric acid it forms a disulphonic acid together with a sulphone (Städel, A. 194, 314; Beckmann, B. 6, 1112; 8, 992).

NITRO- DERIVATIVES.

Nitrobenzophenones $C_6H_5.CO.C_6H_4.NO_2$.

The three isomeric nitrobenzophenones are obtained by oxidising the corresponding nitrodiphenylmethanes (Becker, B. 15, 2090; Basler, B. 16, 2717; Geigy and Königs, B. 18, 2401). The *ortho-* derivative melts at 105°, the *meta-* at 94–95° and the *para-* at 138°.

Dinitrobenzophenones.

Four isomerides have been described; two —viz. *α-dinitro-* (m.p. = 189–190°) and *β-dinitro-* (m.p. = 148–149°)—are obtained when benzophenone is added to concentrated nitric acid (sp. gr. = 1·53), and heated at 60°, the β-modification being the chief product (Städel, A. 194, 349), and two—viz. the *paradinitro-*, melting also at 189°, and the *γ-dinitro-*, melting at 196°—are formed by oxidising the dinitro- derivatives of diphenylmethane melting at 183° and 118° respectively (Doer, B. 5, 797; Städel and Sauer, B. 11, 1747; Städel, A. 218, 344).

AMIDO- DERIVATIVES.

Amidobenzophenones $C_6H_5.CO.C_6H_4.NH_2$.

The *ortho-* and *meta-* derivatives, obtained by reduction of the corresponding nitro- derivatives, have been described by Geigy and Königs (B. 18, 2401).

Paramidobenzophenone (*benzoaniline*) is obtained by heating phthalanil, benzoic chloride, and zinc chloride at 180°, and boiling the resulting condensation compound with alcoholic potash. It crystallises in colourless, lustrous scales, melts at 124°, is sparingly soluble in cold water, readily soluble in alcohol and acetic acid, and yields parahydroxybenzophenone by the diazo- reaction (Döbner, A. 210, 266). Its *methyl-* (Hess, B. 18, 685), and *dimethyl-* derivatives have been prepared.

Dimethylparamidobenzophenone
$C_6H_5.CO.C_6H_4.N(CH_3)_2$.

Preparation.—(1) By heating malachite-green with concentrated hydrochloric acid at 250° (Döbner, B. 13, 2225).

(2) By direct methylation of paramidobenzophenone, and decomposition of the resulting methiodide by heating at 180° (Döbner, A. 210, 270).

(3) 20 kilos. benzanilide $C_6H_5.CO.NHC_6H_5$, 40 kilos. dimethylaniline and 20 kilos. phosphorus oxychloride are mixed together and warmed with continual stirring until a rapid rise of the thermometer indicates spontaneous heating; cooling is then resorted to to keep the temperature below 120°, and the reaction finally completed by heating on a water-bath for one to two hours. The melt may be worked up by two methods. (*a*) It is poured slowly into 100 litres of water and 5 kilos. of hydrochloric acid at 50°, and the resulting orange-coloured liquid allowed to stand; a portion of the ketone separates slowly in a granular crystalline form, and the remainder is precipitated by adding 500 litres of water, and cautiously neutralising with aqueous caustic soda until the odour of dimethylaniline becomes apparent. The precipitated ketone is filtered off, extracted with hydrochloric acid, washed and dried. The mother-liquors contain the excess of dimethylaniline and the aniline formed during the reaction. (*b*) The melt is rendered alkaline, the excess of dimethylaniline separated by steam-distillation, and the solid granular residue, consisting of the condensation product, decomposed by treatment with 100 litres of water and 10 kilos. of hydrochloric acid at 50–70°. The solution, which at first is yellow, rapidly becomes colourless, turbid, and finally deposits a portion of the ketone as a crystalline precipitate, the remainder being obtained by diluting with water and carefully neutralising with aqueous caustic soda, so as to keep all aniline in solution. The ketone is then filtered off, washed and dried. The filtrate contains the aniline formed in the reaction (Farbw. vorm. Meister, Lucius, and Brüning, Germ. Pat. 41,751 of April 10, 1887). Benzomethylanilide may be employed instead of benzanilide (M. L. B., Germ. Pat. 42,853 of Aug. 2, 1887).

Properties.—Dimethylparamidobenzophenone crystallises from alcohol in colourless scales, melts at 90–91°, and is insoluble in water and sparingly soluble in cold alcohol. It is a weak base. When dissolved in chloroform, carbon bisulphide, or hydrocarbons, and warmed with half its weight of phosphorus trichloride, it is converted into a yellow product, probably the chloride $C_6H_5.CCl_2.C_6H_4.N(CH_3)_2$, which is readily reconverted into dimethylparamidobenzophenone by heating with water, and, after purification by precipitation from its solution in chloroform by means of petroleum spirit, readily undergoes condensation with dimethylaniline, forming malachite-green without the presence of phosphorus trichloride or other condensing agent being necessary (Badische Anilin- und Soda-fabrik, Germ. Pat. 27,789 of Dec. 18, 1883). On reduction, it yields a compound, probably the corresponding hydrol

$$C_6H_5.CH(OH).C_6H_4.N(CH_3)_2,$$

which crystallises from alcohol in white needles, melts at 69–70° and forms leuco-malachite-green by condensation with dimethylaniline. Fuming sulphuric acid converts it into a sulphonic acid, melting at 275–276°, and nitrosulphuric acid reacts with it, forming two nitro- derivatives, melting at 133–134° and 173° respectively (M. L. B., *l.c.*).

Diethyl-, methylbenzyl-, and methylphenylamidobenzophenone are described in the patents quoted (M. L. B., *l.c.*).

A second *dimethylamidobenzophenone* has been prepared by heating equimolecular proportions of benzoic acid and dimethylaniline with phosphoric anhydride at 180–200°. It crystallises in concentrically grouped needles, and melts at 38–39° (O. Fischer, B. 10, 958).

Diamidobenzophenones.

Three diamidobenzophenones, viz., the *para*-, α-, and β- derivatives, have been prepared by reducing the dinitrobenzophenones of like name with tin and hydrochloric acid (Städel and Prätorius, B. 11, 744; Städel and Sauer, B. 11, 1747; Städel, A. 218, 349), and a fourth has been obtained by the prolonged heating of pararosaniline or rosaniline with hydrochloric acid (Wichelhaus, B. 19, 110).

Diparamidobenzophenone $CO(C_6H_4.NH_2)_2$, crystallises in needles, melts at 172°, is sparingly soluble in water, and yields dihydroxybenzophenone (m.p. = 210°) by the diazo- reaction.

Trimethyldiparamidobenzophenone

$$N(CH_3)_2.C_6H_4.CO.C_6H_4.NHCH_3$$

is obtained by prolonged heating of pentamethyl violet with hydrochloric acid, and crystallises in aggregates of needles melting at 156° (Wichelhaus, B. 19, 109).

Tetramethyldiparamidobenzophenone

$$N(CH_3)_2.C_6H_4.CO.C_6H_4.N(CH_3)_2.$$

Preparation.—(1) Phosgene is led into dimethylaniline at the ordinary temperature until the increase in weight corresponds with the proportion 1 mol. $COCl_2$ to 2 mols. $C_6H_5.N(CH_3)_2$. The crystalline magma so obtained consists for the most part of dimethylamidobenzoic chloride and dimethylaniline, and in order to complete the reaction the whole is heated at 100° in a closed vessel (Schultz, Chemie des Steinkohlentheers, 2nd ed., i. 685). The product is then treated with water, the excess of dimethylaniline removed by steam-distillation, and the residue purified from the blue dye[1] which persistently adheres to it by repeated solution in hydrochloric acid and precipitation of the filtrate by aqueous soda (Michler, B. 9, 715; Michler and Dupertuis, B. 9, 1900). In this reaction hexamethyltriamidodibenzoylbenzene

$$N(CH_3)_2.C_6H_3(CO.C_6H_4.N(CH_3)_2)_2$$

is formed by further condensation and is separated during the purification of tetramethyldiamidobenzophenone owing to its insolubility in hydrochloric acid; this compound has at present no technical value.

(2) A mixture of 10 kilos. of dimethylamidobenzanilide $N(CH_3)_2.C_6H_4.CONHC_6H_5$, 18 kilos. of dimethylaniline and 8·5 kilos. of phosphorus oxychloride is carefully heated on a water-bath

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[1] This dye has the character of methyl-violet and is always produced in small quantities under these conditions. In the presence of a condensing agent such as aluminium chloride or zinc chloride, the yield is so greatly increased as to afford a means of preparing hexamethylrosaniline on the large scale (compare B. A. S. F., Germ. Pat. 26,016 of Aug. 21, 1883; Eng. Pat. 4,428, 1883; Germ. Pat. 29,943 of July 10, 1884; Eng. Pat. 11,030, 1884).

for two hours, care being taken that the temperature does not rise too rapidly when the reaction sets in, otherwise by-products are formed in considerable quantity. At the end of the reaction, the melt should be a viscid yellowish-brown mass having a slight metallic lustre. The product is worked up by one of two methods: (*a*) It is digested with five times its volume of water containing 1 kilo. of hydrochloric acid at 50–70°, until the condensation product is completely decomposed, then diluted with twenty times the volume of water and the ketone precipitated by carefully adding caustic soda until the odour of dimethylaniline can just be detected; the ketone is filtered off and dried. (*b*) It is rendered alkaline, all dimethylaniline removed by steam-distillation, and the insoluble condensation product separated from the alkaline liquor and decomposed by digestion with a solution of 5 kilos. of hydrochloric acid in 50 kilos. of water at 50–70°. An intense yellow solution is at first obtained, but this rapidly becomes colourless, and after dilution with water and cautious neutralisation with aqueous caustic soda yields the ketone in the form of a crystalline precipitate.

Instead of a dialkylamidobenzamide a disubstituted dialkylamidobenzamide may be employed. Thus tetramethyldiamidobenzophenone can be prepared by heating a mixture of 10 kilos. of dimethylamidobenzodiphenylamine $N(CH_3)_2.C_6H_4.CO.N(C_6H_5)_2$, 12 kilos. of dimethylaniline and 5 kilos. of phosphorus oxychloride on a water-bath for two hours, digesting the product at 50–70° with five times its volume of water containing 1 kilo. of hydrochloric acid until the decomposition of the condensation compound is complete, diluting with 20 volumes of water, neutralising carefully any excess of dimethylaniline by a further addition of acid, and filtering; the residue consists of the ketone mixed with diphenylamine, and the latter can be separated by washing with alcohol or extraction with hydrochloric acid (M. L. B., Germ. Pat. 44,077 of Oct. 27, 1887). These methods can be employed for the preparation of other tetralkyldiamidobenzophenones.[1]

Properties.—Tetramethyldiamidobenzophenone crystallises in silvery scales, melts at 172–172·5° (Fehrmann, B. 20, 2845), at 174° (Graebe, B. 20, 3262), and boils above 360° with decomposition. It is readily soluble in hot alcohol and ether.

Reactions.—On reduction in alcoholic solution with sodium amalgam (Michler and Dupertuis; Nathansohn and Müller, B. 22, 1879) or in amyl alcohol solution with zinc-dust and caustic soda (B. A. S. F., Germ. Pat. 27,032 of Oct. 23, 1883), it is converted into *tetramethyldiamidobenzhydrol*, which dissolves in acetic acid with an intense blue colour (discharged by alkalis), and by condensation with dimethylaniline and subsequent oxidation of the leuco-base yields crystal-violet (ibid.).

Tetramethyldiamidobenzophenone like ketones generally is unable to act directly on the hydrocarbon radicles of aromatic amines, but when converted into its chloride by means of phosphorus trichloride it readily undergoes condensation with secondary and tertiary aromatic amines yielding crystal-violet and similarly constituted blue and green triphenylmethane dyes (Hofmann, B. 18, 767). To prepare the chloride, tetramethyldiamidobenzophenone is mixed with half its weight of phosphorus trichloride (phosphorus oxychloride, pentachloride, tribromide or triiodide, phosgene, or perchloromethyl formate may also be employed), and either cooled or mixed with solvents such as hydrocarbons, chloroform, or carbon bisulphide to prevent resinification. The mixture rapidly acquires an intense blue colour, and the reaction is completed by heating in a water-bath for a few minutes. The chloride can be purified to some extent by precipitating it from its solution in chloroform by means of petroleum spirit, but in the manufacture of triphenylmethane dyes by this method it is never isolated, the secondary or tertiary amine being mixed with the crude product since the purified compound does not undergo condensation even when heated with aromatic amines, unless halogen compounds of phosphorus are present (B. A. S. F., Germ. Pat. 27,789 of Dec. 18, 1883; 29,962 of June 1, 1884; 29,960 of March 21, 1884, expired June 1887; Eng. Pat. 4,850, 1884; 5,038, 1884; 11,159, 1884; M. L. B., Germ. Pat. 34,607, of April 9, 1884; Eng. Pat. 6,311, 1884; Nathansohn and Müller, B. 22, 1888).

When tetramethyldiamidobenzophenone is heated with ammonium chloride or acetate and zinc chloride at 150–160°, or when its chloride is treated in the cold with concentrated aqueous ammonia, it is converted into the yellow dye auramine (B. A. S. F., Germ. Pat. 29,060, of March 11, 1884; 38,433, of June 3, 1886; Ewer and Pick, Germ. Pat. 31,936, of May 9, 1884; Fehrmann, B. 20, 2847; Graebe, B. 20, 3264; *v.* AURAMINE).

When heated for 9 hours at 100° with four times its weight of fuming sulphuric acid containing 20 p.c. of dissolved SO_3, tetramethyldiamidobenzophenone is converted into a monosulphonic acid which crystallises in slender needles from water and alcohol, and when heated at 140–150° with a like proportion of acid containing 40 p.c. of SO_3 until sulphonation is complete yields a disulphonic acid crystallising in long yellow prisms, insoluble in alcohol (M. L. B., Germ. Pat. 38,789 of May 16, 1886).

Tetrethyldiamidobenzophenone

$N(C_2H_5)_2.C_6H_4.CO.C_6H_4.N(C_2H_5)_2$

can be obtained by the action of phosgene on diethylaniline under conditions similar to those adopted in the preparation of the tetramethyl-derivative (Michler and Gradman, B. 9, 1914). It can also be prepared by the methods given in

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[1] Mono- and di- substituted dialkylamidobenzamides are obtained by the action of primary and secondary amines on the chlorides of the dialkylamidobenzoic acids. These chlorides can be prepared either by treating the dialkylamidobenzoic acids with phosphorus trichloride or oxychloride, or more readily by the action of phosgene on dialkylanilines. Dimethylamidobenzanilide, for example, is formed by saturating dimethylaniline with ½ its weight of phosgene in the cold, digesting at 20° until all odour of the gas has disappeared, and then adding the calculated quantity of aniline to the dimethylamidobenzoic chloride so formed, and digesting at 60–80° for five to ten minutes. The product is rendered alkaline by caustic soda and freed from any excess of dimethylaniline by steam distillation, then dissolved in hot dilute hydrochloric acid, filtered, and finally precipitated with caustic soda. Methylaniline, diphenylamine, &c., may be substituted for aniline (M. L. B., Germ. Pat. 44,238 of Aug. 4, 1887).

the Farbw. vorm. Meister, Lucius, and Brüning's patent, No. 44,077. It crystallises from alcohol in scales and melts at 95-96°.

THIO-DERIVATIVES.

Thiobenzophenone $C_6H_5.CS.C_6H_5$.

Preparation.—Thiobenzophenone is obtained by gradually adding 2 parts of aluminium chloride to one part of thiocarbonyl chloride, $CSCl_2$,[1] dissolved in 5 parts of benzene and completing the reaction on the water-bath. The product is carefully treated with ice and extracted with ether; the ethereal solution is washed with soda, then with water, and the ether finally removed by distillation (Bergreen, B. 21, 341).

Properties.—It is an oil which decomposes on distillation, is readily soluble in ether, benzene, and hot alcohol, and reacts with phenylhydrazine and hydroxylamine, yielding respectively the hydrazone and oxime of benzophenone. Other compounds have been described as thiobenzophenones (*cf.* Behr, B. 5, 970; Engler, B. 11, 923), but differ from it in constitution and properties (Bergreen, B. 21, 343).

Tetramethyldiparamidothiobenzophenone

$(CH_3)_2N.C_6H_4.CS.C_6H_4.N(CH_3)_2$.

Preparation.—(1) A solution of 1 part of thiocarbonyl chloride[1] in 3 parts of carbon bisulphide is slowly mixed with 5 parts of dimethylaniline cooled at 0-10° and kept continually stirred. This requires about 3 to 4 hours, and when completed the cooling is discontinued but the stirring kept up for a further 10 to 12 hours, at the end of which time the melt is treated with alkali, the carbon bisulphide and excess of dimethylaniline separated by steam-distillation and the residual thioketone purified by crystallisation (Kern, Germ. Pat. 37,730 of March 18, 1886; Eng. Pat. 12,022, 1886).

(2) Tetramethyldiamidobenzophenone is intimately mixed with one-fifth its weight of phosphoric sulphide and the mixture introduced in small portions at a time into an enamelled vessel heated at a temperature not exceeding 160°. The melt is extracted with water, then with very dilute aqueous sodium carbonate, and finally with water, and the thioketone crystallised from amyl alcohol (B. A. S. F., Germ. Pat. 39,074 of July 2, 1886).

(3) A mixture of 100 parts of tetramethyldiamidobenzophenone, 38 parts of phosphorus oxychloride, and 400 parts of toluene is heated on a water-bath and treated with dry sulphuretted hydrogen until a test specimen no longer dissolves in water with a blue colour; or

A current of phosgene (37 parts) is passed into a solution of 100 parts of tetramethyldiamidobenzophenone in four times its weight of chloroform cooled at 15-20°, and, after the evolution of carbon dioxide has ceased, a solution of 90 parts of sodium sulphide in 800 parts of water is added. In either case the solvent is removed by steam-distillation, and the thioketone purified by crystallisation from alcohol (B. A. S. F., Germ. Pat. 40,374 of October 22, 1886).

(4) Auramine base (*v.* AURAMINE) gives a good yield of the thioketone when its alcoholic solution is saturated with sulphuretted hydrogen at first in the cold and afterwards on a water-bath in a reflux apparatus (Fehrmann, B. 20, 2857; Graebe, B. 20, 3267). Carbon bisulphide brings about a similar change (Fehrmann).

Properties. — Tetramethyldiamidothiobenzophenone crystallises in ruby-red scales showing a bluish lustre, or in a glistening, cantharides-green, crystalline powder, and melts at 194° (Baither, B. 20, 3290), at 202° (Baither, B. 20, 1732; Graebe, *l.c.*). 100 parts of its solution in chloroform at 18° contain 4·58 parts; in ether at 18° 0·27 part, in alcohol at 18° 0·072 part, and in carbon bisulphide at 17°, 1·15 parts; the solution in carbon bisulphide is grass-green by reflected, and dark red by transmitted light.

Reactions.—When warmed with hydrochloric acid it is converted into tetramethyldiamidobenzophenone. When its solution in carbon bisulphide is treated with thiocarbonyl chloride a very unstable colouring matter is obtained, which separates in golden-yellow crusts and dissolves in water forming a deep-blue solution which very rapidly loses its colour; when prepared in chloroform solution and the deep-blue liquid allowed to stand for several days, white crystalline crusts of a compound

$$CCl_2[C_6H_4.N(CH_3)_2]_2 + CHCl_3$$

slowly separate, which on distillation with water decompose into chloroform, hydrochloric acid, and tetramethyldiamidobenzophenone (Baither, B. 20, 1739).

HYDROXY-DERIVATIVES.

Hydroxybenzophenone.

Parahydroxybenzophenone $C_6H_5.CO.C_6H_4.OH$ [CO:OH = 1:4] is obtained by heating benzoic chloride with phenol in the presence of zinc (Grucarevic and Merz, B. 6, 1245), by the action of benzotrichloride on phenol mixed with zinc oxide (Döbner and Stackmann, B. 9, 1919; 10, 1969) and by the diazo- reaction from paramidobenzophenone (benzoaniline) (Döbner and Weiss, B. 14, 1840; Döbner, A. 210, 249). It crystallises in scales, melts at 134°, and when heated with phenol and zinc-dust gives a colouring matter of the corallin type (Graebe and Caro, B. 11, 1350).

Dihydroxybenzophenones.

Diorthohydroxybenzophenone [OH:CO:OH = 2′:1:2] (Richter, J. pr. [2] 28, 285; Graebe and Feer, B. 19, 2609) melts at 59-60° and gives phenol and salicylic acid when heated with hydrochloric acid at 200°.

Orthoparahydroxybenzophenone (*Salicylphenol*) [OH:CO:OH = 2′:1:4], obtained by heating equal weights of salicylic acid, phenol, and zinc chloride at 115-120°, crystallises in pale-yellow scales and melts at 143-144° (Michael, B. 14, 656).

Diparahydroxybenzophenone [OH:CO:OH = 4′:1:4] (Städel and Gail, B. 11, 746), is prepared by the diazo- reaction from diparamidobenzophenone (Städel and Sauer, B. 11, 1747), by heating aurine with water at 220-250° (Graebe and Caro, B. 11, 1348), by heating rosaniline with water at 270° (Liebermann, B. 6, 951; 11, 1435), by fusing phenolphthaleïn with caustic potash (Baeyer and Burkhardt, B. 11, 1299) and by heating parahydroxybenzoic acid and phenol with stannic chloride at 120° (Michael, Am. 5, 86). It crystallises in scales and melts at about 210°. When heated with phosphorus trichloride

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[1] Thiocarbonyl chloride (thiophosgene) is prepared by the reduction of perchloromethylmercaptan $CCl_3.SCl$ by means of stannous chloride (Klason, B. 20, 2380; Kern and Sandoz, Germ. Pat. Anm. K. 5430 of March 19, 1887.

and afterwards with phenol and concentrated sulphuric acid it is converted into aurine (Graebe and Caro, *l.c.*).

Dihydroxybenzophenone [OH:CO:OH = 4′:1:?], obtained by the diazo- reaction from β-diamidobenzophenone (Städel, A. 218, 356), crystallises in small needles and melts at 161–162°.

Dihydroxybenzophenone (*benzopyrocatechol*) [CO:OH:OH = 1:2:3] is obtained by heating pyrocatechol dibenzoate with benzoic chloride and zinc chloride and decomposing the resulting dibenzoyl derivative with alcoholic potash. It crystallises in needles, melts at 145°, and in alcoholic solution gives with ferric chloride a green colour, which becomes blood-red on addition of ammonium carbonate (Döbner, A. 210, 261).

Dihydroxybenzophenone (*benzoresorcinol*) [CO:OH:OH = 1:2:4], prepared under similar conditions from resorcinol dibenzoate, crystallises in needles, melts at 144°, and in alcoholic solution gives a brownish-red colour with ferric chloride (Döbner, A. 210, 256).

Trihydroxybenzophenones.

Salicylresorcinol $(OH)_2.C_6H_3.CO.C_6H_4.OH$, formed by heating salicylic acid, resorcinol, and zinc chloride at 195–200°, crystallises in scales and melts at 133–134° (Michael, B. 14, 656).

Hydroxybenzophenone colouring matters. The foregoing hydroxybenzophenones are, with perhaps the one exception of benzopyrocatechol, destitute of tinctorial power. For the occurrence of tinctorial properties in these compounds it seems to be an essential condition that at least two hydroxyl radicles must be present in contiguous positions in one of the benzene nuclei. Hydroxybenzophenones fulfilling this condition can be prepared by the following methods:—

(*a*) Condensation of fatty or aromatic carboxylic acids or their substitution derivatives with pyrogallic acid (pyrogallol).

(*b*) Condensation of gallic or pyrogallolcarboxylic acids with other phenols, condensation being effected in either case by sulphuric acid, zinc chloride, or stannic chloride (B. A. S. F., Germ. Pat. 49,149 of April 24, 1889; 50,450 and 50,451 of May 28, 1889). The *tri-*, *tetra-*, *penta-*, and *hexa-* hydroxy- derivatives so prepared crystallise without exception in yellow needles; one only of these compounds can find mention here as typical of the series—

Trihydroxybenzophenone

[CO:OH:OH:OH = 1:2:3:4].

Preparation.—Equal weights (50 kilos.) of pyrogallic acid (pyrogallol) and benzoic acid are heated at 145°, and to the fused mass three times the weight (150 kilos.) of zinc chloride is added gradually and with continual stirring. The process is complete at the end of about three hours, and the end of the reaction is recognised when the solution of the melt in hot water gives slender, bright-yellow needles and not scales of benzoic acid on cooling. The melt is then dissolved in 3,000 litres of boiling water, boiled for about two hours with animal charcoal, filtered, and the filtrate set aside to crystallise.

Properties. — It crystallises with 1 mol. prop. H_2O in bright-yellow needles, melts at 137–138°, and yields an *acetyl*- derivative crystallising in white tables, which melt at 119°. The dye gives golden-yellow shades on cotton mordanted with alumina, the shade being more orange in the presence of calcium salts. The chromium lake is brownish-yellow, the iron lake dark olive, and a very beautiful yellow lake can be obtained by printing with a mixture of aluminium acetate and tin salt (stannous chloride) or tin citrate. These colours are in no degree inferior to alizarin, so far as fastness to light, air, acid, alkali, and soap is concerned.

Similar shades are obtained with the hydroxybenzophenones prepared—(1) from pyrogallol and metahydroxybenzoic acid, (2) pyrogallol and parahydroxybenzoic acid, and (3) from pyrogallol and β-resorcylic acid; those from (4) pyrogallol and salicylic acid, and (5) pyrogallol and pyrogallolcarboxylic acid give redder lakes, and those from (6) gallic acid and resorcinol and (7) pyrogallol and gallic acid give lakes of a greenish-yellow shade.

BENZIL $C_6H_5.CO.CO.C_6H_5$.

Preparation.—Benzil is prepared on the large scale by the oxidation of benzoïn

$C_6H_5.CH(OH).CO.C_6H_5$,

a condensation product of benzaldehyde. 200 grams of pure benzaldehyde are heated for a short time with a solution of 20 grams of potassium cyanide in 800 grams of 50 p.c. alcohol, and the liquid allowed to cool. Benzoïn crystallises out in colourless prisms, and is removed by filtration. A further yield of benzoïn can be obtained by heating the filtrate with more potassium cyanide (Zincke, A. 198, 151). The resulting benzoïn is heated with twice its weight of nitric acid (sp.gr. = 1·4) until red fumes are no longer evolved, and a clear, oily, yellow liquid is obtained; the product is then poured into water, and the benzil, which at once solidifies, is purified by crystallisation from alcohol (Zinin, A. 34, 188).

Properties.—Benzil crystallises from alcohol in pale-yellow needles, and from ether, by spontaneous evaporation, in 6-sided prisms, melts at 95°, boils at 346–348° with slight decomposition (Wittenberg and V. Meyer, B. 16, 501), and is insoluble in water, but readily soluble in alcohol and ether.

Reactions.—When distilled over heated soda-lime benzil is converted into benzene and benzophenone (Jena, A. 155, 87), and benzophenone is also formed when it is distilled over heated litharge (Wittenberg and V. Meyer, *l.c.*). On reduction with iron filings and acetic acid or with zinc and hydrochloric acid it yields benzoïn $C_6H_5.CH(OH).CO.C_6H_5$ (Zinin, A. 119, 177), and with sodium amalgam and water yields hydrobenzoïn $C_6H_5.CH(OH).CH(OH).C_6H_5$ (Zincke and Forst, B. 8, 797). It combines with ammonia, yielding imabenzil, benzilimide, benzilam, and lophine (Laurent; Zinin, A. 34, 190; Zincke, B. 16, 890; Japp, B. 16, 2636; Henius, A. 228, 339; Japp and Wynne, C. J. 49, 473), and with aldehydes and ammonia forming glyoxalines and other condensation compounds (Japp and Streatfeild, C. J. 49, 155; Japp and Hooker, C. J. 45, 673; Japp and Wynne, C. J. 49, 464). Alcoholic potash dissolves benzil in the cold with a characteristic violet colour; on heating, the colour is discharged, and the benzil converted into potassium benzilate. When heated with aqueous potash (or soda) no colour reaction is observed, but the benzil slowly dissolves, forming potassium benzilate (diphenylglycollate), $C_6H_5.CO.CO.C_6H_5 + KHO = (C_6H_5)_2C(OH).COOK$, together with a small quantity of diphenylcarbinol $(C_6H_5)_2CH(OH)$ arising from the decomposition of the benzilate (Liebig, A. 25, 25; Zinin, A. 31, 329; Fischer, B. 14, 326 (footnote); Klinger, B. 19, 1868).

Benzil is not attacked by ordinary nitric acid or sulphuric acid. When heated with fuming nitric acid at the boiling-point, however, it yields two isomeric *dinitrobenzils*, which cannot be separated by fractional crystallisation. The nitration product is poured into water, the precipitated mixture of dinitrobenzils dissolved in hot alcohol, and the moss-like crystalline separation [m.p. = 107° or 127°], which forms on cooling, allowed to remain in contact with the mother-liquor for many weeks. Under these conditions a mixture of compact, yellow, octahedral crystals (m.p. = 131°), and thin and almost colourless laminæ (m.p. = 147°) is obtained, which must be separated mechanically. On solution in alcohol the octahedral crystals yield a moss-like separation, which slowly resolves itself into a mixture of octahedra and laminæ; the laminæ, however, appear to be uniform, and crystallise from alcohol in the same form. The octahedral crystals dissolve in 41 parts of boiling and 137 parts of alcohol at the ordinary temperature; the laminæ in 52·5 parts and 290 parts respectively (Sagumenny, B. 5, 1100). The subject requires further investigation.

Dinitrobenzil (the mixed product obtained in this way) yields on reduction an *amido-* derivative, which can be employed for the production of azo- dyes, but has not been isolated from solution. According to Poirrier and Rosenstiehl (Germ. Pat. 44,269 of Aug. 28, 1887; 45,789 of Dec. 9, 1887), the dinitrobenzil, obtained either from benzil according to Sagumenny's directions, or from benzoïn by effecting both oxidation and nitration in one operation, is reduced by heating 5 kilos. with 50 litres of water and 23 kilos. of aqueous soda of 36°B., and gradually adding 10 kilos. of zinc-dust until the solution is completely deprived of its colour. The product is neutralised with 22·6 kilos. of sodium carbonate, filtered, and the precipitated zinc carbonate repeatedly extracted with boiling water. The filtrates on concentration serve for the preparation of azo- dyes, the amount of the amidobenzil in solution being calculated from the 'nitrite-equivalent.' The dyes obtained by combining diazotised amidobenzil with amines, phenols, and their sulphonic acids vary in shade from orange-yellow and red to violet.

A series of yellow and yellow-red dyes have been obtained by the action of benzil on various hydrazinesulphonic acids (R. Meyer, Germ. Pat. 45,272 of March 6, 1888), but do not appear to have found their way into the market.

For further information about benzil and its derivatives, reference should be made to the articles in Watts' Dictionary of Chemistry.

W. P. W.

KHAYA or **KAYA**. The bark of the *caïl-cedra* (*Swietenia senegalensis*) used in Senegal as a febrifuge (*v.* Caïl-cedra).

KIDNEY IRON ORE *v.* Iron.

KIESELGUHR. An infusorial earth, of a white, grey, or greenish powder of low specific gravity, consisting chiefly of the minute silicious shields of diatomaceæ. Large deposits of fossil diatoms have been traced in many parts of the world, but the chief amount of kieselguhr is obtained from Naterleuss, between Hamburg and Hanover. It is found there from the surface down to a depth of about 150 feet. The upper stratum supplies the white kieselguhr. It contains very little organic matter, but some sand; on washing, it gives a very pure and porous product. The second stratum produces grey kieselguhr, containing very little sand, but sufficient organic matter for calcining it. After calcination it forms kieselguhr of the highest quality. The lowest and by far the largest stratum, varying from 50 to 100 feet in thickness, supplies the green kieselguhr, which contains up to 30 p.c. of organic matter. When dry this material glows when heated like peat. It is calcined in small furnaces about 15 feet high and 6 feet wide; these are filled and lighted at the bottom, and no additional fuel is needed. The furnaces are continually replenished at the top, and the calcined product, which has a reddish colour due to ferric oxide, is taken out from the grates underneath. Kieselguhr consists almost exclusively of silica; it resists the action of the strongest acids, but it can be easily made to melt after being mixed with an alkali. Its great porosity makes it very valuable for the manufacture of dynamite. Its high non-conducting power makes it useful for the coating of steam boilers and pipes. It is used by safe-makers, cooking stove and kitchener manufacturers, for making fireproof rooms, and for filling up bulkheads in steamers &c. It has been made into fireproof bricks of low sp.gr. for the setting of steam-boilers, the lining of blast furnaces and the hot-air pipes connected with them, for the backs of fire-places. It has also been suggested as an absorbent for bromine, to be used for disinfecting purposes, and for sulphuric acid. What is termed 'dry sulphuric acid' is prepared by saturating calcined kieselguhr with three or four times its weight of sulphuric acid. The product, containing 75 p.c. of its weight of sulphuric acid, is said to retain the pulverulent form, and can be transported by land or sea in iron vessels without damage or breakage. Kieselguhr is used by manufacturers of ultramarine and by soap makers. A composition for preventing rot and fungus in buildings is made of it; it is also used for polishing metals and for the manufacture of artificial meerschaum (Haacke, S. C. I. 3, 132).

KIESERITE *v.* Magnesium.

KILLAS. A local name used by Cornish miners for the clay-slates of their country (*v.* Slate).

KINETITE *v.* Explosives.

KING'S BLUE *v.* Pigments.

KING'S YELLOW *v.* Pigments.

KINO. Kino is the red, astringent, jelly-like juice obtained by incisions made in the trunks of several trees, and dried without the application of artificial heat. The variety originally introduced by Fothergill in 1757 (Med. Observ. a. Inq. 1, 358) came from the river Gambia in tropical West Africa, where it was derived from the *Pterocarpus erinaceus* (Poiret). This

African or *Gambia kino* was, however, soon replaced by other similar products from Jamaica, the East Indies, and Australia. *Jamaica, West Indian*, or *Caracas kino* is obtained from the *Cocoloba uvifera* (Linn.), a tree inhabiting Florida and the West Indian Islands. The only important kinos at the present day are, however, those which come from India and Australia. The *official, East Indian*, or *Malabar kino* is the product of the *Pterocarpus Marsupium* (Roxb. Corom. Pl., plate 116; Bentl. a. T., plate 81), a tree which attains a height of forty to eighty feet, and occurs throughout Southern India and Ceylon. In the Madras Presidency it is one of the trees the felling of which is restricted by the Government. It affords a valuable timber. The allied *P. indicus* (Willd.) was the source of the kino exported from Moulmein in Lower Burma. Another variety of Indian kino is that furnished by the *Butea frondosa* (Roxb.) and other allied species of *Butea*, and known as *Butea kino, Butea guru, Bengal kino, Palas* or *Pulcs kino*, or *Dhak gum*. It closely resembles official kino, and is largely substituted for it in India. *Australian, Botany Bay*, or *Eucalyptus kino* is the product of numerous species of *Eucalyptus* (Mueller, Ph. [3] 16, 898; Maiden, S. C. I. 1888, 38; Ph. [3] 20, 221 a. 321). Eucalyptus kino is gradually becoming more important, and the better varieties are quite equal in all respects to the kino of Malabar (*cf.* Fl. a. H. 199).

Kino consists of small glistening, angular, brittle, garnet-like fragments, heavier than water, and transparent when in thin layers. When chewed it tastes astringent and colours the saliva blood-red. It is partly soluble in water, entirely soluble in rectified spirit, and almost insoluble in ether. The weak spirituous solution of kino used in medicine sometimes becomes gelatinous. Methods to obviate this have been much discussed (*v.* Indexes Ph.). Fused with potash it yields the trihydroxybenzene *phloroglucinol* $C_6H_3(OH)_3$ 1:3:5 (Hlasiwetz, A. 134, 122), and the dihydroxybenzoic acid, *protocatechuic acid*, $C_6H_3.COOH.OH.OH$ 1:3:4 (Stenhouse, A. 177, 187). When it is distilled alone, orthodihydroxybenzene or *catechol* $C_6H_4(OH)_2$ is formed (Eisfeldt, A. 92, 101).

Treatment of Malabar, Butea, or Eucalyptus kino with ether extracts a small quantity of *catechol*, and perhaps in the case of Eucalyptus kino traces also of *catechin* (Eisfeldt, A. 92, 101; Flückiger, B. 5, 1; Fl. a. H.; Wiesner, Ph. [3] 2, 102). When dilute mineral acids are added to an aqueous solution of kino, a bulky precipitate falls of a substance which has been described as *kinotannic acid*. This compound constitutes the greater part of kino, but it has not hitherto been isolated in a state of purity. It differs from other tannins in its behaviour towards reagents. It is sparingly soluble in water, soluble in alcohol, and insoluble in ether (*v.* Berzelius, Lehrbuch, 3 Aufl. 6, 258; Gerding, Ar. Ph. [2] 65, 283; Hennig, Ar. Ph. (2) 73, 129; 77, 260; 85, 150; Eisfeldt). By boiling kino with dilute hydrochloric acid (1 in 5), a crystalline compound, *kinoïn* $C_{14}H_{12}O_6$, is extracted, which is taken up by ether from the acid solution and may be purified by recrystallisation from water (Etti, B. 11, 1879; 17, 2241; Fl. a. H. 197). It forms colourless prisms which are sparingly soluble in cold, easily soluble in hot water, very soluble in alcohol, and less so in ether. With ferric chloride it gives a red colour. It does not precipitate gelatine solution. Heated with concentrated hydrochloric acid at 120–130° it breaks up into *methyl chloride, gallic acid*, and *catechol*, which indicates that kinoïn is probably *methylcatechol gallic ether*, $C_{14}H_{12}O_6 = C_6H_2(OH)_3CO.OC_6H_4.OMe$. Heated to 120–130° two molecules of kinoïn lose a molecule of water, and are converted into the anhydride *kino red*, $C_{28}H_{22}O_{11}$, identical with that described by Gerding, and which is also obtained from the residue after extraction of the kinoïn from kino by treatment with dilute acid (Etti). Kino red is a resinous compound difficultly soluble in water, easily in alcohol and in alkalis. Ferric chloride colours it dirty green. It gives a precipitate with gelatine solution. It melts at 160–170°, losing a molecule of water, and forming the *anhydride*, $C_{28}H_{20}O_{10}$, a compound resembling kino red. Among the products of the dry distillation of kino red are *catechol* and *phenol* (*cf.* Catechu). A. S.

KINO RED *v.* Kino.

KINOÏN *v.* Kino.

KINOTANNIC ACID *v.* Kino.

KIRSCHWASSER is a spirituous liquor distilled from Morella cherries (Ger. *Kirschen*), and is prepared in Germany and Switzerland. The fruit, having been crushed in vats, is set to ferment and is subsequently distilled.

KISH. An ironworker's name for the masses of impure graphite which are occasionally found in blast furnaces, and which separate out from molten cast iron.

KOLA. Kola nuts are now imported from the West Coast of Africa, and are made into a paste which contains about two per cent. of caffeïne. According to Heckel and Schlagdenhauffen, the fruit of *Heritiera littoralis*, a tree growing in India, in the Philippines, and Molucca, is often found mixed with kola nuts. This fruit belongs to the same family (Sterculiaceæ) as those which give the kola nuts, and is said to possess the same waste-repairing properties as the kola nut, although it contains no caffeïne. It is used as a food-stuff in India.

KOOSS *v.* Resins.

KOSIN or **KOUSSEIN RESIN** *v.* Resins.

KOUMISS *v.* Milk.

KRANTZITE. A variety of retinite, *v.* Resins.

KREMS or **KREMSER WHITE, CREMNITZ WHITE,** *v.* Pigments.

KREOSOL *v. Guaiacum*, art. Resins.

KUNKUR. An argillaceous limestone used in India for the preparation of mortar. It forms an excellent hydraulic mortar (E. Nicholson, C. N. 32, 82).

KUTEERA GUM *v.* Gums.

KYANISING. A process for preserving timber due to Mr. Kyan, of New York, in which a solution of mercuric chloride is forced into the pores of the wood.

KYANITE or **CYANITE.** An aluminium silicate $Al_2O_3.SiO_2$ found in triclinic prisms; generally of a pale-blue colour, sometimes white, or blue with white edges; also grey, green, and black. Occurs usually in gneiss or mica-slate.

KYANOL. Runge's term for aniline.

L

LABDANUM or **LADANUM** *v.* OLEO-RESINS.

LABEL VARNISH *v.* VARNISH.

LABRADORITE *v.* FELSPAR.

LAC-DYE. This dyestuff is obtained from *gum-lac*, a resinous substance incrusting the young branches of a variety of Indian trees, *e.g.*, *Ficus religiosa*, *Butea frondosa*, *Schleichera trijuga*, *Acacia arabica*, &c. These trees are infested with *Coccus lacca*, a scale insect allied to cochineal. The animal punctures the bark of the young branches with its proboscis, draws its nourishment from the sap, which it apparently transforms into the resinous excretion gum-lac.

The twigs, which are frequently covered a quarter of an inch thick with the resinous crust inclosing multitudes of insects, are broken off, exposed to the sun to kill the animals, and then sold under the name of *stick-lac*.

This product is at once used by the Hindoos as a dye-stuff. For this purpose the woody portion is removed, the resinous matter is thrown into tubs, crushed and well washed with water, in order to extract the colouring matter from the inclosed insects. The solution thus obtained is used for dyeing; the washed granular resin is dried and sold as *seed-lac*, or it is further melted, strained through cloth, and finally sold as *button-lac*, *sheet-lac*, and *shell-lac* (*shellac*).

Lac-dye is said to be prepared by precipitating the aqueous solution of the colouring matter with milk of lime, collecting the precipitate on filters, pressing and moulding it into the form of small square cakes, which are then dried.

The dark reddish-brown lake obtained in this manner is insoluble in water, and consists of: moisture 9–11 p.c., ash 15–17 p.c., colouring matter 10–13 p.c., organic impurities 57–65 p.c. The ash consists essentially of silicic acid and silicates of alumina, &c., insoluble in acid (49–50 p.c.), lime (17–26 p.c.), and smaller quantities of ferric oxide, magnesia, alkali, and phosphoric acid. These analyses seem to indicate that during the precipitation with lime a certain amount of clay is probably added, no doubt with a view to facilitate the settling of the flocculent precipitate; also to give the latter more body and plasticity, and thus render it better adapted for moulding into cakes of a non-brittle character.

The pure colouring matter of lac-dye, *laccaïnic acid*, is obtained in the following manner. Finely-powdered lac-dye is boiled with moderately diluted hydrochloric acid, in order to decompose the lake; the decoction is then cooled and filtered. The filtrate contains the bases, phosphoric acid, and some colouring matter. The undissolved residue, which contains the largest proportion of the colouring matter, together with resinous and mineral matters, is well washed and then boiled with a large quantity of water, and the filtered hot solution of colouring matter thus obtained is precipitated by neutral lead acetate. After washing the precipitate several times with hot water, it is suspended in water, decomposed with hydrogen sulphide, and the mixture is boiled and filtered. The filtered solution of colouring matter is evaporated to dryness, and the residue is extracted with boiling alcohol. After mixing the alcoholic solution with a large quantity of ether, and filtering off the impurities and a little colouring matter thus precipitated, the ether is recovered by distillation, and the remaining alcoholic solution is allowed to evaporate spontaneously. The crystals first obtained contain much ash, but this impurity diminishes in each subsequent crop, till at length the pure colouring matter ($C_{16}H_{12}O_8$) is obtained, in the form of a brownish red crystalline powder or crust. Under the microscope the crystals appear as orange-coloured rhombic plates. Laccaïnic acid is readily soluble in methyl and amyl alcohol, acetone, and glacial acetic acid; somewhat slowly, though abundantly, soluble in ethyl alcohol. It is little soluble in water, still less in ether, and quite insoluble in ligroïn and benzene. Its alcoholic solution is not precipitated by ether, and on this fact the above method of obtaining the pure colouring matter is based.

Heated to 180°C., laccaïnic acid decomposes without previous melting. Its aqueous solution has an acid reaction. In caustic alkalis it readily dissolves with a rich crimson colour, which on exposure to air is gradually destroyed through oxidation. With barium, calcium, and magnesium salts it forms insoluble purple lakes, with aluminium salts a crimson lake, and with iron a black lake.

In its general reactions, dyeing properties, &c., laccaïnic acid behaves extremely like carminic acid (cochineal). It differs, however, from the latter by containing less carbon, and by its solution in concentrated sulphuric acid showing in the spectroscope three absorption bands, all more sharply defined and situated decidedly nearer the red end of the spectrum than the corresponding bands of carminic acid. The absorption spectra of the two colouring matters, both in aqueous and in alkaline solution, are identical.

Under the influence of nitric acid laccaïnic acid is changed entirely into picric acid, and not into nitro-coccussic and oxalic acids, as is the case with carminic acid. Heated with concentrated sulphuric acid, laccaïnic acid gives a new colouring matter, which, however, is not identical with the ruficoccin derived from carminic acid. Heated with concentrated hydrochloric acid in a sealed tube to 180°C., it yields a new intermediate substance containing chlorine. By boiling this product with caustic potash in a current of hydrogen to prevent oxidation the chlorine is entirely removed, and on adding acid a new colouring matter is precipitated, which has apparently the formula $C_{28}H_{16}O_{11}$. Its alkaline solution has a violet-blue colour. In ammonia it dissolves with difficulty, giving a brown colour.

Under the influence of melting caustic potash laccaïnic acid yields four crystallisable products which give with ferric chloride a blue, a red, and no colouration, and a black precipitate, respectively. Their constitution has not been determined, but they possess generally the characteristics of oxyacids of the aromatic series.

Before employing lac-dye in dyeing silk and wool it is necessary to grind it, and to decompose the lake by making it into a paste, or even boiling it, with dilute hydrochloric acid, using about equal weights of lac-dye and hydrochloric acid 1·16° sp.gr., and water *ad libitum*. The decoction thus obtained is then employed in the same way as an aqueous decoction of cochineal would be; with tin mordant it gives scarlet, with aluminium crimson, &c., the colours being similar to the corresponding cochineal colours.

In the past, lac-dye has been much used along with cochineal for dyeing scarlets on wool. Practical dyers have always considered that although the colours thus obtained are less brilliant than if cochineal alone had been used, they have more body and are somewhat faster to light and other influences.

Since the introduction of the azo-scarlets derived from naphthalene, which are much cheaper and yield bright colours without the aid of the somewhat expensive tin mordant, the use of lac-dye has diminished more and more, till now (1890) it is of very little importance to the European dyer.

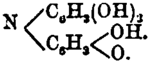
References.—Kerr, 71, 374; Pearson, 1794, 383; Anderson, Monographia Cocci Ceriferi, 1791; Unverdorben, 14, 119; Marquart and Nees v. Esenbeck, A. 13, 286; Buchner, A. 59, 96; John, Chem. Schrift. 5, 1; Funke, J. Ph. Trommsdorff, 18; R. E. Schmidt, B. 20, 1285.

J. J. H.

LAC RESIN *v.* Resins.

LAC VARNISH *v.* Varnish.

LACMOÏD, or **LACKMOÏD**, $C_{12}H_9NO_4$? or



$\mathrm{N}\left\langle\begin{matrix}C_6H_3(OH)_2\\ C_6H_3\left\langle\begin{matrix}OH.\\ O.\end{matrix}\right.\end{matrix}\right.$

A colouring matter obtained by Benedikt and Julius by heating resorcinol with sodium nitrite. Dissolves in water and alcohol, with bluish-violet colour changing to red on the addition of an acid. Used occasionally as an indicator in volumetric analysis (*v.* Acidimetry and Alkalimetry; also Oxazine colouring matters.)

LACTARINE *v.* Albuminoids.

LACTIC ACID or **α-HYDROXYPROPIONIC ACID** $C_3H_6O_3$ was first obtained by Scheele in 1780 from sour milk. Its exact constitution was, however, first ascertained by Liebig and Mitscherlich (A. 7, 47) and by Gay-Lussac and Pelouze (A. 7, 40). It is widely distributed in nature, occurring in the sap of the vine, and in most fermented liquids of vegetable origin, especially in sour milk; it is not, however, present in fresh milk. It has also been found in small quantities in saliva, in the brain and under certain conditions in the gastric juice. The acid obtained by Braconnot, and termed *nanceic acid*, as well as the *thebolactic* acid obtained from opium, have proved to be identical with common lactic acid. On the other hand, the acid obtained by Berzelius from flesh, and further investigated by Liebig, differs from the ordinary lactic acid in certain of its properties, and is therefore distinguished as *paralactic acid*. This will be described later on.

Lactic acid is formed in the fermentation of various sugars, of mannitol, and of dextrin, and also by the action of caustic alkalis on the sugars. It has also been obtained synthetically in a number of ways, the two most important of which are the following:—

(1) Aldehyde unites with HCN forming the nitrile

$$CH_3.CHO + HCN = CH_3.CH(OH)CN,$$

and this on treatment with acids is converted into lactic acid

$$CH_3.CH(OH).CN + HCl + 2H_2O$$
$$= CH_3.CH(OH).COOH + NH_4Cl.$$

(2) By the action of alkalis on α-chloropropionic acid

$$CH_3.CHCl.COOH + 2KOH$$
$$= CH_3.CH(OH).COOH + KCl + H_2O.$$

These two syntheses clearly show that the acid is α-hydroxypropionic acid.

In order to distinguish lactic acid from the allied acids it is frequently called *ethidene-lactic* or *fermentation lactic acid*.

Preparation.—Lactic acid is usually prepared by the fermentation of sugar. According to Bensch's method (A. 61, 177), 6 kilograms cane sugar and 30 grams tartaric acid are dissolved in 26 litres of boiling water, and after standing for six days, a mixture of 250 grams putrid cheese, 8 kilograms sour milk, and 3 kilograms finely powdered chalk added. The temperature is then kept between 30° and 35°, and the whole well stirred daily. After about a week the mass becomes solid with formation of calcium lactate. This is decomposed by H_2SO_4, and the filtrate neutralised with $ZnCO_3$. A simpler plan (Lautemann, A. 113, 142) is to replace the chalk in the original mixture by 2 kilograms zinc white. After about ten days a magma of zinc lactate together with some mannitol is formed, which may be recrystallised from water. The purified salt obtained by either method is dissolved in boiling water, and precipitated with H_2S, the filtrate evaporated to a syrup, cooled, and separated from mannitol and undecomposed zinc salt by extraction with ether. The syrup which remains after evaporation of the ether is then warmed on the water bath.

Harz (Vierteljahr. pr. Chem. 20, 501) gives the following method of preparing the acid. Three parts milk-sugar, 36 parts water, and 0·5–0·75 parts of meal rich in gluten are mixed together, and then one or two teaspoonfuls of yeast and 6 parts soda-crystals added. If the fermentation is started with milk sugar, it may be continued by the addition of cane sugar.

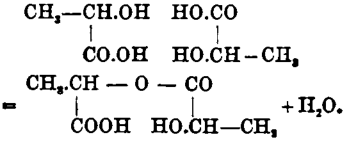
A large number of micro-organisms are capable of causing lactic fermentation of sugar, one of which has, however, a much greater intensity of action than the remainder, and is known therefore as *Bac. acid. lactici*. It consists of short thick cells, generally united in pairs. The solution must be kept neutral, and access of air must be allowed, as well as the necessary nitrogenous food.

For the preparation of the acid from sugar by the action of caustic alkalis, Kiliani (B. 15, 699) recommends the following method. 500 grams cane sugar are mixed with 250 c.c. water, and 10 c.c. of the sulphuric acid employed later on, and warmed in a flask of 2 litres capacity to 50° for 2 hours. To the well-cooled solution 400 c.c. of caustic soda solution (1 part of caustic to 1 part water) are gradually added, the mixture being constantly cooled. The exact quantity of sulphuric acid necessary is then allowed to flow in; the acid is prepared by adding 3 parts H_2SO_4 to 4 parts water, and previously directly compared with the caustic soda solution by titration. A crystal of Glauber's salt is added to facilitate crystallisation, the whole being cooled and well shaken, and allowed to stand 24 hours. The mass is then extracted with 93 p.c. alcohol, filtered on the pump, and half the filtrate neutralised with $ZnCO_3$ on the water bath, then mixed with the other portion, and the whole allowed to stand 36 hours. The separated zinc salt is filtered off, well pressed, recrystallised from water, and converted into the acid as before.

The acid thus obtained forms a syrup of sp.gr. 1·21–1·24, and is soluble in all proportions in water and alcohol, less readily in ether. It is hygroscopic, colourless, and inodorous, but has a very sharp acid taste. The syrup is, however, not the pure acid, but a mixture of the latter with small quantities of water and the anhydride. The pure acid has not yet been obtained, as when the aqueous solution is evaporated the formation of anhydride commences before all the water is driven off, and even takes place in the exsiccator.

For pharmaceutical purposes the acid must be colourless and inodorous, and have a sp.gr. of at least 1·21, and should leave scarcely any residue on ignition. It should not be affected by NH_3 and $(NH_4)_2S$, and should give, at most, only a faint opalescence with $BaCl_2$, $AgNO_3$, $(NH_4)_2C_2O_4$, and should give no precipitate on boiling with Fehling's solution.

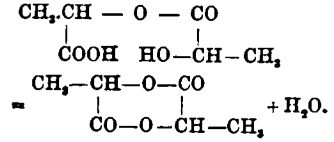
The anhydride above referred to is formed by the elimination of a molecule of water from two molecules of the acid in the following manner, the one molecule acting as an alcohol and the other as an acid:



$$\begin{array}{ll}\mathrm{CH_3{-}CH.OH} & \mathrm{HO.CO}\\ \qquad | & \qquad | \\ \qquad \mathrm{CO.OH} & \mathrm{HO.CH{-}CH_3}\end{array} = \begin{array}{ll}\mathrm{CH_3.CH} \;{-}\; \mathrm{O} \;{-}& \mathrm{CO}\\ \qquad | & \quad | \\ \quad \mathrm{COOH} & \mathrm{HO.CH{-}CH_3}\end{array} + \mathrm{H_2O}.$$

This compound, *lactic anhydride*, or *lactolactic acid*, is at the same time an alcohol, an acid, and an ethereal salt. It is a light-yellow amorphous mass, easily soluble in alcohol and ether, insoluble in water, and is decomposed by alkalis forming salts of lactic acid.

On further heating, another molecule of water is driven off, forming a second anhydride called lactide



$$\begin{array}{ll}\mathrm{CH_3.CH} \;{-}\; \mathrm{O} \;{-}& \mathrm{CO}\\ \qquad | & \quad | \\ \quad \mathrm{COOH} & \mathrm{HO{-}CH{-}CH_3}\end{array} = \begin{array}{ll}\mathrm{CH_3{-}CH{-}O{-}} & \mathrm{CO}\\ \qquad | & \;| \\ \qquad \mathrm{CO{-}O{-}} & \mathrm{CH{-}CH_3}\end{array} + \mathrm{H_2O}.$$

This substance, which is a double ethereal salt, is very slightly soluble in water, and forms white needles melting at 150° and boiling at 255°.

Salts. The salts of lactic acid are all soluble in water, many so readily that they are very difficult to obtain crystalline. They are obtained by direct neutralisation of the free acid, or by double decomposition from the calcium salt.

The K, Na, NH_4 salts are very hygroscopic, and only the last two have been obtained crystalline.

Calcium lactate $(C_3H_5O_3)_2Ca + 5H_2O$ is usually obtained direct from sugar by Bensch's process (*v. supra*). In small quantities it is sometimes prepared by neutralising lactic acid with chalk. It forms cauliflower-like aggregates of microscopic rhombic needles, which are soluble in 9·5 parts of cold, much more readily in hot water, and also soluble in alcohol. It loses its water of crystallisation at 100°, and at 250–275° loses another molecule of water, forming *calcium dilactate* $(CH_3.CH)_2.O.(CO_2)_2Ca$. The product is a vesicular mass, from which alcohol extracts some unaltered calcium lactate, and leaves the new compound behind as a very slightly soluble substance.

Barium lactate $(C_3H_5O_3)_2Ba + 4H_2O$ crystallises with great difficulty, forming cauliflower-like aggregates. It does not lose all its water of crystallisation at 100°.

Magnesium lactate $(C_3H_5O_3)_2Mg + 3H_2O$ is prepared by dissolving lactic acid syrup in 10 times its bulk of water, and neutralising with basic magnesium carbonate. The solution is evaporated until a skin forms, and then allowed to crystallise. It forms small light prismatic crystals, which frequently unite to form crusts. It dissolves in 30 parts of cold and 4 parts of hot water, forming a neutral very bitter solution. It loses its water of crystallisation at 100°.

Zinc lactate $(C_3H_5O_3)_2Zn + 3H_2O$ is best obtained direct from sugar by Lautemann or Kiliani's method. It crystallises better than any other lactate, and forms colourless, well-developed, four-sided rhombic prisms. It loses its water of crystallisation *in vacuo* or at 100°. It dissolves in 60 parts of water at 15°, and in 6 parts at 100°, forming an acid, bitter-tasting solution. It is very slightly soluble in alcohol.

Ferrous lactate $(C_3H_5O_3)_2Fe + 3H_2O$. This salt was introduced into pharmacy by Gélis and Conté in 1840, and was again recommended later on (1847) by Engelhardt and Maddrell. It is best prepared from crude calcium lactate (obtained by Bensch's method) in the following manner. The crude salt is recrystallised from water to which a little lime has been added, and if necessary the operation repeated. To the conc. aqueous solution of the purified salt the theoretical quantity of ferrous chloride is added, and the mixture allowed to stand for three days in a cool place. When no more crystals form the precipitated salt is filtered off, washed with a little alcohol, and dried at 50°.

Ferrous lactate forms greenish-white crusts of needles, or a similarly coloured crystalline powder. It dissolves at the ordinary temperature in 48 parts, and at 100° in 12 parts of water, forming an acid solution with a sweetish chalybeate taste. The solution becomes yellow, and then brown, in the air, ferric lactate being formed, and also undergoes alteration on evaporation in the air, leaving a hygroscopic residue containing ferrous and ferric lactates and some free acid. The dry salt is unaltered in the air, and loses its water of crystallisation when heated to 100° in a current of hydrogen.

Bismuth lactate is prepared by neutralising diluted lactic acid with freshly precipitated $Bi(OH)_3$, and precipitating the salt with alcohol. The voluminous precipitate is filtered off and dried at the ordinary temperature. It forms a white brittle horn-like mass, which only partially redissolves in water.

Paralactic acid. As already mentioned, an acid is contained in flesh which, though very similar to lactic acid, is nevertheless not identical with it. It is obtained from extract of meat by dissolving in 4 parts of warm water, adding 3 times the volume of 90 p.c. alcohol, and evaporating the filtrate to a syrup. This is again precipitated with alcohol, filtered, and evaporated, then acidified with H_2SO_4, and extracted with ether (Wislicenus, A. 167, 302). The raw acid may be purified by conversion into the zinc salt.

Paralactic acid is a syrup which can only be distinguished from lactic acid by the fact that it rotates the plane of polarisation to the right, whereas lactic acid is inactive. The salts strongly resemble the lactates, but are somewhat more soluble in water, and have a lævorotatory action.

Besides these two acids, two other isomeric hydroxyacids have been described. The first of these, *hydracrylic acid* or *β-hydroxypropionic acid*, is obtained by the action of moist Ag_2O on β-iodopropionic acid (Socoloff, A. 150, 167). It forms a syrup which decomposes into water and acrylic acid on heating. The second, known as *ethylene lactic acid*, was obtained by Wislicenus by the action of HCN on ethylene chlorhydrin, and boiling the resulting nitril with NaOH (A. 167, 316). Erlenmeyer, however, could only succeed in obtaining by this reaction hydracrylic acid, mixed with a little ordinary lactic acid (A. 191, 268). Wislicenus also obtained from flesh, in addition to paralactic acid, an acid which he believed to be identical with this ethylene-lactic acid, but it has recently been shown (Siegfried, B. 22, 2713) that this is in reality *acetyllactic acid*.

LACTIC FERMENTATION GUM *v.* GUMS.

LACTOPICRIN *v.* LACTUCARIUM.

LACTUCARIUM. *Lettuce opium.* The inspissated juice of the *Lactuca virosa* (Linn.) and other species of Lactuca (*v.* Woodville, Med. Bot. 1, 31; Bentl. a. T. 160, 161). Lactucarium is sometimes employed in medicine as a substitute for opium, and has often been examined chemically. A list of the earlier investigations, together with a summary of their results, is given by Pereira (Mat. Med. 1853, 2, 1569).

Nearly half the weight of lactucarium consists of the tasteless inodorous compound *lactucerin* or *lactucon*, first obtained in the crystalline form by Lenoir (A. 59, 83).

It has been further studied by Franchimont and Wigman (B. 12, 10); Hesse (A. 234, 243; 244, 268); Kassner (A. 238, 220) and others. Lactucarium is first washed with benzene and then extracted with hot alcohol. From the alcoholic solution crude lactucerin separates in crystals. These are purified by solution in ether, agitation of the ethereal solution with aqueous potash, the addition of alcohol till a precipitate begins to form, filtration, and finally the addition of water, when the lactucerin comes down in microscopic needles (Kassner). Franchimont and Wigman prepared a lactucerin or lactucon from lactucarium derived from *Lactuca altissima* (Bieb.), which gave the formula $C_{14}H_{22}O$. It melted at 296°, was insoluble in water, sparingly soluble in benzene and carbon bisulphide, but dissolved in ether, petroleum ether, and in fixed and volatile oils. By the action of phosphorus pentasulphide a *hydrocarbon* $C_{14}H_{22}$ was obtained, which boiled at 247–252°.

According to Hesse, lactucerin consists of a mixture of the acetates of two isomeric alcohols. Alcoholic potash decomposes the ethers and, on the addition of water, a precipitate of the two alcohols falls, which may be separated by taking advantage of their different solubility in alcohol. *α-Lactucerol* $C_{18}H_{30}O,H_2O$, the least soluble in alcohol, consists of silky needles which melt at 173–181°. It is soluble in chloroform, ether, petroleum ether, and hot alcohol. The *acetate*, $C_{20}H_{32}O_2$ or $CH_3.CO.OC_{18}H_{29}$, which exists in lactucerin, may also be prepared from the alcohol. It is crystalline and melts at 202–207°. It is slightly soluble in cold alcohol and glacial acetic acid, and easily in chloroform, ether, and petroleum ether. The *diacetate* melts at 198–200°, the *propionate* at 152°, and the *benzoate* at 156°. *β-Lactucerol*, $C_{18}H_{30}O,H_2O$, may be obtained in long needles from ether or chloroform. It is more soluble in alcohol than α-lactucerol, and forms an *acetate*, $C_{20}H_{32}O_2$ or $CH_3.CO.OC_{18}H_{29}$, the constituent of lactucerin, which is obtained in crystals from alcohol and melts at 230°. It is less soluble in alcohol and petroleum ether than the α-acetate. Crude lactucerin, examined by Flückiger and Hanbury, melted at 232° (Fl. a. H. 398).

After purifying crude lactucerin by sublimation in a current of carbonic anhydride, Kassner found it to melt at 210°, and on analysis to give numbers agreeing better with the formula of Franchimont and Wigman, $C_{14}H_{22}O$ or $C_{28}H_{44}O_2$, than with that proposed by Hesse. Fusing lactucerin with potash, Kassner obtained a new compound, *lactucol*, $C_{13}H_{20}O$ or $C_{18}H_{19}.OH$, together with acetic acid and hydrogen. Lactucol consists of needles melting at 160–162°. It forms an *acetate* which melts at 198–200°.

Lactucin, lactucic acid, lactopicrin, and lactucerin, as constituents of the Canadian lettuce, *Lactuca Canadensis*, have recently been investigated by Flowers (Ph. [3] 10, 44).

The bitter taste, and probably the medicinal value of lactucarium, depends upon three other constituents, which occur in relatively minute quantities. The first of these, *lactucin*, $C_{11}H_{12}O_3,H_2O$ was studied by Walz (A. 32, 85; J. pr. Ph. 14, 25; N. J. P. 15, 118); Aubergier (C. R. 19, 923); Ludwig (Ar. Ph. [2] 50, 1 a. 129); Kromayer (Ar. Ph. [2] 105, 3); Ludwig and Kromayer (Ar. Ph. [2] 111, 1); and Buchner (R. P. 43, 1). It has a decidedly bitter taste and crystallises in white pearly scales. It is soluble in water, sparingly soluble in alcohol and acetic acid, and insoluble in ether. It reduces Fehling's solution. Of the remaining two constituents, *lactucic acid* is a light yellow mass, becoming crystalline on standing (Ludwig and Walz), and *lactopicrin*, an amorphous bitter mass, soluble in water and alcohol (Kromayer, Die Bitterstoffe, Erlangen, 1861, 79).

Flückiger obtained from German lactucarium, by treatment with carbon disulphide, an *amorphous mass* which melted below 100°. Lactucarium also contains a trace of volatile oil, sugar, gum, albumen, caoutchouc, resin, asparagin, oxalic, citric, and malic acids, and yields 8–10 p.c. of *ash* (*cf.* Kremel, Ph. Centh. 1888, 512). A. S.

LACTUCERIN *v.* Lactucarium.

LACTUCEROL *v.* Lactucarium.

LACTUCIC ACID *v.* Lactucarium.

LACTUCIN and **LACTUCON** *v.* Lactucarium.

LACTUCOL *v.* Lactucarium.

LÆVOBORNEOL *v.* Camphors.

LÆVOCAMPHOR *v.* Camphors.

LAKE ORES *v.* Iron.

LAKES. The origin of their manufacture, as well as of the term 'lake' itself, is seen from the following brief historical sketch :—

According to Pliny, the dried scum collected by the dyers of Tyrian purple from their dye-liquors furnished a costly purple-coloured pigment, employed by painters. The *indicum* of the Roman artists was probably obtained in the same manner from a woad or indigo-vat.

Caneparius, a Venetian writer on dyeing, in 1619, states that it was the custom of dyers to evaporate the waste lac dye-liquors in order to obtain an artificial lac used by artists.

Similar pigments were afterwards prepared or collected from the waste dye-liquors of kermes, brazil-wood, &c. Such pigments were called by the Italians *laccæ*, and these were distinguished from each other by adding the name of the substance whence the colour was derived—*e.g.*, 'lacca di verzino (Brazil-wood), lacca di grana (kermes), lacca di cremise, &c.

As to the word 'lake' itself, the Indian *lac* or *lakh* means a hundred thousand, and refers to the immense numbers in which the lac insects (*Coccus laccæ*) appear at certain seasons on the branches of the trees infested with them.

At the present time true lakes are like those of the early days—namely, insoluble pigments obtained by precipitating solutions of organic colouring matters with metallic salts, &c. They are, indeed, the same coloured precipitates which it is the object of the dyer to produce and fix directly upon the fibre, but they are no longer waste products of the dye-bath, but are specially prepared for the use of artists and others.

The precipitating agent employed in their preparation varies according to the nature of the colouring matter; if the latter is of an acid or phenolic character the active constituent of the former is of a basic character, and *vice versâ*. The essential part of all such lakes consists of colouring matter chemically combined with the active constituent of the precipitating agent. In some cases, no doubt, there may be colouring matter or precipitating agent mechanically mixed with the true lake, the amount varying according to the proportions and the method of preparation adopted; but these must be regarded as more or less adventitious and not essential in the composition of a lake.

Most of the vegetable colouring matters are of a phenolic character, and the metal compounds of some are so insoluble that, to produce lakes from them, it suffices to add to a filtered solution of the colouring matter the solution of some metallic salt, for example, alum. In most cases, however, the acid character of the colouring matter is not sufficiently pronounced to enable it to displace the acid of the metallic salt; hence the further addition of an alkali (*e.g.* sodium carbonate) is necessary, in order to neutralise the strong acid of the salt and to liberate the base, with which the colouring matter then combines to form the lake.

If it is possible to employ an alkaline solution of the colouring matter, a lake may be at once obtained on adding to it a metallic salt solution.

Freshly precipitated metallic hydrates are also capable, in many cases, of attracting and combining with phenolic colouring matters when agitated or heated with their solutions.

It is well to bear in mind that not unfrequently the normal compounds of a colouring matter with a single metallic hydrate are comparatively soluble, and in these cases the addition of a second metallic salt (*e.g.* calcium salts) may be found necessary to bring about the formation of the lake, which then bears the character of a double salt.

All the older lakes, derived from vegetable or animal colouring matters, were produced by one or other of the foregoing methods; and these same methods may be employed with all phenolic colouring matters derived from coal-tar or from other sources, *e.g.*, alizarin, &c.

A variety of pigments are now obtained by precipitating certain basic and acid coal-tar colours from their solutions by making suitable additions, and although they are not in all cases veritable lakes, they usually bear the name 'aniline lakes,' and are therefore most conveniently considered here.

In some cases, no doubt, certain elements of the precipitant combine with the colouring matter, and produce an insoluble pigment to which the term lake may be legitimately extended. In those instances, however, where their production depends upon the property, possessed by many insoluble bodies, of attracting the colouring matters from their aqueous solutions by mere absorption, or in virtue of molecular surface attraction, they cannot be regarded as true lakes. Such insoluble substances as are here referred to act as a base or substratum for the colouring matter; they are termed 'carriers,' and consist of kaolin, aluminium hydrate, starch, &c.

It is quite usual, however, to find such insoluble bodies mixed with all lakes, not as precipitants, but for the purpose of increasing the body or covering power of the pigment, or as diluents in order to obtain pale shades.

Good lakes should never dissolve in the vehicles by means of which they are applied as pigments, otherwise all their covering power will be lost, they are no better than ordinary colouring matters, and what would otherwise be a paint becomes a coloured varnish.

LAKES DERIVED FROM PHENOLIC COLOURING MATTERS.

Reds.

Madder-lake. In the preparation of madder-lake extraction of the madder with *boiling* water is avoided, in order not to obtain any impurities which would cause the production of a less brilliant lake. It is well, first of all, to decompose the glucoside of the madder, and thus increase the actual colouring matter, by steeping in slightly tepid water and allowing the mixture to ferment for twenty-four hours, then wash with cold water and extract with alum solution at 60–70°C., employing about equal weights of madder and alum. The hot filtered alum solution of the colouring matter is precipitated as an alumina lake by adding sodium carbonate, and the precipitate is washed.

Another method is to precipitate impurities from a hot filtered decoction of madder by adding a small quantity of lead acetate, then filter, add a solution of alum, and precipitate with sodium carbonate.

One may also arrange matters so as to precipitate basic aluminium sulphate instead of aluminium hydrate, namely, by adding an insufficiency of sodium carbonate to the cooled solution of alum and colouring matter, and then boiling the mixture.

Garancine is preferable to madder for preparing madder-lake, since it does not contain any of the colouring matter in the form of useless glucoside (ruberythric acid), and impurities have also been for the most part removed. Extract 1 kilo. garancine repeatedly for several hours with 20 litres boiling water containing 0·25–0·5 kilo. alum, and filter hot through flannel. On cooling, the colouring matter separates from the filtrate as a flocculent precipitate. This is collected and dissolved in ammonia, and the filtered solution is precipitated with alum, or stannous chloride, or a mixture of both. The colour intensity of the lake varies with the proportions of ammonia and precipitant employed. A method similar to that described for madder may also be employed in preparing madder-lake from garancine.

Bright carmine-red lakes are obtained if, in the preparation of madder-lake, an ammoniacal solution of cochineal-carmine is employed for precipitating the alum solution, instead of sodium carbonate. This method is adopted to render the lower qualities of madder-lakes more attractive. Cheap qualities of madder lakes are also prepared sometimes by extracting mixtures of madder and Brazil-wood with sodium carbonate, and precipitating with alum or a solution of tin.

So-called 'crystallised-madder-lakes' are such as contain a certain quantity of potassium or sodium sulphate, &c., and are not to be recommended.

'Madder-pink-lake' is simply madder-lake diluted with about seven parts of 'blanc fixe' (precipitated barium sulphate).

Madder-lake is entirely, or for the most part, soluble in caustic potash and soda. If chalk or other diluent is present, this may remain undissolved. Boiled with dilute sulphuric or hydrochloric acid, the lake is decomposed and becomes yellow, alizarin being liberated in the form of a flocculent or crystalline precipitate. In dilute ammonia pure well-made madder-lake is not soluble (distinguishing test from cochineal-carmine).

References.—Colomb, Bl. Mülh. 12, 307; D. P. J. 73, 47; Persoz, Traité de l'Impression des Tissus, 1, 507; Merimé, *ibid.* 1, 505; Robiquet and Colin, *ibid.* 1, 505; Khittel, Polyt. Centr. 1859, 81.

Alizarin-red lake is the modern representative of the old madder-lake. It is made either with alizarin only or with mixtures of alizarin and purpurin, according to methods similar to those employed in the preparation of madder-lake. Very frequently, however, the alizarin-red lake contains, in addition to alizarin, lime, and alumina, a certain amount of some fatty acid, the presence of which renders the lake more brilliant, and less sensitive to the action of dilute acids and alkalis.

According to J. G. Gentele, the finest lakes are obtained by employing a mixture of alizarin and purpurin. An alkaline solution of alizarin is prepared by dissolving 100 parts commercial alizarin (10 p.c. paste) in 4·3 parts caustic soda (70 p.c.); the solution is diluted with a large quantity of water and filtered if necessary. A second solution is made by dissolving at least 40 parts alum in 800 parts water, and adding 2·5 parts calcium chloride dissolved separately in a little water. Larger amounts of alum will be found advantageous. The two solutions are mixed with constant stirring, and, if the whole of the alumina is not precipitated, a sufficiency of sodium carbonate solution to effect this is added. The excess of aluminium hydrate thus precipitated, which makes the lake paler, may be replaced by gypsum or china clay added to the lake after washing.

The following method of obtaining an alizarin-red lake is published by Meister, Lucius, and Brüning. 6·67 parts aluminium sulphate are dissolved in 200 parts water; to this is added a solution of 1 part calcium chloride, and before the calcium sulphate formed has separated, the solution is precipitated with 4·25 parts soda-ash dissolved in 100 parts water. The precipitate is well washed, and dyed by heating for half an hour at 70°C. in a solution containing 3 parts alizarin (20 p.c. paste), 1 part Turkey-red oil (sulphated castor oil), 0·1 part tannic acid. When all the alizarin is taken up by the precipitate, a further quantity of 0·5 parts Turkey-red oil is added, and the mixture is boiled for one hour. The lake thus produced is collected on a filter, well washed, and dried at a low temperature—50–60°C.

Purpurin alone is said to be well suited for the production of red and pink lakes. Dark coloured lakes are obtained by adding a slightly alkaline solution of purpurin to a solution of basic aluminium sulphate, and boiling the mixture. Brighter lakes are obtained by dissolving purpurin in a boiling alum solution, filtering and precipitating with sodium or magnesium carbonate.

In making alizarin-red lake it is very essential that the aluminium sulphate employed be free from iron, if brilliant lakes are desired.

In connection with the production of alizarin-red lake, the following observations of Liechti and Suida (Mittheil. Techn. Gewerb. Museum, Wien, May 1885) are of interest.

Pure aluminium hydrate is incapable of directly forming a lake with alizarin—*e.g.*, when boiled with an aqueous solution of the latter. The addition, however, of calcium salts at once effects the formation of a lake.

Aluminium-alizarin lakes of definite composition are best prepared by mixing solutions of aluminium salts with an alkaline solution of alizarin. Lakes are also produced if a solution of aluminium acetate mixed with alizarin is heated; or if aluminium hydrate is heated with alizarin and ammonia, and the mixture is carefully neutralised with acetic acid; or if a mixture of aluminium hydrate, alizarin, and concentrated sodium acetate solution is heated.

Normal aluminium alizarate $Al_2(C_{14}H_6O_4)_3$ produced by the double decomposition of solutions of aluminium sulphate and ammoniacal alizarin (1 mol. Al_2O_3 to 3 mols. alizarin) forms a purplish-red precipitate, which changes to purplish-black on drying. It is readily soluble in distilled water and in alcohol with a red colour. It dissolves readily in alkalis, especially ammonia, with a fine purplish-red colour.

Basic aluminium-alizarates of definite composition are prepared by proportionately decreasing the amount of alizarin employed in the above-mentioned double decomposition.

$Al_4(C_{14}H_6O_4)_3(OH)_6$ is a bright-red precipitate changing to brownish-red on drying. It is soluble in ammonia with a bright-red colour. $Al_2(C_{14}H_6O_4)(OH)_4$ is also a bright-red precipitate, which gives a red powder on drying. In ammonia it is much less soluble than the foregoing. $Al_4(C_{14}H_6O_4)(OH)_{10}$ is a bright-red precipitate, which still remains a fiery-red powder on drying. It is very sparingly soluble in ammonia. All the above basic aluminium alizarates are insoluble in water and in alcohol.

Alkaline solutions of normal aluminium alizarate and of the basic compound

$$Al_4(C_{14}H_6O_4)_3(OH)_6$$

may be mixed with solutions of sodium phosphate, sulphated oil, soap, &c., without undergoing decomposition, but, on neutralising these mixed solutions with acids, very brilliant red lakes are precipitated.

Normal aluminium phosphate $Al_2(PO_4)$, obtained by precipitation and well washed, cannot be dyed with alizarin. The formation of a lake only occurs when a calcium salt, *e.g.* calcium acetate, is also added.

Aluminium-calcium-alizarin lakes of various composition may be prepared by boiling together definite proportions of pure aluminium hydrate, calcium acetate solution, and alizarin. They form either dark or bright brownish-red precipitates. All are insoluble in water and some are insoluble in ammonia. The amount of calcium entering into the composition of the lakes produced in this manner depends upon the amount of alizarin employed, and *vice versâ*.

The probable formula of normal alizarin-red lake is given as $Al_2Ca(C_{14}H_6O_4)_3(OH)_2$ by the above-mentioned authors.

Cochineal-carmine. In the preparation of this brilliant scarlet lake, cochineal is extracted in tin-lined vessels with a large quantity of boiling water, preferably distilled or rain-water. Certain additions are made to the filtered decoction, and it is then allowed to stand for several weeks or even months in shallow vessels of tin or porcelain, during which period the carmine gradually separates in the form of a fine red powder. The additions referred to vary with different makers, and include the following: potassium binoxalate, acid potassium tartrate (cream of tartar), alum with or without cream of tartar, hydrochloric acid, &c. In all cases alkalinity and the presence of iron must be strictly avoided. The above ingredients may also be added to the water with which the cochineal is boiled, in which case the decoction must be filtered hot, since it rapidly becomes turbid on cooling. The addition of gypsum, calcium carbonate, zinc oxide, &c., so usual in other cases, must be avoided, since these would produce violet-coloured lakes.

The manufacture of cochineal-carmine is somewhat restricted, and the methods employed for producing the finest product are kept secret. The following published processes may serve to indicate the lines on which those interested in the subject should work.

According to Alyon and Langlois 500 grams cochineal are boiled for 1½ hours in 30 litres water containing 25 grams sodium carbonate. The decanted solution is well stirred up with 25–35 grams powdered alum, and then allowed to settle about twenty minutes; the clear liquid is poured off, a dilute solution of isinglass or albumen is added, and the whole is heated until the carmine collects together in the form of a coagulum. After removing the heat and allowing to settle, the supernatant liquid is decanted off, the carmine is collected on a filter, washed, and dried at a low temperature. The deeply coloured filtrate serves for the production of carmine-lake.

Even alum alone may be used as the precipitating agent, according to an old receipt, as follows. Boil 16 parts ground cochineal for ten minutes with about 600 parts distilled water, then add 1 part ground alum, boil a few minutes longer, filter the hot solution and allow the filtrate to stand in shallow porcelain basins. In the course of a few days the carmine separates in the form of a red slimy precipitate, which is collected and dried. The decanted liquor on standing yields a further quantity of carmine of a lower quality; its precipitation is facilitated by the addition of a small quantity of stannous chloride.

The residual cochineal which has thus been only partially exhausted serves for the preparation of carmine-lake.

In other similar receipts a mixture of alum and cream of tartar is used instead of alum only, and in that of Madame Cenette, at one time a celebrated maker of carmine, the effective precipitating agents are said to have been potassium nitrate and binoxalate of potash, the general method of procedure being similar to that just described.

Chinese carmine is said to be prepared by extracting cochineal with a boiling solution of alum, heating the filtered decoction with the addition of a solution of tin in nitric and hydrochloric acid (aqua regia), and finally leaving the liquid to stand till the carmine separates.

Cochineal-carmine is insoluble in water but soluble in alcohol. In ammonia solution it dissolves readily with a purplish crimson colour; from this solution tartaric acid precipitates the original carmine, for although when dried the precipitate has a brownish-red colour it becomes bright red when powdered. An addition of alum solution, however, at once produces a brilliant carmine-red lake. The following analysis of cochineal-carmine is given by C. Liebermann (B. 18, 1969).

Moisture	17 p.c.
Nitrogenous matter	20
Ash	7
Colouring matter	56
Wax	traces

The ash consists of SnO_2 0·67 p.c., Al_2O_3 43·09, CaO 44·85, MgO 1·02, Na_2O 3·23, K_2O 3·56, P_2O_5 3·20. From these analyses Liebermann considers cochineal-carmine to be a peculiar aluminium-calcium-protein compound of the carmine colouring matter, somewhat analogous to the Turkey-red-lake, in which alizarin is combined with aluminium, calcium, and fatty matter. This view is, however, not in accordance with the dyeing properties of the colouring matter of cochineal, since it is impossible to obtain a bright scarlet dye on an alumina mordant with or without the addition of calcium salts; moreover, in dyeing cochineal-scarlet on wool with tin mordants, the addition of lime salts to the dye-bath is injurious. It is of course possible that the colouring matters of cochineal and of cochineal-carmine are not identical and may behave differently.

Carmine-lake is simply an ordinary aluminium or tin lake of the colouring matter of cochineal, produced by adding sodium carbonate to a cochineal decoction containing alum or stannous chloride, or both. One may also add the latter to an alkaline solution of the colouring matter.

Florentine-lake is merely a special quality of carmine-lake, containing usually an excess of alumina, and sold in the form of 'drops.' Low qualities of Florentine-lake frequently contain admixtures of Brazil-wood alumina lake. 'Spurious Florentine lake' is only Brazil-wood lake, to which the commercial form of Florentine-lake has been given.

Venetian-lake, Hamburgh-, Chinese-, Roman-, and scarlet-lakes, are all varieties of Florentine-lake.

Brasil Indian-lake or **lac-lake** is a dark purplish-red lake analogous to carmine-lake, and prepared in a similar manner from the Indian product 'lac.'

Brazil-wood lake is prepared by extracting Brazil-wood or peach-wood with boiling water, adding alum and tin solution to the filtered decoction, and finally precipitating with sodium carbonate, avoiding excess. Another method is to add precipitated and washed aluminium hydrate to a filtered decoction of Brazil-wood. Freshly prepared decoctions are never suitable for the manufacture of these lakes; they should always be oxidised, by exposure to air or otherwise, in order to change the principle brazilin into the necessary colouring matter brazileïn.

Vienna-lake is a species of Brazil-wood lake, prepared in the following manner. A mixture of ground starch (30 kilos.), chalk (10 kilos.), and a little gypsum, is stirred up with a decoction of Brazil-wood; then ground alum (1 kilo.) is added and the whole is well stirred for twelve hours and finally allowed to settle. After decanting the clear liquor, Brazil-wood decoction is again added to the residual precipitate, together with a further quantity of alum (1 kilo.), and the stirring is continued as before. This process is repeated until the precipitate has taken up sufficient colouring matter and acquired the character of a lake. The decanted liquors are agitated with fresh starch, chalk, &c. in order to yield further quantities of lake.

In the foregoing process the alum is decomposed by the chalk, and the alumina precipitate thus produced combines with the colouring matter. At first the lakes appear violet through the presence of excess of chalk, but with the continued addition of alum they gradually acquire a crimson colour.

An 'imitation cochineal-lake,' somewhat brighter than ordinary Vienna-lake, may be made in the same way, but making the further addition of sodium arsenite, or the starch is replaced by finely-ground arsenious acid. In these methods the formation of aluminium arsenite and the presence of a slight excess of arsenious acid seem to be essential to the brilliancy of the colour.

Fine dark carmine-red lakes are obtained by adding stannous chloride and cream-of-tartar to a concentrated old decoction of Brazil-wood.

Rose-pink lakes are made from Brazil-wood decoctions after the manner of 'imitation cochineal-lake,' but employing large quantities of gypsum or kaolin, and taking care to have a slight excess of alum in order to ensure a rose-pink free from any tinge of violet. They are exceedingly fugitive to light.

Yellows.

Persian-berry lake is prepared by extracting Persian-berries two or three times with boiling water, dissolving alum in the combined and filtered liquors, and then precipitating with sodium carbonate, taking care to avoid excess. The precipitate is collected on a filter, washed, and sold in the form of paste. This lake, containing much starch and sold in the dry form, is said to be employed in the colouring of sweetmeats.

Persian-berry carmine is produced if stannous chloride is employed instead of alum in the above process. It is a bright orange lake employed by calico-printers.

Persian-berry lakes may also be made after the manner of Vienna-lake, *i.e.* with the use of chalk, alum, and starch.

It is essential to employ only freshly-prepared decoctions if bright-coloured lakes are desired.

Quercitron-yellow lake or **Dutch-pink** is made according to the method adopted in the case of Venetian-lake, by precipitating a decoction of quercitron-bark containing alum, with chalk. The methods employed in making yellow lakes from Persian-berries may also be used. To ensure bright colours the decoction of quercitron-bark is clarified by adding a little gelatin solution, thereby removing tannic acid. Sometimes milk of lime is used instead, taking care to avoid excess.

It is said that these quercitron colours retain their intensity by gaslight better than all other vegetable yellows, and are hence useful for theatre decorations, &c.

Stil de grain is a low quality of Dutch-pink.

English and **Italian pinks** are other qualities of quercitron-bark yellow lakes.

The above lakes are sold in the dry condition in the form of pyramidal-shaped 'drops.' They never possess the brilliancy of those obtained from Persian-berries.

Galloflavin and **nitro-alizarin** lakes of a yellow and orange-yellow colour respectively may be prepared according to one or other of the foregoing methods, employing an aluminium salt as precipitant.

Maroon and **claret-red lakes** are produced from alizarin with chromium salts.

Purple lakes may be obtained from alizarin in conjunction with iron salts, or from galleïn with aluminium or chromium salts.

Blue lakes are obtainable from alizarin-blue with chromium salts.

Green lakes are yielded by resorcinol-green (dark-green) in combination with iron salts, or by cœruleïn with chromium or aluminium salts.

Brown lakes may be prepared from anthracene brown with chromium salts.

Very few details are published concerning the manufacture of lakes from the above-mentioned phenolic coal-tar colours, but the general methods to be employed are similar to those given for alizarin-red lake, &c.

LAKES DERIVED FROM BASIC COLOURING MATTERS.

These lakes, and also those prepared from acid colouring matters, *i.e.* the *coal-tar colour lakes*, have in recent years rapidly acquired an ever-increasing importance and employment in various ways, *e.g.* in paper-staining and printing, lithography, general decorative painting, &c.

In the preparation of these lakes the 'base' or 'carrier' upon which the colouring matter is precipitated in a more or less insoluble form is a most important element, since it determines in great measure their brilliancy, covering power, and general qualities.

These substrata are usually very finely powdered, insoluble, white, or occasionally coloured, materials, such as starch, kaolin (China-clay), chalk, talc, gypsum, heavy spar, precipitated barium sulphate (blanc-fixe), red-lead, &c. They are well mixed with the colour solution and attract the colouring matter either directly or when certain precipitating agents are added to the mixture. Very frequently, however, they are precipitated along with the colouring matter, and may then consist of aluminium hydrate or phosphate, calcium carbonate or sulphate, magnesium hydrate, &c.

The precipitating agent to be employed in any particular case varies according to the nature of the colouring matter used and the purpose for which the lake is intended.

For lakes employed in decorative painting, finely ground heavy-spar is considered to be the most serviceable. Gypsum and China-clay are also used. The chief base for lakes employed in printing wall-papers is 'blanc-fixe' since it excels all others in giving body and covering power to the lake. Aluminium hydrate and barium carbonate, precipitated along with the colouring matter, are also of considerable importance. For paper-staining and lithographic printing the lakes must possess fineness and covering power in a very high degree, and for these, aluminium hydrate precipitated apart from the colouring matter is highly esteemed. Starch, China-clay, precipitated calcium carbonate, barium carbonate, and blanc-fixe, are also employed.

China-clay is most largely used with the basic coal-tar colours, since for these its attractive power is very marked. Barium carbonate and aluminium hydrate precipitated during the process of forming the lake are chiefly used with the azo- colours. Lead sulphate and red-lead are important bases for the eosin lakes.

The proportions of the various materials employed in making the lakes vary considerably, according to the desired intensity of the lake.

All lakes should be washed with water till the filtrate is neutral and free from soluble salts. They are sold as pastes or powders, the latter being sometimes in the form of light porous blocks or 'drops' of suitable size.

The preparation of the basic-colour lakes may be effected as follows:

a. A solution of the colouring matter is well mixed with finely powdered and well washed China-clay and starch, and allowed to stand for some time with occasional stirring. Even without the aid of any precipitant these carriers attract a certain amount of colouring matter from the solution, and become, as it were, dyed. Other carriers, *e.g.* gypsum, blanc-fixe, zinc oxide, &c., may be used, but their attractive power for the colouring matter is very small, and they serve chiefly as diluents.

b. One may also allow starch alone, or with China-clay, &c., to be mixed with the colour solution for a day or two with frequent stirring, then add a solution of alum, and if this effects no precipitation, a solution of sodium carbonate is added.

Coloured powders, prepared according to the foregoing methods, are not true lakes, and readily give up all colouring matter on repeated washing.

c. True lakes, and of deeper shades too, are obtained by precipitating the colour-base as an insoluble tannate. For this purpose a solution of alum, usually with an addition of some one or other of the above-mentioned 'carriers,' is mixed with the colour solution, a solution of tannic acid is then added, and finally a solution of sodium carbonate in order to make the precipitation more complete. The alum may be replaced by stannic chloride, or tartar-emetic; in the latter case precipitation is facilitated by the further addition of a neutral salt, *e.g.* sodium chloride. Instead of sodium carbonate one may use chalk.

In the above manner lakes are readily made from such basic colouring matters as magenta, phosphine, Bismarck-brown, methyl-violet, malachite-green, saffranine, methyl-blue, auramine, rhodamine, &c.

d. For precipitating the basic-greens, the tannic acid may be advantageously replaced by such yellow colouring matters as contain tannin-like principles, *e.g.* old-fustic, and quercitron-bark, since these not only precipitate the basic colouring matter, but also yield a yellower and more brilliant lake.

In this case gypsum, China-clay, blanc-fixe, &c., is mixed with the fustic-extract solution together with sodium carbonate, and then aluminium sulphate or acetate is added. The yellow lake thus produced is then dyed by adding an aqueous solution of the basic-green colouring matter.

Another plan is to mix the fustic-extract solution and the colour solution, with the addition of the necessary 'carriers,' and then precipitate by adding alum or lead acetate solution, or both.

When these methods are employed with saffranine, scarlet lakes are obtained.

It is said that tannin lakes, such as those referred to, possess the defect of retarding or even preventing the drying of oil paints containing them, and are therefore only suitable for water-colours, paper-staining, &c.

e. Picric acid may also be employed as a precipitant with some basic colouring matters, *e.g.* auramine, night-blue, methyl-blue, &c. With methyl- and malachite- greens it is particularly useful, since it forms very insoluble compounds with the bases of these colouring matters, and also yields yellower and brighter lakes than those obtained with tannic acid.

f. Bichromate of potash along with starch &c. has been used as a precipitant with saffranine, with which it produces a brownish-red lake changing to carmine-red on drying.

g. Blue and violet lakes of great brilliancy may be obtained by mixing certain blue and red colour solutions with precipitated and washed Prussian-blue, which thus becomes dyed.

h. Lakes suitable for some purposes may be prepared by precipitating the colour solution, to which a solution of soap or sulphated oil has been previously added, with aluminium sulphate or other metallic salt. The so-called 'resin colours' are prepared in a similar manner by employing a mixture of colour solution and resin soap (resin dissolved in sodium hydrate), and precipitating with calcium or magnesium chloride. Since the lakes thus produced are soluble in benzene it has been found possible to use their benzene solutions for dyeing silk without injuring its finish, lustre, and general appearance. They are also used for preparing coloured varnishes employed in ornamenting metallic surfaces, wood, leather, glass, &c.

Lakes derived from Acid Colouring Matters.

The most numerous of the acid colouring matters referred to here are the sulphonic-acid derivatives of certain colour-bases, and azo-colouring matters derived from benzene, naphthalene, &c. Some of the phenolic colouring matters which possess special features may also be included under this head, *e.g.* aurin and the eosins.

The best precipitating agents for these acid colouring matters are barium chloride, lead acetate, and aluminium sulphate, since the bases of these salts form more or less insoluble compounds with many of the colour-acids.

Alum, aluminium acetate, calcium, magnesium, or stannic salts, in conjunction with caustic or carbonated alkali, may also be used as precipitants.

As in the case of the basic-colour lakes, so here, the 'base' or 'carrier' upon which the lakes are precipitated is of great importance, and the reader is referred to what has been already said upon this point.

Azo- colouring matters are usually precipitated with barium or lead salts. In the case of reds and scarlets the former are used for the blue shades, the latter for the yellow shades.

The following methods have been published by C. O. Weber (Ch. Tech. Central-anzeiger (1885) [4] 1, 17, 44; (1886) [4] 421, 433, 461) and others.

a. The 'carrier' selected is mixed with a solution of the colouring matter, and the latter is precipitated by adding barium chloride solution.

b. Barium chloride is added to a colour solution containing sodium carbonate and the 'carrier.' This method is adopted in cases where the barium compound of the colour-acid forms a voluminous and gelatinous precipitate, instead of one which is dense and powdery, the object being to throw down barium carbonate along with the colour-precipitate.

c. Barium chloride is added to the colour solution containing sodium aluminate and the 'carrier.' The following receipts give the proportions of materials which may be employed:—

Materials employed	I.	II.	III.
Ground heavy-spar	100	—	—
Blanc-fixe	—	100	20
Azo- colour	10	15	15
Sodium aluminate (70 p.c.)	7·5	11·25	11·25
Barium chloride	15	22·5	22·5

I. is suitable for paint, II. for carpet printing, III. for paper-staining.

Instead of barium chloride one may also use magnesium sulphate or calcium chloride.

d. By using aluminium chloride instead of barium chloride in the last-mentioned (*c*) method, especially for orange and scarlet lakes, products suitable for paper-staining are obtained. The solution of aluminium chloride is added in the cold to the colour solution containing sodium aluminate. Excess of aluminium chloride and the consequent production of basic aluminium salt must be avoided. Use about 13 parts aluminium chloride (1·105 sp.gr.) to 3 parts sodium aluminate (70 p.c.).

e. One may employ as 'carrier' precipitated and washed aluminium hydrate, an addition of sodium phosphate also being found advantageous. The aluminium hydrate, in the form of paste, is mixed with the colour solution containing sodium phosphate, and barium chloride is added. Instead of aluminium hydrate, double the amount of barium or calcium carbonate may be employed. The mixture is effected in the cold, it is then heated to about 70°C., afterwards cooled, filtered, washed, &c. The following proportions of materials have been recommended:

Dry aluminium hydrate (employed as paste)	25
Azo- colour	15
Sodium phosphate	7·5
Barium chloride	15

f. Another method is to mix alum, aluminium acetate, or stannic chloride with the colour solution, and then to precipitate carefully with sodium hydrate, carbonate, or phosphate.

g. Paste colours suitable for the printing of wall-papers may be prepared by adding to a solution of stannate of soda as much Turkey-red oil as will dissolve in it, 'blanc-fixe' is added, then colour solution, and finally, calcium chloride as the precipitant.

Alkali-blue is precipitated from its solution by means of dilute acids or acid salts, *e.g.* alum, the precipitate being attracted, in the moment of formation, by the 'carrier' present.

The 'carrier' (usually starch, China-clay, or chalk) is mixed with the colour solution, alum solution is then added, and the mixture is rendered almost neutral by means of sodium carbonate. Instead of alum solution, aluminate of soda may be added to the colour solution, and then carefully neutralised with hydrochloric or acetic acid.

Aurin or **corallin** yields brilliant scarlet lakes, which are, however, not suitable for oil paints, since the acidity of the latter soon turns the scarlet to orange.

The (*b*) method given for azo-colours may be employed, or the following:

The aurin is dissolved in sodium hydrate, 'blanc-fixe,' China-clay, chalk, or barytes are added, and finally a solution of alum as precipitant. The yellowish hue of the lake caused by excess of alum is removed by adding chalk. Example:

Blanc-fixe	100
Aurin	10
Sodium hydrate (70 p.c.) . .	5
Alum	25

One may also precipitate the alkaline solution by calcium, magnesium, zinc salts, &c. The hue of the lakes varies according to the nature of the precipitants employed.

Eosins. These colouring matters give scarlet and crimson lakes of great brilliancy, some of which (the so-called vermilionettes) are employed as substitutes for vermilion. The usual precipitants are lead salts, 1 part pure eosin being precipitated by 1 part lead acetate or 0·75 lead nitrate.

(*a*) Red-lead, or chromate-of-lead-orange is mixed with a solution of eosin in dilute sodium carbonate, and the whole is stirred vigorously in order to prevent the sediment from adhering to the bottom of the vessel. A concentrated solution of lead acetate is then added, the precipitate formed is collected, washed, pressed, cut into blocks, and dried at a low temperature in order to preserve the brilliancy of the colour.

The following proportions are given by Weber:

	I.	II.	III.	IV.
Red-lead .	20	20	200	20
Eosin . .	1·6	1	0·6	0·35
Sodium carbonate cryst.	0·04	0·025	0·02	0·01
Lead acetate	4·00	2·75	1·75	1·00

For yellowish-reds a yellow shade of eosin is employed; for reds, gradually increasing in blueness, one may use erythrosin, cyanosin, rose-bengale, and phloxin. The admixture of lead carbonate, formed when working according to the above receipts, tends to make the lake bluer in tint.

The employment of sodium hydrate instead of a portion of the sodium carbonate, also the substitution of the red-lead by a greater or lesser amount of some white 'carrier,' tend to increase the blueness of an eosin-lake. If starch is the 'carrier' used, the precipitation should be effected in the cold, and sodium hydrate must not be employed, otherwise the starch would be rendered soluble and transparent.

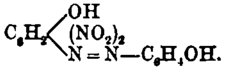
(*b*) Alum may also be employed as the precipitant, but it yields yellower-toned lakes, and the precipitation is not so complete. Aluminium hydrate, in the form of paste (= 2·5 parts dry), is mixed with a solution of eosin (2 parts), and a solution of lead nitrate (1·5 parts) is added; or, the colour solution is mixed with starch or China-clay, and precipitated by means of a solution of alum. For paler shades an excess of alum is added, and precipitated by sodium hydrate. Yellower shades are obtained by the addition of magnesium or zinc sulphate.

Literature.—Lehrbuch der Farbenfabrikation, J. G. Gentele; Die Erd-Mineral-und-Lack-Farben, &c., S. Mierzinski; Die Chemie des Steinkohlentheers, 2, 22, G. Schultz; Journ. Soc. Dyers and Colourists (1890, 6, 32); Instructions issued by several coal-tar colour manufacturers; Weber, Chemisch-technischen Central-anzeigen (1885), 4, 1, 17, 44; (1886) 4, 421, 433, 461. J. J. H.

LAMPBLACK is the soot or finely-divided carbon produced by the imperfect combustion of various substances of a fatty or resinous nature, such as vegetable and animal oils, pinewood, and dead oil; and it may be taken that whatever the combustible material which, on full exposure to the oxygen of the air, produces the best illumination, that material will, if partially deprived of air, produce the greatest amount of sooty deposit. The German mode of manufacturing lampblack consists in collecting it on a woollen cloth exposed to the smoke emitted from resinous woods burning in a close furnace. The cloth being shaken from time to time, the particles are detached and collected. Lampblack is employed in the manufacture of printing-inks and pigments (*v.* INDIAN INK; CARBON).

LANARKITE. A double sulphate and carbonate of lead $PbSO_4.PbCO_3$, found occasionally in monoclinic crystals. More frequently massive or in flexible laminæ at Leadhills in Scotland; also in Siberia, in the Hartz, and in the Tyrol. Lustre, pearly adamantine or resinous. Colour, greenish-white or grey. Sp.gr. 6·3 to 7. Hardness 2.

LANCASTER YELLOW



$$C_6H_2\begin{cases}OH\\(NO_2)_2\\N=N—C_6H_4OH.\end{cases}$$

A colouring matter obtained by P. Greiss, in 1875, by the action of picramic (isopurpuric) acid on phenol. Sparingly soluble in water; soluble in sulphuric acid, with reddish-yellow colour. Dyes silk and wool in an acid bath brownish-yellow. No longer used.

LANDACEIN or **AMYLOID** *v.* ALBUMINOIDS.

LANOLIN *v.* CHOLESTERIN. As the result of numerous observations, this substance constitutes an excellent remedy for cuts and burns. In the case of cuts especially, after a careful anointing with lanolin, scale is never formed, the substance acting, according to Bernh. Fränkel, as a preventive. It is noticeable that cuts when protected by an application of lanolin can be cooled in a rapid stream of water, without danger of removing the lanolin. Bleeding is arrested almost instantaneously.

Lanolin has attracted considerable notice in agricultural circles on account of its property of preserving the elasticity of the hoof and the suppleness of leather. Lanolin owes its great superiority in this respect over other fatty substances to its great capacity for uniting with water, in consequence of which it penetrates better than other fats into moist leather and into the deeper layers of the skin and of the hoof (C. J. 12, 31; S. C. I. 7, 341).

LANTHANUM *v.* CERIUM METALS.

LANTHROPINE *v.* VEGETO-ALKALOIDS.

LAPIS LAZULI. (*Lasurstein*, Ger.) A mineral occasionally crystallised in rhombic dodecahedra, but usually found in compact masses or disseminated through granular limestone. Its value as an ornamental stone lies in its colour, the finest lapis being of a rich Berlin blue; but the mineralogist is acquainted with certain varieties which are green, violet, red, or even colourless. Nordenskjöld regarded lapis lazuli as essentially a colourless mineral, through which pigmentary particles were usually disseminated; and H. Fischer showed, by microscopic examination, that the substance even when crystallised is never homogeneous. The hardness of lapis, though not high (5·5), is sufficient to render it susceptible of polish, thus enabling it to be used as a decorative stone. It was largely employed in ancient Egyptian and Roman art, and is still a favourite material for mosaic work. This stone was the *σάπφειρος* of classical writers, and the iron-pyrites, so commonly disseminated through the lapis, was mistaken for gold. Ground, calcined, and washed, it was formerly much prized and extensively used as a pigment, under the name of *ultramarine* (*outremer*, Fr.). The blue colour has been referred to the presence of a compound of sulphur with sodium and iron; while W. Stein regards it as due to an aluminium sulphide (J. pr. 3, 1871, 38). Heated before the blowpipe, the blue lapis loses colour, and fuses with difficulty to a white glass. In hydrochloric acid it is decomposed, with loss of colour, while gelatinous silica is separated and hydrogen sulphide evolved. The chemical composition of lapis lazuli, which has given rise to much discussion, is illustrated by the following analyses:

	I.	II.	III.
Silica . .	66·9	45·70	43·26
Alumina. .	20·0	25·34	20·22
Ferric oxide .	0·1	1·30	4·20
Lime . .	—	7·48	14·73
Soda . .	10·1	10·55	8·76
Potash . .	—	1·35	—
Sulphur . .	2·9	3·96	3·16
Sulphuric acid	—	4·32	5·67
	100·0	100·00	100·00

I. From S. America, by F. Field. II. From S. America, by Schultz in Rammelsberg's lab. III. Oriental lapis, by Schultz, do. (Sp.gr. of lapis, 2·3 to 2·42). Lapis lazuli is found in limestone, or associated with granite, near Lake Baikal in Siberia, in Thibet, China, Persia, and Chili. It is also occurs in the volcanic rocks of Latium, and in the ejected limestone blocks of Monte Somma (*v.* Vogelsang, Ueber d. natürlichen Ultramarin-Verbindungen, Amsterdam, 1873). F. W. R.

LARCH TURPENTINE *v.* OLEO-RESINS.

LARCH OIL *v.* OILS.

LARDACEIN or **AMYLOID** *v.* ALBUMINOIDS.

LASERPITINE $C_{15}H_{22}O_4$. An alkaloid obtained by Kütz (Ar. Ph. 1883, 221, 161) by extraction with petroleum ether of the roots of the white *Laserpitium latifolium*. Forms large colourless well-formed crystals belonging to the monoclinic system. Melts at 118°; is insoluble in water and dilute acids. Easily soluble in chloroform and ether, slightly soluble in alcohol and petroleum ether.

LAUDANUM. Laudanum is understood in this country at the present day to be the simplest liquid preparation of opium available for medical purposes. The word is an old one, and has undergone considerable change of meaning, but its precise origin has never been ascertained with certainty.

According to one hypothesis the term is borrowed from *laldanum* or *ladanum*, an oleoresin of Greek origin, which is collected from various species of *Cistus* (*v.* OLEO-RESINS), while another derives the word from the Latin *laus*, praise, which is supposed to indicate the high esteem in which the medicine has always been held. In a discussion of this question (Ph. [3] 17, 404, 424, 503, 584 a. 644), it is pointed out by Eagle that according to Mathiolus (Comment. Dioscoridis Mat. Med. Lugduni, 1563) certain Italians applied the term laudanum to labdanum, and thus Littré and Robin (Dict. Méd. Paris, 1877) and others give the Italian equivalents of the two words as synonymous. This statement of Mathiolus would appear to have been the source of the view that laudanum is derived from labdanum, which has been adopted by several lexicographers and writers on materia medica. Hooper (Lex. Med. London, 1848) and Dunglison (Dict. Med. Sc. Philadelphia, 1868) are, however, on the side of the *laus* derivation, and the remarks of such writers as Crollius (Basilica Chymica, Francofurti, 1611), Bruno (Lex. Castello-Brun. Norimbergæ, 1688), Lemery (Pharm. Universelle, 1716), and others are so decidedly in its favour that the weight of evidence at present appears to be with this hypothesis.

But be this as it may, the term laudanum was applied in the seventeenth century to indicate solid or semi-solid mixtures which generally, though not always, contained opium (*cf.* Lond. Dispensatory, 1678). These were gradually replaced by liquid preparations, of which the most celebrated was that of the physician Sydenham, 1644–1689, whose life was written by Dr. Johnson. This was the *Laudanum liquidum Sydenhami* of the London Pharmacopœia of 1720, and is represented by the *vinum opii* of recent medicine. A *tinctura opii* of simpler composition has, however, long taken the lead among galenical preparations of opium. This is a liquid extract made with proof spirit, and represents in all important respects the physiological activity of the crude drug. To this tincture the term laudanum is now applied, both in this country and in the United States, not only by writers such as Pereira (Mat. Med. 1853, 2135) and Stillé and Maisch (Nat. Dispensatory, 1886, 1537), but more especially in the practice of pharmacy. The editors of the British Pharmacopœia for 1885 have also added the term laudanum as a synonym for tincture of opium in a revised issue of that work (*cf.* OPIUM). A. S.

LAUREL CAMPHOR *v.* CAMPHOR.

LAUREL OIL *v.* OILS, ESSENTIAL.

LAURELIC ACID *v.* LAURUS NOBILIS (Linn.).

LAURETIN *v.* LAURUS NOBILIS (Linn.).

LAURIC ACID *v.* FATTY ACIDS.

LAURIN *v.* LAURUS NOBILIS (Linn.).

LAUTH'S VIOLET *v.* METHYLENE BLUE; also THIONINE COLOURING MATTERS.

LAURUS NOBILIS (Linn.). *Bay, Sweet Bay* (*Laurier commun*, Fr.; *Lorbeer*, Ger.).

The classic or noble laurel or bay tree is indigenous to the Levant and is found all along the shores of the Mediterranean. The leaves are used as a flavouring agent, and both the leaves and fruit were formerly employed in medicine.

The fruit, or so-called bay berries, were analysed by Bonastre (J. Ph. [2] 10, 30) and by Grosourdi (J. 1851, 562). Besides water, a large proportion of starch, lignin, sugar, and small quantities of resin, pectin, albumen, and colouring matter, bay berries contain *solid and liquid fat*, *volatile oil*, and a *peculiar camphor*.

From the fat Marsson (A. 41, 330) isolated *lauric acid* $C_{12}H_{24}O_2$, being one of the twelfth members of the $C_nH_{2n}O_2$ or formic acid series of fatty acids. It was subsequently found in numerous other fats (*cf.* Heintz, J. pr. 66, 1). Glycerin trilaurate or *trilaurin*, $C_3H_5(C_{12}H_{23}O_2)_3$ is associated in the fat with the glycerides of oleic, linoleic, palmitic, myristic, and stearic acids (Staub, Nat. Disp. 1886, 874). Grosourdi distinguishes between trilaurin or *stearolaurin* and what he calls *stearolauretin*.

Bonastre (J. Ph. [2] 10, 36; 11, 3) was the first to distil a volatile oil from bay berries. It was further studied by Forcke (Ar. Ph. [2] 17, 177), Brandes (Ar. Ph. [2] 22, 160), and Bley (R. P. 48, 96), and more recently by Gladstone (C. J. 17, 3; 25, 1) and Blas (A. 134, 1). Bley obtained a yield of 0·2 p.c. from old berries. The oil consists of *a terpene*, *laurylene*, $C_{10}H_{16}$, lævorotatory, sp.gr. 0·908 (15°), b.p. 164°; a *sesquiterpene* $C_{15}H_{24}$, lævorotatory, sp.gr. 0·925 (15°), b. p. 250°, and *lauric acid* (Blas; Gladstone) (*cf.* Brühl, B. 21, 157; Wallach, A. 252, 94).

Bay camphor or *laurin*, $C_{22}H_{30}O_2$, was isolated by Bonastre (J. Ph. [2] 10, 32) and further investigated by Delffs (J. pr. 58, 434) and Marsson (A. 41, 329). The yield is about 1 p.c. It consists of prismatic crystals without taste or smell. It is insoluble in water but soluble in alcohol and ether, and is chemically neutral and indifferent.

Grosourdi describes the following substances as constituents of bay berries: *phæosin* or *phæosic acid*, *lauretin*, and *laurelic acid*, but they have not been further examined.

The leaves of *Laurus nobilis* also contain a volatile oil, of which, however, little is known. Barbaglia (Ph. [3] 19, 824) finds that it solidifies at 18° and distils for the most part at 170–175°. That portion distilling at 170° gave the formula $C_{14}H_{24}O$. The volatile oil of the leaves of the allied *Laurus californica* was studied by Stillman (B. 13, 629).

The volatile oils obtained from *Laurus nobilis* must not be confused with others bearing similar names, such as commercial bay oil or bayberry leaf oil, distilled from the leaves of the West Indian tree *Myrcia acris* (DeC.), and which is the flavouring agent in the toilet preparation known as bay rum (Markoe, Ph. [3] 8, 1005; Rüse, Ph. [3] 13, 39); laurel oil of Guiana, natural oil of laurel, or ocotea oil, derived from a tree of Spanish Guiana (Stenhouse, C. S. Mem. 1, 43; 2, 121); or oil of common or cherry laurel, *Prunus lauro-cerasus* (Linn.) which is similar to volatile oil of bitter almonds. A. S.

LAURYLENE *v.* LAURUS NOBILIS.

LAVA. The term lava is properly applied to those products which issue from volcanic orifices in an incandescent and often in a molten condition, presenting, when cooled, the appearance of slag or clinker, and consisting of rock more or less perfectly fused. It differs from other volcanic substances such as the ashes, sand, and scoriæ, not in chemical composition but in the conditions under which it is ejected from the crater. Thus the analyses by Silvestri of lava, scoriæ, sand, and ashes thrown out by Etna in the eruption of 1865 showed the practical identity of constituents in each form of product:

—	Ashes	Sand	Scoriæ	Compact lava
Silica	50·00	49·80	50·00	49·95
Alumina	19·08	18·20	19·00	18·75
Ferrous oxide	12·16	12·42	11·70	11·21
Manganous oxide	·40	·45	·50	·49
Lime	9·98	11·00	10·28	11·10
Magnesia	4·12	4·00	4·20	4·05
Potash	·60	·49	·69	·70
Soda	3·72	3·60	3·40	3·71
Water	·36	·29	·33	·23
Phosphoric acid Titanic acid Vanadic acid Ferric oxide	traces	traces	traces	traces

Of the whole number of chemical elements, eight, viz. oxygen, silicon, magnesium, aluminium, calcium, iron, sodium, and potassium, are those which only are at all usually found in lavas; although the complete list of elements discovered in various examples of volcanic products extends to thirty-one, viz.:

Non-metallic: Boron, carbon, chlorine, fluorine, hydrogen, iodine, nitrogen, oxygen, phosphorus, arsenic, selenium, silicon, sulphur = 13.

Metallic: Aluminium, cæsium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, potassium, rubidium, sodium, thallium, titanium, uranium, zinc, zirconium = 18.

Among the eight elements commonly existing in lava, oxygen makes up nearly one-half of the weight, silicon one-fourth, and aluminium one-tenth. The other five elements vary in their proportions relatively to each other. Silica is present in proportions of from one-half to four-fifths of all lava, and, with the bases, viz. oxides of aluminium, calcium, iron, magnesium, potassium, and sodium, forms the acid silicates of aluminium, calcium, iron, magnesium, potassium, and sodium. In proportion as the acid constituent silica exists in greater or smaller relative quantity, lavas have been distinguished as 'acid lavas' and 'basic lavas': to this classification Professor Judd (Volcanoes, 48) suggests the additional term of 'intermediate lavas.' Under this arrangement, 'acid lavas are those which contain from 66 to 80 p.c. of silica; they are poor in lime, magnesia, and oxide of iron, but rich in potash and soda. The basic lavas contain from 45 to 55 p.c. of silica; they are rich in lime, magnesia, and oxide of iron, but poor in soda and potash. In the intermediate lavas the proportion of silica varies from 55 to 65 p.c.' It may be taken, further, that these three distinctive names correspond with the nomenclature of former writers, viz. trachytes, greystones, and basalt. Since basic or basaltic lavas contain a larger proportion of heavy oxides than the acid or trachytic lavas, it follows that the former possess a higher sp.gr. and may usually be classified according to their weight.

In colour fresh lava ranges from nearly white in the acid to nearly black in the basic. After a time all lavas become reddened on account of the iron present in them being affected by exposure to the weather.

A fourth but much smaller class of lava is one resembling the stony portion of meteorites. Professor Judd suggests for this class the name of ultra-basic lava. This lava contains a very low percentage of silica and a high proportion of iron and magnesia. It has a specific gravity usually exceeding 8; and it is interesting as being composed of those minerals which occur in meteorites, viz. olivine, enstatite, augite, anorthite, magnetite, and chromite.

Under the microscope thin slices of lava exhibit two kinds of materials, a glassy base and crystals of various minerals distributed through it in irregular order and proportion; apparently this variation is to be explained by the rate of cooling to which various portions of the molten mass have been subjected. This, however, does not affect the ultimate chemical composition.

Geologists adopt the following names of lavas, in five main classes, Rhyolites, Trachytes, Andesites, Phonolites, and Basalts; and the glassy and the perfectly crystalline forms are distinguished as follows:

Crystalline forms.	*Lavas.*	*Glassy forms.*
Granite	Rhyolite	Obsidian
Syenite	Trachyte	
Dionite	Andesite	
Miascite	Phonolite	
Gabbro	Basalt	Tachylite

Confining this article to the chemical aspects of lava, it may be said generally that the material ejected from the same volcano at wide intervals of time displays a similar chemical composition. Thus two sets of analyses of I. Etna Lava of (*a*) very ancient date, (*b*) year 1669, and (*c*) year 1865; and II. Vesuvius Lava of (*a*) 1631, (*b*) 1767, and (*c*) 1868, show practical identity:—

I. *Etna Lava.*

—	(*a*) Very ancient	(*b*) Eruption of 1669	(*c*) Eruption of 1865
SiO_2	49·63	48·33	49·95
Al_2O_3	22·47	16·15	18·75
FeO	16·80	16·32	11·21
MnO	0·63	0·54	0·49
CaO	9·05	9·31	11·10
MgO	2·68	4·58	4·05
K_2O	0·98	0·77	0·70
Na_2O	3·07	8·45	3·71

II. *Vesuvius Lava.*

—	(*a*) Eruption of 1631	(*b*) Eruption of 1767	(*c*) Eruption of 1868
SiO_2	48·12	48·20	46·58
Al_2O_3	17·16	17·92	20·00
Fe_2O_3	5·69	5·48	3·20
FeO	5·13	4·75	5·69
MnO	1·20	1·33	1·07
TiO_2	0·22	0·27	0·27
CaO	9·84	8·97	9·09
MgO	3·99	8·51	8·16
K_2O	7·24	7·70	7·35
Na_2O	2·77	2·61	2·74
H_2O	0·08	0·16	0·32

When we come to study the internal structure of volcanoes, however, we are impressed by the fact that lavas of very different chemical composition must have issued from the same vent at successive periods. As a general rule, to which there are not wanting notable exceptions, the first lavas to make their appearance have been of intermediate type; while acid and basic lavas have been ejected at a later period in the history of the volcano. Occasionally we find evidence that lavas of very different chemical composition have flowed from the same vent in frequent alternations.

The following typical lavas were analysed in Bunsen's laboratory:—

—	Hrafutinnuhygyr, near Krabla, north-east of Iceland. Black stony lava	Summit of Elburz	Black basalt from the source of the Euphrates	Hecla, ash of 1845	Compact grey volcanic rock from Kalmanstrenga, Iceland	Ancient lava from Hecla
Silica	75·77	69·65	64·76	56·76	53·08	49·37
Alumina and Ferrous oxide	14·14	19·85	22·31	27·47	28·70	28·66
Lime	1·82	4·40	5·13	6·75	9·92	13·01
Magnesia . .	0·25	2·27	1·91	4·04	5·32	7·52
Potash . . .	2·46	3·83	2·51	2·63	0·61	0·20
Soda	5·56		3·38	2·35	2·37	1·24

V. Volcanoes, by J. W. Judd; Geology for Students, by A. H. Green; Study of Rocks, by Rutley.

LAVENDER, OIL OF, *v.* OILS, ESSENTIAL.

LAZULITE *v.* LAPIS LAZULI and PIGMENTS.

LAZURSTEIN *v.* LAPIS LAZULI and PIGMENTS.

LEAD. Syns. *Blei*; *Plomb*; *Plumbum.* Symbol Pb. At. w. 206·4 (Stas, Bull. Acad. Roy. Belg. [2] 10, 298).

Occurrence.—Lead is said to have been found in the natural state in several localities; in no single case, however, has further examination in these places resulted in a second discovery of the metal. The localities in which native lead has been stated to occur are the Grassington Mines and Alston Moor, certain mines in the province of Guanaxuato in Mexico, and according to Koksharow (J. M. 1875, 873) it has been found in the Kirghis Steppe, where it occurs in hornstone associated with heavy spar and cerussite, also in the gold washings of Katharinenburg, in which it occurs in grains together with gold, magnetic and specular iron ores, also in India (Geol. Survey, India, List of Minerals). The statement that native lead is found amongst volcanic products would appear to be the more reliable one. Some instances of the occurrence of native lead are given by Professor Liversedge, in his Minerals of New South Wales.

A large number of lead compounds are found in nature, a comparatively small number of which can be considered in the light of ores of this metal.

Lead ores.

Lead Ochre, *Litharge*, or *Lead monoxide*, PbO. A rare mineral found at Badenweiler in Baden, at Austin's Mines, Wythe County, Virginia, and is stated to have been ejected from the volcanoes of Popocatepetl and Iztaccituall in Mexico, and found in other localities in Mexico. It is a massive or scaly crystalline opaque solid, of a light-yellow colour, sp.gr. 8.

Minium or *Red Lead* Pb_3O_4. A rare mineral usually found associated with other lead compounds. It is a pulverulent vivid red solid, occasionally mixed with yellow. It is found at Badenweiler, at Austin's Mine, Wythe County, Virginia; in Anglesea, at Grassington, in Weardale, Yorkshire, at Bleialf and Kall in the Eifel district, also at Brillon in Westphalia, and in some localities in New South Wales.

Galena (*Galenite*, *Bleiglanz*, *Lorroche*). *Lead sulphide* PbS. The most abundant of the natural lead compounds, forming the chief commercial source of the metal. It is frequently found in well-defined crystals belonging to the regular system, most usually cubic; it occurs also in combinations of the cube and octahedron, and the rhombic dodecahedron. This mineral is also found in tabular, reniform, or botryoidal masses, coarse or finely granular, and sometimes fibrous masses. It has a metallic lustre, the colour and streak are lead grey; sp.gr. 7·25–7·7, and hardness 2·5. Cleavage of the crystals cubic; fracture of massive varieties conchoidal. It decrepitates before the blowpipe, and on further heating melts, yielding a bead of lead after the sulphur has burnt off. Galena is not unfrequently found in great purity, but more usually contains silver, sometimes gold, also iron, zinc, antimony, and copper. The silver appears to exist as sulphide, as probably also does the gold. It would appear that the silver sulphide does not always exist in the same mode of combination, as in some cases it may be separated by washing, whereas in other instances this is not possible. The opinion that large and well-defined crystals of galena are poor in silver appears to be an erroneous one, as is proved by the analysis of samples of galena obtained from different localities made by R. Smith (Percy's Metallurgy; Lead, 97).

Galena melts at a red heat to a liquid, which easily penetrates clay crucibles, and, heated in the absence of free oxygen, can be volatilised, condensing in the form of crystals. It is decomposed by dilute nitric acid, lead nitrate being formed and sulphur liberated; by concentrated nitric acid it is converted into the sulphate. Hydrochloric acid converts it into the chloride, sulphuretted hydrogen being evolved.

Galena occurs both in stratified deposits and in veins, and is frequently associated with copper and zinc ores. Quartz, calcite, fluorspar, or heavy spar, form in the majority of cases the matrix of galena. In England galena is found in the following localities: Northumberland, Alston Moor, Teesdale, Weardale, Swaledale, and Wensleydale, in Derbyshire, Shropshire, Cornwall, and Devonshire. In Wales this mineral is found in Flintshire, Denbighshire, Cardiganshire, and Montgomeryshire. In the Isle of Man galena is found associated with zinc, antimonial copper and silver ores. In Scotland galena is worked in the Leadhills district, and in Ireland is found in the county of Wicklow. In Germany, a galena rich in silver and associated with spathic iron ore occurs in several localities in the valleys of the Lahn and Sieg; in the Hartz districts and at Freiberg a highly argentiferous galena is found. In Silesia galena is found in the form of irregular deposits, associated with zinc and iron ores. Přibram and Joachimsthal are the chief localities in which galena is found in Bohemia; the ore of these districts is highly argentiferous.

Valuable deposits of galena are found in various localities in France, especially at Huelgoët and Poullaouen in Brittany, at Pontgibaud, Puy-de-Dôme; and at Vialas in the department of Lozère. Galena is found in Spain in Catalonia, Granada, and Linares; it is found also in Belgium at Verdrun, in Savoy and in Siberia.

In Canada galena occurs in several localities in the neighbourhood of Lake Superior. A remarkable vein has been discovered at Silver Lake some six miles north from the head of Thunder Bay. It is also found in several places in Ontario. In the United States extensive deposits of this mineral occur in the States of Missouri, Illinois, Iowa, and Wisconsin. Galena is found in several provinces of Japan, and is widely distributed over New South Wales.

Clausthalite or *Lead selenide*, is a mineral containing lead which like the telluride is chiefly of interest on account of the element associated with the lead.

Cerussite, *Lead carbonate*, *White lead ore*, *Céruse*, *Bleispath*, $PbCO_3$. A mineral occasionally found transparent, usually white, having an adamantine lustre. Found in acicular crystals and in forms resembling arragonite (rhombic), also in stalactitic and crystalline aggregates; massive and earthy, and sometimes as a cementing material of sandstone. Hardness 3–3·5. Sp.gr. 6·4–6·6. It is occasionally found tarnished owing to the conversion of the surface into sulphide by the action of sulphuretted hydrogen formed by the decomposition of galena with which this mineral is frequently associated. Amorphous varieties have a conchoidal fracture. Massive specimens are frequently argentiferous.

Cerussite heated on charcoal before the blowpipe decrepitates and yields at first a yellow, then a red oxide of lead, and ultimately a bead of the metal; nitric acid dissolves it with effervescence.

Specially fine crystals of cerussite are found at Leadhills, at Wanlockhead; in Derbyshire; near Liskeard in Cornwall; and in some of the mines of the United States. Lead carbonate is the chief ore at Leadville, Colorado, where it occurs in deposits between porphyry and limestone; the deposit in some places is as much as 80 feet in thickness. Cerussite is also found near Aachen, at Santander in Spain, in the Cornish and Devonshire lead mines, and at the Seven Churches in Wicklow, Ireland. Large quantities of lead carbonate are found amongst the débris surrounding the ancient lead workings in Derbyshire, in the Mendip Hills, and in Carthagena. These deposits probably owe their origin to the action of the atmospheric carbon dioxide upon metallic lead and the oxidisable lead compounds contained in the slags. Some of the purer varieties of cerussite, such as those found at Mechernich in the Eifel, are used without further treatment in potteries to produce a lead glaze.

Cerussite is found associated with lead and silver ores in several localities in New South Wales.

Lead carbonate is found combined with other lead compounds forming distinct mineral species.

Anglesite, Lead sulphate, Bleivitriol, $PbSO_4$. Rhombic. Combinations similar to those of heavy spar' but more varied. 'The habit of the crystals varies according to the character of the dominant faces, as follows: Group A. Pyramidal to 122, vertically short columnar to 110, horizontal columnar to 011. Group B. Horizontally columnar to 102. Group C. Rectangular tabular to 100, vertically columnar to 110. Group D. Horizontal columnar to 104, rhombic tabular to 001' (Bauerman's Descriptive Mineralogy). The crystals found at Parys Mountain, Anglesea, the original locality for this mineral, are typified by those of Group B. Anglesite is also found massive and granular, and as pseudomorphs after galena. It is very brittle and the fracture is conchoidal. Hardness 3. Sp.gr. 6·12–6·35. Lustre adamantine to vitreous and resinous. Colourless, white yellowish, or brown. Transparent to opaque.

Heated before the blowpipe in the oxidising flame it decrepitates, and fuses to a clear bead which is opaque on cooling. In the reducing flame it gives a bead of metallic lead. Heated with hydrochloric acid it is converted into the chloride of lead. It is soluble in caustic potash or soda.

Anglesite is usually found associated with galena, from which it appears to have been produced by oxidation. By the action of water containing carbonates of the alkali metals or of calcium it is converted into lead carbonate. Pseudomorphs exhibiting this change are not uncommon. The localities in which anglesite is found in addition to the original locality are the following: Cumberland, Derbyshire, and Cornwall; Leadhills and Wanlockhead in Scotland; the Hartz district; Baden, Siegen, Tarnowitz in Silesia; specially fine crystals in the Monteponi Mines, in the island of Sardinia; Linares in Spain; Siberia, Pennsylvania (at Phenixville), Missouri, Massachusetts, the State of New York (Rossie), are amongst the chief localities in the United States. Lead ore containing a considerable quantity of lead sulphate is obtained from Australia; and at Chilote in Peru a compact variety of lead sulphate occurs containing 120 oz. of silver to the ton, the latter occurring in the form of the chloride.

Compounds of lead sulphate and lead carbonate are known, forming distinct mineral species.

Pyromorphite, Phosphate of lead, Green lead ore, Brown lead ore, Linnets,

$$3\{Pb_3(PO_4)_2\}+PbCl_2.$$

Crystallises in the hexagonal system; crystals short hexagonal prisms with flat ends. Crystals usually grouped irregularly in druses; also in botryoidal, reniform, and massive aggregates. Cleavage pyramidal and prismatic, but usually indistinct. Fracture conchoidal. Hardness 3·5. Sp.gr. 5·53–7·2. Colour extremely varied; sometimes colourless, white or grey, usually green, hair- or clove-brown, straw or honey-yellow; the latter less frequent. Lustre resinous, vitreous to subadamantine when transparent; as a rule imperfectly transparent. This mineral has been found in England in Cumberland, Durham, Yorkshire, Derbyshire, and Cornwall. The colour of the mineral consisting of mixtures of phosphate and carbonate of lead obtained at the mines on Cromford Moor, near Wirksworth, Derbyshire, has given rise to the name 'linnets,' from its resemblance to the colour of the linnet. In Scotland pyromorphite is found at Leadhills and at Wanlockhead. In Bohemia it occurs at Přibram, Mies, and Bleistadt; in Saxony at Zschappau, Freiberg, and Johann-Georgenstadt; in Baden at Wolfach and Hofsgrund; in the Hartz near Clausthal; in Hungary near Schemnitz; in France at Poullaouen, Huelgoët, Pontgibaud, and St. Prix; and in Siberia at Beresowsk and Katharinenburg. In the United States of America it has been found at the Perkiomen Mine near Philadelphia, at Phenixville, and in the States of Maine, of New York, Massachusetts, and Connecticut.

Whilst when pure, pyromorphite is a chlorophosphate of lead, and its composition is represented by the formula given above, there is a second variety containing a portion of the phosphorus replaced by arsenic, such varieties having a lower sp.gr. than those containing phosphorus only; a third variety contains calcium and fluorine, and is a mixture of pyromorphite and fluor-apatite.

Pyromorphite heated in a closed tube gives a white sublimate of lead chloride. Heated on charcoal it fuses easily, but is not reduced; the bead on cooling shows crystalline facets and glows at the moment of solidification. It yields metallic lead when fused with soda or borax and metallic iron; in the last case a regulus of iron phosphide is also obtained. Arsenical varieties give the characteristic garlic odour when heated on charcoal in the reducing flame.

Mimetisite, Kampylite, Hedyphane. Lead arseniate $\{Pb_3As_2O_8\} + PbCl_2$. It crystallises in the hexagonal system like pyromorphite, with which it is isomorphous. Hardness 3·5. Sp.gr. 5·5, 7–7·25. Lustre resinous. Colour, white or pale yellow, sulphur or orange-yellow, grey or brown: transparent to translucent. This mineral is found at Caldbeck Fell in Cumberland, the lead mines of Cornwall, and at Beer Alston in Devonshire. It occurs at Johann-Georgenstadt in Saxony, at St. Prix in France, and at Nertschinsk in Siberia, at Phenixville in Pennsylvania, and Zacatecas in Mexico. In certain varieties of this mineral the arsenic is replaced by phosphorus; these are isomorphous mixtures of pyromorphite and mimetisite, and known as kampylite; in other varieties, such as that found at Langbanshytta in Sweden, both phosphorus and calcium are present, being mixtures of mimetisite and chlorapatite, and are known as hedyphane.

Mimetisite exhibits chemical characters similar to those of pyromorphite, save that it gives the odour of arsenic when heated in the reducing flame, and is less easily fused than pyromorphite. It is soluble in nitric acid.

In addition to the above, a large number of minerals are known, consisting of lead compounds, such as *cotunnite* or *lead chloride* $PbCl_2$, which occurs in small brilliant crystals in the lavas of Vesuvius.

Matlockite $PbCl_2.PbO$, small tabular crystals, belonging to the tetragonal system. Hardness 2·5. Sp.gr. 7·21. Transparent or translucent, lustre adamantine. The crystals have a yellow or greenish tint. It is found in the Cromford level lead mine at Matlock.

Mendipite is a rare mineral found in the Mendip Hills lead mines, resembles matlockite in being an oxychloride of lead, and has the composition $PbCl_2.2PbO$. It crystallises in the rhombic system, is found in masses and in columnar aggregates, is of a yellowish-white to pale red colour. Hardness 2·5–3. Sp.gr. 7·1. Heated before the blowpipe it decrepitates and fuses, forming a yellow globule; on charcoal it yields a bead of metallic lead. It is easily soluble in nitric acid. Matlockite behaves in a similar manner when heated before the blowpipe.

Phosgenite, a chlorocarbonate of lead, $PbCl_2 + PbCO_3$, crystallising in the tetragonal system in short columnar or acute pyramidal crystals, which are either colourless, yellow, grey-green, or brown. Transparent or translucent, lustre adamantine, waxy. Hardness 2·5–3. Sp.gr. 6·0–6·2. When heated, fuses readily to a yellow opaque bead, having a crystalline surface; on charcoal yields a bead of metallic lead and acid vapour; is soluble in nitric acid with effervescence, and the solution gives the reaction for chlorides. It is found at Cromford in Derbyshire, at Monteponi in Sardinia, and Tarnowitz in Silesia.

The following is a list of native lead compounds:—

Aciculite, aikinite, belonite, needle ore.

Patrinite $\left\{\begin{matrix} Pb_2'' \\ (Cu_2)'' \end{matrix}\right\} S_3.Bi_2S_3$.

Altaïte. Telluride of lead, PbTe.

Aluminate of lead (hydrated), plumboresinite $\left\{\begin{matrix} Pb'' \\ Al_4''' \end{matrix}\right\} O_7 6H_2O$.

Anglesite, sulphate of lead, lead vitriol, $PbSO_4$.

Antimonial sulphides of lead *v.* Boulangerite, Bournonite, Brogniardite, Freislebenite, Geocronite, Heteromorphite, Jamesonite, Kobellite, Plagionite, Zinkenite.

Antimonate of lead, bleinierite $Pb_3Sb_2O_8.4H_2O$.

Aræoxene, zinkiferous vanadate of lead.

Arsenate of lead *v.* Mimetisite.

Arsenomelane, $2PbS.As_2S_3$.

Binnite—a mixture of arsenomelane and Scleroclase.

Bleinierite, antimonate of lead.

Boulangerite, $3PbS.Sb_2S_3$.

Bournonite (to which is related Wõlchite), $(2PbS.Cu_2S).Sb_2S_3 = \begin{matrix} Pb_2'' \\ (Cu_2)'' \\ Sb_2'' \end{matrix} S_6$.

Brogniardite, $PbAg_2S_2.Sb_2S_3$.

Caledonite $(Pb;\ Cu)CO_3.PbSO_4$.

Carbonate of lead, cerussite, white lead ore, $PbCO_3$.

Cerasin, corneous lead.

Horn lead, chlorocarbonate of lead, phosgenite, $PbCl_2.PbCO_3$.

Cerussite *v.* Carbonate of lead.

Chileïte, vanadate of lead and copper, $(Pb;Cu)_3(VO_4)_2.3(Pb;Cu)O$.

Chiviatite, $2PbS.3Bi_2S_3$.

Chloride of lead, cotunnite, $PbCl_2$.

Chlorarsenate of lead *v.* Mimetisite.

Chlorocarbonate of lead *v.* Cerasin.

Chlorophosphate of lead *v.* Pyromorphite.

Chromate of lead *v.* Crocoïsite, Melanochroïte, Red lead ore, Vauquelinite.

Clausthalite, selenide of lead, PbSe.

Corneous lead, syn. with Cerasin.

Cotunnite *v.* Chloride of lead.

Crocoïsite or crocoïte, chromate of lead, $PbO.CrO_3 = \left.\begin{matrix} Pb'' \\ Cr^{vi} \end{matrix}\right\} O_4$.

Cupreous sulphate of lead *v.* Linarite.

Cupreous sulphatocarbonate of lead *v.* Caledonite.

Cuproplumbite, $2PbS.CuS$.

Dechenite, vanadate of lead, PbV_2O_6.

Descloïzite, $Pb_2V_2O_7$ or $2PbO.V_2O_5$.

Embrothite *v.* Boulangerite.

Eusynchite, syn. with Dechenite.

Freislebenite, $Pb_3Ag_4S_5.2Sb_2S_3$.

Galena, lead glance, sulphide of lead, PbS.

Geocronite, arseniferous schulzite.

Heteromorphite, feather ore, plumosite, $2PbS.Sb_2S_3$.

Hydroaluminous lead *v.* Aluminate of lead.

Kilbrickenite, $6PbS.Sb_2S_3$.

Kobellite $\left.\begin{matrix} Pb_3'' \\ (\frac{2}{3}Sb.'''Bi''')_2 \end{matrix}\right\} S_6$.

Lanarkite, sulphatocarbonate of lead, $PbCO_3.PbSO_4$.

Lead glance *v.* Galena.

Lead, native.

Lead ochre, native protoxide of lead.

Lead ore, green, *v.* Mimetisite and Pyromorphite.

Lead ore, red, *v.* Minium.

Lead ore, white, *v.* Cerussite.

Lead ore, yellow, *v.* Molybdate of lead.

Leadhillite, sulphatotricarbonate of lead, $3PbCO_3.PbSO_4$.

Lehrbachite, selenide of lead and mercury $(PbHg)Se$.

Linarite, cupreous anglesite, cupreous sulphate of lead, $CuH_2O_2.PbSO_4$.

Matlockite Pb_2Cl_2O.

Melanochroïte, phœnicite, phœnicochroïte, $3PbO.2CrO_3 = \left.\begin{matrix} Pb_3'' \\ (Cr^{vi})_2 \end{matrix}\right\} O$?

Mendipite, $Pb_3Cl_2O_2$.

Meneghinite, $4PbS.Sb_2S_3$.

Mimetite, mimetisite, mimetene, green lead ore, $PbCl_2.3Pb_3As_2O_8$. To this is related hedyphane, containing also calcium and phosphorus.

Minium, red oxide of lead.

Molybdate of lead, wolfenite, yellow lead ore, $PbO.MoO_3 = \left.\begin{matrix} Mo^{vi} \\ Pb'' \end{matrix}\right\} O_4$.

Muriocarbonate of lead, syn. with Cerasin.

Nagyagite, foliated tellurium $(Pb ; Au_2).(Te ; Se)$.

Needle ore *v.* Acicoulite.

Oxides of lead *v.* Lead ochre, Minium, and Plattnerite.

Oxychloride of lead *v.* Matlockite and Mendipite.

Patrinite *v.* Aciculite.

Phœnicite or Phœnicochroïte *v.* Melanochroïte.

Phosgenite *v.* Cerasin.

Phosphate of lead *v.* Pyromorphite.

Plagionite, $4PbS.3Sb_2S_3$.

Plattnerite, peroxide of lead, PbO_2. A doubtful species.

Plumboresinite *v.* Aluminate of lead.

Plumbostib *v.* Boulangerite.

Polysphærite, pyromorphite containing calcium.

Polytelite, $4(Pb ; Ag_2)S.Sb_2S_3$.

Pyromorphite, green lead ore, chlorophosphate of lead, $3Pb_3P_2O_8 + PbCl_2$. or PbF_2.

Schulzite, $5PbS.Sb_2S_3$.

Selenate of lead, $PbSeO_4$.

Selenide of lead *v.* Clausthalite and Lehrbachite.

Stolzite, tungstate of lead, $Pb''W^{vi}O_4$.

Sulphate of lead *v.* Anglesite.

Sulphatocarbonate of lead *v.* Leadhillite and Sulzannite.

Sulphide of lead *v.* Galena.

Sulzannite, rhombohedral sulphatotricarbonate of lead, $PbSO_4.3PbCO_3$.

Telluride of lead *v.* Altaïte and Nagyagite.

Tungstate of lead *v.* Stolzite.

Vauquelinite $\left\{\begin{matrix} 3CuO \\ 6PbO \end{matrix}\right\} 4CrO_3$.

Vanadate of lead *v.* Dechenite, Descloïzite, and Vanadinite.

Vanadinite, $3Pb_3V_2O_8.PbCl_2$.

Wōlchite *v.* Bournonite.

Wulfenite, molybdate of lead.

White lead ore *v.* Cerussite.

Zinkenite, $PbS.Sb_2S_3 = \left.\begin{matrix} Pb'' \\ Sb_2''' \end{matrix}\right\} S_4$.

DISTRIBUTION OF LEAD ORES.

Lead ores are abundantly distributed through the rocks of the different geological formations, from the granite to the triassic formation; but most abundantly are these ores to be found in rocks of the Silurian age and in those of the mountain limestone. Whilst many of these deposits are in the form of true veins, some there are which cannot be regarded as true veins. Veins of lead ore which are rich in one formation become suddenly impoverished in passing into another and different rocky stratum. In England three different kinds of deposits of lead ores are distinguished by the miners—viz. (1) rake veins, which are true veins in the geological sense of the word; (2) pipe veins, which are narrow masses, frequently oblong in shape and lying parallel to the rocky strata; (3) flat veins, which are small beds of ore lying in the middle of these strata. Galena generally contains some silver; but lead ores are not always argentiferous, those, however, which occur in crystalline metamorphic rocks are usually so. Further, the lead ores of the older rocks are generally argentiferous, but are not so productive of lead as those of the limestone districts, yet are more persistent in depth.

In England, lead ores are worked in veins and 'flats' in the mountain or carboniferous limestone in the neighbourhood of Alston Moor, where the counties of Northumberland, Cumberland, and Durham meet, and elsewhere in those counties. The lead-yielding districts of Derbyshire, Yorkshire, and the Mendip Hills are in the same formation. The Cornish and Devonshire mines are workings in true veins occurring in the Devonian formation—'Killas' of Cornwall and Devonshire. The lead workings of the Shelve district in Shropshire, of Cardiganshire, of Montgomeryshire, of Leadhills and Wanlockhead in Scotland, and those of the Isle of Man, are in rocks of the Silurian formation; whilst in Ireland, in Wicklow, and Newtownards in the County Down, lead ores are found in granite.

In Germany lead mines are worked in the valleys of the Lahn and Sieg, and these lead-bearing veins are found in Devonian strata. Those of the Hartz district are also in Devonian slates; they yield a highly argentiferous galena and silver ores proper. In the Hartz district there are three centres—viz. (1) that in the neighbourhood of Clausthal; (2) the mines in the vicinity of Andreasberg; and (3) those at Rammelsberg, near Goslar. The Freiberg mines are in gneiss and yield a highly argentiferous galena. The Silesian lead ores are found in irregular deposits in the muschelkalk, and are associated with ores of zinc and iron. A remarkable stratified deposit of lead ore of triassic age is that of Mechernich in the Eifel, where a bed of sandstone is filled in places with nodules formed of sand grains cemented together by galena.

The mines of Bleiberg and Raibel in Carinthia are among the most important lead mines in Austria. Here the ore is a very pure galena associated with molybdate of lead, and is found in limestones of the triassic formation. At Přibram, in Bohemia, the veins are in Silurian strata, and yield a galena very rich in silver.

The mines are from three to four thousand feet deep.

Whilst lead is found in almost every province in Spain, the chief workings are those of the provinces Jaen, Murcia, and Almeria. In the province of Jaen, in the neighbourhood of Linares, two distinct systems of veins occur traversing the triassic sandstones and the granite upon which the former reposes. In the district round Carthagena in Murcia, the lead ores occur in veins and stratified and irregular deposits in Silurian rocks and trachytes. In the province of Almeria lead is found in veins in the mica schists and clay slates of the Sierra Almagrera. Some of the ore of this district is highly argentiferous.

The chief Italian sources of lead are the mines of Sardinia, which may be divided into three types—(1) Ore masses interstratified in Silurian rocks, as in the mine of Monteponi; (2) veins traversing Silurian clay slates, as in the Montevecchio Mine, one of the most important lead mines in Europe; and (3) lodes traversing Silurian limestones, *e.g.* Malacalzetta. The ore of the Montevecchio consists of galena mixed with blende, iron pyrites, heavy spar, siderite, and copper pyrites. It is poor in silver, whilst that at Malacalzetta carries about 40 oz. of silver to the ton. In all cases in Sardinia the ore is galena. There are numerous deposits of lead ore (galena) on the mainland. In the Brusmipiano Mine, in the district of Milan, galena is found associated with cerussite, iron pyrites, jamesonite, copper pyrites, and malachite. At the Morso Alto mine a galena is worked rich in silver, and a highly argentiferous galena is worked at the Boltino mine in the mining district of Florence. In this case the galena is associated with fahlerz, bournonite, and native antimony ore.

The deposits of lead ores of Portugal are very similar to those of Spain. The most important district is that of Mutola, near the Guadiana. The galena contains about 24 oz. of silver to the ton, whereas the cerussite and anglesite associated with it are frequently much richer.

In Greece ores of lead, silver, and zinc occur constantly associated with one another. They occur in mica schists, limestones, granites, and trachytes, sometimes in irregular masses and sometimes in the form of lodes. The chief mining district is that of Laurium, at the southern extremity of Attica.

In Sweden argentiferous lead ores occur in veins in granular limestones belonging to the crystalline slates. The chief mines are those of Sala, of Lofas in Dalecarlia, and of Guldmenshytta in Westmanland.

In France galena containing silver and associated with blende and iron pyrites occurs at Poullaouen in lodes traversing clay slates of Silurian age. The lodes at Huelgoët yield, in addition to argentiferous galena, cerussite, pyromorphite, and also native silver and horn silver. Whilst galena is found and worked in several localities in France, the most important mines are those of Pontgibaud in the Puy-de-Dôme, where lead lodes are worked, which traverse rocks consisting of granite, gneiss, and schists, broken through by dykes of porphyry, and covered by sheets of basalt, beds of cinder, or by flow of lava. The galena is always argentiferous, and is accompanied by blende or iron pyrites, and occasionally by patches of fahlerz.

In Belgium galena is found in numerous places, but the deposits are seldom of sufficient importance to pay the expenses of working. It is frequently associated with cerussite and pyromorphite. A productive lead mine exists at Bleyberg, near Moresnet, where a vein is worked which traverses the carboniferous limestone and the coal measures.

Lead ores are found in various parts of Russia; galena and several other lead minerals occur in a lode at Ekaterinenburg in the Ural. In the Caucasus deposits of galena exist. In Poland are the deposits of galena in the dolomites of the muschelkalk, which have been worked for centuries. The most remarkable mines are those near Olkusk and Boleslaw. Lodes of lead ores occur near Chasing and Kielcé in rocks of Devonian age. Galena associated with fahlerz, molybdenite, iron pyrites, copper pyrites, and blende occurs in deposits in the mining district of Nertschinsk in Eastern Siberia.

Lead ores are found in various provinces of the Indian empire; they occur in beds or pockets, but seldom in veins. Many of these deposits have been worked by natives, but only on a small scale; there are practically no workings carried on at the present time.

Galena is found in many provinces in Japan, but the deposits of this mineral are not particularly valuable. In addition to this mineral, several lead antimony ores are found in Japan.

Australia. In Victoria galena occurs in several localities; that at St. Arnaud is argentiferous. In New South Wales this ore is widely distributed over the colony, but no lead mines are known to be working. In South Australia the mines of argentiferous galena are situated in the southern part of the colony, near Cape Jervis. In the Champion Bay district of Western Australia both lead and copper ores have been found in gneissic rocks, associated with granite and greenstone. In Tasmania argentiferous galena has been found; at the Penguin, and in the neighbourhood of Mounts Roland and Claude. Galena containing silver is occasionally found in the gold-bearing reefs of Coromandel and Thames, New Zealand.

Africa. Argentiferous lead and copper ores are found in some mines in Algeria, and lead ores are known to exist in different parts of South Africa; these ores are found chiefly in the limestone formation extending from the junction of the Vaal with the Orange River in a northerly and then in an easterly direction to Rustenburg, in the north-west of the Transvaal. There is evidence of these ores having at one time been worked by the natives.

In the United States of America argentiferous galena, associated with blende, iron, and copper pyrites, occurs in the Atlantic States in the form of true veins; in the Azoic slates of New York and in the New England States in veins running parallel to the formation; in the State of New York it occurs in irregular deposits in the unaltered Lower Silurian rocks. The chief lead districts are, however, those of the Upper Mississippi Valley and the Missouri. The Upper

Mississippi lead district is comprised within the States of Wisconsin, Illinois, and Iowa, the chief lead-producing district being that of the first named State. The deposits of lead ore are found in the 'galena' or magnesian limestone of the Trenton period of the Lower Silurian formation, and cover an area of about 140 geographical square miles. These deposits assume a variety of forms, *e.g.*, the *sheet*, a solid mass of ore filling a vertical fissure; this is the most characteristic mode of occurrence, in addition to which other forms are distinguished, such as an *opening*, *a crevice with pocket openings*, *cave openings*, *flat sheets*, and *vertical openings*, in all of which masses of lead ore occur in variously formed fissures in the limestone. The principal ore is a very pure galena, poor in silver, crystallising in cubes; it is accompanied by blende and zinc carbonate and a brown iron ore. The chief deposits of the Missouri district are situated in the counties of Washington, Franklin, and Jefferson. The ore occurs as 'float mineral,' a term applied to describe the mode in which galena is found imbedded in the superficial soil overlying the limestones of Lower Silurian age, in which the ore is found in deposits very similar to those in which it occurs in the Mississippi district. The galena is usually associated with iron and copper pyrites, and at the famous Lamotte mine nickel and cobalt ores are found with it. In Utah and the Western States large and irregular deposits of highly argentiferous lead ore occur.

In Canada galena is found in several localities around Lake Superior, a remarkable vein occurring at Silver Lake, some six miles northward from Thunder Bay, and at 500 feet above Lake Superior. A finely crystallised variety of galena has been found on the East Main coast of Hudson's Bay, in strata similar to those in which it occurs in the Mississippi district.

In Mexico lead ores are found in the mines at Guanaxuato and La Concepcion mine, and lodes containing argentiferous galena, quartz, and calc spar occur in the mining district of Tatatila and Zomelahuacan.

ASSAY OF LEAD ORES.

For the purpose of assaying, lead ores are divided into two classes: first, those containing little or no sulphur or arsenic, of which the carbonate of lead is the most important representative; second, such ores as galena, and those minerals containing arsenic, phosphorus, and sulphur.

Assay of ores of the first class. The easy reduction of oxidised lead compounds by carbon renders the assay of ores of this class a comparatively simple operation. The mineral is first carefully reduced to a fine powder by grinding in an iron mortar, and passing it through a sieve of wire gauze, care being taken to obtain a fair sample.

25 grams of the ground ore are well mixed with 37·5 grams of dry sodium carbonate, and from 2–3 grams of charcoal, according to the richness of the mineral. This is next placed in an earthen crucible, which should not be more than half filled by the mixture, and the top covered by a thin layer of sodium carbonate or of common salt. The crucible and contents are placed in a furnace and carefully heated, so that when the effervescence takes place the mass should not swell up and flow over the sides. The reaction may be checked by withdrawing the crucible from the fire, and regulating the draught by the damper. When the evolution of gas has ceased, the heat, which should not have exceeded a dull redness, is raised to a bright red, and the slags are in this manner so liquefied that the lead easily accumulates and forms a button at the bottom of the crucible. The contents having been brought to a state of complete fusion, the crucible is withdrawn from the furnace and the assay poured into a mould; or, after tapping to collect the lead together, the crucible is set aside to cool. If the operation has been successful, the surface of the slag will be smooth and concave and possess a distinct vitreous lustre. After cooling, the crucible or mould is broken and the button of lead extracted. The button is freed from adhering slag by hammering it out on an anvil, and afterwards washing it with a hard brush; slag not removed by this process can usually be got rid of by treatment with dilute sulphuric acid. If the fusion has not been complete, and consequently the lead not completely separated from the slag, then the slag should be broken up in an iron mortar and the lead separated from it by washing.

Argol may be substituted for charcoal as a reducing agent, and borax (fused) is also recommended as a flux; black flux, which consists of finely divided carbon mixed with carbonate of potassium, is also used. The following table contains proportions in which these different reagents should be employed in assaying ores of this class, and also with certain lead products:

—	Sample	Argol	Charcoal	Sodium carbonate	Borax glass	Salt
I.	200 grains	100	—	300	—	200–250
II.	400 "	200	—	400	200	"
III.	400 "	200	—	400	200	"
IV.	400 "	—	50–60	600	—	"
V.	400 "	200	—	400	—	"
VI.	400 "	600	black flux and a cover of borax		—	"

I., II., and III. are proportions recommended by Mitchell; the first for oxides, carbonates, and cupel products, the second for cupel bottoms and other refractory products, and the third for fumes and silicious slags, &c. IV., V., and VI. are proportions recommended by Phillips; the salt is simply used to cover the mixture.

In some cases ores of this class can be assayed by simply heating the ore in a charcoal-lined crucible, and fusion with potassium cyanide has been recommended by the late Dr. Richardson.

The button of lead obtained by any of the above processes is carefully weighed, and its quality judged by its colour and softness; in some cases it is subjected to a complete examination by the ordinary analytical methods. If the substance contains other metals than lead these will usually be found alloyed with this metal; if zinc be among these metals, but small quantities are found in the lead.

Assay of ores of the second class. The most important ore of this class is galena, which may be treated in several ways. One method consists in carefully roasting a weighed portion of the properly ground ore, and then submitting the roasted ore to one of the processes used for ores of the first class. This method is not to be recommended, as it not only requires considerable care and experience, but does not yield the whole of the lead.

A second method consists in fusion of the ore with from 3 to 4 times its weight of dry sodium carbonate in an earthen crucible; instead of sodium carbonate, potassium carbonate may be used, or black flux; in the latter case the complete fusion of the mixture takes a longer time. The operation results in the production of a button of metallic lead, which is separated from the slag in the manner described above. The amount of lead obtained by this method is from 7-9 p.c. below the lead contained in the galena. In the third method use is made of the fact that when galena is fused with metallic iron, the iron combines with the sulphur, and sulphide of iron is produced and metallic lead. Several modifications of this method have been proposed, differing essentially in the manner in which the metallic iron is used. The oldest mode of procedure consists in mixing the finely divided ore with about 30 p.c. of its weight of finely divided iron, which Phillips recommends to be either in the form of small nails or iron wire cut into small pieces. The mixture is heated in an earthen crucible, its surface being covered with a layer of dry sodium carbonate or borax, when the heating has been continued for a sufficient time to bring the whole to a state of tranquil fusion, the crucible is withdrawn from the furnace and allowed to cool. On breaking the crucible a button is found, apparently of uniform composition, but which when struck with the hammer separates easily into two parts, the one the button of lead, and the second and friable portion, the sulphide of iron. This method yields from pure galena 78 p.c. of metallic lead. The loss is chiefly due to the volatility of the galena.

Instead of the metallic iron being used to desulphurise the whole of the galena, it may be used simply to decompose the sulphide of lead which exists in the slag as a double sulphide, formed by a portion of the galena uniting with the sulphide of the alkali metal produced when galena is fused with sodium carbonate or black flux. The iron should be employed in such a form that the excess may be withdrawn when the reduction is completed. The following is a description of the process as recommended by Mitchell, in the Manual of Assaying:—

Two earthen crucibles are prepared by smearing their insides with ordinary black lead, such as that used for domestic purposes, and in each of these are placed, with their heads downwards, three or four large flooring nails. The ore to be assayed is mixed with its own weight of sodium carbonate, the mixture placed in the crucible and pressed lightly down about the nails. On the top of this, place about half an ounce of common salt, and above it an amount of dried borax equivalent to the weight of the ore operated on. The whole is now introduced into the furnace and gradually raised to redness; at the end of ten minutes the temperature is increased to bright redness, at which it is kept for another ten minutes, when the flux will be well fused, and will present a perfectly smooth surface. When this has taken place, the crucible is removed from the fire, and the nails are separately withdrawn by the use of a small pair of crucible tongs, care being taken to wash each well in the fluid slag until perfectly free from adhering lead. When the nails have been withdrawn the pot is gently tapped, to collect the metal into a button, and then laid aside to cool; after which it is broken, and the button of lead removed and cleaned in the usual way. The result is verified by an assay in the second crucible.

This method when carefully conducted is said to yield with pure galena from 84 to 84·75 p.c. of metallic lead, but according to Phillips it is stated to yield 82 p.c. only, and Percy gives the yield of a similar method as from 82-83 p.c. of metallic lead. The chief objection to the process is the liability of fragments of iron becoming detached and firmly adherent to the button of lead. The fragments of iron are produced by the nails being most energetically attacked at the point of contact between the flux and galena, which, when the slag is fused, occupies the lower part of the crucible.

The most satisfactory manner of employing iron in the assay of galena is to make it the material of which the crucible is constructed. A wrought-iron crucible, such as is required for this purpose, may be made of a piece of half-inch iron plate turned up into the form of a crucible and the edges carefully welded; the bottom is closed by a thick iron rivet, securely welded to the sides, and the whole finished on a suitable mandrel. Or, as it is difficult to insure perfect joints by welding, and corrosion is liable to take place at the joinings, the crucible may be forged from a solid piece of bar-iron by hammering it hot over a core the size of the interior of the crucible. The assay is made by first placing the crucible in the furnace and raising it to a dull red heat, then the mixture of ore and sodium carbonate and borax is introduced by means of a long copper scoop, the crucible having been withdrawn from the furnace for the purpose and then replaced. The mixture of sodium carbonate and borax is made of 1 part of the former to 2 parts of the latter, and the ore is intimately mixed with an equal weight of this mixture. The crucible and contents are gradually raised to a red heat, during which time the mass becomes liquid and a considerable evolution of gas takes place. In some ten or fifteen minutes the mixture will be seen to have become quiescent; the crucible is partially withdrawn from the fire and the contents stirred with an iron rod, all particles adhering to the sides being carefully scraped down to the bottom of the crucible, which is then replaced in the furnace and covered with an earthen lid and heated for three or four minutes to bright redness. The crucible is then withdrawn by strong tongs, and the contents poured into an iron pot or an iron mould. The sides of the crucible are next carefully scraped with a chisel-edged bar of iron, and the adhering slag and lead added to the portion poured into the mould. When cold the contents of the mould are easily removed, and the button of lead separated from the slag, washed and weighed. This process is the one most usually adopted in lead smelting establishments, and with pure galena yields from 84·25 to 85·25 p.c. of lead, the lead being free from iron and perfectly malleable.

Dr. Percy recommends the use of argol, which together with sodium carbonate or borax should be mixed in the following proportions: I. For rich ores, comparatively free from vein stuff. II. For poorer ores.

	I. Grains	II. Grains
Ore . . .	500	500
Sodium carbonate	500	350
Borax . . .	—	150
Argol . . .	50	50

Oxidised lead ores may also be assayed by fusion in an iron crucible; in such cases the ore should be mixed with flux as given in II.

In the assay of galena use may be made of the fact that when galena is heated with nitre, the whole of the sulphur is oxidised before any of the metallic lead; so that by using a suitable proportion of nitre the galena may be completely desulphurised and a button of metallic lead obtained. The assay is conducted by mixing the powdered ore with from 30–35 p.c. of nitre according to the richness of the ore, which should be mixed with twice its weight of sodium carbonate. The fusion is made in an earthen crucible and takes place quietly; the slag does not retain any globules of lead. In using this method care has to be taken to adjust the amount of nitre so as to yield as large a proportion of the lead as possible, an excess of nitre resulting in a loss of the lead by reason of its oxidation, whilst too small a proportion of nitre leads to the loss of the metal, as some of the sulphide of lead is retained by the slag. These facts make the assay of galena by this method unsatisfactory. The method may, however, be employed if the amount of silver alone is to be determined, as then by the use of an excess of nitre the lead only is oxidised, whilst the whole of the silver will be contained in the button obtained.

Welsh method of assaying galena.—The method used at some of the lead works in Wales consists in heating the ore in a wrought iron dish, the cavity of which is some 5″ in diameter and 1″ in depth at the centre, and provided on two sides with a groove, serving as a channel through which the molten lead is poured. The dish is provided with a metal cover slightly larger than the cavity of the dish. The iron of the dish itself serves as the reducing agent. The dish is heated to bright redness on a blacksmith's fire, and then 10 oz. of the ore placed in the cavity of the dish and the cover adjusted. The fire is urged for two minutes, the dish is then withdrawn from the fire and placed on an iron support and the cover taken off. The lead is poured off into an iron ingot mould, the slag and iron sulphide being kept back by a piece of wood held before the groove.

After this first pouring the dish and its contents are replaced on the fire and heated to bright redness; in this way a second amount of lead is obtained and poured and cast as before. The lead from these pourings is carefully weighed. In experienced hands this crude method yields very good results, pure galena yielding from 79–83 p.c. of lead; with poorer ores such good results cannot be obtained.

Influence of various substances on the yield of lead in assaying.

A series of experiments has been made by Dr. Percy on the effect produced by different substances when mixed with galena on the yield of lead, the assay being made in an iron crucible and the ore mixed with fluxes. The presence of silica has a more marked influence than either calcium carbonate or barium sulphate, which is accounted for by the higher temperature required to flux the silica in the first stage of the operation. The loss of lead due to the presence of silica is lessened by the presence of lime or iron oxide.

Silver. In the assay the whole of this metal passes into the lead; the amount of silver is separately determined.

Gold. This metal behaves like silver; the amount is usually extremely small.

Copper. Lead ores sometimes contain copper pyrites, grey copper ore, or copper carbonate. In assaying such ores a portion of the metal passes into the lead and some into the slag.

Zinc. When zinc ores are mixed with lead ores in the assay a portion of the metal is volatilised; a part remains in the slag, whilst but a small quantity passes into the lead.

Arsenic. Arsenate of lead, or arsenical iron pyrites, is sometimes associated with lead ores. On assaying such ores the lead is obtained free from arsenic, as a portion passes off volatilised as arsenic or arsenio sulphide, whilst some of the arsenic unites with iron to form a speiss, easily separable from the lead.

Iron. Present usually in the form of iron pyrites, in assaying, this metal passes into the slag as a sulphide of iron combined with sodium sulphide. The lead is but little affected.

Antimony is usually present in lead ores in the form of sulphide; in assaying such ores a portion of the antimony passes into the lead and a hard lead is the result. The manner of conducting the assay may, however, be so varied that either a pure lead or an alloy of lead and antimony can be produced. To obtain pure lead the ore is fused in an open crucible with three times its weight of sodium carbonate, the lead is then liberated in the metallic state, and the antimony being oxidised unites with the soda and passes into the slag. The separation of the metals is rendered the more complete by the presence of the antimony in the slag, which prevents the slag retaining the lead. In assaying ores containing both antimony and silver, they should be heated with a mixture of sodium carbonate and nitre; the latter serves to oxidise the antimony which is retained in the slag, and an alloy of silver and lead obtained. The nitre should be sufficient to decompose the sulphides completely, an excess results in a loss of lead but does not influence the yield of silver, whilst an insufficient supply of nitre may be attended by a loss of silver, owing to the slag still containing some unreduced antimony sulphide.

The estimation of silver in lead ores.—The method of estimating the amount of silver in lead ores consists first in obtaining the lead by one of the processes described above and then submitting the weighed lead to the operation of cupellation, whereby the lead is removed by oxidation in a heated current of air and the metallic silver which is not affected under these conditions is left. This separation is facilitated by making the *cupels*, the vessels used to contain the lead button, of bone-ash, a material which easily absorbs the lead oxide. The furnace commonly used for this purpose consists of fire-clay tiles held together in a wrought-iron framework of the form represented in figs. 1 and 2. The fireplace is formed of the body of the furnace and has openings into it at *d* and *f* through which the fuel is charged, and below is the ash-pit, provided with a door *a*. The 'muffle' *m* is a small D-shaped retort of fire-clay, closed at one extremity and furnished with openings at the sides to allow of a free circulation of air. The muffle is supported on a shelf at one end, whilst the open end fits into an opening in the body of the furnace provided with a door *d'*. The position of the muffle is such that it is heated on every side by the ignited fuel, and is traversed by a current of air from the opening *d'*. The draught is further increased by the iron chimney *e*, which is provided with a shelf on which the cupels may be placed, and thus dried before use.

The cupels or supports on which the lead is heated are small circular dishes slightly hollowed out and made by compressing bone-earth in a mould formed of an iron ring. The bone-earth for this purpose is first passed through a wire sieve, then mixed with water or a solution of potassium carbonate until sufficiently moistened to retain the marks of the fingers. The apparatus used in making the cupels consists of a mould, which is simply a bevelled steel ring, which is placed over a loosely fitting circular iron plate. The mould is filled with the prepared bone-earth, being first slightly compressed with the hand, and finally with a steel die, which is tightly driven into the ring by a mallet or hammer. The die is then withdrawn and the cupel carefully forced out of the ring by a wooden cylinder. The cupels are set aside to dry, and are then ready for use.

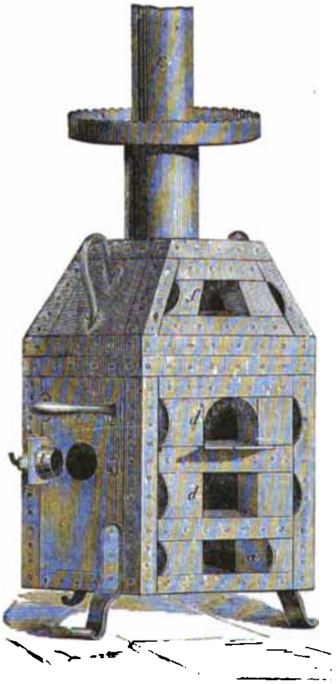


Fig. 1.

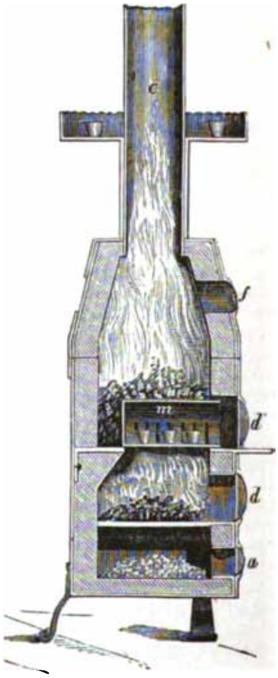


Fig. 2.

In using the apparatus the muffle is first raised to a red heat, and then, after covering the floor of the muffle with a little bone-earth to prevent its corrosion by any lead being spilt on it, six or eight cupels are placed in the muffle, the opening *d'* closed, and the cupels gradually raised to the temperature of the muffle itself. When this is the case, the door is again removed and the weighed buttons of lead placed in the cupels by means of a pair of steel tongs, and the door again replaced. A few minutes suffices to melt the lead, and on opening the door the cupels will be found to contain a bright metallic disc; at this stage the assay is said to be 'uncovered.' The current of air produced by opening the door starts the oxidation of the lead and its conversion into litharge; at the same time a cloud of vapour rises and partially fills the muffle, which either escapes at the opening or passes through the slits in the sides of the muffle. At the same time it will be noted that an annular stain appears on the cupel round the metal, which gradually extends and penetrates into the substance of the cupel, the metallic bead diminishing rapidly. When the oxidation of the lead is almost completed, the bead of metal appears to become agitated by a circular movement, and apparently to revolve with great rapidity. In a short time the movement suddenly ceases, a momentary flash of light is observed, and the bead becomes white. This phenomenon is known as the 'brightening' of the assay, and indicates the completion of the removal of the lead, the cupel containing now a button of silver. The cupel containing the silver is now covered with another kept red-hot for that purpose and then withdrawn, and after remaining on the ledge in front of the muffle for a time sufficient to allow the metal to solidify, the upper cupel is removed, and the globule of silver detached, cleaned, and weighed on a balance turning to ·001 grain. The object of covering the cupel in the manner described is to prevent loss by what is termed the 'vegetation' of the button. This phenomenon is due to the sudden liberation on solidification of the oxygen absorbed by the molten metal, by which the surface of the metal is thrown up into fantastic arborescent forms, and not unfrequently pieces of the metal are projected outwards by this sudden action.

The cupellation is best conducted with the muffle and the cupels at a full blood-red heat, and the vapours rising from the cupel should gradually curl away and be removed by the draught. Too rapid a current of air results in a cooling down of the cupel, and consequent hardening of the litharge round the metal, thus preventing the further oxidation of the lead. If the supply of air is insufficient the assay remains too long in the muffle. When the temperature is too high the cupels are white, the metal they contain can scarcely be seen, and the fume, which is scarcely visible, rises rapidly to the arch of the muffle. With too low a temperature the fumes lie over the bottom of the muffle, and the sides and opening are blackened. Careful attention to the temperature at which the cupellation is performed is required, owing to the fact that silver is sensibly volatile at high temperatures, so that the operation should be performed at the lowest temperature compatible with the absorption of the litharge by the bone-ash.

If the ore contain gold, the whole of this metal is found alloyed with the silver, and its amount may be determined by submitting the silver to the process of parting.

Bismuth may be separated from silver by the same process as lead and copper; tin, antimony, and iron may also be separated from this metal by adding lead sufficient to carry the oxides of these metals into the cupel.

The fuel employed in working a furnace such as that described above is coke or charcoal; furnaces specially built to form part of the structure of the laboratory are frequently used, and there is also a convenient form of assay furnace constructed in which gas is used as fuel.

The amount of silver is, for commercial purposes, estimated in oz., dwts., and grs. per ton of ore. The following table contains the amount of silver per ton of ore, corresponding to the amount obtained from an assay of 400 grs. of the ore:—

400 grains of ore-giving silver	One ton of ore will yield silver			400 grains of ore-giving silver	One ton of ore will yield silver		
grains	oz.	dwts.	grs.	grains	oz.	dwts.	grs.
0·001	—	1	15	0·2	16	6	16
0·002	—	3	6	0·3	24	10	0
0·003	—	4	21	0·4	32	13	8
0·004	—	6	12	0·5	40	16	16
0·005	—	8	4	0·6	49	0	0
0·006	—	9	19	0·7	57	3	8
0·007	—	11	10	0·8	65	6	16
0·008	—	13	1	0·9	73	10	0
0·009	—	14	16	1·0	81	13	8
0·01	—	16	8	2·0	163	6	16
0·02	1	12	16	3·0	245	0	0
0·03	2	9	—	4·0	326	13	8
0·04	3	5	8	5·0	408	6	16
0·05	4	1	16	6·0	490	0	0
0·06	4	18	0	7·0	571	13	8
0·07	5	14	8	8·0	553	6	16
0·08	6	10	16	9·0	735	0	0
0·09	7	7	0	10·0	816	13	8
0·1	8	3	8	—		—	

SMELTING IN REVERBERATORY FURNACES.

The smelting of lead ores, of which galena is the principal one, is carried out either in reverberatory furnaces, blast furnaces, or shallow hearths. The ore is received from the mines dressed and freed as far as possible by mechanical means from the various minerals and gangue material with which it is found associated.

The following are the methods by which the extraction of lead is effected:—

I. *Method of Double Decomposition*, or method by reactions or roast reactions process (Röstreactions Arbeit), or air-reductions process. As the last name implies, air aids in the reduction, and it does so in the following manner.

When galena is roasted at a moderate heat, it is partially converted into the oxide, and a portion is also oxidised to the sulphate; if, after this roasting the temperature be raised, the unaltered galena reacts on the oxide and sulphate of lead formed in the previous stage, and metallic lead is produced, sulphur dioxide being evolved.

These reactions are represented by the following equations:

$$(a)\ \begin{cases} 2PbS + 3O_2 = 2PbO + 2SO_2. \\ PbS + O_2 = PbSO_4. \end{cases}$$

$$(b)\ \begin{cases} PbS + 2PbO = Pb_3 + SO_2. \\ PbS + PbSO_4 = Pb_2 + 2SO_2. \end{cases}$$

II. Method of roasting and subsequent reduction of the oxidised compounds by means of carbonaceous matter (Röstreductions Arbeit).

III. The precipitation process (Niederschlags Arbeit) or method of affinity, in which iron is used to effect the removal of sulphur.

The treatment of a lead ore frequently requires the use of two if not all the above processes.

Smelting in reverberatory furnaces.—The Flintshire process is an example of the method by double decomposition carried out in reverberatory furnaces, which vary somewhat in construction and dimensions.

The following is a description given by Phillips of a *Flintshire furnace.*

The length of the hearth is usually about 11 feet, and its width 9 feet, and under this is an arched vault, extending the whole length of the bed to the fire-bridge. The hearth is made of slag, moulded into the proper form when in a plastic and semi-fluid state. Towards the centre of the hearth is a depression in which the fused metal accumulates, and at the bottom of which is situate the tap-hole. The fireplace is at one end, and before reaching the cavity of the furnace the flame has to pass over a fire-bridge about 2 feet in width, and from 12 to 14 inches below the arch. At the opposite extremity of the hearth are openings communicating with the flue in connection with a lofty chimney. The fuel is supplied through a door at one end of the fireplace, in addition to which the furnace is furnished with six working doors, about 9 inches by 12, protected by heavy cast-iron frames built into the brickwork and closed by iron plates, which can be easily removed when required. The bottom of this furnace is made nearly level with the doors on one of the sides, but is inclined towards the other in such a way as to be from 18 to 20 inches below the middle door, where it communicates with the tap-hole, beneath which a cast-iron tapping-pot is set in the ground. In the top of the furnace is a hopper, from which a fresh charge of ore is let down as soon as that which is being worked is withdrawn.

In working this process, the charge (consisting of 21 cwt. in N. Wales, and from 12-14 cwt. in the north of England) is let down into the furnace, which is still hot from a previous working, and is spread evenly over the surface of the bed of the furnace, care being taken to prevent it dropping into the depression in the furnace-bed or well. During the first hour and a half the charge is frequently stirred, and the supply of air carefully regulated by opening the various doors, the temperature being kept sufficiently high to insure the oxidation of a portion of the galena, but at the same time not high enough to cause the charge to melt. It is during this period of calcination that the lead sulphide is in part converted into lead oxide and lead sulphate. At the end of this period the doors are closed, the fire is made up, then the temperature is raised to bright redness, and maintained at this point for about twenty-five minutes. This rise in temperature causes the charge to become plastic, and a reaction takes place between the unaltered galena and the oxy-compounds of lead, by which lead is produced, and the metal runs down into the well in the bed of the furnace. At the end of this period the doors are opened to cool the furnace and the charge, which, when it has become as pasty as ordinary mortar, is pushed back from the well and spread over the higher part of the bed. The doors are again closed and the temperature raised by addition of fresh fuel; in this way the charge is rapidly run down into the depression in the furnace, and when this is accomplished some slaked lime is thrown on to the surface and, by means of a rake, thoroughly mixed up with the charge. Thus the slags and unreduced ore are cooled and rendered sufficiently pasty to allow of their again being removed and spread over the higher portions of the furnace bed, where they are again calcined as in the first operation. This calcination lasts about half an hour. At the end of this stage the temperature is again raised, and the whole charge is melted down into the well. During this stage it is not infrequent to throw a little coal slack on to the charge. When the charge has in this way collected in the well, some slaked lime is thrown on to it, and the slags pushed back on to the sloping side of the furnace and allowed to drain. The lead which has collected in the well is now tapped, and the slags, technically known as *grey* slags, are withdrawn in pasty lumps through the doors at the back of the furnace. The surface of the metal in the tapping pot is covered by slags and matts, which retain mechanically a considerable proportion of metallic lead, the separation of which is effected by stirring with a paddle and throwing on to the surface some coal slack, and this is well worked up with the molten metal. A considerable evolution of gas takes place, this is ignited, and the heat produced suffices to melt and liberate the metal confined in the slag. The slag is then skimmed off, thrown into the furnace, and the lead ladled out into cast-iron moulds.

Before introducing another charge, the tap-hole is opened to allow the lead produced from the slag and skimmings to run into the metal pot, where it remains until the next charge is run off. The tap-hole is again closed, and another charge of ore dropped into the furnace from the hopper.

This process may, therefore, be summarised as follows:—

(1) Calcination of the ore at a low heat, whereby a certain amount of lead sulphide is converted into lead oxide and lead sulphate.

(2) Melting down of the charge, during which the unaltered lead sulphide reacts upon the oxidised products and a separation of lead occurs.

(3) The admixture of lime with the molten charge and the 'setting up' of the slags, a further separation of lead from the interaction of the sulphide and the oxy- compounds of lead, and the production of an excess of lead oxide and lead sulphate over the lead sulphide present.

(4) The tapping of the metal which has accumulated during the operation, and the drawing of the slags in a pasty condition.

In Flintshire the ores smelted by this method yield 75–80 p.c. of lead by the dry assay, and of this 90 p.c. is obtained by smelting in reverberatory furnaces, the remaining 10 p.c. being obtained by subsequent treatment of the slags (of which about 4 cwt. per charge is produced) and fume. The time required for the working of the charge is from five to six hours.

In some cases, in Flintshire, another process of extraction is used, similar to that employed at one time in Cornwall. The mode of treatment consists of two operations:

(1) Calcination of the ore.
(2) Melting down of the calcined ore.

Each operation is effected in a distinct furnace. The method is a combination of all the different processes for the extraction of lead, utilising

(1) The air reduction process,
(2) The desulphurisation of galena by iron,
(3) The reduction of oxidised lead compounds by carbonaceous fuel.

The ore treated in Cornwall consisted principally of galena associated with blende and sulphurised copper ores, and also a silicious gangue. Furthermore, it contained a considerable amount of silver. These ores yielded on an average 60 to 70 p.c. of lead containing about 35 ounces of silver to the ton.

The first operation, or calcination, was performed in a reverberatory furnace having three working doors, one on either side of the furnace, and the third on the side opposite the fire-bridge, and smaller than the others. Below the bed of the furnace was an arched chamber, into which the calcined ore was raked through holes in the bed opposite each of the lateral working doors. The furnace was built of ordinary rubble-work, lined internally with nine inches of fire-brick. The doors were hung in a cast-iron framework, or had the sides protected by slabs of granite. The charge was introduced through a hole in the roof merely closed by a slab. The charge varied from 25 cwt. to 3 tons, but usually consisted of about 1 ton 18 cwt. to 2 tons, and was spread over the furnace bed and calcined at a high temperature, regulated so as to prevent clotting. The operation lasted from fifteen to eighteen hours, the charge being raked over every hour, and at the end was raked through the holes in the furnace bed into the vault below, from whence it is conveyed into the flowing or melting furnace, which is very similar to the Flintshire furnace.

This furnace had five working doors, two pairs on either side, and the fifth on the side opposite the fire bridge, as in the calcining process. Near one of the lateral working doors the hearth sloped to the one near the bridge, where the tap-hole is placed, from which the metal &c. ran into an iron pot placed outside the furnace, near to which was a small pit to receive the regulus or slurry. The metal pot was also provided with a channel to convey away the slag.

The charge for such a furnace consisted of two tons of calcined ore, and was brought into the furnace through the back working doors. The charge was first spread over the sloping hearth, the doors closed, and the temperature raised until the charge was melted down, requiring some two or three hours.

In some cases, as with pure ores, the lead produced in this stage was tapped off, but more usually the charge was mixed with lime and culm (anthracite coal) and set up on the higher part of the furnace bed.

In some cases fluorspar was used as a flux, and 1 or 2 cwt. of scrap iron was added to assist in the decomposition of the lead sulphide.

The doors were again closed and luted, and the charge melted down. The furnace was then tapped, and the molten metal flowed into the metal pot, followed by the regulus or slurry, consisting chiefly of iron sulphide and containing the principal proportion of the copper. The regulus ran over from the metal pot into the pit below, and after a time the slag began to make its appearance; the lip of the pot is then stopped with ashes, and the flow of the slag directed along the channel by which it was conveyed out of the building.

The whole operation of melting, from the time of introducing the charge to the tapping of the metal, took about eight hours. The slag was generally sufficiently free from lead not to require subsequent treatment. The regulus was treated for the lead and silver it contains, and then when sufficiently rich in copper sold to the copper smelter.

In calcination 6 cwt. of coal were required for every ton of ore, the melting down requiring about 8 or 9 cwt. The lead obtained was usually hard, and required softening at a high temperature to remove the antimony which it contained.

A modification of the Flintshire process is used in France, the following description of which, as practised at Couëron, is taken from the late Mr. Phillips's account given in his Elements of Metallurgy:—

The construction of the furnaces at Couëron, Loire Inférieure, France, will be readily understood by reference to the accompanying woodcuts.

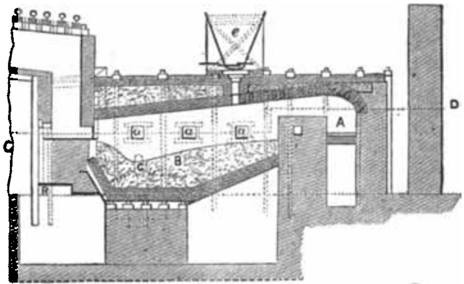


Fig. 3.

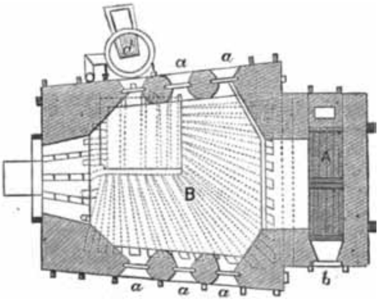


Fig. 4.

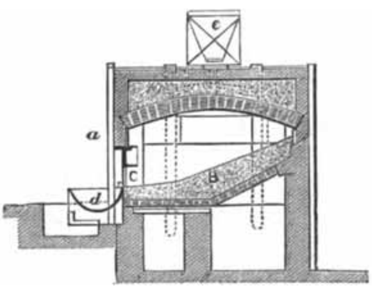


Fig. 5.

Fig. 3 is a longitudinal section.

Fig. 4 is a horizontal section on the line CD.

Fig. 5 is a transverse section through the tapping-hole.

The fireplace A is of the usual dimensions, and the hearth B, instead of being on an arch, as is commonly the case in North Wales, is supported on iron bars, on which is laid a course of flat tiles. On these is placed a course of fire-bricks on edge, on which is arranged the usual slag bottom. The furnace has the ordinary number of working doors, *a*, with a fire-door *b*, and a tapping-hole *c*; there is a small fireplace below the pot *d*, to prevent the too rapid chilling of the lead during the process of ladling into moulds.

Although similar in form and dimensions to the ordinary Welsh furnace, it differs from it in one important particular, namely, in having the tapping-pot placed near the flue end instead of under the middle door.

This arrangement gives a larger surface to the hearth for roasting the charge, and permits of the lead being collected in the coolest part of the furnace, where it is least exposed to loss from volatilisation.

The mode of working varies with the nature and composition of the ores treated. This variation depends principally on the length of time required for roasting the ores before subjecting them to the higher temperature of reactions. Pure ores, especially those containing a notable proportion of carbonate or sulphate of lead, require very little previous roasting, whilst those containing blende, pyrites, &c., must be calcined for a considerable time before smelting.

In general the ores treated are derived from Sardinia, and contain on an average about 81 p.c. of lead, and but little silver. They are tolerably free from impurities, being composed of galena associated with carbonate and sulphate of lead, and a calcareous gangue, in which are found small quantities of blende, calamine, ferric oxide, and silica. The cobbed ores, before delivery to the furnace, are ground between rollers and passed through sieves of eight holes to the linear inch. A charge of ore weighs 27 cwt.

Two men are employed at each furnace, one of whom, the chief, works on the fore-side and takes a leading part in the work to be done.

In the treatment of rich ores the ordinary method of working consists in roasting them in such a manner that more than one half of the sulphide of lead present in the ore is converted into a mixture of oxide and sulphate. On raising the heat of the furnace to bright redness the oxide and sulphate formed in roasting react on the undecomposed sulphide in the charge, producing metallic lead, sulphurous anhydride, and a residue of slag.

The process is thus divisible into two well-marked and distinct operations:

I. Calcination or oxidation.

II. Smelting or reduction.

I. *Calcination.*—Supposing a charge to have been just worked off and the residual slags withdrawn, the furnace will be empty and at a red heat. The damper having been lowered, the charge of ore in the hopper, *e*, is let down through the opening in the arch, and spread evenly over the furnace bottom by means of rabbles. This done, the working-doors are closed, but the fire-door is left open and the fire damped with cinders, in order so to moderate the heat that the charge may become red-hot without clotting. The charge is thus left undisturbed for some time. During the first hour it is once or twice lightly rabbled; at the expiration of that time, after being well turned with the paddle, it will be found to be red-hot throughout. The damper is then lowered so as to leave just sufficient draught for the free escape of the gaseous products of calcination. The working-doors are now left partially open to admit the air necessary for the oxidation of the galena, and under its oxidising action the charge soon acquires a high temperature. Care must, however, be taken to prevent the heat from increasing so much as to cause softening of the ore. When the heat is properly controlled a white crust, consisting of a mixture of oxide and sulphate of lead, in which the former predominates, is rapidly formed on the surface of the charge, and no fumes are visible.

The surface is renewed from time to time, about every quarter of an hour, either by rabbling or by paddling. The requisite heat is maintained in the furnace during this process by firing with cinders only, which are preferable to coal for that purpose, not merely on account of their lower value, but also because they give a steadier heat and do not yield gaseous hydrocarbons to interfere with the oxidation.

The alternate raking and paddling of the charge is continued at regular intervals, until on examination, it is thought to be sufficiently desulphurised, which is generally the case at the end of from four to four and a half hours.

The grate is then freed from clinker, coal is thrown on the fire, the damper is opened, and a brisk fire is got up; thus in a few minutes the heat in the furnace is so raised as to lead to a *commencement of the reactions period.*

II. *Smelting.*—As soon as the firing has commenced, the ore lying at the back and extreme end of the furnace is raked towards the bridge. With the increase of temperature which now takes place, the roasted ore soon begins to soften and to give off white fumes, thus showing that the reactions which result in the liberation of metallic lead have commenced. Great care and attention on the part of the smelter are, however, necessary, in order to prevent too great a loss of lead by volatilisation during the heating up of the charge. The ore must on no account be allowed to liquefy, and as often as it shows a tendency to fuse, some slaked lime in powder is thrown on the charge and well worked into it with a rake. By this means, and by carefully regulating the draught, the charge can be heated to the required temperature without fusion. Lime must be frequently added during the process, but in small quantities at a time. The consumption of lime amounts altogether to about 2 p.c. of the ore treated.

Shortly after the reactions commence globules of lead may be seen on the surface of the charge, and before an hour has elapsed a certain quantity of lead has drained down the slope of the hearth into the well. The charge, having in due time attained the temperature of bright redness, it must not be fired too hard, therefore both the draught and the firing are so regulated that the heat is kept at the requisite degree without going beyond it.

The reactions are much aided by frequently rabbling and turning the ore; but as the working doors must remain open for this purpose it follows that a large quantity of air enters the furnace, thus oxidising the sulphide in the ore, and so cooling the charge that the flow of lead becomes interrupted. When the cooling is judged to have been carried sufficiently far, the charge is rabbled, the doors closed, and the fire so urged as to fill the furnace with flame during several minutes; then, on re-opening the doors and paddling, the flow of lead recommences as before.

At the expiration of from two and a half to three hours from the commencement of the reactions, a considerable amount of lead will have accumulated in the well. A first tapping is then made, the lead being received in the tapping-pot, under which a small fire has been previously lighted in order to warm it, and to maintain the lead in a melted condition; the tap-hole is stopped with a plug of stiff clay.

The thick dross which rises to the surface of the lead, and which contains a certain quantity of sulphide removed from the charge by the hot lead and again separated on cooling, is skimmed off with a shovel and put back into the furnace. A little fine coal, together with some burning cinders and lime, is now thrown on the lead, which is vigorously agitated with a small paddle and stirred until it is clean. It is then skimmed, the skimmings being put on one side and the clean lead ladled into moulds.

The firing, paddling, and cooling of the charge are repeated several times, until at last the residue becomes dry and gives out but little lead. Thereupon the heat in the furnace is considerably increased, but not in a degree to fuse or flow down the charge, and towards the close of the operation the matters remaining on the hearth consist to a great extent of oxides.

The pot skimmings, composed of cinders and lead matt, are now thrown into the furnace and well paddled with the charge, the reaction of the sulphide of lead and cinders on the oxide and sulphate producing a further yield of lead. When this has ceased and it is seen that no more can be extracted without a very high heat and the addition of coal to the charge, the grey slag is raked through the middle door at the back of the furnace, and the second and last tapping is made.

The whole period of reactions occupies from 5 to 5½ hours. After the withdrawal of the slags, the bottom is examined, and if it is corroded into holes, or in any way injured, is repaired by putting into the cavities a mixture of grey slag and lime and beating it smooth with the paddle. It is of great importance to maintain the bottom perfectly smooth and with a good slope on all sides towards the tap-hole. A little lime is now spread over the bottom, and a fresh charge is at once let down into the furnace; the damper having previously been lowered to prevent loss of fine ore by the draught. The weight of coal consumed is equal to 40 p.c. of the ore smelted. The produce of lead per charge of 1,350 kilos. of ore (at 81 p.c. of lead) is 15 pigs weighing 901 kilos. and 290 kilos. of slags containing 50 p.c. of lead. Hence the total loss of lead in the reverberatory furnace is 3·52 p.c. by volatilisation, but of this a certain proportion is recovered from the fume collected in the condensers and flues. A larger percentage of lead in pigs might be obtained by adding more coal to the charge towards the end of the process and firing hard, in order to reduce part of the lead left in the slags. It is, however, considered more economical to limit the production in the reverberatory to about 80 p.c. of the lead contained, and to carry the richer slags to the blast furnace. This is especially the case when the blast furnace is connected with good condensers and long flues.

It will be seen from the foregoing description that the process of reverberatory smelting adopted at Couëron differs principally from that generally employed in England, in there being (1) no melting or flowing down of the charge; (2) the long preliminary calcination of the ore before commencing the reactions.

The position of the tap-hole near the flue end of the furnace gives a longer slope to the hearth, and allows of heavier charges being worked; at the same time the lead produced is collected in the well at a greater distance from the fire.

Spanish furnace or boliche.

In the south of Spain the smelting of lead ores has been carried on for many centuries in a form of furnace known as the *boliche*. It consists of two chambers, separated from one another by a fire-bridge. One of these only is used for the reduction of the ore, and the second, which is situated between the first and the chimney, serves apparently to moderate the draught.

The fireplace projects from one side of the hearth, and is without a grate; the fuel, consisting of wood, is supplied through a door at the end of the fireplace.

The smelting hearth inclines towards the working door, situated at the end of the longer axis, immediately within which is a receptacle in the floor for the collection of the metal.

The boliche is constructed of rubble work, cemented together by clay and strengthened by buttresses built at the angles.

The interior is lined with fire-brick, the lining for the hearth consisting of a species of clay resulting from the decomposition of talcose schists, known as 'laja' or 'laguena,' or of a mixture of this clay with broken galena.

The English firms smelting lead ores in the Linares district use a boliche constructed of sandstone and without any special lining, the sandstone being bound together by means of iron braces.

The method of smelting is in principle similar to the Flintshire process, and the process is divided into three operations:

1. *Caldeo*, or calcination, occupying from 1 to 1½ hours.
2. *Blandeo*, or sweating, lasting from 4 to 4½ hours.
3. *Corrida*, or running down, occupying the remainder of the shift, *i.e.* from 2 to 3 hours.

The ore thrown into the furnace through the working door is first spread evenly over the surface of the hearth and then calcined. When the calcination is completed the temperature is raised and the running down of the charge begun. The slags are dried up after the completion of the melting down by throwing into the furnace the ash and breeze from the ashpit. The metal is tapped into a vessel, in which it is stirred with dry leaves, and finally ladled into moulds.

The yield of the boliche is about 80 p.c. of the lead of the ore as given by the dry assay. The grey slags contain from 45 to 50 p.c. of lead and represent 15 to 17 p.c. of the charge. These slags are subsequently treated in a blast furnace. The charge of a boliche consists of 60 arrobas, or 13 cwt. 1 qr. 16 lbs., and requires for its reduction 1,550 to 1,750 lbs. of brushwood. It is stated that the lead obtained by using the boliche is softer than that produced in the Flintshire furnace, but Mr. Phillips states that the difference in quality is not very marked. The difference is supposed to be due to the fact that in the boliche the smelting is effected at a much lower temperature. At Linares boliches have been built so as to burn a mineral fuel, but the result of working has in no way shown this form of furnace to be superior to the English reverberatory furnace.

Bleiberg process.—At Bleiberg in Carinthia, reverberatory furnaces of a special construction are used, two being usually built side by side and arranged to work into one chimney.

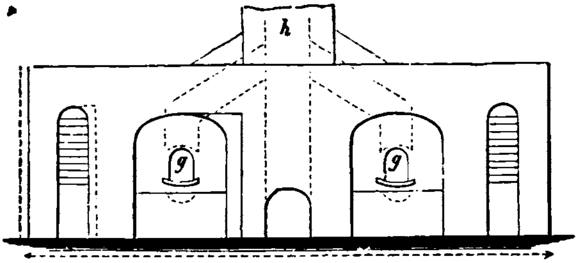


FIG. 6.

Fig. 6 represents a front elevation, and fig. 7 a horizontal section. The hearth is about 10 feet long, and at the back near the fire is about 4 feet 10 inches wide. This width is maintained for about half the length of the furnace, when it is gradually reduced, until at the working door it is about a foot wide. The hearth is sloped from the back and also from the two longer sides, thus forming a depression in which the metal may collect and flow into the metal pot, *a*, in front of the working door, *g*.

The hearth is formed of a lower layer of beaten clay and an upper one of fused slags, having a united thickness of about 6 inches. The fireplaces, P, P, P, are built parallel to the longer axis of the furnace, and separated from the latter by a fire-bridge. The products of combustion pass into the chimney, *h*, by a flue above the working door. The grate is of stone, having a greater inclination than the hearth, and is traversed by openings for the admission of air.

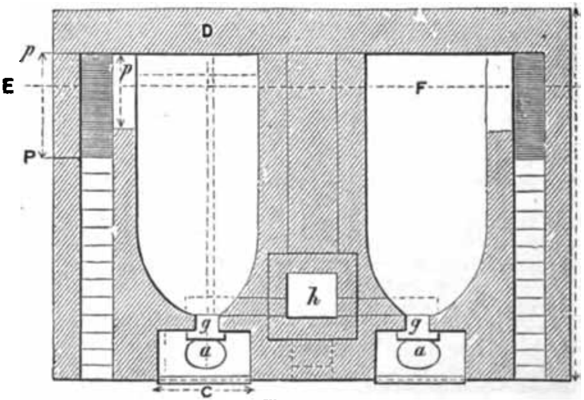


FIG. 7.

The fuel employed is wood, but in some cases brown coal is used, and then the stone grate is replaced by one with iron bars.

The galena smelted at Bleiberg is associated with cerussite, anglesite, and molybdate of lead, also with zinc blende, calamine, and willemite. The zinc ores are separated mechanically and treated for zinc. The lead ores are delivered to the smelter either in the rough state or in the form of slimes. In the former state on assaying they yield from 65-70 p.c. of lead, in the latter from 60-65 p.c.

In smelting, a charge of 375 lbs. of ore is thrown into the furnace through the working door and spread over the hearth. This is calcined at a temperature low enough to prevent the softening of the charge—the calcination occupying three to four hours—the charge being raked over at intervals. The temperature is next raised to bring about the usual reaction between the oxy- compounds and the unaltered galena, the charge being carefully rabbled to promote a thorough admixture, and thus aid the reactions. This operation lasts from three to four and a half hours, the metal produced constantly flowing into the depression, and thence to the metal pot. At the end of this operation the slags are dried up by the addition of ashes and breeze, and then withdrawn from the furnace. The lead produced from the ore in this way, amounting from 125 to 150 lbs., is supposed to be specially pure, and is known as '*Jungfernblei*,' or 'virgin lead.' After the withdrawal of the slags a second charge of ore is treated, the slags produced being left in the furnace, and to them the slags from the previous smelting are added. These slags are free from sulphide and contain lead in an oxidised state only. The temperature is raised and charcoal added, the whole being intimately mixed with the rabble. The oxidised lead compounds are in this way reduced in from seven to eight hours, about 150 lbs. of lead being produced.

The complete working of the two charges will occupy from twenty-one to twenty-three hours, the yield of lead being usually about 2½ p.c. below that obtained in the dry assay.

Smelting galena with iron in reverberatory furnaces.—A method depending on the 'process of affinity' was at one time used in France in the reduction of a silicious Spanish galena. The furnace used was constructed with a hearth sloping from the fire-bridge to the working door. In front of the furnace, below the working door, is the tap-hole, in front of which is the metal pot for receiving the metal. Above the working door is a flue communicating with a chimney for the removal of the products of combustion &c., the fireplace being at the end of the furnace opposite the door. The method of working consisted in introducing a charge of some 800 lbs. of galena, to which was added some 200 lbs. of scrap iron; the mixture was then heated and stirred from time to time, the galena in this way being reduced by the iron, lead and sulphide of iron are produced. The contents of the furnace are, at the end of the operation, run into the tapping-pot, in which the lead collects, and the matt and slag are allowed to flow over on to the floor. Both the matt and slag contain lead, for which they are subsequently treated in a blast furnace.

Galena containing 80 p.c. of lead yielded by this method from 67–70 p.c. of metal, the matt contained from 5–12 p.c. of lead, and from 4–5 p.c. are found in the slag, whilst 4 p.c. would be volatilised. This method of reduction of raw galena with iron in reverberatory furnaces is stated to be wasteful and expensive.

Smelting in Cupolas or Blast Furnaces.

Cupolas or blast furnaces are employed not only for the reduction of slags obtained in the smelting conducted in reverberatory furnaces, and of the various drosses produced in the purification and desilverising of lead, but also for the smelting of ores which by reason of the minerals associated with them and their poverty in lead are unsuited for treatment in reverberatory furnaces. This reduction is effected either by a treatment of the raw ore in the blast furnace, or by submitting the ore to a preliminary roasting and subsequently smelting it in a blast furnace.

In the treatment of raw ores the reducing agent is iron, which is added to the charge either in the form of metallic iron, as was at one time practised at Clausthal, or the iron is replaced by the basic silicates of iron, obtained as slags in refining and puddling of iron, or from copper smelting. In some cases the iron required is added in the form of iron ores. The fuel usually employed is coke. This mode of smelting of raw ores is dependent on the decomposition of lead sulphide by metallic iron yielding metallic lead and iron sulphide. When basic silicates of iron or other iron compounds are used, the iron required for the reduction is obtained by the reduction of these compounds by the carbon of the fuel or the carbon monoxide produced by its combustion. The iron sulphide formed unites with some lead sulphide and the sulphides of other metals, such as copper and silver, present in the ores, forming a fusible matt or regulus, which being lighter than lead collects above the metal in the hearth of the furnace, and is tapped out with the metal, from which it is easily separated. Some of the sulphide of copper in the ore is reduced to metallic copper, and this alloys with the lead, as also does the silver which may have been reduced by iron and lead.

Antimony and arsenic sulphides, if present, are reduced by the metallic iron, the metals combining with the lead, or being in part volatilised and thus occasioning a loss of lead. As will be seen, these sulphides must also lead to an increased consumption of iron, and also a greater yield of matt. In addition to lead and matt, a fusible slag is formed, which consists chiefly of a silicate of iron and contains lead, which is recovered from it by re-smelting in the blast furnace with another charge of ore. This is repeated until the amount of lead present is sufficiently reduced to allow of its being thrown away.

From the matts produced as described, a further amount of lead is obtained by roasting the matt and smelting the roasted matt in a small cupola, an operation which produces, in addition to lead, a second matt and slag. A similar treatment of the second matt may, as at Clausthal and Freiberg, yield a further quantity of lead, and a matt in which, where lead ores associated with copper are smelted, the copper is sufficiently concentrated to serve for the extraction of the copper. The reduction of lead ores in blast furnaces is more usually preceded by a roasting of the ore, conducted as a rule in reverberatory furnaces, and in this manner the whole of the galena is converted into oxide and some sulphate, and finally the roasted ore is heated to a temperature sufficiently high to effect a partial fusion or render the mass of roasted material pasty. In this latter stage a portion of the lead oxide reacts with the silica associated with the ore, producing a silicate of lead. The roasted ore is next passed on to the blast furnace, where it is smelted with coke and suitable fluxes into the composition of which iron, either as metallic iron or as a basic silicate, enters. In some instances the iron compounds required for the decomposition in the blast furnace are supplied by the iron ores associated in the first instance with the lead ores. This is the case in the smelting as conducted at Freiberg. In the melting down in the blast furnace the oxy- compounds of lead are reduced in part by the carbonaceous fuel, but chiefly by the iron, which in presence of carbonaceous matter is able to decompose the lead silicates. The product of this smelting should consist of lead, containing the greater portion of the silver present in the ore, and a slag consisting essentially of silicates of iron, lime, alumina, and magnesia and not more than 3 p.c. of lead. Highly silicious lead ores are smelted at Pontgibaud in this manner, the roasted ore being treated with a mixture of scrap iron, limestone, and lead slags in a blast furnace. At Couëron, the silicious ores are roasted and smelted in a blast furnace together with the grey slags produced in the smelting richer ores in reverberatory furnaces in the manner already described, to which are added agglomerated fume and iron slags. When the calcination of the ore is complete and the sulphur entirely removed by oxidation, the products of the subsequent smelting in the blast furnace consist of lead and slag only, but otherwise a matt or regulus is formed in addition, as at Freiberg. The matts produced are treated in a manner similar to that already mentioned, being first roasted and subsequently smelted in a special cupola, or are returned, after roasting, to the blast furnace and smelted with a fresh charge of ore.

Various forms of blast furnaces have been used in different lead-smelting districts for the reduction of lead ores. The older forms of furnace, such as used at Clausthal and Freiberg, and the Castilian furnace used for the smelting of Spanish slags and introduced into this country for the treatment of slags, have been replaced in late years by furnaces of newer construction; such as the Rachette furnace, the horizontal section of which is rectangular, with two long sides and two shorter. In each of the longer sides are placed three or more twyers, and there is a single twyer in each of the two shorter sides; the hearth is provided with a tap-hole on each of the narrow sides. The hearth bottom slopes downwards toward each narrow end. Water twyers similar to those used in iron-smelting are also used. Another of the improved forms is the Pilz furnace, which is cylindrical in form, wider at the top than the bottom, with a circular or octagonal section inside and supplied with from five to eight twyers. These furnaces are charged from the top, the gases being drawn off either by a vertical pipe leading to condensing flues, or by a lateral one. These furnaces have been further improved by replacing the brickwork in the hottest part of the furnaces by an annular cylinder of iron, provided with apertures for the twyers and an opening through which the slag flows. The sides of the cylinder are kept cool by a constant stream of water circulating through it. Blast furnaces provided with water-jackets are in use at Freiberg, at Couëron and Pontgibaud (*v.* Phillips, Elements of Metallurgy), and at Lead ville the Rachette furnaces used there are provided with this arrangement. Water-jacketed furnaces for smelting lead ores and also for smelting slags have been erected in this country by Mr. W. Maynard Hutchings.

Smelting of lead ores at Clausthal.—As an example of the practice of the 'iron precipitation' process, the treatment adopted at Clausthal may be cited, for a more detailed account of which the reader is referred to a series of papers by J. Clark Jefferson, A.R.S.M., in Engineering, vols. 24 and 25, from which the following account is taken.

The ores smelted at Clausthal consist of an argentiferous galena, associated with copper pyrites, fahlore, bournonite, zinc blende, spathic iron ore, iron pyrites, brown spar, quartz, calc spar, heavy spar, clay-slate, and greywacke. The minerals are first submitted to mechanical treatment and supplied to the smelter in the form of *schlieg*, of which the following may be regarded as representing the average composition:

Lead . . .	50·7	to	73·6	per cent.[1]
Silver . . .	0·555	,,	0·185	,,
Copper . . .	0·02	,,	0·6	,,
Zinc . . .	0·3	,,	4·1	,,
Antimony . .	0·02	,,	0·3	,,
Iron . . .	0·4	,,	3·7	,,
Sulphur . .	8·5	,,	14·2	,,
Alumina . .	0·07	,,	1·5	,,
Lime . . .	0·2	,,	1·4	,,
Insoluble residue .	5·9	,,	32·4	,,

The old method of smelting practised at Clausthal consisted in reducing the *schlieg* by fusion with metallic iron and coke in a blast furnace 20 to 25 feet high and 3 feet square in the widest part. The form of furnace has gradually been altered, as also the method of treating the ores; the chief change in this latter has been the replacement of the iron by the iron silicates obtained from the copper works in the Lower Harz, and also the use of the iron residues left by the extraction of copper from burnt pyrites by the wet method. In respect to furnace development it will be sufficient to describe the later model of furnace used, which is the third form in use at Clausthal, the construction of which will be understood from the accompanying diagram.

Fig. 8 is a front elevation; fig. 9, sectional elevation; and figs. 10, 11, 12, and 13, horizontal sections. *a*, is shaft of the furnace; *b*, iron charging funnel; *c*, waste gas pipe; *d*, blast main; *e*, four vertical blast pipes; *f*, socket blast pipes; *g*, four water twyers; *h*, flue to condensing chamber; *i*, sheet-iron casing; *j*, bearers carrying sheet iron casing; *k*, iron tapping hearth; *l*, fore hearth; *m*, breast stone; *n*, iron column for supporting the bearers; *j*, *o*, copper piping to convey water to the twyers; *p*, outlet water pipe from the twyers; *q*, cast-iron cistern for water from the twyers; *r*, perforated sheet boxes to prevent a stopping up of the pipe *p*; *s*, cast-iron foundation cylinder; and *t*, slag gutter.

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[1] Kerl. Grundriss der Metallhüttenkunde, p. 60.

The furnace is built on a cast-iron foundation plate 1·5 inches thick; on this rests the main wall, which is 4 feet high, 4 feet 2 inches inside, and 7 feet 2 inches outside diameter. The space inside this brick wall is filled to a height of about 2 feet 3 inches with slag bricks, on the top of which is a layer of clay 1 foot in thickness, and this again covered flush with the top of the main wall with brick. In the centre and forming the bottom of the hearth is a slab of fire sandstone 16 inches thick. The shaft of the furnace built on this foundation is for a height of 7 feet built of fire-brick, and the remainder, 10 feet, is built of ordinary brick, the thickness being that of two bricks throughout the whole height. As will be seen, the section of

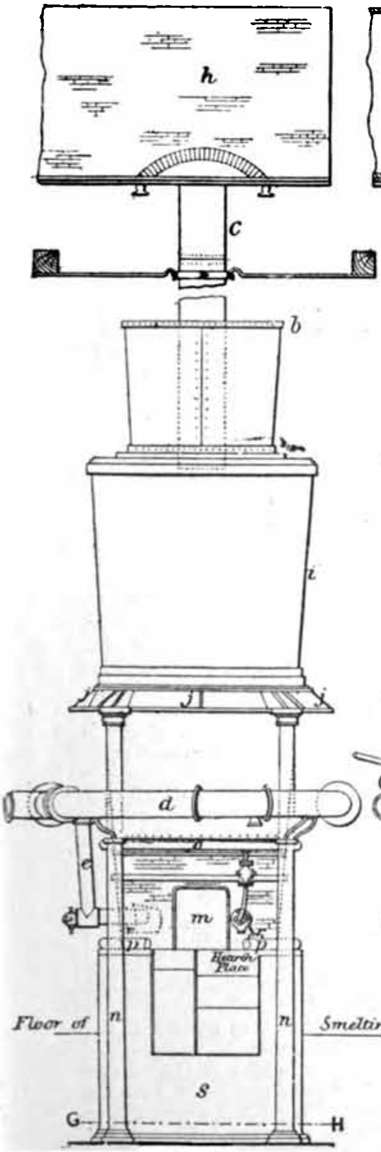


FIG. 8.

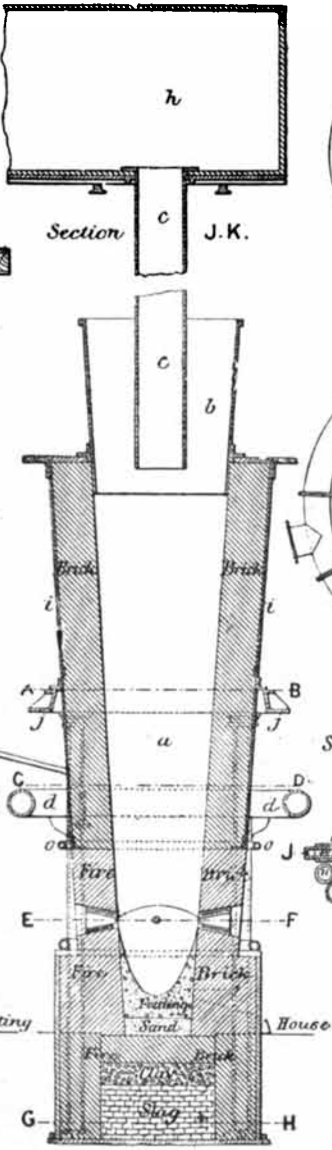


FIG. 9.

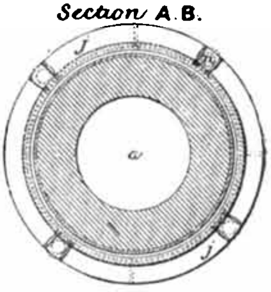


FIG. 10.

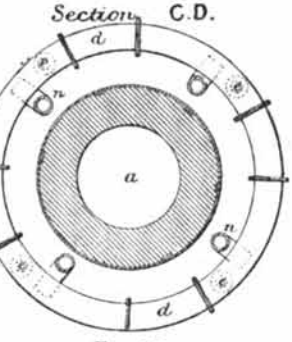


FIG. 11.

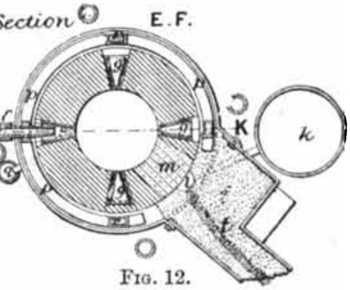


FIG. 12.

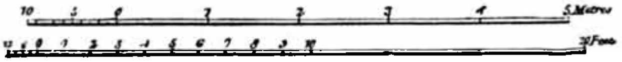


FIG. 13.

the furnace gradually enlarges; its diameter at the hearth is 3 feet, and 5 feet at the extreme upper end. The height of the furnace is about 25 feet to the charging opening, and 21 feet 6 inches to the top of the boshes. The furnace bottom is made of clay and coal dust, resting on the slab of sandstone, and hollowed out as shown in fig. 9. The four twyers are symmetrically arranged some 30 inches from centre to centre; the diameter of the circular blast main is 60 inches.

The materials smelted in these furnaces consist of ore in the form of *schlieg*, lime, roasted lead matt, slags obtained in smelting ore, and schlieg, as also a proportion of slags obtained from the smelting of regulus, together with slags obtained in smelting copper pyrites at Oker, known as Oker slags, or the residue left in the wet extraction of these copper ores. These two last-named materials supply the iron required for the reduction of the lead ore, the former in the form of silicate of iron, and the latter containing iron in the form of the sesquioxide. The following analyses give the composition of these materials; I. of Oker slags (Hampe, 1874), II. of the residue obtained from the wet extraction method.

	I.		II.
SiO_2	21·87	SiO_2	5·30
Al_2O_3	4·95	PbO	2·06
FeO	54·99	CuO	2·19
CaO	0·11	Sb_2O_3	0·15
MgO	3·09	Fe_2O_3	77·77
CuO	3·71	Al_2O_3	3·74
MnO	2·34	ZnO	0·31
ZnO	3·80	MnO	0·36
S	2·45	CoO NiO	0·1
PbO	1·33	CaO	3·32
Sb	·04	SO_3	4·83
NiO	·33	S	0·2
K_2O	1·19	MgO	0·17
Na_2O	0·60		
	100·80		100·50

The materials composing the charge are prepared on the charging floor and thrown into the furnace with the fuel, the mineral and flux being disposed in layers alternating with layers of coke. The following is an example of the composition of the charge.

	Cwt.
Ore	100
Lead fume	1·01
Lead scrapings from the smelting house	0·63
Roasted lead regulus	47·51
Schlieg scrapings from the charging floors	1·21
Oker slags	60·00
Slags from the same process	3·70
Regulus slags	42·0
Slags from schlieg smelting	54·00
	310·06

The products obtained are work-lead (*Werkblei*), lead regulus (*Bleistein*), and a slag containing more or less of lead. The lead, as is shown by the following analyses, contains many metallic impurities, a portion of which are derived from the minerals associated with the galena and some from the materials used in the reduction.

Lead	98·8378	98·9648
Copper	0·1862	0·2838
Antimony	0·5743	0·7685
Arsenic	0·0009	0·0074
Bismuth	0·0039	0·0082
Iron	0·0035	0·0028
Zinc	0·0025	0·0028
Nickel	0·0023	0·0028
Cobalt	0·0016	0·0003
Cadmium	trace	trace
	99·6130	100·0414

The lead is refined at Lautenthal, or if it contains sufficient silver is desilverised by Parkes' process.

The following analysis gives the composition of the lead regulus:

Sulphur	26·877
Iron	53·112
Lead	10·655
Copper	4·620
Silver	0·03
Antimony	0·267
Arsenic	—
Zinc	2·110
Manganese	0·385
Cobalt and nickel	0·306
Lime	0·383
Magnesia	0·054
Silica	0·510
	99·309

The lead regulus is roasted in heaps, wood being employed as fuel, and in some cases coal, the roasting process occupying altogether some two months. The heaps are constructed as follows; first a layer of about 3 inches of powdered slag is spread on the ground, on this is placed a layer of pine wood, 100 cwt. of regulus requiring 110 cubic feet of wood for complete roasting. The regulus to be roasted is spread over the wood in a pyramidal heap, 14–20 feet broad, 20–30 feet long, and 5–6 feet high, and containing some 2,000–3,000 cwt. of regulus. The ignition is effected by setting fire to shavings placed under the wood. The first firing lasts from 8 to 10 weeks. After the heap has burnt out, it is broken up and the insufficiently roasted separated, to be again submitted to a similar roasting. When by this roasting the sulphur has been sufficiently reduced, but not completely burnt away, the regulus is then smelted in the ore furnace, and this mode of treatment is adopted so long as the copper in the regulus does not amount to more than from 6–7 p.c., in which case the roasted regulus is smelted in a low blast furnace with slags from ore smelting and coke. This operation yields a work-lead amounting to 7–9 p.c. of the roasted regulus treated, and a regulus in amount varying from 24–42 p.c. of the roasted regulus. The amount of lead obtained is 75 p.c. of that contained in the regulus, the remainder being lost by volatilisation. This lead contains antimony and from 0·4 to 1·5 p.c. of silver. The regulus produced in this operation is again roasted and smelted, and thus a regulus produced which now contains some 20 p.c. of copper and is next treated for copper.

The following are analyses of the slags obtained in smelting ore in the blast furnace, the principal constituent of which is silicate of iron:

	I.	II.
Silica . . .	40·22	38·7
Barium sulphate .	0·82	2·9
Alumina . .	7·89	8·8
Lime . . .	4·95	5·0
Ferrous oxide .	33·35	33·4
Magnesia . .	1·38	0·9
Zinc oxide . .	3·41	4.8
Lead oxide . .	1·96	2·4
Manganous oxide .	1·89	1·5
Potassium oxide .	1·15	0·9
Sodium oxide .	0·59	0·3
Oxides of nickel and cobalt . .	0·04	0·2
Iron . . .	1·68	—
Copper . . .	0·21	0·2
Silver . . .	0·0006	0·0016
Phosphorus pentoxide . .	0·56	0·2
Sulphur . .	0·81	1·4
	100·9106	101·6016

Lead-smelting at Freiberg.—The treatment of the great variety of minerals smelted at Freiberg for lead consists essentially of two sets of operations; first, the roasting of the ore to desulphurise it as completely as possible; secondly, the smelting of the roasted ore in blast furnaces and thus producing a work-lead, a matt or regulus, and a slag. The matt produced is submitted to repeated roasting and smelting operations, pretty much as practised at Clausthal.

The mines of Saxony from which the ores smelted at Freiberg are chiefly derived supply a great number of different mineral species which are classified as follows: (1) Lead ores, (2) copper ores, (3) arsenical ores, (4) zinc ores, (5) sulphur ores, (6) silver ores. The first class represent all minerals which contain above 15 p.c. of lead, and these are again subdivided into two groups: (1) '*Bleiische Erze*,' plumbiferous ores, containing from 15–30 p.c. of lead; (2) lead glances, in which the amount of lead in some cases is as much as 80 p.c. The mean lead content of the ores may be stated as 40 p.c., and this is associated with 150 grams of silver per 100 kilograms. The following represents the average composition of the '*bleiische Erze*':

Lead	15–20 p.c.
Sulphur	30 „
Zinc	10 „
Arsenic	7–15 „
Silver	60 grams per 100 kilograms.

The copper minerals known as '*kiesblendige Erze*' are constituted of three species, viz. iron pyrites, copper pyrites, and zinc blende; the copper varies in amount from 1–3 p.c. Arsenical minerals are constituted of arsenical pyrites containing about 10 p.c. of arsenic, and the zinc minerals consist essentially of blende containing from 30–40 p.c. of zinc. All these various minerals are more or less argentiferous. Those minerals containing above 20 p.c. of sulphur are classed as sulphur minerals.

For the purpose of calcination the ores are divided into two classes; those containing at least 20 p.c. of sulphur and not more than 25 p.c. lead are submitted to a preliminary roasting in kilns so arranged that the sulphur dioxide produced may be utilised in the manufacture of sulphuric acid. In this operation a portion only of the sulphur is removed, the greater portion being reduced by roasting the partially desulphurised ore with raw ores which from their composition are unsuited for roasting in kilns. This second and final calcination is performed in reverberatory furnaces known as the 'Sinteröstöfen,' consisting of two beds, one above the other, the lower bed having the grate at one end, at the opposite end is a passage communicating with the upper part along which the heated gases pass and are finally conveyed from the furnace by a flue which communicates with condensing chambers.

This form of calcining furnace with two beds has been replaced by a furnace with a single bed, and with working doors upon both sides, in which the ore is charged at one end from a hopper placed above, viz. at the end furthest from the fire. The ore is spread in a layer over this portion of the furnace bed, and after remaining in this part for a given time it is moved on to the next portion of the bed, and its position filled by a fresh charge. In this way the charge is gradually moved along the furnace to the fire-bridge, and at this point it is subjected to a heat sufficiently intense to effect a partial fusion or agglomeration and is then withdrawn. In this manner the ore is continually submitted to a gradually increasing temperature, whereby the sulphur of the sulphides is burnt away and oxides produced, which in the final heating react with the silica and produce silicates.

The construction of the new 'Fortschauflungsröstöfen' will be understood from the accompanying figures, for the drawings of which as also for much information respecting the present practice of lead smelting, the writer is indebted to Mr. W. Maynard Hutchings, general manager of the lead works of Messrs. Cookson & Co., Newcastle-on-Tyne.

Fig. 14 is a front elevation of the furnace, which is constructed of brickwork with a lining of fire-brick, and stayed together with iron standards and crossbars. In this is also shown the hopper *a* for charging ore, the ten working doors *b*, the door *c* for the withdrawal of the charge, and the door *d* for charging fuel into fire-grate.

Fig. 15 represents a vertical section, showing the fire-grate *e*, fire-bridge *f*, and the bed of the furnace, constructed of iron plates supported by pillars of brickwork, which are cooled by circulation of air below; upon these plates are built the materials composing the bed of the furnace. *g* is the opening in the roof through which the ore from the hopper is discharged into furnace bed, *h* the flue leading to a series of condensing chambers.

Fig. 16 is a plan of the furnace, and figs. 17 and 18 are vertical sections through CD and FG respectively.

The charge of unroasted minerals and roasted minerals is carefully prepared so as to attain as nearly as possible the following conditions.

(1) The amount of lead shall not exceed 20–25 p.c., an amount which experience has shown serves well as vehicle for the silver.

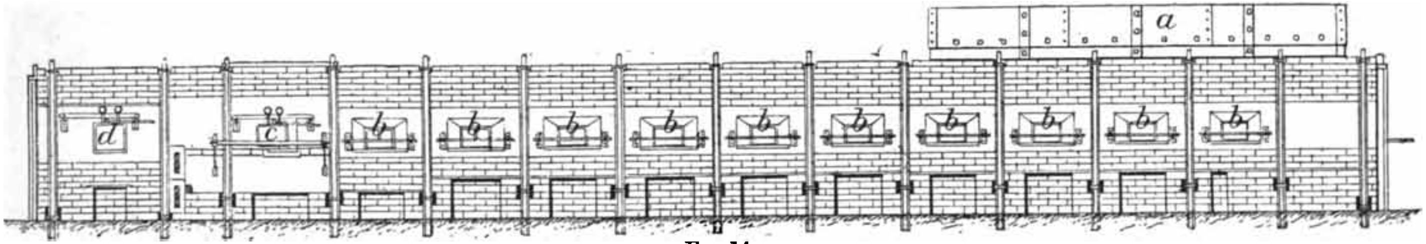


FIG. 14.

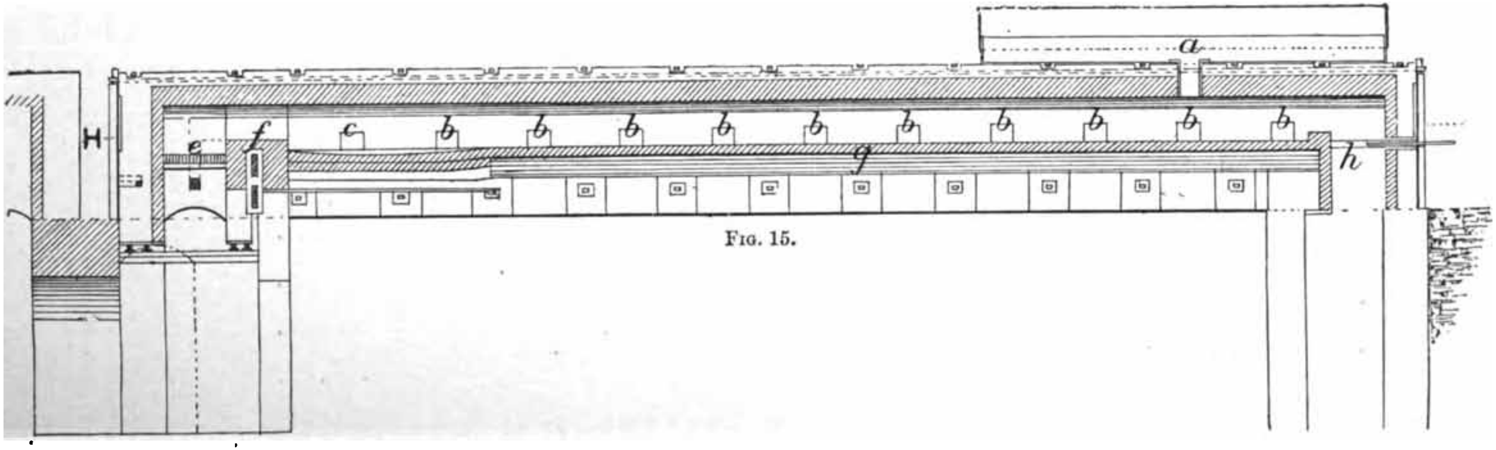


FIG. 15.

(2) The amount of zinc should not exceed 10 p.c., a greater proportion of zinc rendering the separation of slag and matt unsatisfactory owing to the viscosity of the slags.

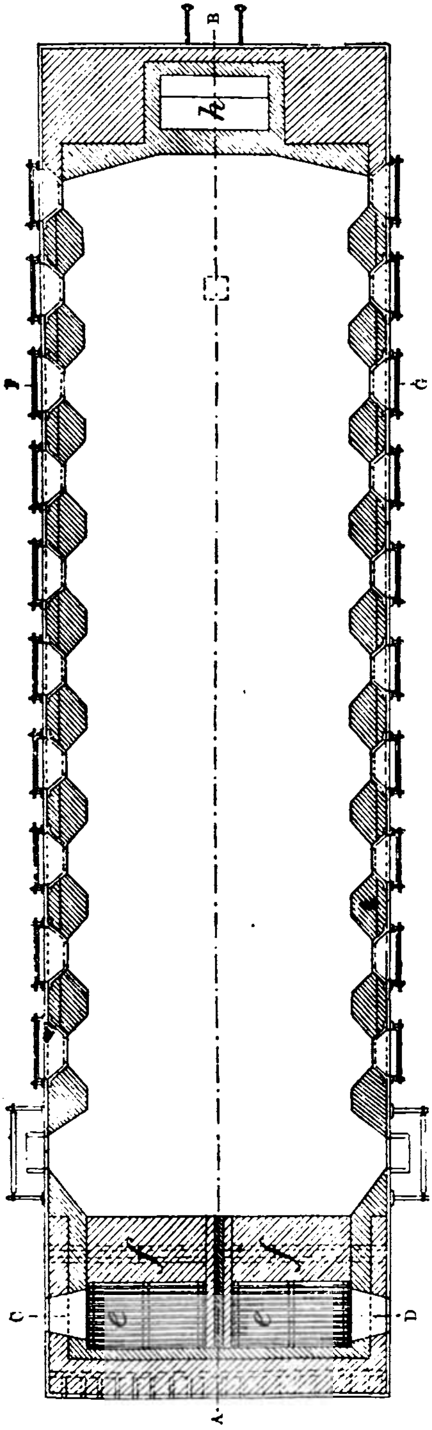


Fig. 16.

(3) Silica should be present to the amount of 20–25 p.c., and thus insure the production of slags consisting essentially of protosilicates of iron.

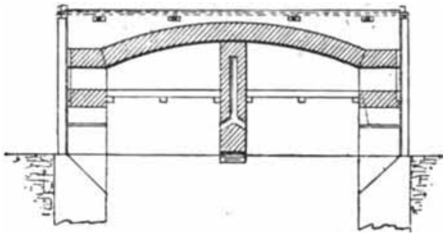


Fig. 17.

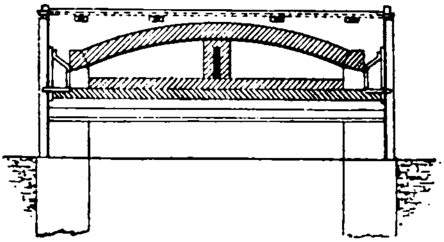


Fig. 18.

The amounts of lead, silver, copper, zinc, and silica are assayed to ascertain whether the above conditions have been fulfilled. The following are two examples of such assays:

—		Lead p.c.	Copper p.c.	Zinc p.c.
No. 1	Before roasting	22	2·5	—
	After roasting	21	2·5	10
No. 2	Before roasting	25	5·5	8
	After roasting	22	5·4	10

—		Silica p.c.	Silver grams per 100 kilograms
No. 1	Before roasting	—	75
	After roasting	27	67
No. 2	Before roasting	14	100
	After roasting	20·7	102

By calcination the amount of sulphur is reduced to about 2 p.c. The proportion of iron in the charge is never assayed, in fact as much iron pyrites as possible is added, and in some cases iron ores also.

The following are two examples of a charge prepared for roasting:

	No. 1	No. 2
Galena	41·00	37·20
Bleiische Erze	7·47	11·00
Iron pyrites	43·33	40·46
Silicious iron pyrites	4·50	4·81
Silicious minerals	1·60	6·53
Residues from zinc manufacture	2·10	—
	100·00	100·00

The proportions of crude to roasted ore in the above mixture are as follows:—No. 1: Crude ore 53·88, roasted ore 44·03. No. 2: Crude ore 60·73, roasted ore 39·27.

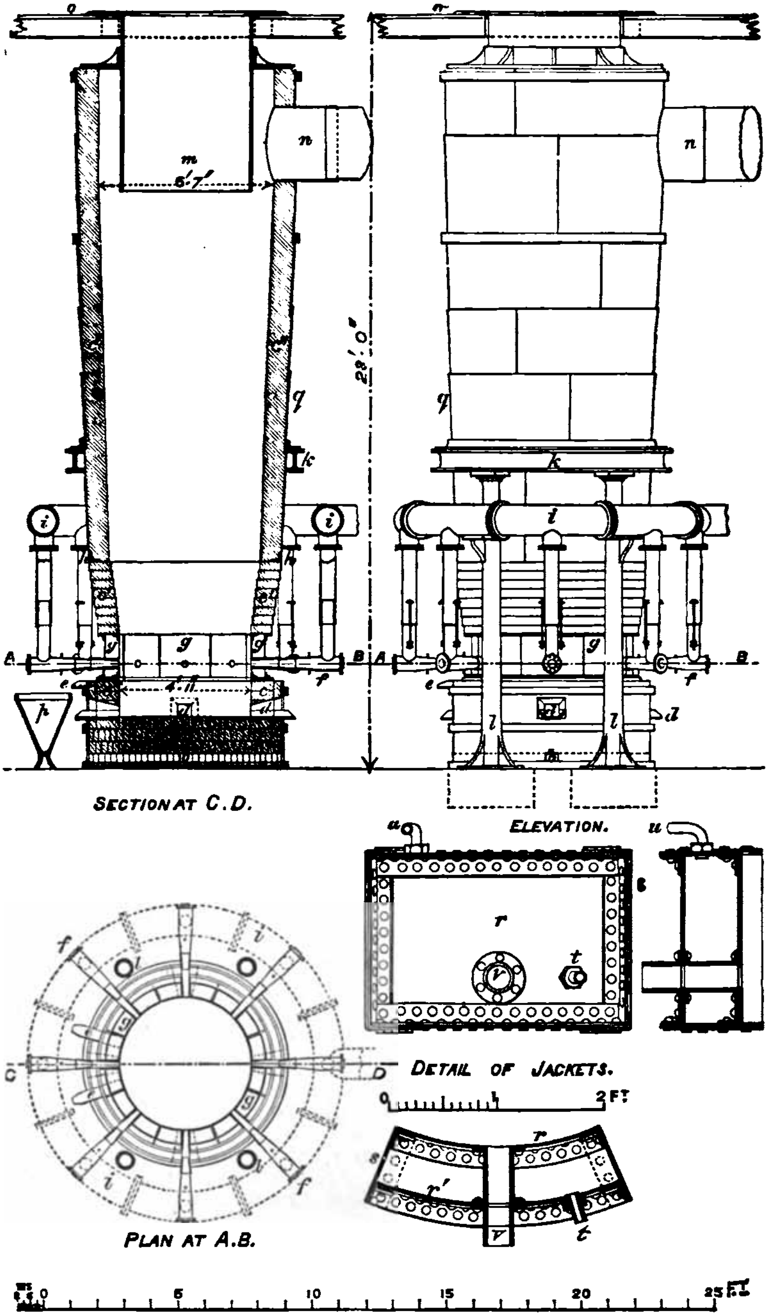


Fig. 19.

Smelting for lead in blast furnace.—The roasted ore is next reduced by fusion with coke in a blast furnace, the most recent form which has been adopted at Freiberg being a circular Pilz furnace resembling that used at Clausthal, from which it differs in the manner of drawing off the gases and also the arrangement used for charging the furnaces, and in having the sides of the furnace in the zone of fusion constructed of cast-iron boxes through which water circulates. The accompanying illustrations (taken from Percy's Metallurgy; Silver and Gold, part 1, p. 542) represent the Pilz furnace used at Freiberg in 1878. It is 25 feet high, is circular in section, 4 feet 11 inches diameter at the hearth, and gradually widening to 6 feet 7 inches at the top, and is supplied with eight twyers.

a, the hearth bottom, composed of four courses of bricks, the lowest common brick, resting on a circular plate of iron 1¼ inches thick, then three courses of fire-bricks, and is encased in boiler-plate, made in segments screwed together and further strengthened by hoops of wrought iron; *b*, channel extending through the brickwork and open at both ends; these channels, of which there are two, at right angles, allow of the escape of moisture; *c c*, brickwork forming the inner and upper part of the hearth; *c′c′*, brickwork of the boshes; *c″c″*, brickwork forming the shaft; *d d*, the tap holes, of which there are four; *e e*, two slag lips, along which the slag flows into the slag pot *p*, consisting of a cast-iron conical vessel; *f f*, blast pipes, the horizontal portions of which can be moved to and from the twyer holes; the vertical portions are supplied with a sliding screw by means of which they may be moved up and down; *g g g* are water-jackets made in sections, and of wrought iron, the construction of which is shown in detail in the accompanying illustrations. Water-jackets may also be constructed of cast iron instead of wrought-iron, each segment being provided with an aperture for the twyer and also pipes for conveying the cold water and for the outflow of the heated water; *h h*, ring of angle iron, riveted to the outer case, serving for the support of the shaft during the repairing of the lower part of the furnace; *i i*, blast main of cast iron; *k*, ring of iron supported by the four cast-iron pillars *l l*; *m*, cast-iron cylinder, flanged at the top and inserted into the mouth of the furnace, in order that the fume and waste gases may be drawn off by the pipe *n*; *o*, charging floor; *q*, outer iron casing of the furnace. The water-jackets are composed of wrought-iron plates ⅜ of an inch in thickness, and are riveted to angle-iron 2⅜ inch by ⅜ inches; *s s* are side plates overlapping by 2¼ inches top and bottom; *t*, pipes for supplying cold water; and *u*, pipe for the outflow of cold water; *v*, twyers, which are 2¾ inches diameter.

The following are four examples of the '*lit de fusion*' for such a blast-furnace, in tons of 1,000 kilograms:—

—	*a.*	*b.*	*c.*	*d.*
Roasted minerals	40·	40·	40·	35·
Foreign minerals (crude)	1·20	0·6	0·6	0·6
Jewellers' sweepings	0·8	0·5	1·0	1·0
Residues from the manufacture of arsenic products (roasted)	6·00	6·00	6·00	7·00
Slags	27·5	25·	27·5	27·5
Matt after a second roasting	1·00	1·00	1·00	1·00
Unroasted matt	0·75	0·75	0·75	0·75
	77·25	73·85	76·85	72·85

The products consist of a work-lead, a matt, occasionally a speiss, slags, and fume. The yield of work-lead from each of the above charges was the following:

a.	6 tons	450 kilograms
b.	7 „	760 „
c.	7 „	940 „
d.	5 „	850 „

The lead contains many metallic impurities —*e.g.* copper, arsenic, antimony, bismuth, tin, iron, and sometimes cobalt and nickel; the proportion of silver present is very variable, and dependent upon the proportion of foreign rich minerals used in the charge. If above a certain percentage of cobalt and nickel are present in the materials smelted, a speiss is produced containing lead, copper, cobalt, nickel, and also silver. The average amount of matt produced from the above charges would be 1 ton 900 kilograms, and would contain from 15–20 p.c. of lead and from 10–12 p.c. of copper.

The slags produced consist chiefly of protosilicates, and are highly ferruginous. They contain 4–5 p.c. of lead, and, on an average, from 10–20 grammes of silver per 100 kilograms, in consequence of which they are in part returned to the blast-furnace and in part used in the subsequent smelting of the matt. The following is an analysis of slag produced as above:

Silica	32·2
Tin oxide	0·6
Lead oxide	4·9
Ferrous oxide	42·4
Zinc oxide	10·0
Alumina	7·3
Lime	4·1
Sulphur	0·4
	101·9

The amount of coke consumed is some 190 kilograms per ton of roasted ore smelted.

The matt produced in the blast-furnace is first roasted in kilns and then in stalls, and the roasted matt is smelted in a blast-furnace similar to that used in smelting the ores, producing in this way a further quantity of lead, a second matt, and slag. The following is an example of the '*lit de fusion*' for first matt smelting:

	Tons
Slags from ore smelting	37·5
Matt (after three roastings)	6·0
Matt (crude)	0·6
Foreign copper ores	1·8
Slags from previous smelting	2·5
'Abzug' from liquating furnace	1·6
Cupel bottoms	1·2
Drosses	1·5
	52·7

The amount of lead produced from these quantities was 3 tons 65 kilograms; this lead is very impure, and contains on an average 400–500 grams of silver per 100 kilograms. The matt called second matt will contain 10–12 p.c. of lead, 12–15 p.c. of copper, and 140–150 grams of silver per 100 kilograms. The slags are usually thrown away, as they contain from 0·5–1 p.c. of lead, and 1–2 grams of silver per 100 kilograms. These slags are occasionally used for building purposes. The coke consumed is 110 kilograms per ton of matt, &c.

This second matt, obtained in the operation described above, is treated in exactly the same manner as matt No. 1, and a further amount of work-lead rich in silver is obtained, which is submitted to liquation, and a third matt containing from 20–25 p.c. of copper, which is subsequently treated for the extraction of copper.

The different leads produced in the smelting of ore and of the matts are very impure, containing about 5 p.c. of total impurities, amongst which are arsenic, antimony, tin, iron, zinc, bismuth, copper—at times cobalt and nickel. The purification and desilverising of the work-lead will be subsequently described.

In Colorado, at Leadville, lead ores are smelted in blast furnaces of the Rachette type, provided with water-jackets and also with a syphon-tap which has been introduced into blast furnaces in this country and on the Continent. The syphon-tap is a contrivance consisting of an oblique channel penetrating the bottom of the hearth of the furnace, by which the lead rises into a basin placed outside the furnace, and from which as it accumulates the lead is ladled out into moulds. The ores smelted at Leadville are locally styled *sand carbonates* and *hard carbonates*. The former consist of lead carbonate containing silver chloride, whilst the latter are a porous silicious material containing lead carbonate and silver chloride associated with hydrated oxide of iron and manganese. In some cases the ores contain considerable quantities of argentiferous galena, which is frequently covered with a coating of carbonate of lead. The chief foreign ingredients, which are but few, are clay, limonite, and silica. Pyromorphite and anglesite are found in small quantities, as are also oxidised compounds of copper, arsenic, and antimony. In some mines bismuth and vanadium ores are found, and silver is found combined with iodine and bromine in addition to chlorine. The fuel used in smelting these ores is coke and charcoal, limestone, hæmatite, and limonite being employed as fluxes, but in many cases the ores contain sufficient admixture of iron compounds to enable them to be treated directly in the blast furnace. The pig lead obtained, which is known as *base-bullion*, carries from 100–250 oz. of silver per 2,000 lbs., and from 0·25–0·14 oz. of gold; this is treated for silver and gold in the Eastern States. Each unit of lead produced requires the expenditure of 1½ units of fuel. For further details the reader is referred to an article by S. F. Emmons on Lead-smelting at Leadville, published in the Report on the Precious Metal Deposits of the United States, Washington, 1885.

Smelting on Shallow Hearths.

The furnace known as the 'ore hearth,' or 'Scotch hearth' is the one chiefly used in smelting galena in the northern counties. It varies considerably in dimensions and in external form at different works, but consists essentially of a shallow rectangular hearth built of cast iron, set in brickwork or stone. Fig. 20 is a vertical section of the 'ore hearth,' A the hearth bottom, 22 inches square, the iron plate being about 3 inches thick; the sides are also composed of iron of the same thickness, and the depth of the hearth will be about 4½–6 inches. In front of the hearth is the work-stone B, sloping from the front edge of the hearth to the metal pot C, in which the lead is maintained in a molten state by a fire below. The work-stone is about 8 feet long, 18 inches broad, and 2½ inches thick; it has a raised border of about an inch high on its two sides and along the front, and a narrow channel 2 inches wide and 1 inch deep runs diagonally across it. The work-stone is embedded in fireclay or a mixture of slime, ore, and bone-ash. At the back of the hearth is a prism of iron, called the back-stone, D, upon which rests the bellows-pipe, and above it is another prism E, called the pipe-stone, with an opening below to receive the bellows-pipe. The blast-pipe enters at a height of some 6½ inches above the level of the upper end of the work-stone, and when in work will be about 4 inches above the level of the metal in the bed. The hearth is covered by a hood of brickwork, opening at the back into a flue leading to the fume condensing chambers. Behind the hearth is a blind flue or pit into which 'hearth-ends' and other matter coming off with the fume may fall and collect, and from which it is removed as required. At the side of the hood is an opening in the brickwork communicating with the hearth, through which the ore and fuel are charged. The opening in front can be regulated by a movable iron plate, which in some cases is in the form of a sliding shutter, which by means of a counterpoise can be raised or lowered in its groove so as to nearly close in the front of the hearth.

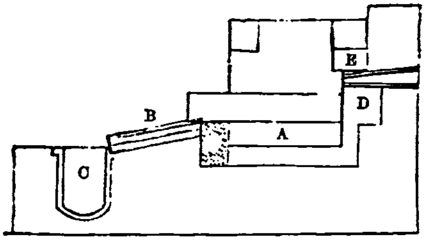


Fig. 20.

The fuel used is either coal or peat, now more usually coal, and the blast is supplied by a Roots blower, and the ore may be either added in the raw state, or, as is more usual, after it has been roasted in a reverberatory furnace. The working of this hearth requires the constant attention of two men, and at the end of each shift the bottom should be nearly filled with lead, which in the molten state forms the bottom on which the charge rests. The mass of agglomerated ore, slag, and coke left at the end of each shift is called the 'browse.' In working, a fire of coal is made on the hearth, and then a moderate blast turned on. Ore is next thrown on, and when the hearth is provided with a shutter, this is closed down. After the lapse of a few minutes, the charge is stirred by a poker and fresh ore and fuel added from time to time. At intervals the shutter is raised and a portion of the charge drawn on to the work-stone, and then the workman picks out the grey slags, which are pushed aside and ultimately thrown on to the floor of the workshop at the side of the hearth. The other portions of the charge drawn on to the work-stone are broken up and returned to the hearth, the contents of which are set up so as to distribute the blast, and fresh ore added in small quantities. As the lead forms it flows into the well, and overflows along the channel in the work-stone into the pot in front of the hearth, from which it is ladled into moulds. Towards the end of a shift no fresh ore is added, but the 'browse' is thoroughly worked up alone, and when the blast is stopped, the grey slags are separated from it, and a portion of the lead from the metal pot ladled back into the well in the hearth so as to fill it for the next shift. The process is essentially an air reduction process; the object being to oxidise the ore and then by subsequent admixture with ore to bring about the reactions between the unaltered sulphide and the oxy- compound resulting in the formation of lead. Formerly, as has been already stated, the ore was treated in the raw state, but is now more generally submitted to a calcination, by which a portion of the sulphur is removed and the slimes agglutinated, thus enabling them to resist the force of the blast and reduce the amount passing away in the form of 'hearth-ends' and fume. The influence of this previous calcination in reducing the fume and loss &c. is shown by the following results obtained by Mr. Norman Cookson, in smelting 400 tons of ore, yielding on assay 81 p.c. of lead, one half of which was smelted raw and the other half after roasting (*v.* Local Government Report, 1878–9. Supplement containing the Report of the Medical Officer, 1878, 289).

	200 tons roasted	200 tons raw
Lead, first fire . .	73·10	60·80
Lead in grey slags . .	2·50	1·80
Lead in fume, hearth-ends, loss, &c. .	5·40	18·40
	81·00	81·00

A description of the ore-hearth and its working was given by the late Hugh Lee Pattinson, and published in the Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne for 1831.

The American hearth, which was first introduced at Rossie, New York, and has been subsequently used in other parts of the United States, is very similar in construction and working to the Scotch hearth. The bottom is constructed of cast iron, 24 inches square, 12 inches deep, and 2 inches in thickness. The two sides and back are formed into an air-chest, 14 inches high and 6 inches wide, through which the air passes and from which it is conveyed by a pipe to the twyer, which is placed at the back of the hearth, as in the ore-hearth. In front of the hearth is a sloping work-stone, with diagonal channel, along which the metal flows into a metal pot. This mode of constructing the American hearth, with an air-chest, serves the double purpose of cooling the sides of the hearth and supplying hot air for the blast. The hearth is worked like the ore-hearth, the bottom being filled with lead, which forms the bath upon which the charge floats. The fuel used is wood or pine charcoal, and the galena to be treated should be broken up into pieces not exceeding ⅛ of a cubic inch in size. The furnace may be kept in constant work for six days of the week, and requires two attendants during each shift. The fuel consumed produces little more than 2½ times its weight of metal; the daily yield of lead is about 7,500 lbs. Experiments have been made with this form of hearth in various places in Europe, but it has not been adopted permanently at any one.

Slag hearth.—The various rich slags obtained by smelting in reverberatory furnaces, or in the ore-hearth, are usually smelted in a special blast furnace, known as the slag-hearth. In some establishments the Castilian blast furnace with three twyers is used, whilst in others furnaces similar in type to the Pilz furnace, and provided with water-jackets, are employed.

The ordinary slag-hearth is furnished with one twyer, and has the form of a deep hearth or shallow rectangular furnace. It is built of fire-brick and cast-iron, incased in common brickwork, leaving an opening in front. The outer casing is prolonged, forming a shaft which is connected with the flues for condensation of fume, &c. The bottom is formed of a plate of cast iron, styled the *bed-plate*, and laid with a slight inclination forwards; on the bed-plate are placed two cast-iron *bearers*, which carry the side walls of the furnace. In front is a plate of iron, the fire-stone, placed so as to leave an interval of seven inches between its lower edge and the bed-plate; the back of the furnace below the twyer is formed of another plate of iron. In front of the bed-plate is a cast-iron trough, the lead trough, which is usually divided into two unequal parts by a partition forming a part of the casting. The larger of these divisions corresponds in width with that of the bed-plate, and at the bottom of the partition is a hole through which the molten metal flows into the smaller division of the trough. The slags flow from an opening in the stopping of the breast into the larger division of the lead pan, and flow over from this into a pit sunk in the ground, through which a current of water flows. The outer brickwork surrounding the hearth is supported by iron plates braced together with tie-rods, the twyer passing through the plate which supports the back stone on which the nozzle rests. The outer brickwork is built so as to leave an opening in front of the hearth, and there is also an opening at one side for charging the furnace. The bed-plate is covered to within an inch of the twyer with coarsely sifted coal cinders, thus forming a bottom which slopes with the bed-plate towards the lower edge of the firestone. The space in front of the ash bottom, between the bearers and firestone, is plastered up with clay. The ash bottom serves as a filter to separate the slag from the lead, which percolates through to the bed-plate and then flows through openings in the clay stopping into the lead trough. This also is filled with cinders, through which the lead passes and finds its way to the bottom and through the partition into the smaller division of the trough, whilst the slag flows over into the slag pit, the sudden cooling of which by the water determines its disintegration, and renders easy the separation of any inclosed particles of metal. The fuel employed is coke and peat, and in commencing to work with this furnace, after making the bed of cinders as described, peat is piled up above the bed and ignited, then the blast turned on. When the peat is burning, coke is thrown into the furnace and a layer of grey slags added. This is continued as the operation proceeds, alternate charges of fuel and slag being added; lead is produced and a slag, 'black slag,' free or nearly free from lead. Occasionally a bar of iron is thrust through the layer of cinders to liberate the slags and lead. The lead obtained from ore-slags is not as pure as that obtained at the first smelting, it is whiter and much harder, and is afterwards submitted to the calcining process to soften it. In some cases iron slags are added with the fuel and grey slags; especially when the grey slags contain much lime is this addition useful, the formation of an easily fusible slag being in this way promoted.

SOFTENING AND DESILVERISING.

The lead obtained by smelting may contain, in addition to silver, antimony or copper and other oxidisable metals, which may be present in quantities sufficient to interfere with the desilverising process; the metal is, therefore, when necessary, submitted to an operation known as *improving* or *softening*.

The *improving* or *softening* is effected in a reverberatory furnace, the bottom of which consists usually of a cast-iron pan, about 2 inches in thickness, length about 10 feet, width 5 feet 6 inches, and 10 inches in depth. All the angles of the casting are carefully rounded to prevent breakage by expansion or contraction, and the softened lead is drawn off by a hole bored in the bottom, near the outer edge, which is stopped by a well-fitting iron plug held in its place by a weighted lever. Such furnaces are usually made to hold from 8–12 tons of molten lead.

The fireplace is about 20 inches wide, and has a length equal to the width of the cast-iron pan, from which it is separated by a bridge two feet wide. The height of the furnace above the pan at the bridge end is 16 inches, and at the other end it is 8 inches.

The charge is either introduced in the form of pigs or is first melted in an iron pot set in brickwork at the side of the furnace, and subsequently ladled into a sheet-iron gutter, by which it is conveyed to the furnace. A softening furnace has been constructed with the iron pot for melting the hard lead, built above the calcining furnace, and so arranged that the heat required for the fusion is supplied by the furnace fire. The molten lead is run into the calcining pan by raising a plug at the bottom of the pot, the opening in which is immediately above the pan and a little to one side of the fire-bridge.

In this furnace the molten lead is submitted to the action of heated air, whereby the easily oxidisable impurities are converted into oxides, which, floating on the surface of the bath, are removed by an iron rake; in this way a fresh surface is constantly exposed to the action of the heated gases, and thus the greater portion of the impurity is removed. The progress of the operation is judged by taking a sample in a ladle and casting it in an iron mould, when the calcination has been completed the surface will present a peculiar flaky crystalline appearance. The calcined or softened lead is then tapped into an iron pot, from which it is ladled into the pig moulds, or is run from the furnace by a movable iron gutter into a series of pig moulds placed in readiness in front of the furnace.

In some districts hard lead is improved in a furnace with a slag bottom, which allows the operation to be conducted at a much higher temperature, and more rapidly than in iron pans. In Germany a marl bottom is used, whilst in some establishments these furnace bottoms are constructed of wrought-iron plates in form of a long shallow rectangular pan, the sides and bottom of which are lined with a lining of firebrick. Furnaces of this construction are made to hold as much as 70 tons of molten lead.

The calcined dross removed from the lead is reduced with coal, and the slag produced reduced in the slag hearth or in a cupola. In this way a very hard lead is obtained, which is again calcined, and the drosses formed yield on reduction a lead sufficiently rich in antimony to be sold to typefounders.

Leads containing a considerable proportion of copper are submitted to liquation before softening. The liquation is effected by heating the pigs of lead in a reverberatory furnace, the bed of which slopes from the fire-bridge and terminates in a sump or lead-pot at the flue end. The pigs are piled up at the upper end of the furnace-bed and subjected to a low heat; the lead first melts and flows down into the pot, whence, after skimming, it is ladled into moulds. The more refractory dross containing the copper, nickel, and a portion of the arsenic, and also sulphur, is left behind.

SILVER CONCENTRATION — DESILVERISING AND LEAD REFINING.

Concentration of silver in lead.—The improved or softened lead is, before separating the silver from it, next submitted to a process having for its object a concentration of the silver to an extent sufficient to render its extraction economical. The silver concentration or enriching of the lead is performed either by the Pattinson, the Rozan, or the Parkes's process. The first two of these processes are alike in principle and are founded on the observation made by the late Hugh Lee Pattinson, of Newcastle-upon-Tyne, that when lead containing silver is melted and the molten mass allowed to cool slowly, at the same time being constantly stirred, then, at a temperature near the melting-point of lead, crystals begin to separate out. If the crystals so produced are separated they are found to contain a smaller proportion of silver than the original lead, whilst the liquid alloy from which the crystals have been separated are proportionately richer in silver. This discovery was made the basis of a patent by Hugh Lee Pattinson, for 'An improved method of separating silver from lead,' the date of the patent being October 28, 1833, and at the meeting of the British Association held at Newcastle-upon-Tyne in 1838 the process was described in a paper by Mr. Pattinson. The introduction of this method of enriching lead has made it possible to extract the silver even when it is present in amounts so small as from 2–3 ounces to the ton, the desilverised lead retaining from ⅛–⅜ ounce of silver per ton. With present (1890) prices it would not, however, prove remunerative to Pattinsonise lead containing less than 4 ounces of silver per ton.

Pattinsonising, Pattinsonage, Pattinsoniren. The operation is conducted in large cast-iron hemispherical pans, capable of holding 6 to 10 tons of molten lead. The small 6-ton pots are now rarely used, and in some establishments pots capable of holding 18 tons of lead are employed, the larger size requiring the use of cranes in working the ladles. A series of nine to twelve of these pots is placed side by side in a line and resting on brickwork supports. Each pot is provided with a separate fire-place, the heated gases from which are conducted round the pan by a circular flue and thence pass into a flue running the whole length of the pots by which the gases are conveyed to the chimney. In addition to the large pots, there are sometimes smaller pots placed at the side between the larger pots, and heated by a separate fire; these serve to hold some melted lead for the purpose of heating and cleaning the ladles. Along both sides of the erection in which the pots are built is a platform on which the workmen stand. The pot at one end of the series is smaller than the others, being about two-thirds the capacity, this is called the *market pot*, which receives the poor lead and from which the lead is run into the pig moulds. The other apparatus used in this process consists of perforated ladles made of iron ½ inch in thickness; when worked by hand the ladle would measure 16 inches in diameter and 5 inches deep, the holes being ⅜ inch in diameter, whilst when cranes are used the ladle would measure some 20 inches in diameter, 6 inches in depth, and the holes would be ¾ of an inch. The handle of the ladle is some 9 feet 6 inches long, and ½ an inch in thickness. In addition to the ladle, a chisel-pointed bar or *slice* is used in stirring the lead.

Fig. 21 shows the arrangement and mode of setting a range of pots.

The method of working will be best understood by supposing the lead to be treated contains some 20 ozs. of silver to the ton; the metal in the form of pigs would be charged into one of the pots about midway between the *market pot* and the *rich pot*, the fire is set on and the lead melted; by the melting the surface of the metal is covered with a layer of dross, which is carefully removed by a ladle and the fire withdrawn. Water is sprinkled on the surface of the molten bath to promote cooling, and as the metal cools a cake is formed on the surface, which is detached and broken up by means of the slice, and the pieces stirred into the liquid. As the cooling proceeds the mass is kept continually stirred and after a time crystals begin to make their appearance. The crystals are now removed by means of the large perforated ladle, which is plunged into the liquid and then gradually raised, the side of the pot serving as a fulcrum; the ladle is raised until it is completely out of the bath and is brought into a tilted position, and whilst in this position the crystals are allowed to drain. When drained the contents of the ladle are transferred to the next pot on the left, supposing the market pot to be

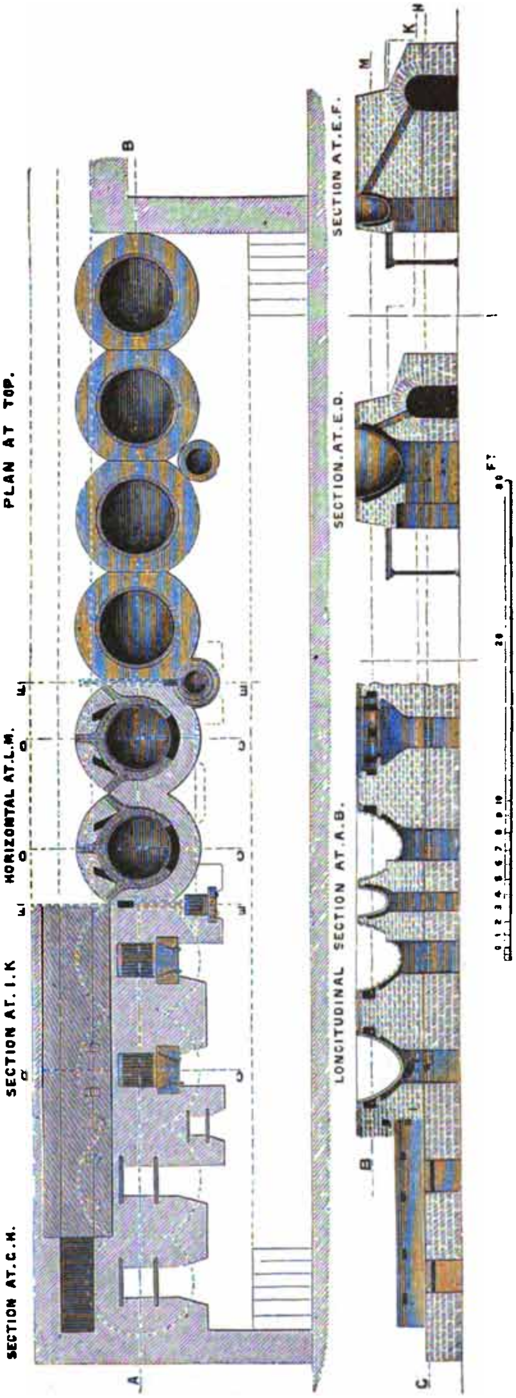


FIG. 21.

at the left extremity of the range. This operation is repeated until two thirds of the original charge has been transferred in this way. The remaining third, which represents the rich alloy, would be transferred to the next pot on the right —*i.e.* toward the *rich pot*. The rich bottoms, as they are called, will contain 40 ozs. of silver to the ton, and any lead that may be on hand having a similar silver content would be added to the enriched bottoms. The poorer lead from this single operation would contain about 11 oz. and similarly any lead to hand of this assay would be added to the metal obtained by this operation. A second charge would be next introduced into the pot in which the first operation was conducted and would yield further quantities of poorer lead and enriched bottoms, the former transferred to the left and the latter to the next pot on the right. The poorer lead would be similarly treated and from it a further quantity of still poorer lead would be produced, which is passed on to the next pot to the right and so on until the lead which reaches the market pot will contain some 10 dwts. of silver per ton; the enriched lead gradually meanwhile making its way to the *rich pot*, but in the richer pots the separation is less complete than in the poorer ones, and the enrichment is not so rapid. In working the last pot, after two thirds of the metal in form of crystals have been transferred, the enriched bottoms will consist of crystallised and liquid alloy, and the latter is separated from the former by pressing the mass with the back of the ladle, the fluid portion, the richer in silver, runs through the holes in the ladle and is removed by an ordinary ladle. Working in this manner a market lead is obtained at one end of the range in which the silver is reduced to the amount already stated, and at the other end of the range is produced lead containing from 600 to 700 ozs. of silver to the ton, beyond which it is not possible to push the concentration by this method.

In the above description it has been assumed that the method of thirds or the high system was employed. This is the method most usually adopted in practice, but for special purposes the low system or method of eighths is sometimes used, in which seven-eighths of the contents of the pots are transferred to the poorer pot. In some works the method of seven-eighths is used for 'riching up' rich leads to the refinery grade of about 600 ozs. In the seven-eighths system the lead should treble itself in assay in each operation, but seldom is this the case. In the two-thirds system each operation is supposed to result in the doubling of the silver content of the lead, but in practice this only obtains with leads ranging downwards from about 50–60 ozs. of silver per ton.

As at each melting of the lead the metal is oxidised and a layer of dross formed on the surface, the bath is carefully skimmed after each melting and the drosses collected for future reduction. With a 20 oz. lead, the amount of drosses formed is 25 p.c. of the weight of the metal. The continual drossing of the metal naturally effects a purification of the lead, as the dross produced consists not only of lead oxide, but also of the oxides of the more easily oxidisable metals present. The value of the Pattinson process as a means of not only enriching the lead, but also of purifying it, is shown by the fact that lead to be used for white-lead-making is frequently Pattinsonised, although the amount of silver present may be very small. Further, Mr. Baker, of Sheffield, concludes that copper and iron are both separated with the silver in this process, which is true when the amount of copper does not much exceed ·025 p.c.

The Rozan process or Pattinsonising by steam.—This process of crystallising by steam was first introduced in the works of Messrs. Luce and Rozan at Marseilles, and has been described by Rozan in the Berg und Hüttenmännische Zeitung for 1874, and also by Mr. Norman C. Cookson in a paper published in the Transactions of the Newcastle Chemical Society for 1878. This method of desilverising has been practised for many years at Mr. Cookson's works. In this system steam under pressure is forced into molten lead, and by the continual agitation of the mass produced in this manner the production of crystals poor in silver is favoured, and the separation of an enriched fluid lead facilitated. Mr. Cookson, in the paper already referred to, is inclined to the opinion that the steam serves a second purpose, producing a chemical effect and aiding in the oxidation of the antimony, copper, iron and arsenic, and other oxidisable metals present. This oxidation may be due to the air carried into the pot by the steam. In any case leads such as rich Spanish leads containing as much as from a half to three-quarters p.c. of foreign metals may be treated by this system without having been previously calcined or softened. The following is the description of the plant and mode of working given by Mr. Cookson in the paper already referred to:—

'The pot marked M (fig. 22) is simply a melting-pot, and the lower pot C is the working, or, as it is commonly called, the crystallising pot. To illustrate the working, we will suppose the C pot contains fourteen tons lead crystals from a previous operation, assaying, say, eighty ounces of silver per ton, and the M pot seven tons original lead of similar silver content already melted; a moderate fire is set away in the firegrate of the C pot, and the contents of the M pot are skimmed of their dross; the hot lead from the pot M is then run on to the warm crystals in the C pot, and, with the assistance of the moderate fire already referred to, the whole contents of this pot (now twenty-one tons) are rapidly brought into a melted and working condition, when the charge is carefully skimmed; the M pot is at the same time charged with seven tons of lead containing

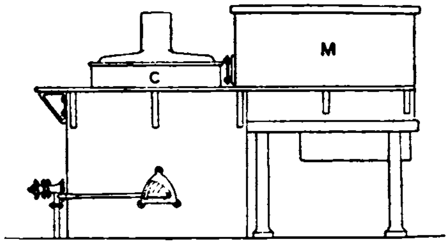


Fig. 22.

about forty ounces silver per ton of lead, as this will be the assay of the crystals resulting from the operation shortly about to commence in the c pot. The fire under this pot is next drawn, and a small fire under each of the tapping spouts is set away, the object of this being to prevent the lead setting in them when tapping out the rich lead later on. Steam at fifty to fifty-five lbs. per square inch is next admitted through the valve v, and is distributed evenly through the pot by the baffle plate *b* (fig. 23). To hasten the cooling and consequent crystallisation, thin streams of water are allowed to run on to the surface of the lead. This might be thought to cause the lead to set on the top, but the violent action of the steam entirely prevents this, and the crystals as formed and the liquid lead are uniformly distributed through the pot, and a more perfect crystallisation is effected than can be obtained in the old Pattinson process. When the workman sees that the charge is ready, *i.e.* when about two-thirds are in crystals and one-third liquid, he taps out through spouts at either side of the c pot the rich liquid lead, the poorer crystals being retained in the pot by perforated plates which effectually keep them back. This liquid lead is run into moulds containing 3½ tons each, and the blocks as they set are lifted out by cranes and arranged in a semicircle, where they await their turn to be again and again operated on. This process of crystallising, as in that of Mr. Pattinson, is repeated until the crystals are sufficiently poor in silver not to require further treatment, when, being fit for market lead, they are melted and run into pigs of the usual size, or into 3½-ton blocks, according to the purpose for which we require them. As regards the rich lead, it is worked up until its silver contents are of the standard fit for the refinery. A large portion of the foreign metals contained in the original lead is skimmed off in the state of oxides; and anyone seeing these oxides for the first time will be struck by the fact that those from the operations in the richer charges will be very dark in colour, some in fact almost black, this being due to the impurities contained, while as they come down in silver contents they have the yellowish colour proper to the oxides of lead. A large portion, however, is carried off up the funnel above the c pot, with the escaping steam, and is deposited in the condensing chambers, of which we have several of good size. These oxides are of various metals, that of lead being in the proportion of 80 to 85 p.c., the remainder consisting of the oxides of copper, antimony, arsenic, iron, &c., but principally of the two first named.'

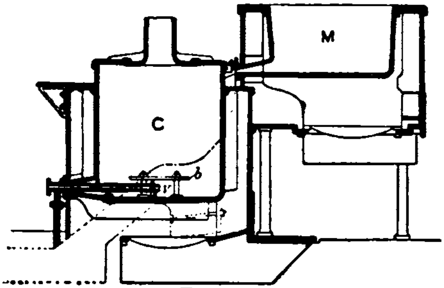


Fig. 23.

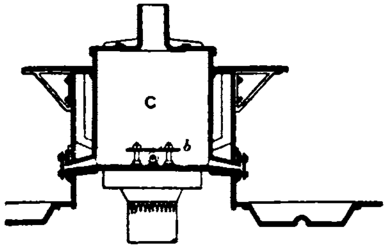


Fig. 24.

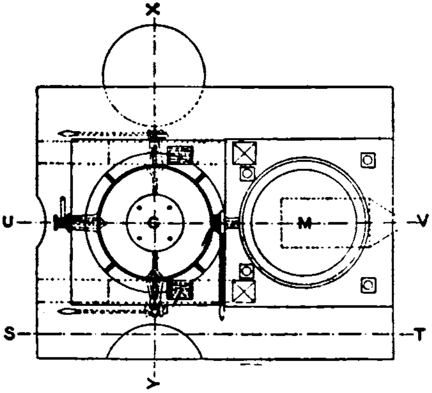


Fig. 25.

In the accompanying illustration of the plant used in the Rozan process, fig. 25 is the plan of a battery, fig. 22 is an elevation along the line s t, fig. 23 a section along the line u v, and fig. 24 a section along the line x y.

The following table taken from Mr. Cookson's paper gives the silver assays of twelve crystallisations taken from an average of 350 operations:—

Ounces per ton of lead.

570–315–202–112·5–62–33·75–19·5–10–5–2·5–1·25–14 dwts.

Mr. Cookson summarises the advantages of the Rozan system, as follows:—

'1. The entire saving of the cost of calcining all ordinarily hard leads, and in the case of extra hard leads, such as Greek lead, a very large saving.

'2. A cost for labour not exceeding one-fifth.

'3. A cost for fuel of about two-fifths.

'4. A saving of one-third in the oxides produced, which advantage any lead manufacturer will fully appreciate.

'Its defects are:

'1. A large capital outlay.

'2. A constant expense in repairs and renewals.'

The advantages of the system would appear to considerably outweigh the defects. The arrangement of the pots at different levels considerably reduces the labour of working a charge, and at Messrs. Cookson & Co.'s establishment at Howden-on-Tyne, the working is still more simplified by having attached to each battery of Rozan pots a hydraulic crane, by which the blocks of lead, which are cast with an iron eye in circular moulds shown in section in fig. 24, can be raised and lowered into the melting-pot or moved into any position at will. In fact, such is the perfection of the system of hydraulic cranes at this works that from the time the crude lead enters the work until it makes its exit as 'market lead' it is hardly ever touched by hand, but moved from place to place by cranes.

Parkes's system.—The method of desilverising lead by Parkes's process depends on the fact that when lead containing silver is melted with zinc, and the fluid mixture allowed to cool, the portion which first solidifies consists of a mixture of silver, lead, and zinc, and contains nearly the whole of the silver. Patents for this process were granted to Mr. Alexander Parkes, of Birmingham, in the years 1850, 1851, and 1852; and in 1859 the method was put in practice at Llanelly. It was subsequently tried at Tarnowitz, and, owing to the difficulties experienced in its working, finally abandoned at both places. The chief difficulties were (1) the removal of the zinc from the desilverised lead, which could not be performed sufficiently well to make the lead marketable; (2) the separation of the silver from the zinc alloy was attended by considerable loss; (3) the recovery of the zinc from the rich lead was somewhat difficult to accomplish.

The difficulties experienced in the use of this method have led to the proposal of several modifications of the original process, and the method as practised now at several establishments in this country, on the Continent, and in America, is comparatively simple, and is conducted as follows. At a height of some eight or more feet from the floor level the several pots used in the process are set in brickwork, each being provided with a separate fireplace. The number of these pots will be determined by the quantity of lead to be treated. At one establishment visited by the writer the number of pots was five, two larger ones capable of containing 25 tons of lead, and three smaller ones each holding about 6 tons. The lead is charged into one of the larger pots and melted, and, when melted, a slab of zinc is laid in the bath and the temperature raised until the zinc melts. When this temperature has been reached, the remainder of the zinc to be added at this stage is thrown into the bath and the whole thoroughly well stirred. After stirring for a quarter of an hour the metal is allowed to cool, and, as soon as the crust of zinc alloy has become sufficiently solidified, it is removed by a perforated ladle, and the skimming continued until the lead begins to set. The skimmings are transferred to one of the smaller pots. The lead is again heated to the melting-point of zinc, and a further quantity of zinc thoroughly stirred into it, the cooling and skimming repeated as before, and the skimmings transferred to the smaller pot. After this second addition of zinc the entire operation is repeated with a third portion of zinc, and the pot subsequently carefully skimmed. The proportions of zinc used in the various additions will vary according to different practices. The following may be taken as representative of one method of working. The lead contained 550 ozs. of silver; the total zinc required was 1,130 lbs., which was distributed as follows: first addition 340 lbs. of zinc, for the second 340 lbs. also, and the remaining 450 lbs. were used in the last. The total amount of zinc used is determined by the richness of the lead, in accordance with the following table, which has been confirmed by experiments conducted at Clausthal:—

Lead containing		grams of silver for 1,000 kilos. required			
Lead containing	250	grams of silver for	1,000 kilos. required	1¼	p.c. of zinc.
„	500	„	„	1¼	„
„	1,000	„	„	1½	„
„	1,500	„	„	1¾	„
„	3,000	„	„	2	„
„	4,000	„	„	2	„

The desilverised lead left in the larger pot after skimming the third time is tapped or siphoned out, and run into an improving furnace placed at a lower level, where it is kept at a red heat for several hours and occasionally skimmed, the progress of the calcination being watched by withdrawing small samples, which are cast in a mould, and from the appearance presented on cooling the state of the lead is determined. When thoroughly calcined the lead is tapped into a cast-iron pot and then run into pig moulds.

The skimmings which accumulate in the smaller pots containing silver, lead, and zinc are gently heated to effect by liquation a separation of a portion of the lead and the argentiferous alloy which is separated from it by a perforated ladle. The eliquated lead so obtained is added to the next charge of lead to be desilverised, whilst the solid alloy is next submitted to distillation, by which means the zinc is distilled off and obtained in a form in which it can be used over again, and a part in a pulverulent state consisting of zinc and zinc oxide. To this end the alloy is charged into a large fireclay crucible placed in a vertical furnace, heated by coke, and provided with a movable top, consisting of an iron framework with slabs of fire-clay, and moved by a small crane. The mouth of the crucible is closed by a hemispherical cover provided with a tubulus for conveying the vapours of zinc to a vertical condenser, which stands on a vessel for receiving the condensed zinc. By this arrangement the crucible is converted into a retort in which the zinc-argentiferous alloy is distilled, the zinc volatilised, leaving behind the enriched lead, which is ladled out of the crucible. In this way some 40 p.c. of the zinc is collected in the metallic state and 20 p.c. in the form of dust mixed with oxide. Both are free from silver. The proportion of zinc recovered varies very much with the amount of zinc used, *i.e.* with the silver assay. Taking for an example the zinc used in the case cited above, 50–55 p.c. of this zinc would be got back by distillation and a very little of it in the form of powder. Parkes's process, when worked as above described, is stated to cost considerably less than either of the other processes, and yields a market lead containing less silver.

Cupellation or Refining.

The enriched lead obtained by either one or other of the above methods is next submitted to the process of cupellation or refining, in which the lead is oxidised and converted into litharge, and metallic silver obtained. In England the refining is performed in a reverberatory furnace, the bottom of which, called the test or cupel, is movable, and into which the lead is fed at intervals from a melting-pot in which the rich lead is melted, and poured by a ladle into an iron gutter, serving to convey it to the test. In some cases the 'rich bars' are pushed down 'feed pipes,' so that they project into the furnace and are melted off as required. The oxidation of the lead is effected by means of a blast of air produced by a fan or other blower or by a steam injector. An English refinery in which two cupels can be worked at the same time is represented in figs. 26 and 27.

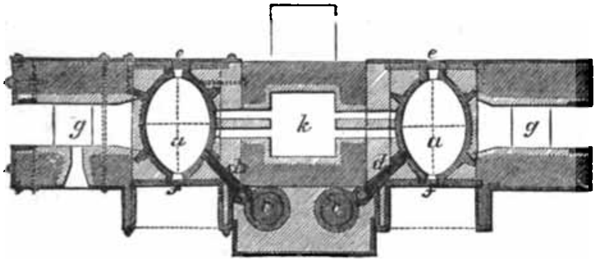


FIG. 26.

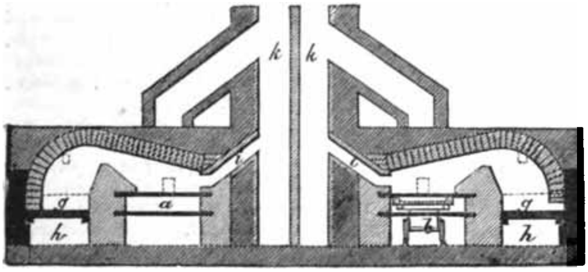


FIG. 27.

a, *a* are the position of the tests, one of which is shown resting on the iron waggon, *b*; *c*, *c* the melting-pots for the rich lead; *d*, *d* the iron gutter to supply the test; *e*, *e* the point where the blast enters; *f*, *f* the opening along which the litharge flows into iron pot placed below; *g*, *g* the fire-grates and *h*, *h* the ash-pits; *i*, *i* the flues, and *k*, *k* the chimneys.

The test or cupel is made of bone ash finely ground and prepared by moistening with a dilute solution of pearl ashes. This mixture is placed within an oval iron framework, consisting of an iron ring *a*, *a* (fig. 28). This ring, known as the test ring, is held together by iron bars, *b*, *b*.

The mixture of bone ash and pearl ashes is beaten down thoroughly with iron rammers into this framework, and the centre of the mass scooped out by means of a small trowel, giving the test the form represented in the accompanying illustrations, thus forming a reservoir for the molten metals. It has been proposed to mould these tests by presses worked by hydraulic power. The test before use is allowed to dry in the air for some time and then placed on an iron waggon and run into position under the furnace; it is then wedged tightly against an iron ring built in the masonry. The fire is next lighted, and the test slowly and carefully heated, so as to thoroughly anneal it. When perfectly dry, the temperature is raised to a dull redness and the test is filled with rich lead. The lead is first covered by a greyish dross, which, as the heating continues and the temperature rises, gradually gives place to the formation of litharge. The blast is now turned on and the oxidation of the lead takes place, the litharge produced is blown by the blast to the mouth of the refinery and flows over the gate into an iron pot, placed below. These iron pots are built on wheels and when filled with litharge are removed; the cake of litharge is easily detached after cooling, and is subsequently reduced, as will be described later on. As the oxidation proceeds, fresh lead is added to the test, and if a large stock of rich leads have to be treated, then the refining is only conducted sufficiently far to produce an enriched alloy, in which the silver amounts to about 8 p.c. of the contents of the test. The concentrated argentiferous lead is tapped into an iron pot run on wheels, placed under the test bed, which is pierced by a drill. When the concentrated rich lead has been run off, the hole is made up with a pellet of bone ash kept in its place by an iron plate, and another charge is introduced. By this removal of the enriched lead, a distribution of silver through a large quantity of litharge is avoided. The concentrated rich lead is finally refined in another test. The end of the operation is indicated by the appearance of the surface, the brightening of the plate, as it is styled; the blast is then turned off and the fire removed from the grate. When the lead has been completely removed, the silver is usually tapped out into ingots direct, through a hole in the bottom of the test. In some cases the plate of silver is allowed to set, and when this has taken place the wedges are withdrawn and the test is

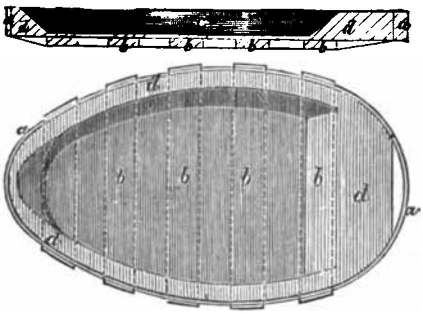


FIG. 28.

lowered on to an iron waggon, on which it is removed and then allowed to cool. The plate, when solid, is detached from the test, and brushed with an iron brush to remove any litharge, slag, or bone ash.

In an ordinary refinery 4 to 5 cwt. of lead can be worked off in an hour, and the fuel required would be from 6 to 7 cwts. of coal per ton of lead oxidised. The plate of silver will vary in weight from 10,000 to 20,000 ounces, and is usually pure, containing about 99·7 to 99·8 p.c. of silver. The test bottoms are saturated with litharge and contain some silver; they are usually broken up and those portions free from lead picked out to be used over again, whilst the remainder is smelted in a blast furnace. It has been proposed to extract the test bottoms with acetic acid, thus producing a solution of lead acetate and recovering the bone ash.

German Refinery.

In Germany the rich or enriched argentiferous lead is cupelled in a furnace known as the *Treibofen*, consisting of a reverberatory furnace with a circular hearth, and having a fireplace at one side. The bottom of this furnace is not movable, as in the English refinery, but composed of firebricks, on which lies a solid stratum of slag, and this again is covered by a coating of marl, well beaten down with iron rammers. The bottom is regularly hollowed out from the sides towards the middle, where a hollow is cut about an inch deep for the reception of the silver. The layer of marl is renewed for each operation. A dome of iron, plastered over with marl, covers the bed, and is moved as required by means of a crane. There are five openings into the side of the furnace, one serving to admit the flame from the fireplace, two smaller ones, near together, for the twyers by which the blast of air is forced on to the surface of the metal, and the litharge produced blown towards a fourth opening, by which it escapes in a fused state. The twyers are usually provided with valves, styled 'butterflies,' which serve to diffuse the blast over the surface of the metal. The fifth opening into the furnace is provided for the introduction of the lead. In working with unsoftened lead the charge for one operation would consist of about 5 tons of metal, some three-fourths of which would be introduced into the furnace before lighting up, the remainder being added from time to time as the cupellation proceeds. Much larger charges are treated when softened lead is used. The mode of working is as follows: the charge of lead, in form of pigs, is piled up in the middle of the hearth, and covered with wood, which is ignited by throwing on to it some burning charcoal. The iron dome is next let down and luted all round with clay. The blast is turned on and the fire in the grate made up. In the course of some three or four hours the lead has melted down and the bath is covered by a layer of dross, which is dark in colour and consists of a mixture of the oxides of the metallic impurities contained in the lead, and is called the *abzug*; it is raked out at the opening for the removal of the litharge. After the removal of the *abzug* the surface of the metal becomes clearer and in a short time acquires a peculiar circular movement; the dross now rising to the surface is purer and more fluid than the *abzug*. This second product forms what is known as the *abstrich*, and is an impure litharge, which, as it is produced, flows through channels cut in the breast of the furnace. The temperature is kept sufficiently high to maintain the *abstrich* in a state of fluidity. The formation of *abstrich* is succeeded by the production of pure litharge, which flows out of the furnace through the channels already mentioned. After the litharge-stage has commenced, the remainder of the metal to be cupelled is added in small portions at a time; the pigs of lead being so placed that the lead gradually melts and leaves behind the more refractory *abzug* unmixed with the metal. The full charge of metal having been added, the operation is continued and the temperature maintained sufficiently high to keep the silver in a molten state until the greater portion of the lead has been oxidised and the bright metallic surface of the molten silver is observed. The blast is then turned off and the fire is damped down; water is also thrown on to the metal to harden it, and the cake of *blicksilber* is withdrawn from the furnace freed from marl, litharge, &c. The *blicksilber* contains from 90 to 95 p.c. of silver and is refined in small reverberatory furnaces, the beds of which are made of bone ash, or some material serving like bone ash, for the absorption of the litharge formed by exposing the *blicksilber* at a temperature above the melting-point of silver to the oxidising action of the air.

The cupellation of a charge of 10 to 15 tons of lead lasts from 70 to 80 hours, and the loss of metal amounts to from 3 to 6 p.c.

Reduction of Litharge and Pot Dross.

The litharge produced in the cupellation of argentiferous lead, as also the various drosses formed in the Pattinson process, are reduced to the state of metal. The reduction is in this country usually performed in a reverberatory furnace, the sole of which slopes from the fire-bridge to a point near the flue, where an iron gutter, built in the furnace bed, serves to convey the molten lead to an iron receptacle outside the furnace. The reducing agent employed is coal. The sole of the furnace is prepared by covering it with small coal which is partially coked by the heat, and thus a porous covering is formed on the brickwork of the furnace bottom. On to this sole, so prepared, the litharge broken into lumps and mixed with coal is thrown, the ignition of the fuel and the reducing gases in the furnace soon effect a reduction of the litharge, and the molten lead trickling through the porous mass gradually finds its way into the metal gutter, by which it is conveyed to the metal pot. The charge is turned over from time to time, and when the reduction is completed the residue, termed *cinders*, is raked out. The litharge cinders are, together with other lead refuse, such as test bottoms, &c., treated in a cupola or slag-hearth, whereby a further quantity of lead is obtained from them.

In some establishments the litharge is reduced in blast furnaces similar to those employed in smelting ores; the fuel used is either coke or charcoal, and the litharge is mixed with slags from a previous reducing operation. The lead produced by reduction of the litharge is softened and desilverised when necessary, and inasmuch as the litharge produced towards the completion of the cupellation is richer in silver than that formed in the earlier stages, it is frequently reduced apart from the rest, and yields a lead containing from 70 to 100 ounces of silver per ton.

Refining lead by electrolysis.—A process, due to Keith, for refining lead by electrolysis, has been in use at New York for some years. The anodes of the electrolysing cells are made of the furnace lead, which is cast in thin plates about 4 ft. long, and weighing 45 lbs.; these are inclosed in muslin bags, which serve to retain the gold and silver and other insoluble matters. The cathodes are plates of pure lead, and are placed about 2 inches from the anodes in a bath consisting of a solution of lead sulphate in sodium acetate. The bath is heated by steam to about 38°C., and the electricity is supplied by a Weston dynamo, working at 1,500 revolutions per minute. When the electric current is passed through such a series of cells the anodes are corroded and dissolved, an equivalent amount of lead being precipitated on the cathodes as a loose crystalline powder, which falls to the bottom of the cell, whilst the matters formed by the disintegration of the anodes are collected in the muslin bags. The action is continued until only 2 or 3 p.c. of the lead forming the anodes remains undissolved. In a series of 48 decomposing cells each containing 50 anodes, 10 tons of 180-ounce silver lead with 2¼ p.c. of antimony and arsenic, can be refined daily by a 12 horse-power steam engine. The precipitated lead contains 11 grains of silver per ton, and is compressed by hydraulic pressure before melting.

Condensation of Lead Fume.

In consequence of the volatility of lead at high temperatures a certain proportion of the metal and some of its compounds are carried away by the heated gases in the operations of smelting, refining, reducing, &c. To prevent the loss and minimise the nuisance which would arise from allowing the gases produced in these various operations to pass direct into the chimney, the furnaces are connected with a series of flues or condensing chambers in which the gases are cooled and so deposit some of the solid matter held in suspension, before they issue from the chimney. These flues are cleaned out at stated intervals, and the 'fume' collected. The lead exists in the 'fume' chiefly in the form of sulphate and oxide, and is recovered by roasting and smelting it alone or mixed with ores and slags. A certain proportion of silver is always found in fume lead, the amount being considerably less than that obtained directly from the ores from which it was produced.

The method of fume condensation most usually relied on, and the one stated to be the most efficient, is simply to connect up the various smelting and other furnaces in a works with a series of long flues of large transverse area. In some establishments the flues used for this purpose have an aggregate length varying from 3–5 miles, and a cross section of from 6 feet by 7 feet to 8 feet by 9 feet. Jets of steam and water have in some cases been introduced at different points in the flues with the object of facilitating the fume deposition; but lead smelters differ in opinion as to the advantages gained by the use of either steam or water. Various devices have been proposed to effect a condensation of lead fume without the necessity of constructing long flues or large condensing chambers.

Stagg's condenser consists of a large rectangular chamber divided by partitions springing alternately from the top and bottom of this chamber, leaving free spaces above and below; the lower part of the chamber is filled with water, so that the gases pass first down one side of a partition through the water, and rising in the next compartment pass over the next partition and down again through the water. The gases are drawn through the chamber by means of air-pumps attached to the exit flue. The fume is in its passage through the condenser thus drawn through water, and the greater portion of the solid particles is removed, the solid matter collecting in the water is drawn off from time to time into tanks where the fume subsides.

In Stokoe's method of condensing, the gases are drawn off from a flue by means of a fan and are then forced into the condenser, which consists of two chambers placed side by side; these chambers are divided into several compartments by partitions which alternately reach the top and dip below the surface of water at the bottom of the chamber. The chamber is divided horizontally by two floors made of open joists upon which faggots are laid, thus forming filtering beds, which are washed by water in the form of fine spray falling from a cistern on the top of the condenser. The gases extracted from the flue by the fan are forced through the series of compartments of the condenser and meet in their passage with the fine spray of water, and must also pass through the several filtering beds, where the fume as it collects is washed away by the water which accumulates in the lower part of the chamber. When the water has reached a certain height it is drawn off into tanks, and here the solid matter collected by the water gradually separates out.

In 1878 Messrs. Wilson and French patented a condenser, which has been adopted at the Sheffield Smelting Company's works and also by Messrs. Bewick and Partners, Limited, of Hebburn-on-Tyne. At Messrs. Bewick's works the gases from the ore-hearths and slag-hearths and reverberatory furnaces pass first into a long flue, which ascends the ballast hill at the back of the works, and after making a circuit round the top of the hill, the gases are drawn off from the flue down a series of narrow flues to the condensers. In this way the gases are thoroughly cooled before they reach the condenser, and a certain portion of their solid burden will have been deposited in the flues, which are cleaned out from time to time; the remainder is obtained in the condenser. The condenser consists of a wooden box *aa*, fig. 29, having a shelving bottom where the solid matter arrested collects, and a tap *b* at the lowest point, by which the contents of the condenser are run off from time to time. The box is filled with water to the level of *c*. The gases are forced into the box by a fan, along the pipe *h*, which opens into a chamber *g*, formed by a partition running parallel with the side of the box. Below, this chamber opens into a series of triangular tubes *i*, running across the box;

these tubes are perforated above, and through these fine openings the gases are forced into the water by which the box is partially filled. Near the surface of the water at *d* is fixed a series of three or four copper wire screens, or screens made of wickerwork, and held in position by the supports *e* and *f*. The gases pass out finally by the pipe *j* in the top of the box, and are conducted by flues to the chimney. By this arrangement the gases are forced through a layer of water of a given depth, and further intimate contact between the water and the particles of the fume &c. is insured by the wickerwork or copper wire screens. The fume &c. arrested by the water collects in the lower part of the box, and is drawn off into settling tanks, and after removing the greater portion of the water, it is dried and smelted. With three wire-gauze screens and a depth of 8½ inches of water, Mr. French states that at the Sheffield Smelting Company's works, the quantity of lead and silver arrested amounts to from 95–98 p.c. of that contained in the smoke as it leaves the furnace.

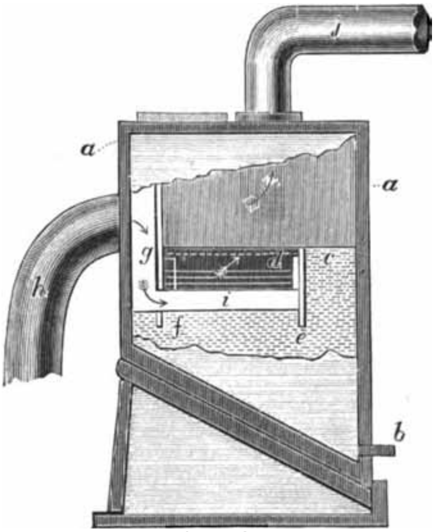


Fig. 29.

The application of electricity to fume condensation has been suggested by Professor O. Lodge (S. C. I. 5, 572–575), and its use patented by Walker. In using electricity it is proposed to line a portion of the flues with spikes, and to hang well-insulated wire netting, studded over with ragged edges and spikes, in the middle of the flue. In the case of large chambers a number of wire nets are suspended and arranged parallel to one another; these nets are to be kept alternately negative and positive. These conductors so arranged are connected with an electrostatical machine, such as Wimshurst's or Voss's, and the fume condensation effected by the continuous brush discharge from the surface of the conductors. Experiments have been made with this method at the Bagillt works of Messrs. Walker, Parker & Co., Limited, and yielded satisfactory results when working on a small scale, but did not prove successful when applied to the flues of the works. One of the chief difficulties, however, is that of efficiently insulating the conductors.

Composition of lead fume.—The following analyses taken from Dr. Percy's work on the Metallurgy of Lead (p. 451) will serve as examples of the composition of lead fume. The samples analysed were collected from the flues of the lead-smelting works at Bagillt, and represent the fume from reverberatory furnaces and slag hearths.

Lead oxide . .	46·54	62·26	46·88
Lead sulphide . .	4·87	1·05	—
Ferric oxide and alumina . . .	4·16	3·00	10·00
Zinc oxide . .	1·60	1·60	4·14
Lime . . .	6·07	3·77	6·73
Sulphuric anhydride .	26·51	25·78	14·15
Insoluble residue .	10·12	1·97	14·40
Carbonaceous matter	—	—	3·37
	99·87	99·43	99·67

Properties and Uses of Metallic Lead.

Properties of lead.—Lead is a bluish grey metal, the freshly cut surfaces exhibiting a distinct metallic lustre, which soon disappears owing to superficial oxidation. Its crystalline character is well shown by the beautiful fern-like crystalline growths which are seen on the pigs of best market lead, or as they form on the surface of a casting as the molten metal gradually cools. It can easily be obtained in the form of regular octahedrons by melting lead and allowing the molten metal to partially solidify, and pouring off the portion still remaining liquid. It is deposited in arborescent forms, known as the lead tree, by the decomposition of a solution of lead acetate either by zinc or by electricity. Lead is a very soft metal, is easily cut by a knife or scratched by the nail; it readily receives impressions and leaves a streak on white paper. It is very malleable and is ductile. Rolled lead is more ductile than cast lead; both its malleability and ductility are injuriously affected by the presence of impurities. Lead is a metal of feeble tenacity, a wire $\frac{1}{12}$th of an inch will not support a weight of 20 lbs. When struck with a hammer pure lead emits a dull sound; the presence of antimony, however, makes it sonorous, hard lead being easily distinguished from soft lead by this property. The presence of antimony, zinc, arsenic, and silver increases the hardness and brittleness of this metal. The hardness of lead is also increased by repeated meltings; this is stated to be due to the formation and dissolution by the molten metal of the oxide of lead formed by the action of the air. In practice it is found that the lead is improved by every melting.

The sp.gr. of lead is variously stated by different observers. According to Schweitzer (Am. 7, 174), it varies between 11·344 and 11·377 at 4°C. St. Claire Deville (Phil. Mag. [4] 11, 144) gives the following as the results of his observations on lead prepared in different ways:—

(1) Cooled slowly from fusion, 11·254; (2) Cooled quickly from fusion 11·363; (3) Electrolytic lead, 11·542; (4) Lead obtained by electro-

lysis, then fused and cooled quickly, 11·225. The influence of pressure on the sp.gr. of lead is shown in the following results obtained by Spring (B. 16, 2724). (1) Not pressed, 11·350 at 14°C.; (2) Once pressed, 11·501 at 14°C.; (3) Twice pressed, 11·492 at 16°C. The sp.gr. of molten lead is given as 10·37 and 10·65 by Roberts-Austen and Wrightson (A. Ch. [5] 30, 181), and 10·952 by Quincke (P. 135, 642).

Lead begins to melt at 325° and is completely fused at 335°; its boiling-point has been determined by Carnelley and Williams (C. J. 35, 1879, 566) and is stated by these observers to lie between 1450° and 1600°C.

The specific heat of lead according to Regnault is 0·0314 at temperatures between 10° and 100°C., and for molten lead according to Person it is 0·0402 between 380°-450°. The latent heat of lead is such that 1 part by weight of lead in solidifying gives out heat sufficient to raise 5·369 parts by weight of water by one degree centigrade. It is an inferior conductor both for heat and electricity.

Lead is tasteless, but emits a characteristic odour when rubbed between the fingers. It can be welded in the cold by pressing the clean surfaces together.

Lead is easily oxidised by exposure to the air, and in the finely divided state, as obtained by the decomposition of the tartrate by heat, it is pyrophoric. Pure dry air, freed from carbon dioxide, has no action upon lead, nor is it attacked by air-freed water; but easily suffers corrosion under the combined influence of air and moisture, or of water and air. By the action of air and water the hydrate of lead is produced, which dissolves in the water and is converted into a basic carbonate by the carbonic acid present. The action of water on lead is materially influenced by the presence of small amounts of salt dissolved in the water; nitrates are supposed to further the action—this is especially true of ammonium nitrate—whereas chlorides, sulphates, carbonates, and phosphates are said to retard the action. Chlorides, sulphates, and carbonates, especially the latter, diminish the solvent action of nitrates and in some cases destroy it altogether. The action of distilled water on lead is reduced by addition of chlorides, sulphates, and carbonates. Water saturated with carbonic acid under ordinary pressure has but little solvent action on lead, but when saturated with carbonic acid under a pressure of six atmospheres, the solvent action is considerably increased. In this case also the presence of ammonium nitrate and of potassium carbonate tends to retard the action. These conclusions are drawn from a series of observations on the influence of salts on the solvent action of water on lead, made by M. M. Pattison Muir (C. N. 33, 102, 125, 145; 34, 223, 234) who has also studied the influence of salts on the solubility of the basic carbonate $(PbCO_3)_2Pb(HO)_2$, which is formed on the surface of the exposed lead or deposited at the bottom of the vessels. The order of the solubility of the basic carbonate agrees very nearly with that of metallic lead in solutions of the same salts (Muir, C. J. 31, 660). The influence of small quantities of free sulphuric acid on the corrosion of lead by water has been studied by W. Carleton Williams (S. C. I. 6, 111-113). In these experiments distilled water saturated with air was used to dissolve certain salts, and to these solutions sulphuric acid in amounts equivalent to from 1 to 5 grains per gallon was added, and the amount of lead dissolved from pieces of sheet lead immersed in these different solutions was determined. The presence of 1 grain per gallon of free acid notably increases the action, a greater quantity of lead in a given time being found in the solution than when the salt solutions are used alone. The total action as measured by the loss of lead is less in presence of free sulphuric acid than with the salt solutions alone. Allen (C. N. 46, 145-146) found that water taken direct from the main in one town in Yorkshire, and having an acid reaction, when left in contact with lead, dissolved an amount of lead equivalent from 0·42 to 0·56 grains per gallon, but after the water had been made slightly alkaline the amount of lead dissolved was equivalent to 0·14 grains per gallon only. Considerable attention has been given in recent years to the important subject of the action of drinking water on lead, as in several districts in this country cases of lead poisoning have arisen and have been attributed to the action of the water supply on the lead pipes used for conveying the water. Messrs. Crookes, Odling, and Tidy refer the activity of water towards lead as due to a deficiency of silica, and are of the opinion that from 0·5 to 0·7 parts of silica per 100,000 is sufficient to prevent the action. In many cases the corrosion of the lead pipes would appear to be due to the presence of a free acid in the water supply, as is apparently the case with one of the water supplies of Sheffield, and also the water supply at Huddersfield (Allen, *l.c.*, also C. N. 46, 88). The waters most liable to act upon lead are those obtained from upland gathering grounds, waters which are soft and usually of remarkable purity. The activity of such waters is by many attributed to the presence of free acid. Professor Percy F. Frankland, in a paper read before the London Section of the Society of Chemical Industry (S. C. I. 8, 241-247), has described a series of experiments made in investigating the action on lead of a soft water from an upland gathering ground. In these experiments pieces of leaden service pipe, 2 feet long and closed at one end, were used, and the pipes were filled with water completely and the open end closed by a cork. Since the water in question attacked both new and tarnished lead, old pipes taken from the services where the water was used were also employed in the experiments. The amount of lead in the water was determined after it had remained in contact for a day. Its activity was found to be destroyed by agitation with carbonate of calcium, also by the addition of sodium carbonate, in amounts equal to 5 parts per 100,000. The addition of sodium carbonate was observed to have the same effect in the case of several waters experimented on. Sodium phosphate, unless present in considerable amounts, has no influence. Lime was found to behave like sodium carbonate in the case of new pipes, but to increase the activity of the water towards old pipes. Further experiments with distilled water and the water supply of Dundee (Frankland and Frew, S. C. I. 8, 247-250) have shown (1) that the activity of a water towards lead may, according to its composition, be either increased or diminished by increased pressure; (2) that water containing oxygen has its activity diminished, whilst the activity of water containing carbonic acid is not materially affected by increased pressure up to two and a half atmospheres; (3) that by very slow filtration through extremely finely-divided flint a small proportion of silica is dissolved; (4) that the water after such filtration has less action on lead, both in the case of distilled water and of soft potable waters submitted to investigation; (5) that the activity of soft water is very materially reduced by the addition of small proportions of carbonate of soda. Professor Frankland finds that carbonate of soda retains its protective action even at 100°C., and also that the alkaline waters from the artesian wells in the London basin are without action on lead. These waters are especially rich in silica.

Inasmuch as air facilitates the solvent action of water, an intermittent water supply is favourable to the contamination of water, and as lengthened contact with lead in the case of an active water will naturally result in a considerable proportion of the metal being dissolved, it is advisable, as was recommended by Crace-Calvert in connection with the Manchester water supply, to run off the water that has been standing over night in the pipes, as such water may, by the long contact with lead, be unfitted for drinking purposes. The neglect of such precautions may be attended with serious results (*v.* Allen, *loc. cit.*).

Lead is dissolved easily by dilute nitric acid; the action of concentrated acid is arrested by the formation of the nitrate of lead in white granular crystals. Dilute hydrochloric and dilute sulphuric acids do not attack lead, but it is dissolved by boiling concentrated hydrochloric and sulphuric acids, lead chloride and lead sulphate being formed.

Composition of commercial lead.—Market lead, owing to the perfection of the methods of desilverising and refining, is usually pure, containing traces of antimony, copper, iron; occasionally zinc, tin, bismuth are found, and small but varying amounts of silver are usually present. The following analyses serve to illustrate the composition of commercial lead:—

—	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*
Copper	0·0014	0·0526	0·0053	0·0004	0·0002	0·012 to 0·046	0·05 to 0·1	0·00011
Antimony	0·0037	0·0074	0·0074	0·0011	0·0013	0·016 to 0·04	0·02 to 0·1	0·00016
Iron	0·0016	0·0015	0·0015	0·0003	0·0014	0·001 to 0·035	0·02 to 0·05	0·00037
Zinc	0·0016	0·0018	0·0018	0·0007	0·0003	traces to 0·009	—	0·00013
Silver	0·008	0·0040	0·0040	0·0001	0·0009	—	—	—
Bismuth	—	—	—	0·0034	0·0555	—	—	0·00063
Tin	—	—	—	0·0001	—	—	—	—
Arsenic	—	—	—	—	—	—	—	0·00005
Total of foreign metals	0·0163	0·0673	0·0200	0·0061	0·0596	0·032 to 0·110	0·09 to 0·25	·00145
Specific gravity	—	—	—	11·358	11·314	11·365 to 11·395	11·869	—

(*a*) Bleiberg. (*b*) Newcastle; both analysed by Hampe. (*c*) Lead manufactured by Foster, Blackett & Wilson, Newcastle-on-Tyne, analysed by Michaelis (1868) (Kerl, Huttenkunde, 19). (*d*) and (*e*) Schweitzer (*loc. cit.*). (*f*) Lead from Upper Hartz, purified by Pattinson's process. (*g*) Freiberg lead, refined by Pattinson's process. (*h*) Lead from Ems, desilverised by zinc and refined by steam. *f*, *g*, and *h* are quoted from analyses given by Kerl (Huttenkunde).

Lead is largely used in building construction in the form of sheets, gutters, spouts, &c., also for the manufacture of pipes for gas and water, for making shot and solders. Its power of resisting the action of acids &c. renders it of great service in the construction of chemical plant, *e.g.*, sulphuric acid chambers. The lead preferred for the construction of sulphuric acid chambers is that obtained by remelting old lead, which is hardened by a small amount of antimony. Experiments of Johnson and Calvert (C. R. 56, 401), of Hasenclever (W. J. 1872, 239), and of Bauer (ibid. 1875, 364) have shown that ordinary leads resist the action of sulphuric acid more effectively than pure lead.

Sheet lead.—For the manufacture of sheet lead market lead is cast in a plate several inches in thickness by running molten metal into a mould consisting of a large rectangular iron framework. When the plate is somewhat cooled it is transferred to the rolling mill, which consists of a pair of massive iron rollers, about 18 inches diameter and some 8 feet wide, which are worked by engines with reversing gear. The rolls are placed in the middle of a long bench, a little wider than the rollers, and about 3 feet high; at intervals of a foot along the bench are placed wooden rolls on the same level as the rollers, which serve to facilitate the movement of the sheet to and fro. By passing and repassing of the plate between the rollers it is gradually extended into a sheet, which, when too long for manipulation in the ordinary way, is cut into smaller sheets which are rolled separately. Or the sheet may be doubled over, the surface being previously chalked to prevent the adhering of the two sheets, and the doubled sheet rolled out to the required thickness. The lead having been rolled out, the edges and ends of the sheets are cut straight and the sheet wound on to a cylinder at the end of the bench.

Lead pipes are usually made in machines worked by hydraulic pressure. Over the piston of the press is a reservoir which contains the metal, and which may be heated by an annular fireplace. The reservoir is filled with molten lead by a spout through an aperture in the top; when filled the spout is withdrawn and the aperture closed tightly by an iron plug, kept in position by an iron key. The size of the pipe is regulated by a steel die of the diameter of the outside of the pipe fitted at the top, the internal diameter of the pipe being determined by a mandril which passes directly through the centre and is moved upwards by the rising piston, the semi-molten metal being at the same time forced through the die. As the pipe passes out at the top it is coiled on to a drum. The pipes used for gas-services are usually made of metal to which either tin and antimony have been added directly, or these metals may be supplied by the addition of a harder lead containing them.

Lead shot is made by alloying the metal with arsenic, which is added either in the form of white arsenic or arsenical dross from the improving furnace. The addition of arsenic serves to impart a greater fluidity to the metal and increases the tendency of the metal to assume a spherical form in passing through the air. The molten metal is made to run through cullenders pierced with holes, and to fall through a considerable height into vessels holding water. The height required for the fall is either secured by means of a shot tower, or, as in some places, by means of a deep well, the shaft of an old coal pit being in some cases adapted for this purpose. The size of the shot is determined by the size of the holes in the cullender, by the height from which the lead falls, and by the temperature and consequent fluidity of the molten metal.

The shot, taken from the vessel in which they have solidified, are sorted by sieving into different sizes, and the imperfect ones separated by causing the shot to roll down an inclined polished metal surface, the globular ones running down easily, and are collected in a box at the bottom of the inclined plane, whilst the imperfect ones remain on the sides of the plane. The shot are finally polished by shaking them with a little plumbago in a cask revolving on a horizontal axis.

LEAD COMPOUNDS USED IN THE ARTS.

Lead oxide, *lead monoxide*, or *plumbic oxide* PbO. The two commercial varieties of this compound are *massicot* and *litharge*. The former is obtained when molten lead is heated at a moderate temperature in the air, the molten lead being constantly stirred. It is the product formed in the first stage of the manufacture of red lead. After grinding and levigation it is obtained as a brownish-yellow powder. Another variety is obtained as a lemon-yellow powder by heating white lead (the basic carbonate).

Litharge is produced when the oxidation of the lead takes place at a temperature sufficiently high to melt the oxide formed, as in the cupellation process of which it is one of the products. When litharge is manufactured for sale, the purest lead is submitted to cupellation; if the lead used is not quite pure, then the portions of litharge first formed and that produced towards the end of the operation are rejected. The litharge as it forms is collected in large iron pots fitted on wheels, in which it is allowed to cool slowly. When the pots are emptied, the litharge 'falls,' the central portions which have cooled more slowly being somewhat lighter in colour and possessing a scaly crystalline structure. The more friable portion is broken up and passed through a circular temse or screen, the litharge collected and packed in casks and sold as *flake litharge*. That portion of the litharge which does not fall, but remains in hard coherent masses is ground between horizontal stones in a stream of water, by which the powdered litharge is carried into settling tanks in which it accumulates. The litharge after separating from the water is dried at a low heat in a reverberatory furnace, packed, and sold as *levigated litharge*. The colour of lead oxide varies from lemon yellow to reddish yellow, and on heating it becomes brownish-red. The specific gravities of different varieties of lead oxide are given by Geuther (A. Ch. 219, 60–61) as follows:

Yellow cryst. 9·29 at 15°; red cryst. 9·126 at 15°; red cryst. 9·125 at 14°; red powder, 9·09 at 15°; and red, very pure, 8·74 at 14°.

Litharge is used in the arts in the manufacture of flint glass, as a glaze for earthenware, for the preparation of lead acetate, lead nitrate, lead plaster, and for drying oils.

Red Lead, *Minium*, or *Plumbic Tetroxide* Pb_3O_4. The manufacture of red lead consists in the oxidation of lead, which is effected at two stages, the first process being the conversion of the lead into massicot or the 'drossing' of the lead, and the second the conversion of the monoxide into tetroxide or a red lead of the required shade. These operations are usually conducted in two different furnaces. The first of these, the drossing oven, is a low-arched furnace with a bed of fire-brick laid on a bed-plate of cast iron having raised borders on each side and at the back. The bed of the furnace is made to slope slightly towards a median line, and also from back to front. On either side of the furnace bed is a low wall, the spaces between which and the wall of the furnace form the two fireplaces. In front are three openings closed by hinged doors of cast iron; the two side ones communicate with the fireplaces, and serve for the introduction of fuel, whilst the central one, which is larger than the other two, serves for the introduction and the working of the charge, as also to allow of the escape of the products of combustion, which pass into an arched space or hood of brickwork in front of the furnace, this hood forming in fact the base of the short vertical chimney attached to each furnace. In front of the working door is hung a chain with a hook at the end; this serves as a fulcrum for the rabble used in working the charge. Below the working door a space is formed by two vertical plates of cast iron on brick walls, resting on a slab of stone or plate of iron on the floor, and supported by the iron plate which forms the lower part of the front of the furnace. This space in front serves to collect any of the oxidised product which may fall in transferring it to the waggons. The length of the furnace is about 11 feet, and the width between the bridges is about 8 feet 4 inches. The 'colour oven' is in most essentials similar to the 'drossing oven;' the bottom is flat and the slope from back to front not so great as in the latter. Coal is used as fuel in these ovens; in some cases where the ovens are constructed with fire-grates and ash-pits, small coal may be used.

The mode of working is as follows. A charge of from 22 to 31 cwt. of pig lead is introduced into the furnace, and a dam is made across the furnace of rough oxide with lead intermingled obtained from the grinding &c. of a previous charge. The temperature is so regulated as to melt the lead, which forms a pool behind the dam; the molten lead is agitated by means of a rabble and splashed over the furnace bottom. In this way the oxidation is promoted, and as the oxide forms it is pushed toward the back of the furnace, the still unoxidised lead flowing to the front, and as the oxidation proceeds the pool becomes smaller and smaller. The oxidation is promoted by adding some slag lead from time to time, the antimony contained in it being favourable to a rapid drossing. This addition of slag lead, whilst it curtails the length of the operation, is not permissible in the manufacture of the better varieties of red lead, such as are used in the manufacture of flint glass; the red lead used for this purpose should not contain copper. In practice it is found the oxidation of the lead is so materially promoted by the use of slag lead, that in many works special alloys of antimony and lead are prepared and used to replace slag lead in the manufacture of the best varieties of red lead.

When the oxidation is completed the charge is raked out into iron waggons, and in these allowed to cool. It is next passed to the grinding mill, where it is ground between millstones with a regulated supply of water. The heavier particles of lead oxide and metallic lead which sink in the troughs leading to the settling cisterns are collected and used in the drossing oven to dam up the charge of lead. The finely ground massicot is carried by the stream of water into settling tanks where it subsides, and after the water has been run off, it is transferred to iron barrows, in which it is conveyed to the 'colouring' oven, upon the bed of which the contents of the barrows are emptied. The mass is thus quickly dried, and is then spread out over the bed of the oven in furrows and ridges resembling a ploughed field, and heated at a carefully regulated temperature for some hours, until it has assumed the required shade. The oxidation is aided by stirring the mass from time to time, and the progress of the operation watched by withdrawing a sample by means of a paddle, and from the appearance presented by the sample the completion of the operation is determined. When hot the red lead has a rich purple tint, which when the oxidation is completed, assumes a bright red colour on cooling.

A variety of this same compound, styled orange lead, is made by submitting white lead to a similar process. The lighter particles of white lead which form as a froth in the grinding and levigating white lead are collected, and when heated in the red lead ovens yield a very soft and bright coloured orange lead.

The red lead is withdrawn from the ovens, and after cooling is re-ground and dried, and after sieving is packed in barrels. Orange lead is ground and levigated, as the decomposition of the carbonate requires a temperature so high that some of the oxide of lead produced is partially fused.

Red lead is a granular crystalline powder, the colour of which varies somewhat, this variation is supposed to be in part due to the presence of orange lead formed from the carbonate of lead contained in the massicot, and produced by the absorption of carbon dioxide from the air, but in all probability it is to be accounted for by the difference in composition of the lead from which the red lead is made. When heated, red lead assumes a darker shade of red, becoming violet and ultimately black, regaining its original tint on cooling. The specific gravity of red lead, as given by different observers, varies from 8·62 to 9·19 (Clark's Constants of Nature, 47). When strongly heated it yields oxygen, and is converted into the monoxide. It is decomposed by nitric acid, the nitrate of lead and the puce-coloured peroxide PbO_2 being formed; when digested with nitric acid and a little sugar, the red lead is completely dissolved. Red lead is used as a pigment, in the manufacture of flint glass, as a cement in making steam-joints, and in the manufacture of secondary batteries. Commercial red lead may contain some metallic lead, lead sulphate, and also oxides of antimony, tin, copper, and iron.

White lead, Céruse, Blanc de Plomb, Bleiweiss. The commercial article known as white lead is essentially a basic carbonate of lead, of the formula $2PbCO_3.Pb(HO)_2$, which is produced by the decomposition of a basic acetate of lead by means of carbon dioxide. The method of manufacture which according to experience yields a white lead best adapted for the production of paint, one of the chief uses of white lead in the arts, is a modification of the old Dutch process.

The Dutch method consists in exposing thin sheets of metallic lead, rolled into coils and placed in earthenware pots containing a small amount of vinegar, to the combined action of the acetic acid contained in the vinegar, air, moisture, and carbonic acid; this latter and the heat necessary to further the corrosion of the lead being obtained by the fermentation of horse manure and stable litter, in which the earthenware pots and their contents are embedded. The 'blue' or metallic lead is gradually corroded and converted into white lead, which after being separated from the unaltered metallic lead, is ground and washed.

The English method differs from the Dutch method chiefly in the replacement of horse dung and stable litter by spent tan in a state of fermentation, and the substitution of dilute acetic acid, prepared from pyroligneous acid, for the vinegar. The substitution of spent tan for stable litter minimises the risk of discolouration of the white lead by the production of sulphuretted hydrogen, but the fermentation is somewhat slower, and consequently the conversion of the 'blue' lead into white lead requires a greater length of time. The lead used for the manufacture of white lead should be of the purest and softest description, and the manufacturer usually purifies the lead used for this purpose by the Pattinson, the Rozan, or the zinc process already described. The presence of small amounts of copper or antimony tends to produce a white lead having a dull grey tint. A red or pink colour, at times observed in the manufacture of white lead, has been attributed to the presence of a suboxide of lead by Bannow and Kraemer (B. 1872, 545, and 1873, 21), an explanation admitted by Lorscheid, whilst according to Baker the colouration is said to be caused by the presence of finely divided oxy-compounds of silver. The lead is cast into thin sheets of lattice work or gratings, so as to expose a large surface to the corrosive action of air and acid vapours &c., by pouring molten lead on to a sloping grooved iron plate, from which, on solidifying, the crates, buckles, plates, straps, or wickets, as they are variously styled, are easily detached. Some of this lead is cast in thin circular discs or stars. In some of the works in this country and in America, the 'plates' and 'wickets' are cast by machinery. The machine consists of an endless band of square plates of iron linked together, each plate being a mould, into which the lead is poured as the plates are slowly moved under the spout of the lead-pot. The castings are delivered at the end on a leather belt covered with plates of sheet iron to prevent the hot lead injuring the leather, and are thus carried away from the machine. This machine can make from 50–60 castings per minute. The corrosion of the lead is effected in what are known as stacks, which are built in brickwork chambers, a series of which are usually built side by side along one side of a shed. The dimensions of the chambers vary at different works, the most convenient dimensions being an area of 12 ft. by 20 ft., or 16 ft. sq., and a height of some 25 ft. The front wall of the chamber is provided with an opening, 4 ft. wide, running from the top to the bottom, serving for the introduction of the materials used in the construction of the stack. As the building of the stack proceeds the opening is closed by boards fitting into slots. The stack is built up as follows. First, the floor of the chamber is covered with a layer of ashes, upon this is spread spent tan, already in a state of fermentation; the height of this first bed of tan is some three feet. The tan is beaten down and the surface levelled, and on the bed so formed is placed a series of earthenware pots, which are partially filled with diluted acetic acid containing from a two to three p.c. of acetic acid. These pots are placed together, leaving a space about 6 in. wide between the outside rows and the walls of the chamber. The pots ordinarily used are of two sizes; the larger ones, which are provided with a rim on the inside, are placed on the outer edges of the series, and in the mouths of these pots are placed the discs of metallic lead, resting on the rims already mentioned. These larger pots serve to support the wooden bearers which carry the flooring boards used to cover in the bed. In some establishments pots of one size only are used, and the flooring boards are supported by blocks of wood. On the top of the earthenware pots are placed the crates of metallic lead, so as to form a layer of lead about 5 in. in depth; between the lead and the cover of flooring boards is left a space of from 6 to 8 in. The space between the walls of the chamber and the pots is filled in with tan on all sides, the opening in front being closed by boards. On the bed so constructed another bed is built in exactly the same way, with the exception that in the construction of the upper beds the layer of tan is only about one foot in thickness. In this way the chambers are filled up to a height of some twenty or more feet, with beds consisting of pots, lead, and tan, the topmost bed being covered with a layer of tan. In stacks of an area of 12 ft. by 20 ft., a bed will represent 8 tons of lead, which will lie on about 1,000 pots of 5½ in. diameter, containing 200 gallons of diluted acetic acid. The weight of lead in a stack will vary with different practices, with the size of stack and weight of wickets. In stacks 28 ft., by 14 ft., each bed might represent as much as 7 tons of lead, and with twelve beds the total lead being 84 tons. As the building of the stack proceeds the opening in front is gradually built up with loose boards, and when the stack is completed the opening at the top is left unclosed, so that the stack may be examined from time to time, and if necessary the tan rearranged, as during the fermentation the system of beds gradually falls away from the side walls. In some cases it is usual to provide ventilation in the form of wooden spouts placed in the corners of the chamber; these spouts are pierced with holes which may be closed by tan. Such ventilators are only used in stacks of large area, and they provide an escape for the steam which is produced in considerable amounts during the first stages of the fermentation; in the case of smaller stacks this takes place with sufficient regularity at the surface of the side walls. After the stack is built it is left to itself for about three months, and during this time the fermentation of the tan proceeds producing heat, the temperature in some cases rising to 140°F., which serves to volatilise the acetic acid and water, and at the same time develop carbon dioxide. Under the combined influence of these agents the blue lead is gradually converted into white lead. At the end of the time mentioned above, the stack is unloaded, the top covering of tan is removed, the bark which is not mouldy is used to add to fresh tan in the construction of another stack. As the covering of boards is removed, the corroded crates and discs are loaded into trays and carried away to the mill, in which the white lead is separated from the unaltered metallic lead. The 'corrosions' preserve the form of the castings of the metal, but are more bulky, and present a white opaque appearance, and vary in texture. The best corrosions are hard and porcellanous, and can be easily handled without crumbling, whilst the poorer are of a floury character and crumble easily when touched. In places the white lead is discoloured; the discolouration may be either due to the tarry matter present in the acid used or to the droppings of water from the tan. Before removal of the corrosions from the stack, each layer as it is exposed is thoroughly moistened with water. The white lead taken direct from the bed is not uniform in composition; it consists mainly of a basic carbonate $2PbCO_3.Pb(HO)_2$, but some of the corrosions approximate more nearly to a body of the formula $3PbCO_3.Pb(HO)_2$, whilst in some cases the composition is very nearly that of the normal carbonate of lead $PbCO_3$. All white lead corrosions contain some lead acetate locked up in the particles, and this is dissolved out in the washing and grinding to which the corrosions are next submitted. It is usual to find the earthenware pots quite empty and dry, or at the most a few may contain a little water; the pots are washed and drained, and when dry are used over again. The pieces of white lead which fall on the bed of tan are picked up by hand, the surface of the bed is also raked and a further quantity of white lead is got from the tan by washing it on sieves in a stream of water.

The trays of corrosions are taken from the stack to the grinding mill, where the unaltered or blue lead is separated from the white lead and the latter finally ground into an impalpable powder. The mode of conducting the grinding and levigation varies in different works; the trays are usually sunk in a cistern of water and the contents are directed by means of rakes between corrugated rollers running under a stream of water. The emptying of the trays is effected in this manner to insure a complete soaking with water, and thus further obviating the production of clouds of poisonous dust. The production of dust in the treatment of the corrosions is greatly reduced by watering them before they are removed from the stacks. After the blue lead has been separated, the white lead is crushed by passing through a pair of smooth rollers, made of gun-metal, and raked about over a perforated plate under a constant spray of water. The coarse white lead next passes to horizontal grinding stones, to which it is fed by a ladle or by an endless band. After passing through these stones the white lead issues in the form of a thick white mud, and is again passed through other grinding stones until it has been reduced to a state of subdivision so fine that it is carried along by the stream of water to the settling tanks; the white lead which settles out in the troughs used to convey the water to the tanks is returned to the grinding stones. The grinding and levigating are conducted in such a way that the water may be used over and over again, and is usually found to contain lead salts in solution, which, before discharging the water, are precipitated by sodium carbonate. In the tanks the white lead gradually settles and forms a thick white paste, from which the water is siphoned off, and when the mud has attained a sufficient consistence it is ladled out into the dishes used for drying it. The dishes are shallow clay saucers, 12 in. diameter and 3 in. deep, and made of clay similar to that employed in making flower pots. The dishes are stacked in drying stoves upon shelves made of iron bars, the stoves are heated by iron pipes made to circulate round the floor of the stove, and connected with a fireplace outside the stove, the products of combustion from the fire passing through the pipes. In this way the pulp, which contains some 25-30 p.c. of water, is gradually dried, the temperature of the stoves should not rise above 180°F. The white lead when dry is taken from the stoves and either packed in casks or ground and mixed with oil to form a paint. Boiled linseed oil is used for this purpose, from 8-9 lbs. of oil is needed for every hundredweight of white lead. During the grinding some manufacturers add a small quantity of a blue colouring matter such as Prussian blue or indigo to the white lead to modify the somewhat yellowish tint due to the stains from the bark.

The explanation given by Liebig in his Handwörterbuch der Chemie of the chemical changes which take place in the corrosion of the lead in the stacks, has been practically substantiated by the experiments of Hochstetter (J. pr. 20, 338, 353). These experiments demonstrate the first change to be the conversion of the lead into a basic acetate by the agency of air and acetic acid vapours. The basic acetate of lead is next converted into white lead and the normal acetate of lead by means of carbon dioxide and aqueous vapours. The normal acetate is next converted into white lead, and acetic acid liberated by the combined action of carbon dioxide and aqueous vapour. The acetic acid so liberated is free to take part in the corrosion of a further quantity of blue lead, the conversion of which into a basic acetate precedes the formation of the basic carbonate. The basic carbonate $2PbCO_3.Pb(HO)_2$ is according to Hochstetter not only the product of this combined action, but is also formed when carbon dioxide is passed into a solution of the basic acetate of lead. Further, this compound resists the action of carbon dioxide alone, and can only be converted into the normal carbonate in presence of free acetic acid. In the light of this investigation white lead would appear to consist of carbonate and hydroxide of lead in the proportion of two molecules of the former to one of the latter, and the increased proportion of the carbonate frequently observed is to be explained as due to an admixture of normal carbonate produced by the action of carbon dioxide in presence of acetic acid vapours upon the basic carbonate. All white lead corrosions contain some normal acetate, but the amount of this compound will be less in white lead made by the Dutch or English methods than that produced by the German method in which the production of carbon dioxide, acetic acid, and aqueous vapour ceases simultaneously.

The proportion of lead corroded when working in stacks is from 50-70 p.c., the average result will be about 65 p.c.; the increase in weight is 20 p.c. of the lead used. The uncorroded lead is collected and after drying is weighed and remelted to be used over again.

The percentage of corrosion is chiefly determined by the thickness of the wickets, some manufacturers prefer to cast heavy wickets, and get a low percentage corroded, as it is found that the 'blue' lead is so much more efficiently separated from the 'white' lead.

The German method, as practised at one time at Krems, and now chiefly at Klagenfurt, consists in exposing thin sheets of metallic lead suspended in wooden boxes to the action of the vapours produced from a mixture of wine lees and vinegar, which is spread over the bottom of the boxes. The boxes are packed in stoves heated to about 85°F. This mode of procedure has been modified by suspending the sheets of lead in heated chambers, on the floors of which are placed vessels containing diluted acetic acid, air and carbonic acid gas being led into these chambers.

Whilst this method is much more rapid than the English method, it labours under the disadvantage that the white lead produced does not compare favourably with that produced by the older and slower procedure.

French or Clichy method.—The process by which lead is manufactured in France is due to Thenard, and consists, first, in the production of a solution of basic acetate of lead by digesting litharge with a pyroligneous acid of a sp.gr. 1·056; the litharge is added to the acid in a vessel in which it is kept constantly agitated by mechanical means until the sp.gr. of the solution is 1·145. The liquor is then run into another vessel, in which insoluble matter, such as lead, lead sulphate, silver chloride, &c., settles out, and the clarified solution is conveyed into a vessel where it is exposed to the action of carbon dioxide, which is forced through it by means of a fan and distributed throughout the liquid by a series of small pipes. The carbon dioxide used is produced by heating a mixture of coke and chalk in a kiln, the gases from the kiln passing into a vessel in which they are washed, and are then drawn off by a fan and forced into the decomposing vessel. The gas is passed through the solution of acetate for 12 to 14 hours, the white lead produced is allowed to settle out, and the solution of normal acetate pumped back to the vessel, in which it is digested with litharge and converted into basic acetate. The white lead is run off into a tank and repeatedly washed with water; the first washings, as they contain acetate of lead, are used over again for the production of basic acetate.

Milner's process.—This method of manufacturing white lead consists, first, in the production of a basic chloride of lead by the action of litharge, common salt, and water, upon one another; the change takes place when these substances are mixed with one another at the ordinary temperature; the mixture swells up, becoming gradually white and pasty. The reaction is attended by a considerable evolution of heat, and the solution becomes alkaline. This decomposition is, on the large scale, effected in a pug mill made of white pine, the arms of American elm; the litharge used is flake litharge which has been carefully ground and levigated; it is mixed with salt and water in the proportion of 1 of salt, 4 of litharge, and 16 of water. These materials are mixed with one another, the agitation being continued for three hours, as it is found that unless a sufficient time is allowed, the mass becomes stiff and pasty, and has to be removed from the mill by hand, whereas if the mixing be continued for the time specified, the mass obtained is more fluid, and can be easily removed. The mixture of basic chloride of lead and caustic soda so obtained is next run into a large iron cylinder with spherical ends, the cylinder is lined with lead, and is 16 feet high and about 8 feet diameter. In the top end of the cylinder are two openings, one serving to introduce the mixture from the pug mill, and the second is closed by a valve by which the pressure is regulated. In this vessel the conversion of the basic chloride of lead into a basic carbonate is effected by means of carbon dioxide, which is introduced by a pipe, the portion inside the vessel being provided with a number of perforations for the distribution of the gas. At one side of the lower part of the cylinder is a tap for the withdrawal of the white lead and of samples, which are taken from time to time during the carbonation. The carbonator is supplied with paddles or stirrers attached to a horizontal shaft running across the cylinder, and set in motion by machinery. As in the Clichy process, the carbon dioxide is produced by heating a mixture of limestone and coke in a kiln, from which it passes up a coke tower, in which it is washed by a stream of water and then forced by a pump or fan into the carbonator. The fluid mixture of basic chloride, caustic soda, &c., is submitted to the action of carbon dioxide until it is completely converted into white lead and common salt. The completion of the conversion is ascertained by the appearance and properties of samples withdrawn from the carbonator. The end of the reaction is shown by the liquid no longer exhibiting an alkaline reaction, the mixture forming a viscid, homogeneous mass, which, when shaken up in a glass vessel, by which it is partially filled, coats the sides, forming a uniform very thin layer like frost on a window pane, and after standing a few seconds, the clear liquor separates from the carbonate, leaving arborescent patterns on the sides of the glass. If after this point has been attained the gas be passed through the mixture, the product loses its value, becoming granular and no longer coats the glass, but settles out rapidly. At the end of the carbonation the charge is run off into cisterns in which it is thoroughly washed with water to free it from salt, and, when completely washed, it is drained and dried in the usual manner. The white lead made by Milner's process resembles in composition that produced by the methods already described, and, like these products, is well adapted for use as a paint. This method of white lead manufacture was recently in operation at the Sankey White Lead Company's works, near Warrington, and at one time employed at one of the white lead establishments on the Tyne, but has been abandoned at both places.

Many processes have been devised for the manufacture of white lead; the production of white lead by the decomposition of a basic nitrate of lead with carbon dioxide has been made the basis of one of the proposed methods. Another proposal is to submit a pasty mixture of litharge and lead acetate solution to the action of carbon dioxide, and it has been suggested to utilise the corrosion of finely-divided granulated lead by air, water, and carbon dioxide as a method of making white lead. Attempts have also been made to manufacture white lead by precipitating solutions of basic acetate of lead with solutions of sodium carbonate. These and many other processes have been suggested and patented; and whilst basic carbonates of lead, or mixtures of the normal carbonate and lead hydroxide, are yielded by these methods, none have proved sufficiently successful to supplant the older methods, the greater portion of white lead manufactured at the present time being that produced by the English method, which, despite the slowness of the first stage and the dangerous character of several of the subsequent operations, maintains a supremacy. It would appear that the slow conversion of lead into white lead, such as obtains in the Dutch and English methods, is favourable to the production of this substance in a form possessing high covering properties, and specially adapted for use as a pigment. To perfect this mode of manufacture, what is needed is a method of detaching the corrosions, of washing and drying the white lead, which will minimise the risks of poisoning to the workpeople. Despite the regulations in force at all white lead manufactories in this country and the constant medical examination of the individuals engaged in these processes, cases of lead-poisoning are not infrequent, and in some instances these terminate fatally. Careful and frequent medical examination and immediate attention to the first symptoms of lead-poisoning have proved in the experience of a manufacturer with whom the writer is acquainted that it is possible to produce white lead by the English process without serious consequences to the people employed. No doubt one of the chief obstacles in the enforcement of the sanitary regulations is the negligence and carelessness of the workpeople themselves.

Properties of white lead.—White lead is a white, earthy, heavy powder, which, from its behaviour to polarised light, undoubtedly possesses a crystalline structure. Examined under the microscope, it appears to consist of rounded, circular, or oval grains. The grains are transparent; they vary in diameter from 0·0001 to 0·00004 of an inch. Commercial white lead varies in composition, and is apparently a mixture of the basic carbonate $(PbCO_3)_2.Pb(HO)_2$ and normal carbonate of lead, $PbCO_3$. This view of the constitution of white lead is not only supported by the observations that samples of white lead have been found on analysis to have a composition represented by the formulæ $3PbCO_3.Pb(HO)_2$ and $5PbCO_3.Pb(HO)_2$, and in some cases to consist of nearly pure $PbCO_3$, but is borne out by the investigations of Hochstetter, already referred to. For Hochstetter has shown the basic carbonate $(PbCO_3)_2.Pb(HO)_2$ to be the product of the action of carbon dioxide on a solution of the basic acetate of lead, and also of the action of sodium or potassium carbonates on the solution of the basic acetate. This compound is also produced by the action of carbamide on a solution of the basic acetate of lead (Bourgeois, Bl. 50, 83-85; C. J. Abstr. 1889, 21). Further, this basic carbonate is converted into the normal carbonate by carbon dioxide in presence of acetic acid, and it is conceivable that in the stacks the compound $(PbCO_3)_2Pb(HO)_2$ should be in part converted in this way into the normal carbonate, and thus the varying composition of commercial white lead may be explained. The presence of the basic carbonate, or at any rate of a proportion of lead hydroxide, would appear to be essential to a white lead in order that it may be useful as a pigment and of good covering power. This conclusion is borne out by a series of experiments made by Wigner and Harland, who, by artificially preparing mixtures of lead carbonate and lead hydroxide, have shown that the covering power, the opacity, and the ease with which it can be applied as a pigment are greatly impaired when the proportion of carbonate to hydroxide exceeds that of three molecules of the former to one of the latter. In mixing white lead with oil, a considerable rise in temperature is observed, and it is supposed by white lead makers that a portion of the oil is saponified in this process. If this be the case, then it is probable that the lead hydroxide takes part in this decomposition of the oil, and an explanation is given of the fact that those corrosions, which consist mainly of the normal carbonate of lead are practically worthless as pigments. The covering power of white lead is further dependent upon the density; the greater the density the smaller the amount of oil absorbed and the thicker the colour. The covering power may be tested by triturating equal weights of the samples to be compared with equal quantities of linseed oil, and then determining the weights of equal volumes of the pigments thus obtained; that having the greater density will possess the higher covering power.

Weise (Monatschr. des Gewerbe-Vereins Cöln; also D. P. J. 208, 434) has examined different corrosions obtained by the German method, and concludes from the analysis of the same that the best varieties are those approximating most nearly to the composition of the basic carbonate $2PbCO_3.Pb(HO)_2$, and that an increase in the proportion of normal carbonate results in a reduction of covering power. The following are the analytical results obtained by Weise:

	Lead oxide	Carbon dioxide	Water	
1.	86·80	11·16	2·00	Best quality
2.	86·24	11·68	1·81	Seconds—still good as a paint
3.	86·03	12·28	1·68	Thirds—useful as a paint
4.	84·69	14·10	0·93	Residue from washing apparatus
5.	83·47	16·15	0·25	Useless for paint
6.	93·70	5·31	0·90	”

The following represent the composition of the normal carbonate and of the basic carbonate:

	Lead oxide	Carbon dioxide	Water
Normal carbonate	83·52	16·48	—
Basic carbonate $2PbCO_3.Pb(HO)_2$	86·32	11·36	2·32

The pigments known as Venetian, Hamburg, and Dutch whites are made by mixing white lead with heavy spar, Hamburg white containing these materials in the proportion of 1 to 3, and Dutch white in the proportion of 1 to 2.

Substitutes for white lead.—Several proposals have been made to replace the basic carbonate of lead by other compounds of this metal. Amongst these may be mentioned the oxychloride of lead which was at one time manufactured at Washington, in the county of Durham, by a process patented in 1849 by the late Hugh Lee Pattinson. In this process lead chloride is produced by treating finely-ground galena with concentrated hydrochloric acid; the chloride of lead formed in this way separates out by reason of its sparing solubility in water. The lead chloride is collected together and dissolved in hot water, and this solution is treated with a quantity of milk of lime sufficient to neutralise any free acid and precipitate any iron which may be present, the solution being during this operation maintained at a temperature sufficiently high to keep the lead chloride in solution. After allowing the oxide of iron to settle out, the clear liquor is run off into a vat, and then treated with half the quantity of lime required to decompose the lead chloride. The oxychloride of lead so produced is collected, drained, and washed, and finally dried in stoves on porous earthenware plates. The composition of the oxychloride of lead is represented by the formula $PbCl_2Pb(OH)_2$ or $PbCl(OH)$; it is a white solid, possessing considerable covering power, and at one time was used as a paint. The manufacture of Pattinson's white lead at Washington has been given up for many years.

Lead sulphate is another of the compounds which it has been proposed to utilise as a white lead. In 1839 Richardson suggested the preparation of this compound by decomposing a solution of lead acetate, made by dissolving litharge in acetic acid, with sulphuric acid. The pigment styled 'galenite' is said to be a basic sulphate of lead, and can be made by treating finely-powdered galena at a low red heat in open retorts. Lead fume consists chiefly of lead sulphate, and occasionally a paint of a greyish shade is made with the fume collected in French's and other forms of fume condensers.

Hannay's 'new white lead' is essentially a sulphate of lead produced directly from galena, which is placed with live coke in a furnace of special construction, and volatilised and oxidised by a blast of air. The fume thus produced is conducted into specially-constructed condensers, which are very similar to French's condenser, where it is collected. The material is washed, and finally dried. The patentee also describes the treatment of this condensed fume with various oxidising agents, such as aqua regia, to complete in this way the conversion of the sulphites and other similar compounds into sulphate. By this method a powder of great whiteness is obtained, which is stated to have considerable covering power and to form a useful paint when mixed and ground up with oil.

If, as has been already mentioned, a partial saponification of the oil by white lead takes place when the white lead is mixed with oil, it is not easy to understand how any normal salt of lead can efficiently replace white lead.

Lead Poisoning.

The salts of lead, more especially the soluble ones, are strongly poisonous, and since lead is a cumulative poison its salts and compounds, such as the oxide and carbonate, produce serious results if taken into the system even in minute quantities for any length of time. One of the forms in which lead is introduced into the system is by the use of drinking waters, some varieties of which easily attack the lead of the pipes used for conveying the water. Again, the workpeople engaged in the manufacture of lead and lead compounds, more especially white lead, are liable to suffer from the poisonous action of the compounds of this metal. In course of time the disease becomes chronic, the symptoms of which are pain in the abdomen, constipation, loss of appetite, thirst, a nervous prostration known as lead palsy, epileptic fits, and total paralysis. One of the signs of chronic lead poisoning is a blue line at the edges of the gums, due to the deposition of lead sulphide. This line is frequently seen in the case of painters and decorators, who are liable to this form of poisoning, produced in their case by the white lead used in making paint. The blue line is also to be observed in the workpeople engaged in the manufacture of white lead, or in manufactures in which this compound is employed. A portion of the lead taken into the system is excreted by the kidneys, and in cases of chronic lead poisoning it is stated that the administration of potassium iodide aids in the elimination of lead from the system. The mode in which the compounds of this metal are distributed in the different organs of the body is illustrated by the following results of an examination made by the writer in conjunction with Dr. Drummond and Professor Oliver in the cases of three workpeople who succumbed to the influence of this form of poisoning:—

Description of organ, &c.	Lead found expressed as metallic lead in parts per million			Lead in grains calculated on total weight of organ		
	I.	II.	III.	I.	II.	III.
Large intestine	14·6	37·7	—	—	—	—
Small intestine	9·2	—	—	—	—	—
Muscle	3·1	—	—	—	—	—
Lung	2·2	7·6	—	—	—	—
Heart	6·7	4·12	5·0	0·0243	0·0189	0·0164
Mamma	4·8	—	—	—	—	—
Kidney	15·5	10	13·3	0·027	0·0229	0·0261
Spleen	14·7	12	39·	0·0198	0·0341	0·0853
Liver	47·7	37·8	41·6	0·918	1·000	0·728
Cerebellum and pons	36·9	—	—	—	—	—
Grey matter of basal ganglia	53	—	—	—	—	—
Brain { grey matter of cortex	40·9	—	—	—	—	—
white substance	18·9	—	—	—	—	—
Spinal cord	—	1·16	—	—	—	—
Brain	—	9·8	21·6	0·688	—	—
Cerebellum	—	24·8	8·59	—	—	—
Pons	—	22·6	—	—	—	—
Brain and cerebellum	—	—	—	—	0·779	0·634

P. P. B.

LEADHILLITE, $5PbSO_4.9PbCO_3.4PbO.5H_2O$. A mineral found in Scotland and in Sardinia (*maxite*), crystallising in monoclinic prisms (Laspeyres, Zeit. f. Kryst. 1, 194).

LEAF GREEN. *Chrome Green v.* Pigments.

LEATHER. When the skins of animals are treated with infusions containing any of the vegetable tannins, the gelatinous tissue is converted into the tough imputrescible substance known as leather, while the process by which it is made is called 'tanning.' Certain mineral salts, as well as oils and fats which undergo oxidation in the skin, have a somewhat similar effect. It is proposed in the following article first to describe the structure and chemical composition of skin, and the preliminary processes it has to undergo to deprive it of hair and to render it fit for tanning, and then to deal with the different tanning materials and the various processes by which they are employed in practice.

The skin, as it exists on the animal is much more than a mere covering, and contains a variety of organs, both of sense and of secretion, and some knowledge of its anatomy is necessary to a proper understanding of the tanning process.

The skin consists of two layers, which arise in embryonic development from the inner and outer layers of the ovum, and which throughout retain the strongly-marked differences which correspond to this diversity of origin. The *epidermis* or outer layer of the skin is derived from the outer layer (epiblast) of the ovum, while the inner layer, *corium*, *derma*, or *cutis*, together with all the other connective tissues of the body, takes its rise from the middle of the ovum (mesoblast). Though the skins of different animals differ in details, that of the calf, of which a section is illustrated in fig. 1, may serve as a type of most of those used in the manufacture of leather. The outer layer or *epidermis* consists, as has been said, of simple nucleated cells, which at the surface are dead, hardened, and flattened, but where they rest on the *corium* are soft and spherical, and constitute the so-called 'mucous layer' (*rete mucosum*). This is not supplied directly with blood-vessels, but derives its nourishment from the fluids of the *corium*. Here growth takes place, and the cells probably multiply by fission, though this has not been actually observed. The hairs, though deeply rooted in the *corium*, are really products of the *epidermis* which surrounds them and passes down into the *corium* in the form of a bulb-shaped sheath. The nourishment of the growing hair is supplied by a knob of connective tissue called the hair-papilla, furnished with blood-vessels, and passing up into the centre of the hair-bulb. The hair itself is composed of modified and hardened cells, forming exteriorly irregular overlapping scales, giving the outline a serrated appearance, which is especially marked in wool. Within this 'hair-cuticle,' as it is sometimes called, is the fibrous portion of the hair, composed of long spindle-shaped cells, and sometimes in the centre of this is a cellular pith containing air. The hair, except in white animals, contains a good deal of pigment, and some is also present in the epidermis cells forming the hair-sheath. The new hair, both in fœtal development and in ordinary growth, begins as a thickening of the *epidermis* layer, forming a knob which gradually sinks into the *corium*, and becomes a bulb in which the hair is developed and forces its way to the surface much as an onion does to the surface of the ground. In animals which change their coats in spring the young hair generally originates in this way from a new bulb formed below the old one, and passes up into the old sheath. This deep-seated origin explains the great difficulty found in removing these young hairs for technical purposes. Beside the hairs, sudoriferous and sebaceous glands are similarly developed from the *epidermis*. The sebaceous glands are seated round the stems of the hairs, and their ducts discharge oily matter which serves as a lubricant into the hair sheaths near the surface of the skin. The sudoriferous glands are more deeply placed, usually extending even below the hair roots; they are less convoluted than in man, and discharge through narrow sinuous ducts to the surface.

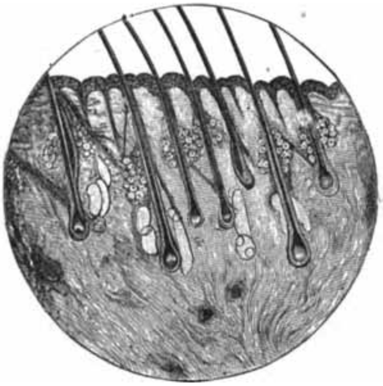


FIG. 1.

The *corium* consists mainly of connective tissue, which, on boiling with water, readily dissolves, and is wholly converted into gelatin. In most animals the principal part of the hide (*pars reticularis*) is composed of bundles of interlacing fibres, each of these bundles being formed of a multitude of fine fibrils. Towards the outer surface these bundles disappear, and the separate fibrils combine in a closely-matted felt (*pars papillaris*), which is technically known as the 'grain.' In the pig, and possibly also in the seal, this close-textured part is thick, and is all that is valuable for tanning, the reticular part being so slightly developed as not to be distinguishable from the looser fatty tissue (*panniculus adiposus*), which underlies the true skin. Consequently, these skins are remarkable for extreme toughness. In addition to this gelatinous structure, the true skin contains certain yellow fibres called 'elastic,' and distinguished by their very difficult solubility in boiling water, acids, and alkalis.

Between the *corium* and the *epidermis* is an extremely fine membrane, known as the hyaline layer. This is very difficult to demonstrate microscopically, but has been separated in some technical operations, and is probably the cause of the clear brown or buff colour of the grain surface of tanned leather, while the finely-matted tissue below it remains nearly white.

The *corium* has also blood vessels, nerves, and minute muscles for erecting the hairs; but none of these are of much technical importance, and for further details the reader may be referred to Procter's Text-Book of Tanning, or to the larger anatomical works.

A few words must, however, be said about the practical microscopic examination of skin. For this purpose it is necessary to produce extremely thin sections, and the skin must be previously hardened. To this end it may be cut into strips about ½ inch long by ¼ inch wide, with their length at right angles to the direction of the hair, which should be cut short with scissors, with which also the loose fatty subcutaneous tissue should be removed. The strips are placed in a closed vessel with several times their volume of methylated spirit diluted with an equal quantity of water. The next day this must be replaced by stronger alcohol, and finally by absolute. In 4–8 days the hide will be hard enough to cut, and may be held between the finger and thumb, and shaved by a drawing cut with a very sharp razor flooded with alcohol and resting on the tip of the forefinger. The cut should begin at the grain side, and must be exactly parallel with the hairs to give good results. For this reason a microtome is of very little service, as it is more difficult to adjust the fragment of hide in it than to make the sections by hand. They are floated off the razor in alcohol, and must be stained in order to make the details visible. Various methods of staining are described in the microscopic text-books, one of the simplest being to immerse in aqueous solution of picrocarmine. The carmine stains the connective tissue and the nuclei of the cells red, while the structures derived from the *epidermis*, the *erectores pili* muscles, and the blood vessels, absorb the picric acid only, and become yellow. The section may now be soaked in glycerin to clear it, and examined in a drop of glycerin under a thin cover-glass; or may be permanently mounted in glycerin or Farrant's fluid; but for this purpose it is generally better, instead of clearing with glycerin, to soak the sections again for some time in absolute alcohol containing a little picric acid, till quite deprived of water, clear in clove oil, and mount in a drop of solution of gum dammar in benzol, or of Canada balsam.

Kathreiner has described a method which, while it is less striking for demonstration of the different tissues, is better adapted for practical work when a knowledge of the general appearance of the structures has been attained. The fresh hide (and it is important in preparing type specimens that the animal should not have been killed more than a few hours), is cut into small strips as described, and then immersed for 4–8 days, according to the thickness of the hide, in about twelve times its volume of an aqueous solution containing 1 p.c. of osmic and 2½ p.c. of chromic acids. This solution must be kept from light and dust in a stoppered bottle and in a cool place. Care must be taken to avoid the fumes, which cause severe catarrh of the mucous membranes. The hide pieces must now be soaked in about twelve times their volume of absolute alcohol several times renewed for 4–8 days, and are then cut as described. No further staining is required, as the chromic acid colours the tissues yellow, while all traces of fat, as for instance, the oily matter of the sebaceous glands, are stained grey or black by the osmic acid. They may be cleared at once with clove oil, in which they may be examined, or mounted in dammar.

A third method may be mentioned which is very useful for rapid observations, especially when it is desired to ascertain how far the cellular structures have been affected in preparing the hide or skin for tanning. The section, which need not be so thin as when intended for more detailed study, may be cut either after a short hardening in alcohol, or in the case of hide swollen with lime, simply by cutting a small strip ¾ through from the grain, and turning it back so as to put the tissue on the stretch, and then cutting from flesh to grain with a razor flooded with distilled water. If the wet section be placed in a drop of water on a slide under a cover glass, and examined by reflected light with a 1-inch objective, the fat glands will be seen as yellow masses embedded in the white fibrous tissue. If now the section be moistened with a mixture of equal parts of glycerin and glacial acetic acid, the connective tissue will become quite transparent, and the glands and hair-roots may be examined, even with a pretty high power, by transmitted light.

The *epidermis* and its products, hair, horns, hoofs, &c., all belong to the class of keratins, which are allied to coagulated albumen. They can hardly be said to be soluble in water, though by prolonged boiling under pressure they are finally dissolved to an extract which does not gelatinise on cooling. The softer structures are easily soluble in dilute caustic alkalis in the cold, while hair and horn only yield to strong solutions aided by heat. They are reprecipitated by acids, and Dr. Putz has taken a patent for a new tanning method in which these precipitates mixed with oil are used as a 'filling' for alumed leather in place of flour and egg-yolk. Lime and other alkaline earths act like the alkalis, and hence milk of lime, while it scarcely attacks the hair, easily loosens it, by dissolving and softening the *epidermis* and root-sheaths. Strong solutions of alkaline and alkaline-earthy sulphydrates, on the other hand, seem to attack the harder tissues by preference, and reduce the hair to pulp without affecting the *epidermis* cells so much as milk of lime.

The fibrous connective tissue forming nearly 95 p.c. of the *corium* is wholly soluble in boiling water, by which it is converted into gelatin, which is not identical with it, but differs only in molecular arrangement or hydration. Connective tissue is soluble in dilute acids, from which it is precipitated by neutralisation, as a fibrous mass, without the sticky feel of gelatin, into which it is immediately converted by heat. Strong acids and alkalis also dissolve the fibrous tissue, and at the same time convert it into gelatin, and usually other products. Rollet has shown that dilute solutions of the alkalis and alkaline earths swell and split the fibrous bundles up into extremely fine fibrils, at the same time dissolving a part of their substance, which he supposed to be of an albuminoid character, but which Reimer (D. P. J. 220, 167) has shown to be a mere product into which the whole of the fibrous tissue may be converted by sufficiently prolonged action of the solvent, and which he has named coriin. It may be precipitated by neutralising the alkali with acetic acid. Excess of acid swells and renders it transparent, though it does not actually dissolve it, but it is readily soluble in alkalis. It may be dissolved in 10 p.c. solution of sodic chloride and in certain concentrations of other chlorides, but is reprecipitated either by saturating or by much diluting the solutions. By the same reagents it may also be extracted from the hide. Beside coriin, the prolonged action of alkaline solutions on hide yields ammonia, tyrosin, caproic and amido-caproic acids, and other products.

Beside gelatin, the hide contains a small proportion of albumen derived from the blood, or rather from the lymph with which the connective tissue is lubricated and nourished. This has, of course, the ordinary reactions of blood albumen.

Hides and skins reach the tanner in very various states. Most of those from animals killed in this country are either fresh or very slightly salted, but those from greater distances are treated in various ways to preserve them. Perhaps the simplest and best is the use of salt, either sprinkled on the flesh side repeatedly, or used in the form of brine. In this way most European hides, and many of those from North and South America, are cured. In countries remote from the sea, hides are frequently first salted and then dried, so as to save weight in carriage, and at the same time to preserve them better. This is called 'drysalting.' A still commoner method, especially where salt is scarce and costly, is simply to dry the hide or skin either by hanging in the shade or by stretching on the ground in the sun. Many hides from Texas and Central and South America are thus treated, as well as smaller skins from more temperate countries. The hides of the small cattle of India, called 'kips,' are dried and then plastered on the flesh side with a mixture of lime and water avowedly to preserve, but really to weight them. Sometimes a portion of arsenic is used to prevent the ravages of insects. It has been proposed in Germany to substitute sulphate of soda for common salt in the curing of skins, both on account of the tax on salt, and because it retains the water, and consequently the weight in the hide better. The advantage of this to the tanner does not seem obvious. In Russia and other cold climates, hides are sometimes preserved by freezing.

Preparation of hides for tanning.—Preliminary to any other treatment, it is necessary to soften hides and skins, and to free them from blood and dirt. When fresh, a few hours, or at most a day or so in one or two changes of fresh water is sufficient to accomplish this; and for sole leather the cleansing does not need to be so thorough as for the finer sorts, while too long soaking is apt to lead to incipient decomposition, and to yield a soft and light-weighing product. Where goods are salted, a much more thorough washing is desirable, and it is advisable to give frequent changes of water to remove the salt as rapidly as possible, and prevent that solvent action on the fibrous tissue which, as has been pointed out, takes place with salt solutions of moderate concentration.

When hides have been dried, a mere soaking is in most cases insufficient to produce complete softening, and in addition mechanical and chemical means have to be employed. Eitner has pointed out that the higher the temperature at which the original desiccation took place the greater is the difficulty of softening; calfskin which had been dried at 60°C. refusing to soften sufficiently for tanning either by soaking or mechanical means. This is analogous to the fact that gelatin dried at 130°C. becomes insoluble even in boiling water. For thin skins, such as calf or sheep, dried in the open air in temperate climates, a simple soaking of some days in cold fresh water, assisted by working over the beam with a blunt knife, is enough. On the other hand, for the sun-dried kips of India or the heavy ox hides of Texas and South and Central America, such treatment would be quite ineffectual, and the method has usually been adopted in this country of soaking for two or three weeks in water, which being seldom changed and highly charged with organic matter from previous parcels of hides, is in a state of active putrefaction. Such soaks will soften much more rapidly than fresh water, and are effectual where even prolonged treatment with it would fail. In India, hides are softened by the native tanners within twenty-four hours, by plunging them into pools in which all the refuse of the tannery is allowed to collect and putrefy. It has, however, come to be recognised by observant tanners that this putrid soaking is very dangerous and unsatisfactory, especially where the hides are destined for sole leather, since it has always a destructive effect on the tissue, and it is found that an equally satisfactory softening may be much more safely and rapidly effected by the judicious use of warm water, aided in some cases by the addition of small quantities of sulphide of sodium. When the hides or kips are so far softened that they can be bent sharply without danger of breaking the fibre, they are worked in the 'stocks' or 'hide-mill,' which is a machine in which two large hammers or plungers work the hides with a sort of kneading action. Some tanners successfully substitute for this rather violent treatment a drumming with warm or tepid water in a rotating 'tumbler' like an immense barrel-churn. A machine in use on the Continent for the same purpose consists of two rollers studded with rounded pegs, or of which one is grooved and the other pegged. The hides are passed back and forwards between these, and undergo a sort of kneading action. When the hides or skins are thoroughly softened they are ready for depilation.

Depilation.—With a few exceptions, which scarcely come properly under the head of 'leather,' it is necessary to remove the hair preparatory to the tanning process. Probably the oldest way of doing this is by putrefaction, or as it is technically called, 'sweating.' This was formerly accomplished by leaving the hides or skins, folded or laid together, in a warm and moist place, till the destruction of the *epidermis* liberated the hair. But though the *corium* was somewhat more resistant to putrefaction than the mucous layer of the *epidermis*, the putrefactive change frequently spread into it, and injured at least its surface. This simple form of sweating may now be considered practically obsolete, and where putrefaction is still employed, it is by what is known as 'cold sweating,' which, though little used in England, is almost universally employed in America in the treatment of dried hides. In this method the hides are suspended from tenter-hooks in well-ventilated chambers, usually almost buried in soil or spent tan, so as to maintain an equable temperature (which is generally somewhere between 15° and 20°C., the higher the more rapid being the action). The air is kept saturated with moisture, and the temperature regulated by admitting steam under a false bottom, or a spray of water from pipes provided for the purpose. The hides, which if dried must previously have been thoroughly softened, are ready for unhairing in 3-7 days, and during the latter part of the time must be examined from hour to hour, and, as soon as the hair is loosened, taken down and placed in piles on the floor. As the thick parts take longer to unhair than the thinner, and the process proceeds more rapidly at the top than the bottom of the chamber, the position of the hides must be altered as the action progresses. When the hair is fully loosened, it is removed either by scraping with a blunt two-handled knife on a sloping 'beam,' or by fulling with stocks. Some American tanners now give a light liming before unhairing to slightly plump the goods and check the decomposition.

In England, both for sole and dressing goods, the hair is almost universally loosened by the use of lime. The pits are usually, though by no means invariably, worked in sets of three, of which one is old and nearly exhausted, the second pretty good, and the third freshly made or strengthened. The duration of the process is very variable, ranging from 4 or 5 to 14 days or more, and the quantity of lime used is yet more indefinite, being variously stated at from 1 lb. to 12 lbs. per hide. The fact is, that, lime being very scantily soluble in water, any quantity beyond that required to maintain a saturated solution has but little effect. Lime is only soluble to the extent of about 1½ oz. per cubic foot, but of course is continuously absorbed by the hide, so that an excess is required which may be less the more often the hides are moved and brought in contact with fresh portions of the lime liquor. Hides lime well and rapidly, suspended from frames in pits, especially if rocked or frequently shaken, and in any case the more frequently they are moved and the better and more uniform the action. In America they are usually tied together by the shanks and wound from one pit to another over a 'reel' or skeleton drum, turned by hand or power. The old lime liquors become charged with ammonia and organic products from the hides, which materially modify their action, rendering more lime soluble, but diminishing its plumping effect. One result of this is that hides unhair more readily out of a somewhat old lime than they do out of one freshly made, and a change from an old into a newer and stronger lime sometimes actually sets the hair firmer at first, by plumping the tissue and so grasping the root-bulbs. If hides be limed for 3 or 4 days in a sharp new lime in which they are frequently drawn, and are then transferred into a pit of water maintained at a temperature of 40°-50°C. for 24 hours, they will part readily with their hair, and at the same time be to a considerable extent freed from lime. This plan, which is of American origin, and is sometimes called the Buffalo method, may be highly recommended for sole leather, giving good weight and colour and a firm solid texture. Of course, the relative amount of liming and hot water may be varied to a considerable extent.

Unhairing may also be hastened by warming the limes themselves. The heat increases the solvent power of the lime, but at the same time checks the plumping, and the tendency is to produce a soft and porous leather. Hence the method is ill adapted for sole, and even for dressing leather requires to be employed with caution, and it is doubtful whether the same effects are not better obtained in other ways.

It has naturally been proposed to substitute the caustic alkalis for lime, and it is probable that it might be done in some cases with advantage, or at any rate that small quantities might be added to the limes to hasten their action; but so far their use has not found much favour with tanners, except as constituents of such secret preparations as 'Inoffensive.' One cause of this is probably that from their easy solubility and powerful action, great care is required, and where used by 'rule of thumb,' serious injury is readily done to large quantities of costly raw material. It is one of the virtues of lime that, from its very limited solubility, it is almost impossible to destroy a pack of hides by its use, and the injury which it does when carelessly handled is often attributed to other causes. Naturally it would be thought that the alkalis would be easily removed from the hide by simple washing, and that the solubility of their soaps would favour the removal of grease; but it is found that alkalis form a sort of compound with hide-fibre, from which they can scarcely be removed until they have first been neutralised with acid, while practically the grease is not saponified but merely emulsified, and for this purpose lime answers just as well as a stronger alkali.

In liming sole leather the principal object is to enable the hair to be removed and to free the hide from grease with as little solution of its fibrous structure as possible. The English tanner frequently desires also to raise or swell the hide, and so to split up the fibrous bundles into their constituent fibrils as to prepare it for tanning, though it is probable that this may be better and more economically done by the presence of acid in the earlier tanning liquors, or in some cases by the direct use of an acid bath. It is a question on which there is still much difference of opinion whether the unhairing is best accomplished by the use of strong fresh limes for a short time, or of old and weak limes charged with ammonia for a longer period. It is certainly dangerous in hot weather to let them get too stale and loaded with organic matter, as in this case even the presence of caustic lime does not prevent putrefaction, which is fatal to the manufacture of plump and solid leather. In fact, by microscopic examination of such stale limes it is easy to detect the presence of active bacteria. A plan which presents considerable advantages is to use fresh and moderately strong limes, to which, say, one-third of their volume of old lime liquor has been added. If in any case the liming is too low, it will be impossible to eradicate grease from the hides of very fat cattle, though the leather may be of excellent quality. In the manufacture of dressing leather a somewhat more thorough liming is generally desirable, since it is not only required to remove the hair but to dissolve a proportion of the cementing matter of the fibrous tissue, and so render the leather softer and more pliable. This is especially true in the manufacture of glove or 'glacé' kid and lamb leather, in which the property of stretching in any direction is largely dependent on a proper liming. In the continental manufacture of these goods it is customary to 'sharpen' the limes by the addition of realgar (arsenic sulphide). This produces, with the lime, calcic sulphydrate, and possibly sulpharsenate, which considerably hasten the unhairing. The sulphydrate seems to be the most active agent, and the desirability of finding a substitute for the very poisonous red arsenic led Böttger to propose the use of calcic sulphydrate, prepared directly by passing hydrosulphuric acid into milk of lime. This produces a paste which is greenish from the presence of traces of sulphide of iron, and which acts as a rapid depilatory, and if applied as a paste on the hair-side will in a few hours reduce the hair to a pulp, while from the rapidity of the action, the hair bulbs and the various glands are much less affected than with an ordinary liming. Mixed with lime in smaller proportion and used in pits in the ordinary way, it loosens the hair rapidly without actually destroying it, principally by attacking the mucous layer, since the harder part of the epidermis frequently comes off with the hair roots in it in sheets of considerable size. Unfortunately for its use in practice, for which otherwise it is excellently fitted, it keeps very badly, and must be freshly made as required, which is both costly and troublesome. A concentrated solution of calcic sulphydrate was recently produced by the Washington Chemical Company, and promised to be a valuable depilatory; but unfortunately its manufacture proved unremunerative. Gas-lime, which often contains a considerable quantity of calcic sulphydrate has been used as a substitute, but is too uncertain in its composition to be satisfactory, and has been almost superseded as a gas-purifying agent by oxide of iron. None of these disadvantages attend the use of sulphide, or more strictly speaking, sulphydrate of sodium, which has been strongly advocated by Eitner, the energetic director of the Austrian Government Research Station at Vienna, to whom the leather trade probably owes more of scientific improvement than to any other man of the present day. It is now manufactured on a considerable scale commercially, in a crystallised form; it keeps well and possesses great depilatory powers, both alone and in union with lime, with which it forms calcic sulphydrate and caustic soda. A paste containing 4–5 lbs. to the gallon of water, and thickened with lime to a soupy consistence, will, if painted on the hair side of a hide, completely destroy the hair in a few hours, so that it may be swept off with a stiff brush. This mode of proceeding has been much recommended for sole leather, and it makes a firm and solid article, but the difficulty of getting it so thoroughly brushed into the hair that it will destroy every part of it, is very considerable, while, if any part has been missed, the short hair is very difficult to remove. For this reason, and because it leaves all the hair-roots and glands in the skin and so prevents a clean buff, it is only suitable for very common classes of leather, though it will do good service on dried hides instead of the cold sweat. Used in pits in conjunction with lime to the extent of about ½lb. per hide, it does not materially injure the hair, while it quickens the unhairing and yields good weight and excellent quality; but it must be borne in mind that sulphides do not swell the hide like caustic alkalis, so that the after process of tanning must be so arranged as to get the plumping in the liquors. Where plumpness is not desirable, but a tough, solid texture is required, as in some descriptions of light leathers, its use would promise special advantages.

The total soda existing in commercial sulphide of sodium as sulphide and carbonate or caustic may be determined with standard acid, using methyl-orange as an indicator, since this colour is quite unaffected by the presence of either hydrosulphuric or carbonic acids. The sulphur is advantageously estimated by ammoniacal zinc solution, using alkaline lead tartrate as an indicator by placing drops of it and of the solution being tested near each other on filter paper. Solutions containing sulphide of sodium together with dissolved sulphur and polysulphides obtained by boiling together caustic soda or soda ash and lime possess considerable depilatory power, but it is not easy to determine the amount of available sulphur. Somewhat similar solutions are obtained by forcing air through the 'tank waste' of alkali works suspended in water, or naturally in the 'bog-liquor,' which in some works drains from the waste-heaps, and where these can be cheaply obtained, they may in some cases be advantageously used.

Examination of lime liquors.—Considerable information may often be obtained by a simple examination of lime liquors. Free ammonia may be determined by placing, say, 80 c.c. of the liquor in a shallow dish on a flat glass plate, and over it in a second dish, supported on a glass triangle, 10 c.c. of normal acid. The whole is covered with a small bell glass, rendered air-tight by smearing the edges with vaseline, and allowed to remain for twenty-four hours, when the whole of the ammonia will have been absorbed by the acid, which may be titrated with normal alkali. The sample should be drawn from the middle of a lime pit well plunged up, and rapidly filtered in a funnel covered with a clock-glass.

The lime in the portion from which the ammonia has been withdrawn may now be estimated with normal or decinormal acid, using methyl-orange as an indicator. This will give the amount of lime (and any other alkalis present) existing in a free state or in combination with organic matter and weak organic acids. Litmus is unsuitable for the purpose from the presence of these weak organic acids, which render its end-reaction quite indefinite but do not affect methyl-orange so much. For the same reason this indicator will be found very useful for many determinations required in a tannery. An estimate of the organic matter present is obtained by evaporating 50 c.c. of the filtered liquor to dryness in the water-oven in a platinum crucible, weighing, and then igniting and estimating by loss. This method can of course lay no claims to strict accuracy, but is sufficient to give valuable information as to the condition of the liquor; and, if a uniform course of liming be adopted, as to the amount of matter dissolved out of the hides in the process, or the comparative quantities by different liming methods. For more accurate work the liquor might be evaporated to dryness with the addition of a little excess of hydrochloric acid to retain ammonia, and some powdered pumice or other absorbent material to render the removal of the dried residue from the basin practicable, and the nitrogen estimated by combustion with soda-lime or cupric oxide. It is easy to calculate very approximately the amount of matter which the nitrogen represents, since both the gelatinous and horny tissues contain about 17·5–18 p.c. of nitrogen.

Bateing and drenching.—If lime or other alkalis have been used in depilation, they must be removed before tanning, and in sole leather it is desired to do this with as little loss of pelt as possible. Commonly a mere suspension in water is considered sufficient, and when the water is hard, a little lime is added to remove the free carbonic acid and hydric calcic carbonate present, which would form insoluble carbonate with the lime contained in the hide, and afterwards by combining with tannin would produce bad coloured leather. A further cleansing may be effected by 'scudding,' or working the grain-side with a blunt knife on a beam, which expresses much of the *débris* of hair-roots and fat glands, as well as lime. When a clean buff is desired this precaution should never be omitted.

It is, however, impossible really to remove the whole of the lime by soaking in water, since it forms a sort of loose compound with the fibrous tissue, from which it can only be dislodged by the aid of acids. Nesbit has recently patented the use of water highly charged with carbonic acid for this purpose, and there is no doubt that it will remove lime without the least injury to the pelt, while it leaves the grease of the hide in a mechanical condition favourable to its removal by scudding. The patentee also proposes it as a substitute for the bateing of dressing leather, but as this is usually required to soften, as well as to remove lime, it can hardly entirely replace it, though it may be useful as a preparation.

The removal of the lime may, however, be well effected by other agents beside carbonic acid. Very dilute sulphuric acid will perform the same service satisfactorily, though great care has to be used to add it in small successive doses as it is absorbed by the hides, to keep them in constant motion, and to avoid even a small excess. Some trouble is often experienced in the use of commercial acids from the precipitation of the iron which they contain as an impurity on the fibre of the hide, where it subsequently produces stains by combining with the tannin. Weak vegetable acids and the ammoniacal salts of the stronger acids may also be used. For sole purposes hydrochloric acid should be avoided, as the chlorides have a great effect in preventing the plumping of the hide which is so desirable in this class of leather. Instead of actually removing the lime it is sufficient in many cases to convert it into a neutral and insoluble form, as, for instance, by the action of hydric or neutral phosphates, oxalates, or arsenates. Borax and boracic acid have also been patented for the purpose. Recently 'creasotinic' acid, a mixture of higher homologues of salicylic acid, has been employed for this purpose with some success; and is at the same time a powerful antiseptic.

In the case of most light leathers where softness is aimed at, it is found necessary to use, either alone or as a supplement to some process of removing the lime, a putrefactive or fermenting bate, which has the effect of reducing ('abateing') the plumpness of the hide, and at the same time of softening it by attacking the fibrous tissue. Either an infusion of dung (dogs', pigeons', or hens') called *bate* or *puer* (the latter probably having some connection with the French *puant*), or of bran (drench), and frequently both, are used successively. Probably the putrefactive organisms themselves are active agents of the process. Tiffany's bate, which has been used to some extent in America, consists essentially of glucose with the addition of some nitrogenous material which renders it a suitable nutritive fluid when dissolved in water for the rapid multiplication of bacteria.

It should be noted that glucose, independently of putrefactive action, has the power of dissolving both lime and connective tissue; but in Tiffany's bate the solution is too dilute for this to come prominently into play.

In the preparation of 'shaved' and 'dressing' hides, a bate may contain about 1 peck of hen or pigeon dung to 25 or 30 hides, in which they are handled frequently for 3–7 days. This time may be much shortened by warming the bate and working the goods with a drum or paddle tumbler. The latter consists of a tank or pit, generally having a curved bottom to favour the motion of the liquid, and agitated by a paddle-wheel with 6–8 floats. A short 'stocking' out of the bate is also sometimes employed with good effect. Tumbling with warm water before bateing will wash out a good deal of lime and reduce the plumpness, and so save both time and material; and French tanners make excellent shaved hides and calf-skins without bateing by careful working at the beam, long washing with cold water (during which probably a slight putrefactive action takes place), and the use of weak and stale liquors. Shaved hides are so called because, after the bateing, the thicker parts of the butt are reduced by shaving on an upright beam with a currier's knife with a turned edge.

Still lighter and more flexible sorts of leather, such as morocco and kid, are usually puered with putrid dog-dung infused in hot water, and strained through a basket. This is frequently followed, after scudding, by a drench made by pouring boiling water on bran, and allowing to ferment. In this case lactic acid seems to be one of the most active products, though its plumping action is controlled by the putrefactive fermentation going on at the same time. Wood (S. C. I. 9, 27) has shown that starch is destroyed by the active ferment, and considerable quantities of methane evolved. In hot and thundery weather the lactic ferment is liable to be replaced by the butyric, when the skins plump rapidly and become transparent, and are finally perforated or dissolved. The best precautions are to scald out the tubs thoroughly, and to wash the bran before use with cold water to remove the flour, which furnishes the nourishment required by the butyric ferment.

In the brief space available it is impossible to give more detail as to these preparatory processes, which are, however, of the first importance from a practical point of view. From the scientific, it must only be noted that the plumping and 'falling' which the fibrous tissue suffers through the action of various reagents, is closely connected with osmose, and is at least as much a physical as a chemical phenomenon; and, like most other details of the trade, offers a most promising field for investigation.

Tanning materials. Before speaking of the actual tanning process, a few words must be said about the chemistry of the vegetable products on which the operation depends.

The tannins, or tannic acids, are widely distributed through the vegetable kingdom, and form a large and varied class, differing considerably in chemical constitution as well as in properties. The one point which they all have in common is the power of precipitating gelatin from its solution as an insoluble compound. They are also all derivatives of the aromatic series of carbon compounds, and, so far as is known, all contain either pyrocatechol $C_6H_4(OH)_2$ or pyrogallol $C_6H_3(OH)_3$, and sometimes the isomer of the latter, phloroglucol. This difference of origin corresponds to a well-marked difference in properties. As a rule the pyrogallol tannins give a blue-black with ferric acetate, and a whitish deposit on the surface of the leather, well known to the tanner as 'bloom'; while the pyrocatechol derivatives give a greenish black, and deposit red insoluble matters, probably anhydrides of the tannins. Oak bark occupies an intermediate position, yielding both bloom and reds, and apparently containing both pyrogallol and pyrocatechol. In such cases, however, it is not very certain whether we have to do with a complicated tannin or with a mixture of two dissimilar ones, since tannins, being neither crystallisable nor volatile, are very difficult to separate. It is known that many of the bloom-yielding materials, such as myrobalanes, contain gallotannic acid, which yields no bloom, and ellagitannic acid, which yields a copious bloom of ellagic acid.

It is of course only the pyrogallol tannins which yield gallic acid as a decomposition product, while the pyrocatechol tannins contain the corresponding protocatechuic acid. Many of the pyrogallol tannins yield glucose on decomposition, but in the pyrocatechol class it seems to be absent.

A complete list of tannin-yielding plants would embrace a large part of the vegetable kingdom, but the following are those in most extensive practical use.

Oak bark is one of the oldest and best of tanning materials, producing excellent but not heavy leather; and, from its comparative weakness in tannin (8–12 p.c.) its action is somewhat slow. It yields a good deal of whitish bloom.

Valonia, the acorn cup of the *Quercus Ægilops* and *Q. Macrolepis*, yields a tannin very similar to that of oak bark, but giving more bloom and a darker colour, and at the same time a heavier leather.

Myrobalanes, the fruit of *Terminalia Chebula* (India), contains 25–30 p.c. of gallotannic, and ellagitannic acids, and, consequently, blooms freely. It gives good colour and fair weight, and though alone it yields a porous and soft leather, it is very useful in mixture with dark coloured materials, such as hemlock extract, for sole leather, and as a cheaper substitute for sumach, on the lighter descriptions.

Divi-divi, pod of *Cæsalpinia coriaria* (S. America), contains 30–50 p.c. of a tannin somewhat similar in effect to that of valonia. It produces a heavy-weighing leather, but is dangerously liable to a sudden fermentation, which produces a deep-red stain on all leather in contact with it.

Sumach, the ground leaves of *Rhus coriaria*, &c. (Sicily), yields 16–24 p.c. of tannins very similar to those of myrobalanes, but paler in colour. It is principally used for light leathers, though occasionally a warm sumach liquor is used to brighten the colour of heavy tannages.

Mimosa bark, the product of several species of acacia, principally Australian, contains 20–30 p.c. of a red tannin derived from pyrocatechol, and yielding no bloom, but giving considerable weight and firmness to the leather. An extract has recently been introduced into commerce.

Hemlock bark, known in this country principally in the form of extract, is produced by the hemlock pine, *Abies*, or *Tsuga Canadensis*, of North America. The bark contains 8–10 p.c., and the extract 20–30 p.c. of a tannin similar to that of mimosa, but giving a larger proportion of red anhydrides, and consequently a heavier leather, but at the same time one of a still more pronounced colour, which is less easily modified by other agents. It is the staple tanning agent of North America.

Gambier (*Terra Japonica*), pale catechu, an inspissated extract from the leaves of *Uncaria Gambir* of the East Indies, contains 30–40 p.c. of a peculiar catechol tannin, which penetrates leather rapidly, but has less astringency and adhesion to the hide fibre than most other tannins. These properties make it very valuable in certain stages of the tanning process, though alone it produces a leather of very inferior quality. Cutch (dark catechu), though somewhat similar in its chemical relations, is a very different product practically, and is derived from the wood of *Acacia Catechu* and *A. Suma*, and, consequently, more allied to the mimosa bark, which has already been described. Gambier comes to this country in blocks of about 2 cwt., covered with mat and pasty in the centre, and also in cubes of about an inch square, which are much purer, and internally are quite white with crystals of catechin. Cutch comes in masses of a glossy dark-brown fracture, and is principally used for dyeing.

Exhaustion of tanning materials. — Most tanning materials require to be ground before lixiviating. This is accomplished either by a mill, on the principle of the ordinary coffee mill, with grooved iron or steel cones, or by one of the numerous forms of 'disintegrator,' in which the grinding is done by dashing the material against a serrated or grated casing, by beaters revolving 2,000 or 3,000 times a minute. Valonia and myrobalanes are frequently crushed between fluted or toothed steel rollers. The actual exhaustion takes place in this country mostly in large square sunken vats, constructed like the other pits of the tannery and worked in series, the liquors being either pumped from one to the other or allowed to run through wooden boxes, connecting the space below the perforated 'false bottom' of one pit with the top of the next. In America the 'leaches,' as the extracting vessels are called, are usually immense circular tubs, fitted with perforated 'false bottoms' and with rotating 'sprinklers,' like those in use in breweries. This suits the American conditions, where the tanning material is cheap and not very strong, as it exhausts the bark to a fair degree very rapidly; but it is scarcely sufficiently thorough for the stronger and more costly materials in use here. Imperfect exhaustion is one of the most serious sources of waste in tanning, and the residues deserve more careful testing than is usually given to them.

Quantitative determination of tannins.—Many methods have been proposed for the purpose, several of which are capable of application under special conditions, but the only two which have stood the test of general practical work, and each of which is valuable for different purposes, are the hide-powder method, which is the gradual development of the work of several chemists, among whom Simand may be specially mentioned, and the permanganate and indigo process of Löwenthal.

The first of these is the only one which permits of an actual gravimetric determination of the tanning matter absorbable by hide, and is recommended for the valuation of extracts and tanning materials, but requires a pretty concentrated tannin solution, and where this cannot readily be obtained, as in testing waste liquors and residues of tanning materials, the method of Löwenthal is very useful, permitting the use of very dilute solutions, but having the disadvantage of giving only relative results except with gallotannic acid.

The hide-powder process consists in passing a solution of the tannin to be tested through a filter formed of finely powdered hide, which absorbs and removes all available tannin. If a measured portion of this filtrate and an equal quantity of the original infusion be evaporated to dryness and the residues weighed, it is obvious that the difference will give the actual weight of tannin absorbed. It is conducted as follows. A sufficient quantity of the extract &c. is dissolved in boiling water to give approximately a 1 p.c. solution when made up to 250 c.c., and after cooling is carefully filtered. As many extracts continue to deposit insoluble reds or ellagic acid after the solution is cool, it is a question how long the solution should stand before filtering, since most of the reds act as tannins while in solution, and of course would be estimated as such.

A piece of tolerably strong glass tube, about four inches long and one inch diameter and open at both ends, is fitted with a tight cork in which is inserted a piece of slender tube about 12 inches long bent into the form of a siphon, with the shorter leg in the cork, the end of which is covered with muslin containing a minute tuft of cotton wool to act as a strainer. The wide tube is now filled with the very fine and highly purified hide-powder (manufactured by the K. K. Versuchs-Station für Leder-Industrie, at Vienna, and by Dr. Roth at Berlin and sold by Messrs. Mawson & Swan at Newcastle), and covered at the open end with a piece of muslin held in its place by an elastic band or a bit of thread. The powder must not be rammed, but merely shaken in as closely as possible. The wide tube is now placed in a deep beaker, which is gradually filled with the tannin solution so that the hide-powder may be uniformly wet by capillary absorption, which will take about an hour. The solution is then drawn over the siphon by gentle suction with a piece of india-rubber tube, when it will continue to drop slowly and regularly. The first 30 c.c. should be rejected as containing a large proportion of the traces of soluble matter contained in the hide-powder; and the next 50 c.c. collected and evaporated at 100°C. in a weighed crucible or basin, and the residue weighed, while 50 c.c. of the original carefully filtered solution is treated in the same way. It is desirable to make a blank experiment with distilled water on the hide-powder employed, from which a correction for solubility of the hide-powder may be deduced and applied as a correction to the actual analysis. Should gallic or other fixed acids be present in large quantity, a portion is retained by the hide-filter and reckoned as tannin. Hence in such cases it may be advisable to use the Löwenthal method, which is less affected in this way if gelatin be used as a precipitant. Should glucose be present in large quantity a slight error would be caused in the opposite direction by its solvent power on hide-tissue. Neither of these circumstances is likely to introduce serious error in the practical use of the method on fresh extracts and tanning materials.

It is easy to obtain infusions of the requisite strength in working upon extracts, but with solid tanning materials the case is different, as the quantity of water is insufficient for complete extraction in the ordinary way. It has, however, been proved by Eitner, that no loss of tannin as estimated by the hide-powder method is caused even by prolonged boiling in a closed apparatus; and he has contrived one on the principle of Soxhlet's tube, in which the liquor is boiled continuously in a flask, and the steam condensed and allowed to filter back through the material to be exhausted (Gerber, January 1, 1887). Very good results may also be attained by simply exhausting with small successive quantities of hot water in an ordinary funnel loosely plugged with cotton wool, and placed in the neck of a flask in which the liquid is allowed to boil down. It is best to boil the powdered material first in a small quantity of water, and filter off the strong liquor so obtained into a separate flask, before beginning to concentrate the weaker liquors. This saves the bulk of the tannin from long boiling, and the whole is finally made up to 250 c.c. Treatment in a Von Schroeder's extractor with subsequent concentration of the weaker liquors also answers well. It consists of a pewter cylinder of about 5 inches deep and 2¾ inches diameter, fitted with a perforated piston covered with a piece of muslin. The tanning material is exhausted in this with successive portions of hot water, and the liquid strained off by pressing down the piston, and a fresh portion of water is added before the piston is withdrawn, so as to pass through and wash the muslin. 25 grams of oak bark and 10 to 15 grams of valonia or extract are suitable quantities to use.

The Löwenthal method is volumetric, and, as very much weaker infusions are required, the above quantities may be made up to a litre. The material may either be boiled briskly for half an hour in a large flask, allowed to cool and made up with the solid residue to 1 litre, or it may be treated in the Von Schroeder extractor with about five or six successive quantities of boiling water, and digested each time for half an hour in the water bath. The indigo solution is made by dissolving 5 grams of pure sodic or potassic sulphindigotate (Gehe's *Carminum cœrul. op.* answers well), in a litre of distilled water, adding 50 c.c. of concentrated sulphuric acid and filtering. The permanganate contains 1 gram of the pure salt per litre.

For a titration 20 c.c. of indigo, and about 400 c.c. of water free from organic matter are placed in a large beaker, which is provided with a stirrer consisting of a perforated disc of earthenware attached to a glass rod, so that it can be worked up and down like a churn. The point of the burette is capped with a short tube drawn to a capillary point, and capable of passing about 1 c.c. in 10 seconds. This is allowed to run full tap into the beaker, which is vigorously stirred the whole time. The colour changes first to green, and then to pure yellow, and as it approaches the latter, the flow must be checked and the last drops added very cautiously. The quantity of permanganate used will be that required to oxidise 20 c.c. of indigo. If the process be now repeated with the addition of 5 c.c. of the tannin infusion, the excess required to destroy the blue will correspond to that required to oxidise the astringents added, and should not exceed two-thirds of that required for the indigo alone. A second estimation should not differ from the first by more than 0·1 c.c.; and the results added together will correspond to the total astringents in 10 c.c. of the infusion (*a*). But as gallic acid and other bodies always present in tanning materials are oxidised like tannin itself, it is necessary to make a second titration after removing the tannin and estimate by loss. For this purpose 50 c.c. of the original infusion is mixed with 28·6 c.c. of a 2 p.c. solution of Nelson's or other pure gelatine, and 10 c.c. of dilute sulphuric acid (containing 1 vol. of concentrated in 10), and is then saturated with salt, which will bring the total volume up to 100 c.c. The whole is well shaken, with the addition of a little kaolin to aid subsidence, and allowed to stand for half an hour, when it may be filtered quite clear. The titration is repeated twice with 10 c.c. of the filtrate (equal to 5 c.c. of the original solution), and the results added = (*b*). To calculate the percentage of tannin in terms of gallotannic acid it is necessary to compare these results with those from pure tannin, but as this is practically unattainable, Von Schroeder has shown that the purest commercial may be substituted with little error if 1 gram of the dry commercial be reckoned as equal to 1·05 of the pure (the impurities having a higher permanganate value than tannin itself). If the moisture be determined in a sample of air-dry tannin, and it be preserved in a carefully closed bottle, it will be easy to calculate the quantity equal to 3 grams of pure tannin, and dissolve it each time in a litre of water. If 5 c.c. of this solution be titrated twice, as before, and the added result called c, the quantity of tannin x contained in the tanning material under examination will be $c:(a-b)::3:x$. It is essential to calculate always by comparison with actual tannin, as it is found that the quantity of permanganate required to oxidise a given quantity of tannin varies according to the rapidity with which it is added. Accurate results may be obtained by conducting the titration in an ordinary beaker or white basin, adding the permanganate drop by drop, and stirring with a glass rod, if care be used to perform all titrations in the same way and approximately in the same time. For the same reason no relation can be given between tannin and oxalic acid, but oak-bark tannin may be taken to consume about as much permanganate as two-thirds its weight of gallotannic acid. Hide-powder may be substituted for gelatin in removing tannin, but seems on the whole to offer no advantages. Hunt has shown (S. C. I. April, 1885) that saturation with salt causes partial precipitation of gallic acid, and recommends the use of 25 c.c. of gelatin solution and 25 c.c. of saturated salt solution containing 50 c.c. concentrated sulphuric acid per litre. In this case the precipitation of the tannin is not always quite complete.

Tannage of sole leather.—As this is a simple and typical case of vegetable tanning it may be described in some detail. Professor Knapp, in his classical essay on the Nature and Methods of Tanning (Natur und Wesen der Gerberei, Munich, 1858), adduces powerful reasons for believing that leather is not an actual chemical combination of the gelatinous fibres of the hide with tannin, but rather that the action is a surface one in which they are coated with an insoluble matter which protects and makes them resistant to solvents and decay. Whether this is wholly true or not, it harmonises with practical observation as regards sole leather. It has been said that both acids and alkalis swelled the fibrous bundles and split them into finer fibrils, so offering a larger surface and more finely divided texture, and to produce a heavy and solid tannage it is found necessary that this should take place either before or during the tanning process. The English sole-leather tanner usually accomplishes it by the action of lime in depilation; the American, who unhairs by sweating, has to secure it by a separate treatment with sulphuric acid, while in other cases where sulphides or low liming are the agents of depilation, it is partly accomplished by these and partly by the organic acids present in the earlier tanning liquors. When a hide swollen with lime is brought into tanning liquors the weak acids present rapidly neutralise the alkali, and the hide, previously plump and firm, becomes soft and flaccid and falls in thickness. If little acid is present in proportion to tannin this action takes place very gradually, and the tannin, which penetrates rapidly in the alkaline state of the hide, fixes the fibre in a swollen condition, and a plump rapid tannage is obtained, which, however, is often deficient in colour from the tendency of the lime to form tannates which darken in drying. If, on the other hand, the hide, comparatively freed from lime, is brought into liquors where acid predominates over tannin, the tissue, at first soft and flaccid, swells gradually and combines with the tannin in an acid condition, again producing a plump leather and of good colour, since lime tannates are easily soluble in the acids present. But if, on the other hand, the unswollen hide comes into liquors which have insufficient acid to plump it, or if, having been swollen by lime, it is allowed to fall back as before described, the tannin will fix it in this fallen condition, and it will be impossible afterwards to plump it or to make thick leather.

The free acid capable of dissolving lime tannate in a liquor is easily determined directly by adding saturated lime-water from a burette to a measured quantity of liquor, till it forms a permanent cloudiness; 10 c.c. of liquor should require from 5–15 c.c. Some of the acids which dissolve lime are too weak to produce any perceptible plumping effect on the pelt.

For common sole and strap leather the first of these methods may perhaps be adopted with advantage. In this case the hides or 'butts' (from which the bellies and shoulders have been trimmed in the beam-house) are simply suspended in limy water to remove the scud and loosely adhering lime, and are then brought into weak liquors, which have already lost most of their strength in previous use, and which may advantageously contain a considerable proportion of gambier, which has the property of penetrating quickly without much contracting or drawing the grain. These liquors should be contained in deep pits in which the hides may be freely suspended, if possible without touching each other, and in which they may be kept in constant motion without exposure to the air, which would darken them by oxidising the alkaline tannates. This is best accomplished by suspending from frames to which an oscillating or traversing motion is given by power, but shaking frequently by hand will fairly answer the same purpose. The butts or hides rapidly take a bright orange colour, and must be moved gradually forward into stronger liquors as the grain becomes set. It is difficult at this stage to state the suitable strength of liquor, since the specific gravity of these old liquors depends more on the impurities than on the tannin present, but they may range from 10° to 16° of the barkometer (sp.gr. 1·01–1·016) and the liquor should contain no acids strong enough to redden methyl-orange, but should give a purplish red to litmus paper.

If, on the other hand, it be desired to make a leather of first-rate colour and quality, the hides should be freed as perfectly as possible from lime by scudding and the use of some of the other methods already mentioned, and should come into weak liquors of oak bark, gambier, or other bright coloured materials, which must contain a sufficient proportion of free acid to prevent entirely the rapid orange colouration which has been mentioned; the butts should colour much more slowly and then take rather a brown than an orange tint. This acidity may be obtained by using in the later parts of the process such materials as ferment and produce acetic and other acids, as for instance light oak bark, and myrobalanes, but it will sometimes be difficult to secure sufficient without the direct addition of acetic or other vegetable acid. Mineral acids, such as sulphuric and hydrochloric, must be avoided. The goods must gradually be moved into stronger liquors, but care must be taken throughout to keep the acid in excess of the tannin, so that the butts gradually plump up and remain plump, and it must be borne in mind that so far as swelling is concerned, acid and tannin is antagonistic. Putrid or stale liquors (which are often styled 'sour' but contain little or no acid) must be sedulously avoided in every sort of sole-leather tanning.

In the American treatment of 'acid' sweat-leather the sides are usually, but not always, coloured before plumping in a sweet and moderately strong hemlock liquor, and the acid used with water only, but if the colouring and plumping are done together, a sweet fresh hemlock liquor is used with the vitriol so as to tan the grain before it is much affected by the acid. The butts receive all their plumping in this acid vat, and are then tanned in liquors which contain no vitriol. Good results are not to be attained by adding vitriol in small quantities to the handler liquors.

After the colour is fully set, and the butts by whatever method are fairly plumped in the suspenders, the rest of the process is very simple. The butts are laid flat in 'handler' pits, generally with liquor only, but sometimes with a little solid dusting material as the butts get forward. In these pits the goods are handled once a day or oftener, and the liquors are constantly changed and strengthened. This is the stage in which hemlock and other dark-coloured materials can be introduced with least injurious effect. When the butts are coloured nearly or quite through, they are placed in 'layers,' with stronger liquor and solid tanning material, such as bark and valonia, strewed between them, and they are allowed to remain undisturbed for periods of from one to six weeks, according to the age and character of the goods and the practice of the tanner. This is repeated till the goods are fully tanned, when they are raised and drained, or sometimes washed from adhering 'dust' and strong liquor in a warm sumach liquor, and taken up into the drying lofts, where they customarily receive a slight oiling and are hung up till about half dry. They are then laid in a pile to soften and equalise the moisture ('sammed'), and the grain is struck out either by hand with the 'pin' (a two-handled knife with a triangular blade), or by machine; again slightly oiled, somewhat further dried, and rolled twice and finally dried off in a warm loft. The exact dryness or 'temper' for the different operations is a matter of great importance, but is not easy to describe in writing, and it is besides somewhat influenced by the tannage. It is not uncommon to improve the colour of the grain by washing it with an aniline or other colour in the interval between striking and rolling 'off.'

Dressing leather. Hides intended for 'shaved' hides are generally light, not exceeding 60 lbs. in raw weight; those for 'dressing' or 'common' hides may be somewhat heavier. They are unhaired with lime and bated with hen or pigeon dung, and 'shaved' hides are shaved over the thick parts of the butt, and with a currier's knife of which the edge is turned in a peculiar way with a slender steel. They are coloured by frequent handling, or better by the use of a paddle tumbler, in a sweet liquor sufficiently strong to colour and set the grain in a distended condition, so that, as the inner portions shrink under the further astringent action of the liquor, it becomes wrinkled up into a network of fine furrows. After this the tannage is conducted similarly to that of sole leather, but with much weaker liquors and tanning materials, selected to produce a soft and pliable leather. Acidity of the liquors which would swell the hide and produce a hard leather must be carefully avoided, while stale and so-called 'sour' liquors will soften and supplement the action of the bate, of course at the cost of a further loss of weight and firmness. In the shed, dressing hides are simply oiled and dried, but it is now more general to curry them wet out of the pits, an operation which is rather mechanical than chemical, but which consists in scouring out the bloom or deposit of ellagic acid which has formed in the surface, shaving down, and treating with oil and tallow.

Enamelled, patent, or japanned leather. These names are applied to the various kinds of leather which are finished with a bright waterproof surface similar to the lacquered work of the Japanese, the first generally denoting leather so finished on the grain side, and with a grained surface. The colour is commonly, but not invariably, black. The leather may be tanned with a variety of materials, but must be well scoured and curried with but little oil or dubbin, and it is necessary that the hides should be well freed from grease by careful scudding before tanning. It is claimed that Nesbit's process is particularly valuable for this sort of leather. The skins are stretched on boards or frames, and coated with a linseed oil varnish thickened with Prussian blue, lampblack, and other pigments. The frames are then slid into grooves in a sort of closet heated by steam to 70°–80°C., and when the coat is dry the process is repeated till the requisite thickness is obtained, each coat being smoothed with pumice before applying the next. In France and Germany the japan is frequently dried in the sun. The American tanners are particularly skilful in treating large thin hides in this way. They are divided by the splitting machine into several thicknesses, and both the grain and flesh splits are frequently enamelled, the flesh split receiving a preliminary coating of thick boiled linseed oil and turpentine to form a sort of artificial grain.

Morocco, when genuine, is produced from goat-skins, but an article of equal quality is made from the rough-haired or 'blue-back' seal, and an inferior description, called 'French morocco,' from sheep-skins. The skins are unhaired by liming, puered with dog-dung, and passed through a bran drench, and are tanned with sumach, first in paddle-tumblers, and then in handlers. With sheep-skins the process is frequently much hastened by sewing them into bags, which are filled with sumach liquor and a little air, and are floated in a sumach bath and then laid on a shelf to drain and press. After a day's treatment they are again filled with a fresh sumach liquor, and this is usually sufficient to complete the tannage. When dried, these are called 'crust-roans.' The dyeing is either done by brushing on a table, or by folding down the back, or pairing, so as to protect the flesh-side as much as possible, and drawing through a dye-bath, which is generally of aniline colours or dye-woods. The grain receives a slight glaze of albumen and is polished by means of glazing machines by friction under agate, glass, or hard wood, and is sometimes impressed with an artificial grain by engraved or electrotyped rollers; the grain being afterwards raised or improved by the operation known as 'boarding.'

Russia leather is tanned with willow, larch, and probably other barks, and is dyed with Brazil wood grounded with perchloride of tin. Its peculiar odour is due to the essential oil of birch-bark tar, which is applied during the tanning process. Many imitations made in England and on the Continent are scented by a small proportion applied, mixed with oil, to the flesh-side.

'Chamois' or wash-leather is a totally different product from those which have been already described. The ordinary article is made from the flesh-splits of sheep-skins, and is thoroughly limed so as to dissolve as much as possible of the cementing substance of the fibres, and so produce softness. The lime is then removed by a short bran-drench, and after the superfluous moisture has been pressed out, the skins are oiled on a table with fish or whale oil, folded in cushions, and worked under fulling stocks for two to three hours, and then shaken out and hung up for a short time to cool and partially dry. The process is repeated again and again until the water has been entirely replaced by oil, and they are then laid in a pile in a warm place, when a sort of fermentation takes place with a considerable production of heat caused by the oxidation of the oil, and the skins take a yellow colour. The surplus oil is now removed either by pressure ('degras'), or by washing with potash or soda lye, from which 'sod oil' is recovered by neutralisation with sulphuric acid. Though it is not known that any chemical change takes place in the fibres, which probably are simply coated with the products of the oxidised oil, the leather is extraordinarily resistant both to boiling water, acids, and alkalis, and yields no gelatin to the former.

Crown leather (Preller's, or Helvetia leather). This leather, which is remarkable for its toughness, may be regarded chemically as intermediate between 'chamois' and kid, as it is produced by the action of oils and fats in conjunction with an albuminous 'filling' quite analogous to the egg-yolks and flour which are used in the kid manufacture. As the leather is employed for belting, picker straps, and other mechanical purposes, well flayed hides of medium substance are most suitable. They are unhaired by sulphides or sweating, or by a very short liming hastened by mechanical motion, so as to lessen injury to the fibre. For the sake of appearance they are grained and coloured by working for 1–2 hours in a paddle tumbler in a moderately strong chestnut, hemlock, or other tanning liquor. They are then swollen (if not unhaired with lime), by paddling for a few hours with about 8½ oz. of sulphuric acid per hide, washed through clean water, and hung up till half dry. They are next spread on a table and covered on the flesh with a layer of tanning paste ¼ inch thick. This may be composed of 7 parts wheat flour, 7 parts horse grease, 1 part salt, and 1–2 parts tallow. (Originally ox-brains were used in the mixture, but are not necessary.) They are then folded in bundles and are placed in a large drum studded with pegs inside, and warmed by the injection of moist air to about 30°–40°C. according to the hardness of the fats employed, in which they are worked for 8–12 hours, at the end of which time they are again partially dried and coated with the fat-mixture, and the process repeated four or five times. The hides are then washed in water, and sometimes with a little soda, and are curried by setting out on both sides, and boarding to raise the grain. The yield is only about 30–40 p.c. of the raw weight of hide.

Calf- and glove-kid. As it is impossible in the limits of an encyclopædia article to give working details where the greatest nicety is required in every stage of manufacture, and as the general outlines are the same in both these products, it will suffice to take them together, briefly indicating how the different qualities of each are produced. In calf-kid considerable firmness is required, together with great pliability, while in glove-kid, which is not only made from actual kid-skins, but also to a large extent from fine lambskins, not only the greatest softness, but the property of stretching in every direction without tendency to spring back, is essential. This characteristic difference is due not only to the different character of the skins employed, but to the fact that in the latter case special care is taken in the beam-house so to dissolve the cementing matter of the tissue that the separate fibres can move over each other without adherence. Hence the calf-skins are usually unhaired simply by a rather thorough liming, while the kids are treated with limes which in addition contain realgar (red sulphide of arsenic), which is mixed with the hot slaked lime. In both cases the skins are puered, first with a bate of dogs' dung, and then with a bran drench; and in both cases, but especially in the latter, the washing and working on the beam is very thorough, since unless the fat-glands and scud are very completely got rid of, it is impossible to dye the skins uniformly and properly. The tannage is accomplished in a drum containing a mixture of flour, alum, salt, and egg-yolks, with sometimes an addition of olive oil, thus being in principle a combination of mineral tannage with that of oil and albumen described under 'crown leather.' Calf-kid are then shaved on the flesh, and are dyed black by grounding with a mixture of stale urine, or that and bichromate of potash with logwood; sometimes by brushing, and sometimes by folding grain-side out, and passing through a bath of the dye-liquor, darkened and fixed by a wash of ferrous sulphate. They are then grounded with a moon-knife (a round knife with a central handle), rubbed over the grain with a mixture of wax, soap, and gum, and ironed to give them a gloss.

In glove-kid the dyeing process is much more complicated, and most of the tannage is washed out with warm water, which necessitates a second feeding in the drum with egg-yolk and salt. The colours are produced by a great variety of dyes and mordants, among which the juice of a variety of berries may be mentioned. Aniline dyes are now rarely used alone, but are frequently employed as a final wash to brighten the colour. After dyeing, the skins are wrung out or 'sleeked' out with a brass plate on a beam, dried, and again slightly damped and stretched by drawing over a blunt knife which is fixed on a post; an operation which is called 'staking.'

Mineral tanned leather. The use of alum and salt in the production of kid leather has already been mentioned, and though in that case the quality is largely influenced by the additions of flour and egg-yolk, it has been known from the earliest times that leather may be made by the agency of alum and salt alone; and the process is still used in the curing of skins with the hair on, and in the manufacture of 'white leather' for laces, &c. Though the salts of alumina, iron, chromium, and some other metals adhere so strongly to the surface of the hide fibres as to be withdrawn by them from solution, and even from combination in such double salts as alum, where only the sulphate of alumina takes any part in the process, it has never been shown that any real chemical combination takes place, as it probably does at least to some extent in the vegetable tannages, and it is here that Professor Knapp's theory already quoted finds its strongest support. If hide is dried before tanning it becomes hard, horny, and translucent, because the fibres are glued together by the dissolved coriin between them, and Knapp has shown that any agent which precipitates the coriin, and prevents its adhesion, will produce a species of tannage preserving the flexibility and opacity which are characteristic of all forms of leather. Thus if the water be merely removed by absolute alcohol, in which coriin is insoluble, a product is obtained which, if kept flexible by stretching during drying, is almost indistinguishable from alumed leather, although it consist only of hide fibre, and by wetting is at once reduced again to the condition of raw hide. Coriin is also insoluble in concentrated salt solutions, especially in presence of acids, and salts (like alum) of acid reaction, which thus prevents the adhesion of the fibres and produces a softer leather than alum alone, which yields an imperfect tannage of a horny character. Not only is the aluminic sulphate separated by the attraction of the fibre from the potassic sulphate of alum, but the aluminic sulphate itself which is deposited is rendered somewhat basic, while a certain quantity of free sulphuric acid is found in the alum liquor. Aluminic sulphate or acetate may be substituted for the alum without any change in the result, and chromic and ferric salts used with common salt produce similar leather but with a greenish or orange colour respectively. If in place of normal, basic ferric salts are used, which may be made by oxidising ferrous sulphate with nitric acid, the skin takes up considerably larger quantities, and leather weighing nearly 50 p.c. of the wet raw hide may be obtained, but somewhat coarse in fibre and inclined to crack. Professor Knapp took out a patent for this process of tanning, but it has not proved a commercial success.

Strong as is the attraction of the fibre for certain metallic salts, it is insufficient to prevent their being removed in great part by persistent washing, and hence mineral tanned leather is unsuited to stand wet without a further treatment to fix the tannage. For this purpose Professor Knapp has proposed the use of soap baths, which by double decomposition form insoluble stearates and oleates with the metallic base. Carbonates of the alkalis may also be used, which precipitate alumina and ferric and chromic oxides on the fibre.

The use of chromates in tanning was long ago suggested by Cavallin, who used ferrous sulphate to reduce the chromic acid and to give the leather a colour more akin to that of bark-tanned. This idea has been revived and patented with some variation by Heinzerling, and great efforts have been made to work the method on a commercial scale, but without much apparent success. He uses bichromates in conjunction with salt and alum, while: he leather is afterwards saturated with paraffin-wax and resin to render it more resistant to water. H. R. P.

LEATHER BROWN. *Bismarck Brown v.* AZO- COLOURING MATTERS.

LECIMICROONIN, LECIMICROZYMASE, LECITHOZYMATE, LECITHOONIN *v.* ALBUMINOIDS.

LEDITANNIC ACID *v.* LEDUM PALUSTRE (Linn.).

LEDIXANTHIN *v.* LEDUM PALUSTRE (Linn.).

LEDUM CAMPHOR *v.* CAMPHORS; also LEDUM PALUSTRE.

LEDUM PALUSTRE (Linn.). *Marsh tea, Wild rosemary; Lédon* (Fr.); *Porsch, Sumpfporst* (Ger.). Marsh tea is a shrub, some three feet in height, belonging to the natural order ericaceæ, which inhabits marshes, generally, throughout the northern hemisphere. Its inflorescence consists of umbels of white or pale rose-coloured flowers. The leaves possess acrid narcotic properties, and were formerly made use of in medicine. A strong decoction is now sometimes applied in veterinary practice to destroy cutaneous parasites, and it is also employed to kill vermin in furniture.

The most important constituents of the leaves are volatile oil, camphor, a glucoside and tannin. The *volatile oil* obtained by distilling the leaves with water was examined by Willigk (Sitz. W. 9, 305) and Fröhde (J. 1861, 692). It contains a *terpene* $C_{10}H_{16}$, boiling at 160°, an *oxygenated oil* $C_{10}H_{18}O$, perhaps *ericinol*, boiling at 240–242°, and camphor.

Ledum camphor $C_{15}H_{26}O$, a homologue of common camphor, was examined in 1796 by Rauchfuss (J. der Pharm. 3, 1 a. 189) and afterwards by Meissner (B. J. 13, 170), Grassmann (R. P. 38, 53), Buchner (R. P. 38, 57; N. R. P. 5, 1), Willigk (Sitz. W. 9, 302), Rizza (J. R. 19, 319), Iwanow (J. 1879, 909), Trapp (B. 8, 542), Hjelt a. Collan (B. 15, 2501). The camphor crystallises out abundantly when the volatile oil is placed in a freezing mixture, and may be separated and purified by recrystallisation from alcohol. It sublimes readily in needles, which melt at 104–105°, and boil at 292°. It is soluble in alcohol, ether, chloroform, and benzene. Heated with acetic anhydride at 150° a *sesquiterpene* $C_{15}H_{24}$ is obtained, which boils at 264°, and at 0° has a sp.gr. 0·9349 (*v.* CAMPHORS).

Marsh tea contains small quantities of the *glucoside ericolin*, $C_{34}H_{56}O_{21}$ (?) (Rochleder a. Schwarz, Sitz. W. 9, 308; 11, 371) a compound which occurs generally in ericaceous plants (Kawalier, Sitz. W. 9, 297; Thal, J. 1883, 1402). It is an intensely bitter, yellowish-brown, sticky resin (*v.* ERICOLIN). By the action of dilute acids it breaks up into glucose and *ericinol*, $C_{20}H_{26}O$ (?). The latter compound is also a product of the action of dilute acids on pinipicrin, a glucoside occurring in the needles of the Scotch fir (Kawalier, Sitz. W. 11, 350; 13, 515). Ericinol is a colourless oil when first obtained, but it soon oxidises and turns brown when exposed to the air.

Leditannic acid $C_{15}H_{20}O_8$ (?) was examined by Willigk (Sitz. W. 9, 302), Rochleder a. Schwarz (Sitz. W. 9, 307), Rochleder (Sitz. W. 44, 493), and Thal (J. 1883, 1402). By treatment with dilute acid it is converted into *ledixanthin*, $C_{30}H_{24}O_{12}$ (?), but no sugar is formed. The tannin of the horse-chestnut appears to give the same compound when treated with dilute acids, and is perhaps identical with leditannic acid. Distilled alone leditannic acid yields an oil and *catechol* $C_6H_4(OH)_2$. A. S.

LEGUMIN. *Vegetable caseïn.* The distinctive albuminoid of the seeds of the *Leguminosæ*, found also in some other seeds; it closely resembles in composition and properties the caseīn of milk. It occurs mixed with other albuminoids in the seeds, and is with difficulty obtained in a pure state.

Legumin was discovered by Einhof in 1805, and has been investigated by Proust, Vogel, Boullay, Braconnot, Liebig, Dumas and Cahours, and others, and especially by Ritthausen.

The avenin of oats (Norton) appears to be identical with legumin. Ritthausen divides plant caseïn into legumin, conglutin, and gluten-caseïn, which differ a little from each other in their composition and in a few of their properties. The first and third are albuminates, and the second a plant globulin, being soluble in a dilute salt solution, and precipitated on dilution with water.

The three forms of plant caseïn are all but slightly soluble in water, but easily soluble in dilute alkaline solutions, in solutions of alkaline reacting salts, and in very dilute acids. They are precipitated from alkaline solutions by dilute acids and by rennet. They always contain a small quantity of phosphoric acid, apparently only partly combined with bases.

Voelcker found from 1·38 to 2·18 p.c. of phosphorus in legumin prepared from peas and beans, and Norton ·8 to 2·3 p.c. in legumin from various sources.

The solubility of the plant caseïn of seeds in water is largely due to the presence in the seeds of a small quantity of alkaline phosphate.

Conglutin is easily soluble in a 5 p.c. solution of common salt, and on diluting with water the greater part of it is precipitated; and that remaining in solution can be precipitated with copper sulphate.

The three forms of plant caseïn on decomposition with sulphuric acid, yield ammonia, tyrosine, leucine, glutamic and aspartic acids, but the latter in different ratios. Legumin yields about 1·5 p.c. glutamic acid and 3·5 p.c. aspartic acid, conglutin yields about 4·0 p.c. glutamic acid and 2·0 aspartic acid, and gluten-caseïn yields about 5·3 p.c. glutamic acid and ·3 p.c. aspartic acid. Legumin yields about 17–18 p.c. of leucine (Hlasiwetz and Hebermann). Treated with baryta water it yields ammonia, carbonic, acetic, and oxalic acids, tyrosine, leucine, alanine, and other amido- acids, and gluco- proteïns, especially $C_7H_{14}N_2O_4$ (Bleunard). Sp.gr. 1·285–1·36 (Dittmar).

Ritthausen obtains legumin from peas, haricots, beans, lentils, vetches, &c., by the following process. The seeds are finely powdered, macerated with about eight times their weight of cold water for six hours, the liquid decanted and strained, and the residue again macerated with water. In some cases, notably with beans and lupins, the solution is acid, and in such cases it is desirable to add to the water used in extracting the seed sufficient caustic potash solution to render the mixture very feebly alkaline, otherwise much less proteïd will be extracted from the seed. The strained extract is allowed to settle for some time at a low temperature, 4°C., and when clear, or nearly so, decanted and precipitated with dilute acetic acid (1 : 8), adding only just sufficient acid to complete the precipitation, and keeping the temperature low. The precipitate is collected on a filter washed with 50 p.c. alcohol, which causes it to shrink and separate easily from the filter; the precipitate is then further washed and extracted with dilute alcohol, strong alcohol, and with ether; then pressed, again washed with alcohol, and dried in a vacuum over oil of vitriol.

If the product is still impure it may be purified by dissolving it in the cold in a very dilute solution of caustic potash (·1–·2 p.c.), and, after decanting from any insoluble matter, reprecipitating with dilute acetic acid.

When pure the legumin is completely soluble in a large volume of water; and when heated with sulphuric acid mixed with its own volume of water, pure legumin completely dissolves, forming a clear brown-yellow solution, which gives no precipitate on dilution with water.

Conglutin is obtained in a similar manner from sweet and bitter almonds and from lupins. It contains rather more nitrogen, is more glutinous, and more soluble in acetic acid than legumin, besides being completely soluble in dilute salt solution. Also, its compound with copper oxide differs a little from the legumin copper-oxide compound.

The conglutin obtained from lupins is partly insoluble in a 5 p.c. solution of salt, *i.e.* it contains legumin. Gluten-caseïn is specially present in the seeds of *gramineæ.* To obtain it the flour of the seeds is washed with cold water to free it from starch and the remaining gluten dissolved in very dilute caustic potash solution, and precipitated with acetic acid. The precipitate is washed with alcohol 60–70 p.c., then with 80–85 p.c. alcohol, and redissolved in the cold in a ·2 p.c. solution of caustic potash and reprecipitated with acetic acid. The precipitate is then purified by washing with water by decantation, extracting with alcohol of 70 p.c. at 35°C., with absolute alcohol and with ether; again washing with alcohol and drying over oil of vitriol. Gluten-caseïn forms a grey-white, curdy, flocculent mass, and on drying assumes an earthy rather than a horny consistence. It swells up in acetic acid, and is only very slightly soluble therein, though that from some plants is more soluble than that from others. Similarly, the gluten-caseïn of rye is much more easily soluble in ammonia than that of wheat.

Ritthausen formed compounds of plant caseïn with copper oxide by dissolving the finely-powdered proteïd in water containing ·2–·3 p.c. of potassium hydrate, largely diluting the solution with water, and adding a solution of blue vitriol and as much caustic potash as is necessary to dissolve the precipitate first formed and give the whole solution a violet colour. The clear solution is then neutralised with dilute sulphuric acid, and the precipitate collected and washed with water till it ceases to give a reaction for sulphates.

Legumin thus treated gives a precipitate containing from 13·5 to 15·5 p.c. of CuO, and the proteïd is unaltered by the treatment.

Conglutin is, to a slight extent, decomposed by the treatment, and yields a compound containing about 11·6 p.c. of CuO.

Gluten-caseïn is but slightly altered by this treatment; but its copper oxide compound is somewhat soluble in water, and contains about 14 p.c. CuO.

The legumin obtained from several sources by Ritthausen was found by him to be partially soluble in dilute solutions of salt; but there was little or no difference in composition between the soluble and insoluble portions. The composition of legumin and its allies, as given by Ritthausen, varies somewhat according to their source, and also according to the method used for the determination of their nitrogen. In some of the earlier analyses the determinations of nitrogen by the soda-lime method gave low results. From the most trustworthy results, in which the nitrogen was determined by Dumas' method, the following percentages are calculated:

—	Legumin from peas and beans	Legumin from oats	Conglutin from sweet and bitter almonds	Conglutin from yellow lupins	Gluten-caseïn
C . . .	51·5	51·6	50·4	50·8	50·2–52·9
H . . .	7·0	7·5	6·9	6·9	6·8–7·0
N . . .	17·1	17·5	18·6	18·4	17·1–17·4
S . . .	·4	·8	·4	·9	·9–1·5
O . . .	24·0	22·6	23·7	23·0	22·0–24·1

A similar proteïd has been found in walnuts, hazel-nuts, candle-nuts (*Aleurites triloba*), paranuts (*Bertholletia*), castor-oil beans, cherry kernels, plum and apricot kernels, and earth nuts (*Arachis hypogæa*).

Ritthausen obtained the following percentages of legumin from different seeds:—French beans 11 p.c., peas 5·4 to 9·4 p.c., horse beans 10 p.c., Mazagan beans 18·7 p.c., and lentils 5·2 p.c. From sweet almonds he obtained 15 p.c. of conglutin, and from lupins 20 p.c.

The whole of the nitrogenous matter of these seeds is not in the form of legumin; other albuminoids are present. Thus field beans contain about 24 p.c. of nitrogenous matter, peas about 23 p.c., and lentils 25 p.c.

In China and Japan a kind of vegetable cheese, known in the latter country as *tofu*, is made from the seed of the soy bean (*Soja hispida*). This leguminous seed contains about 37 to 40 p.c. of nitrogenous matter, and about 20 p.c. of fat, being a very concentrated food.

The cheese is made by soaking the beans in water, pounding them, and straining through a sieve, which removes most of the starch, boiling the residue with water, and straining the solution through cotton-cloth and pressing the residue. The strained liquor, containing the nitrogenous matter (legumin &c.) and fat, is precipitated by the addition of the brine formed on the deliquescence of common sea salt; the precipitate pressed and cut into cakes is ordinary *tofu*. It contains about 89 p.c. of water, the dry matter being nearly two-thirds nitrogenous matter and one-third fat, with small quantities of carbohydrates and ash. A drier product is obtained by freezing these cakes of cheese, and then thawing by exposure to the sun. On thawing, a large quantity of water runs off, leaving a spongy, somewhat horny residue, known as *kori-tofu*.

Analyses of these products gave the following results:

—	Fresh tofu	Frozen tofu or kori-tofu	Dry matter from frozen tofu
Water . . .	89·0	18·8	—
Ash . . .	·5	1·6	2·0
Fat . . .	3·2	28·8	35·4
Nitrogenous matter .	6·5	48·8	60·1
Carbohydrates	·8	2·0	2·5
	100·0	100·0	100·0

E. K.

LEHRBACHITE *v.* Selenium.

LEIPSIC YELLOW. *Normal lead chromate v.* Chromium.

LEITHNER'S BLUE. *Cobalt blue v.* Pigments.

LEMNIAN EARTH. A red, yellow, or grey earthy substance, somewhat resembling fuller's-earth, and consisting of a hydrated silicate of aluminium, with more or less iron. It takes its name from its occurrence at Lemnos, an island in the Greek archipelago, where, in consequence of its reputed medicinal virtues, it was formerly regarded as sacred. The earth was dug only once a year, with much ceremony, and, after mixture with goat's blood, was made into small cakes or balls, which were sealed by the priests, whence it was termed *terra sigillata*.

F. W. R.

LEMON YELLOW *v.* Barium chromate and Chromium.

LEMONS, OIL OF *v.* Oils, essential.

LEMON-GRASS OIL *v.* Oils, essential.

LEPIDINE *v.* Quinoline.

LEPIDOLITE *v.* Lithium, also Mica.

LEPTANDRA. *Culver's Root.* The rhizome and rootlets of *Leptandra Virginica* contain a resin leptandrin. It is used as a cathartic in biliousness or constipation.

LETTUCE OPIUM *v.* Lactucarium.

LEUCANILINE *v.* Triphenylmethane colouring matters.

LEUCIN. *Amido-caproic acid v.* Fatty acids.

LEUCOMAÏNES *v.* Ptomaïnes.

LEUKOGALLOL *v. Pyrogallol,* art. Phenol and its homologues.

LEUTORCINOL *v. Cresorcinol,* art. Phenol and its homologues.

LEVIGATION. Levigation is the mechanical process by which hard substances are reduced to a very fine powder by grinding them with water. The process is used principally in the preparation of pigments. On a small scale the substance is ground with a 'muller.' The muller is a piece of hard stone, convenient in shape and size to hold in the hand, and carefully flattened and polished on one side. The pigment to be ground is mixed with water on a large square slab of stone, preferably marble, and then ground with the muller. The finest artists' colours are ground in this way. On the large scale the pigment is first thoroughly mixed with water in a pug-mill. It is then ground between millstones similar to those used for flour, or under edge runners. Sometimes the millstones are replaced by three horizontal granite rollers, between which the pigment is ground. A mill with stones 2 feet in diameter will grind 15 cwt. of paint in 11 hours. A. P. L.

LEVULIN *v.* Dandelion.

LEVULOSE. *Sucro-levulose, Lævo-glucose, Fruit-sugar* (*Lévulose, Chyliarose,* Fr.; *Linksfruchtzucker,* Ger.), $C_6H_{12}O_6$.

This sugar occurs with its isomer dextrose in honey and in many fruits. It is produced, together with an equal proportion of dextrose, by the inversion of cane sugar.

According to Nicol (Z. 14, 177), the inversion is best conducted by dissolving 3 grams of cane sugar in 4 c.c. of water, to which 20 drops of hydrochloric acid (1·11 sp.gr.) have been added, and heating the solution on the water bath for thirty minutes. The cane sugar is thus decomposed into levulose and dextrose, one molecule of water being assimilated

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

The inversion may also be induced by heating with dilute sulphuric acid or by alkalis, or even by carbonic acid gas, especially under pressure, or by prolonged heating of the aqueous solution alone. An aqueous solution becomes slowly inverted at the ordinary temperature on keeping, except when it has been sterilised by boiling, and is kept out of contact with air.

When the inversion is induced by acids, the acid must be neutralised before separation of the levulose, by addition of baryta when sulphuric acid has been employed, or by silver oxide with subsequent passage of sulphuretted hydrogen through the filtrate when hydrochloric acid has been used.

After prolonged heating at 165°–170°C., cane sugar becomes converted into a mixture of *levulosan* ($C_6H_{10}O_5$) and dextrose, without change of weight. On fermenting the aqueous solution of the mass with yeast the dextrose is decomposed, while the levulosan remains unchanged, and may afterwards be converted into levulose by treatment with dilute acids.

Levulose may be separated from dextrose in invert sugar as follows. 6 grams of finely-powdered slaked lime is added to every 100 c.c. of a neutral ice-cold 10 p.c. solution of invert sugar, and the solution, which at first sight is merely milky, is agitated, the vessel being preferably immersed in ice-cold water until it acquires a creamy consistency. The mass, which consists of the difficultly soluble calcium levulosate $CaO.C_6H_{12}O_6.H_2O$, together with the easily soluble calcium dextrosate, is filtered through linen and strongly pressed to remove the greater part of the liquid, and is suspended in water and decomposed by addition of oxalic acid or by passage of carbonic acid gas. The filtered solution is evaporated *in vacuo* over sulphuric acid with production of anhydrous levulose.

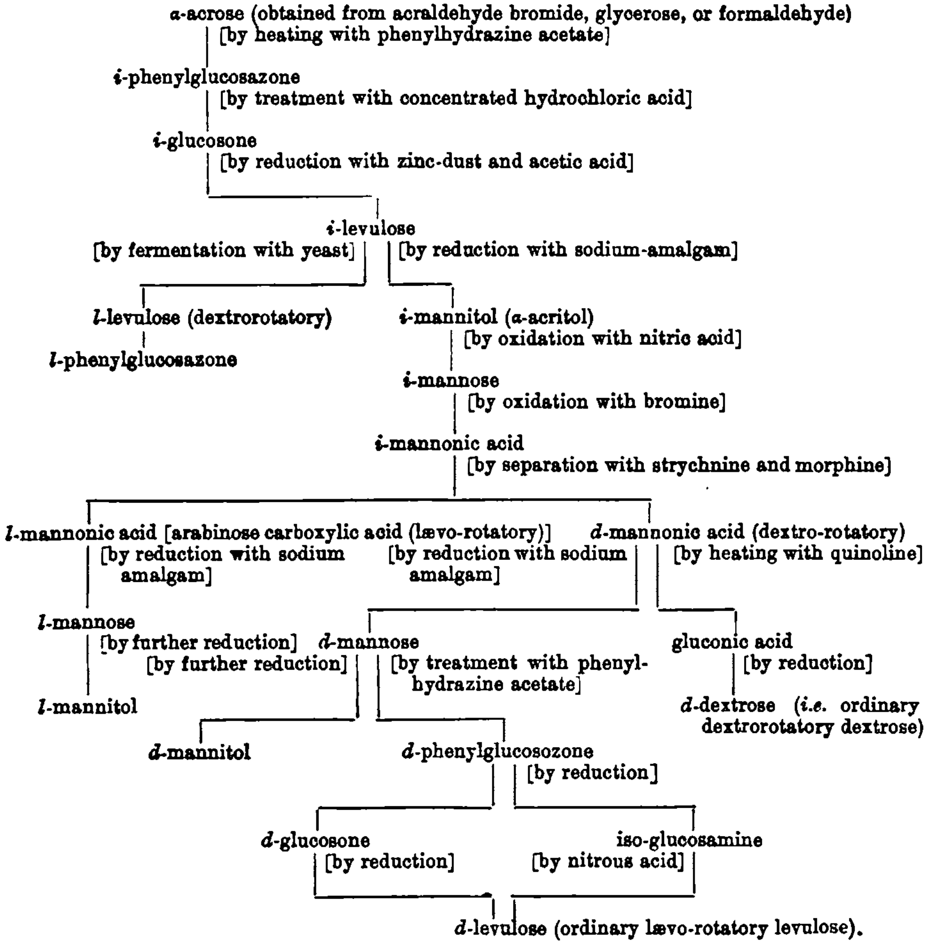
For the preparation of pure levulose, *inulin*, which is completely converted into that substance on boiling alone or with dilute acids, is usually employed.

Jungfleisch and Lefranc (C. R. 93, 547) dissolve inulin in 10 parts of water, and digest at 100°C. for twenty hours, the solution being then evaporated to a syrup, and purified with alcohol and animal charcoal.

This method is preferable to treatment with acids on account of the difficulty in the latter case of separating the levulose from the by-products.

Levulose is not produced by the hydrolysis of any glucoside.

E. Fischer (B. 23, 370–394, 799, 805; Abs. C. J. 1890, 466) has effected the synthesis of levulose, mannose, and dextrose. The mode of derivation of these carbohydrates, and their relation to *α*-acrose, may be seen from the following table:—



As usually prepared, levulose is a colourless, uncrystallisable syrup, which becomes anhydrous at 100°C., or when dried *in vacuo* over sulphuric acid. It may, however, be obtained in crystals, the best process, according to Jungfleisch and Lefranc, being as follows. The syrup is repeatedly washed with cold absolute alcohol, and is left for some time in a cold place. The mass gradually deposits crystals, and finally solidifies. On dissolving it in hot alcohol and cooling the solution most of the levulose separates as a syrup, but the mother liquor on standing deposits thin, colourless, silky needles, sometimes as much as a centimetre in length and usually grouped in spherical concretions. The crystallisation is usually induced by the introduction into the solution of a few crystals of levulose. Such addition also induces crystallisation from an aqueous solution.

Hönig and Hubert (M. 8, 529) have obtained levulose in combined octahedra and prisms belonging to the rhombic system.

Levulose is less crystalline but more soluble in water and much sweeter than dextrose. It is also rather sweeter than cane sugar. It ferments less easily than dextrose, and when treated in aqueous solution with chlorine or bromine yields glycollic acid, whereas dextrose yields gluconic acid.

According to Soxhlet the relative reducing powers of levulose and dextrose on Fehling's solution, in 1 p.c. solution, are 475 to 518; but Allihn finds that if the solutions be boiled for thirty minutes (instead of for two minutes, as in Soxhlet's experiments), their reducing powers are identical. On Knapp's mercurial solution their action is the same, but on Sachsse's mercurial solution their actions are 100 (levulose) and 148·6 respectively. On treatment with sodium amalgam and water, levulose yields mannite.

Levulose is more readily decomposed by acids, but less readily by alkalis, than dextrose. One of the products of its treatment with caustic soda or baryta is lactic acid (Sorokine, Russ. Chem. Soc. 1885, 368).

When heated to 170°C. it yields *levulosan*.

The crystals melt at 95°C., and, according to Jungfleisch and Lefranc and to Hönig and Jesser (M. 9, 562), are not hygroscopic, which statement is not confirmed by Herzfeld (A. 244, 274).

Levulose has the property of rotating the plane of polarised light to the left; various numbers have been obtained for its specific rotatory power by different observers. Thus, for the sodium line, Hönig and Schubert (M. 8, 529) have obtained −87·84° at 22°, while Hönig and Jesser (M. 9, 562) give −113·96° at 20°, and Herzfeld (A. 244, 274) has obtained −77·81° at 20°.

The specific rotatory power usually taken is −98·8° at 15°C. for the sodium line. This power decreases by 0·6385° for each degree centigrade of increase in temperature. This property is taken advantage of in determining its proportion in presence of other sugars, the rotation being first observed at a low temperature and then at about 100°C.

The lævorotatory power of levulose is so much in excess of the dextrorotatory power of dextrose, that cane sugar, when inverted, becomes lævorotatory in the proportion of 38° for each 100° of dextrorotatory power previously possessed.

LIBAVIUS, FUMING LIQUOR OF. *Stannic chloride* $SnCl_4$ *v.* TIN.

LICHENS. According to modern ideas, these curious and interesting plants are of a compound character, and are considered to be algæ upon which fungi are supported. Many species have been employed from the earliest times in medicine, dyeing, and as food stuffs (Mémoires sur l'utilité des lichens, par Hoffmann, Amoreux, et Willemet, Lyon, 1787). From about the year 1300, certain species have been employed for the production of the purple dye-stuff '*orchil*' or '*archil*,' since, as shown by modern researches, they contain peculiar colourless principles which, under the combined influence of ammonia and atmospheric oxygen, yield the purple colouring matter *orceïn* (*v.* ARCHIL). Under the name of '*Crottle*' or '*Crotal*,' with various descriptive prefixes, several species have been, and even still are, directly applied in dyeing buff and brown colours on home-spun woollen yarn in different parts of the United Kingdom—*e.g.* in the Highlands of Scotland, Wales, &c. Those lichens—*e.g.* Iceland moss (*Cetraria islandica*)—which serve as food stuffs contain a starch-like substance termed *lichenin*, which is capable of conversion into glucose.

The following list includes the principal lichens which have been submitted to chemical examination:

Alectoria sarmentosa, Ach.; *v. Evernia ochroleuca*.

Bæomyces roseus, Pers.; *v.* analysis by Brandes (Berl. Jahrb. 25, 1, 38).

Biatora lucida, Fr. Contains usnic acid (Knopp, Götting. gelehrte Anzeiger, 1843, 2 u. 3 Stück, 16; A. 49, 122; J. pr. 31, 196).

Borrera ciliaris v. Parmelia ciliaris.

Calicium chrysocephalum, Ach. This yellow lichen, growing on oak, birch, pine, &c., was found by Hesse to contain a yellow crystalline substance, calycin (B. 13, 1816).

Cetraria aculeata, Fr. Contains moss-starch (lichenin) and lichenic (fumaric) acid, but no cetraric acid (Weppen, Ph. C. 1838, 12).

Cetraria islandica, Ach. Contains starch, not deposited in granules, but uniformly distributed among the cells (lichenin); cetraric acid, lichenstearic acid, thallochlor (the green colouring matter of lichens), fat, sugar, gum, yellow extractive matter, brown lichenulmic acid formed from cetraric acid, and another body undetermined (Knop and Schnedermann, 55, 144; J. pr. 36, 107); also alumina (Knop, J. pr. 38, 347) and a pale yellow bitter principle (Berzelius, Schweigger's J. Ch. Ph. 7, 332). The lichenin, which is convertible into sugar, is present in such large quantity that this lichen can be used for food (Schmidt, A. 51, 29).

Cetraria glauca. Contains lichenin (Berzelius, Scherer's A. 3, 288; Schweigger's J. Ch. Phys. 7, 336).

Cetraria vulpina v. Parmelia vulpina.

Cladonia digitata, Hoffm. Contains usnic acid and starch (Knop, A. 49, 119; J. pr. 31, 196).

Cladonia bellidiflora, Schær. Contains 1·18 p.c. mineral matter, of which 0·59 p.c. is soluble, and 0·59 p.c. insoluble (Thomson, A. 53, 252)

Cladonia macilenta, Hoffm. Contains usnic acid and starch. (Knop, A. 49, 119; J. pr. 31, 196).

Cladonia uncialis, Hoffm. Contains usnic acid and starch (Knop, A. 49, 119; J. pr. 31, 196).

Cladonia pyxidata, Fr. Contains a large quantity of lichenin (Schmidt, A. 51, 29). Contains 6·09 p.c. mineral matter (Thomson, A. 53, 252).

Cladonia rangiferina, Hoffm. (*Lichen rangiferinus*, L., *Patellaria rangiferina*.) Contains usnic acid (Rochleder and Heldt, A. 48, 2), a large quantity of lichenin (Schmidt, A. 51, 29), also cladonic acid (Stenhouse, A. 155, 58), which is identical with the β-usnic acid of Hesse (A. 117, 343).

Cornicularia vulpina v. Parmelia vulpina.

Evernia furfuracea, Mann. (*Parmelia furfuracea*, Ach.) Contains usnic acid (Rochleder and Heldt, A. 48, 9); *v.* also analysis by John (Chem. Schr. 6, 41).

Evernia ochroleuca, Fr. (*Alectoria sarmentosa*, Ach.; *Evernia sarmentosa*, *Parmelia sarmentosa*, Ach.) Contains usnic acid (Knop, A. 49, 122; J. pr. 31, 196).

Evernia prunastri, L. (*Lichen prunastri*, *Parmelia prunastri*, *Lobaria prunastri*.) Contains evernic and usnic acids (Stenhouse, P. M. [3] 32, 300; A. 68, 55; 155, 55). Rochleder and Heldt found lecanoric acid, but not usnic acid (A. 48, 1). Stenhouse considers that Rochleder and Heldt must have examined some other lichen.

Evernia sarmentosa v. Evernia ochroleuca.

Evernia vulpina v. Parmelia vulpina.

Gyrophora pustulata, Ach., T. and B. (*Umbilicaria pustulata*, Hoffm.) From Norway. Contains gyrophoric acid, resin, and humus matter (Stenhouse, Tr. 1849, 458; A. 70, 218).

Isidium corallinum, Ach. Contains a large quantity of calcium oxalate (Braconnot, A. Ch. [2] 28, 319). This lichen is known as 'white crottle.'

Lecanora atra, Ach. From this lichen, collected in the mountains surrounding the western part of Palermo, Paterno and Oglialoro obtained atranoric acid $C_{19}H_{18}O_8$, a yellow crystalline substance, m.p. 175°C., very similar to usnic acid; also a colourless crystalline substance of weak acid character, m.p. 190°C. (Gaz. Chim. Ital. 7, 1877; C. N. 35, 264; B. 10, 1100). Hesse (B. 10, 1324) considers Paterno's yellow acid to be cladonic acid, and his atranoric acid to be hydrocarbonusnic acid.

Lecanora crenata, Myl.; *v. Lecanora ventosa.*

Lecanora concolor. Probably contains chrysophanic acid.

Lecanora hæmatomma v. Parmelia hæmatomma.

Lecanora parella, Ach. (*Parmelia parella*, Schær.) Contains parellic acid, lecanoric acid, tannin matter, three different fats, bitter extractive matter, chlorophyll, inulin (?), and gummy matter. The mineral constituents are sodium and potassium chlorides and sulphates, calcium and magnesium carbonate, calcium phosphate, alumina, and ferric oxide (Schunck, A. 54, 257, 274; 41, 161). This lichen is known as 'light crottle.'

Lecanora rubra v. Parmelia rubra.

Lecanora tartarea, L. (*Patellaria tartarea*, Dec.; *Parmelia tartarea*, Ach.) Contains erythric acid, synonymous with F. Nees v. Esenbeck's 'remarkable resin' (Brandes' Archiv Apoth. 16, 135), also with Heeren's erythrin, and with Kane's erythrilin (Schweigger's J. Ch. Phys. 59, 313). Schunck found crustaceous lichens belonging to *Lecanora*, &c., collected on the basalt rocks of the Vogelsberg, in Upper Hessia, to contain lecanoric acid as well as erythric acid (A. 41, 157). In a specimen from Norway, Stenhouse found gyrophoric acid (A. 70, 218; Tr. 1849, 458). Braconnot found it to contain large quantities of calcium oxalate (A. Ch. [2] 28, 319). This lichen, known as 'crottle' *par excellence*, is, or was, employed in dyeing purple.

Lecanora ventosa, Ach. Contains usnic acid and another crystalline substance (Knop, A. 49, 122; J. pr. 31, 196).

Lecanora vitellina, Ach. Probably contains chrysophanic acid.

Lecidea geographica, Schær. From the Brocken. Contains usnic acid (Knop, A. 49, 122; J. pr. 31, 196).

Lecidea candida, Ach. (*Psora candida*, Dec.) Contains a large quantity of calcium oxalate (Braconnot, A. Ch. [2] 28, 319).

Lecidea lucida v. Biatora lucida.

Lichen barbatus v. Usnea barbata.

Lichen dealbatus, Ach.; *v. Variolaria dealbata.*

Lichen parietinus, L.; *v. Parmelia parietina.*

Lichen prunastri v. Evernia prunastri.

Lichen rangiferinus, L.; *v. Cladonia rangiferina.*

Lichen vulpinus, L.; *v. Parmelia vulpina.*

Lobaria prunastri v. Evernia prunastri.

Ochrolechia parella and *O. tartarea v. Lecanora parella* and *L. tartarea.*

Parmelia barbata v. Usnea barbata.

Parmelia caperata, L. This lichen is known as 'stone crottle.'

Parmelia ciliaris, Ach. (*Borrera ciliaris.*) Analysis by John (Chem. Sch. 6, 39).

Parmelia ceratophylla, var. *physodes*; *v. Parmelia physodes.*

Parmelia furfuracea, Ach.; *v. Evernia furfuracea.*

Parmelia hæmatomma, Ach. (*Patellaria hæmatomma*, Hoff.) Contains usnic acid and another crystalline substance in small quantity (Knop, A. 49, 122; J. pr. 31, 196), also large quantities of calcium oxalate (Braconnot, A. Ch. [2] 28, 319).

Parmelia lentigera, Ach.; *v. Squamaria lentigera.*

Parmelia omphalodes, L. (*Parmelia saxatilis*, var. *omphalodes*, L.) Contains 8·12 p.c. mineral matter, of which 0·33 p.c. is soluble and 7·79 insoluble (Thomson, A. 53, 252). Under the name of 'black crottle,' this lichen is employed for dyeing a brown colour on homespun woollen yarn in the Outer Hebrides (Lewis and Harris).

Parmelia parietina, Ach. (*Lichen parietinus*, L.) Contains chrysophanic acid (Rochleder and Heldt, 48, 12). It is identical with Schrader's 'resinous yellow of wall-lichen' (Berl. Jahrb. Pharm. 1819), also with Herberger's 'parmelia yellow' (Buchner's Repert. Pharm. 47, 179, 202; A. 12, 342), and with Thomson's parietin (P. M. J. [3] 25, 39; Edin. New. Phil. J. 37, 187; J. pr. 33, 210; A. 53, 252). This lichen also contains wax, stearin, parmelia red, uncrystallisable sugar, bitter extractive matter, parmelgliadin (lichenin), chlorophyll, soft resin, gum, ethereal oil, lichen fibre, calcium lichenate, sodium and calcium chloride, and traces of calcium phosphate (Herberger). Thomson found it to contain parietin (chrysophanic acid), a crystallisable sugar, and 6·8 p.c. mineral matter, consisting of silicic acid, alumina, and aluminium phosphate, ferric oxide and ferric phosphate, sodium-chloride, -sulphate, and -phosphate. A variety of *Parmelia parietina* growing on sandstone rock, and not on trees, like that of Rochleder and Heldt, was found to contain chrysopicrin (vulpic acid) by Stein (J. pr. 93, 366; Zeitsch. Ch. Pharm. 7, 97). Compare C. Schmidt (A. 51, 29); Sander (Ueber die Wandflechte, Sonderhausen, 1815, and Kast. Arch. 8, 431); Monnhardt (Dissert. sist. Lobariæ parietinæ Analysin chem. Kieloniæ, 1818); Schröder (Berl. Jahrb. 1819, 44; Markowitz (Scherer's Ann. Chem. 1, 438).

Parmelia physodes, Ach. (*Parmelia ceratophylla*, var. *physodes*.) Contains physodin and two colourless crystalline substances (Gerding, Brandes' Ar. Ph. [2] 87, 1), also ceratophyllin (Hesse, A. 119, 365). This lichen, popularly known as 'dark crottle,' is employed in various parts of the United Kingdom in dyeing a brown colour on homespun woollen yarn.

Parmelia prunastri v. Evernia prunastri.

Parmelia radiosa, Ach.; *v. Placodium radiosum.*

Parmelia roccella v. Roccella tinctoria.

Parmelia rubra, Ach. Contains a large quantity of calcium oxalate (Braconnot), A. Ch. [2] 28, 319.

Parmelia saxatilis, Ach. Contains usnic acid, lichenin in small quantity, and 6·91 p.c. mineral matter (Schmidt, A. 51, 29; Overbeck, Brandes' Ar. Ph. 82, 150).

Parmelia saxicola, Ach.; *v. Placodium ochroleucum.*

Parmelia sarmentosa, Ach.; *v. Evernia ochroleuca.*

Parmelia tartarea, Ach.; *v. Lecanora tartarea.*

Parmelia ventosa, Ach.; *v. Lecanora ventosa.*

Parmelia vulpina, Ach. (*Lichen vulpinus*, L.; *Corniculeria vulpina*, Dec.; *Cetraria vulpina*; *Evernia vulpina*). Contains vulpic acid or vulpulin (Bebert, A. 2, 342; J. Ph. 17, 696). Berzelius (J. 12, 256) and Gerhardt erroneously considered vulpic acid to be identical with chrysophanic acid. It is considered to be identical with Stein's chrysopicrin by Bolley, Strecker, and by Stein himself. Compare F. Möller and A. Strecker (A. 113, 56; J. pr. 79, 468; A. Ch. [3] 58, 486); W. Stein (Zeitschr. Ch. Pharm. 7, 97; 8, 47; J. pr. 93, 366; Brandes' Ar. Ph. 118, 230); Bolley and Kinkelin (Zürich. Mitth. 1865; J. pr. 93, 354). Spiegel (B. 13, 1629) examined *Cetraria vulpina* collected in Pontresina, Switzerland, and found it to contain 1·5-2 p.c. vulpic acid; a sample from Norway contained 4 p.c. vulpic acid.

Patellaria hæmatomma, Hoff.; *v. Parmelia hæmatomma.*

Patellaria rangiferina v. Cladonia rangiferina.

Patellaria rubra, Hoff.; *v. Parmelia rubra.*

Patellaria tartarea, Dec.; *v. Lecanora tartarea.*

Patellaria ventosa, Dec.; *v. Lecanora ventosa.*

Peltigera canina, Hoff. Contains lichenin (Schmidt, A. 51, 29).

Pertusaria communis, Dec. Contains a large quantity of calcium oxalate.

Pertusaria dealbata v. Variolaria dealbata.

Physcia ciliaris v. Parmelia ciliaris.

Physcia parietina v. Parmelia parietina.

Placodium ochroleucum, Dec. (*Parmelia saxicola*, Ach.). Contains large quantities of calcium oxalate (Braconnot, Am. Ch. [2] 28, 319).

Placodium radiosum, Dec. (*Parmelia radiosa*, Ach.). Contains large quantities of calcium oxalate (Braconnot, *l.c.*).

Placodium elegans and *murorum v. Squamaria elegans* and *murorum.*

Psora candida, Dec.; *v. Lecidea candida.*

Ramalina calicaris, Fr. var. *fastigiata.* Contains large quantities of starch (lichenin), colouring matter, and bitter substance, and a small quantity of saccharic acid (Berzelius, Scherer's A. 3, 97); also usnic acid (Rochleder and Heldt, A. 48, 9).

Ramalina calicaris, Fr. var. *fraxinea.* The ash contains a large quantity of ferric oxide, but scarcely a trace of potassium carbonate (John, Chem. Schr. 6, 37); soluble and coagulable albumen (Berzelius, Scherer's A. 3, 208); lichenin and usnic acid (Rochleder and Heldt, A. 48, 9). The latter is identical with the α-usnic acid of Hesse (A. 117, 297).

Ramalina scopulorum, Ach. Contains 4·18 p.c. mineral matter, of which 0·33 p.c. is soluble and 3·84 p.c. is insoluble (Thomson, A. 53, 252).

Roccella frutectosa. From California. Contains roccellic and erythric acids (Hesse, A. 199, 353).

Roccella fuciformis, Ach. (*Roccella tinctoria*, var. *fuciformis*.) This well-known 'orchella weed' is largely imported, for the purpose of manufacturing orchil and cudbear, from Angola, Zanzibar, Madagascar, Ceylon, and Lima. It contains erythric acid (Heeren's erythrin, Kane's erythrilin), roccellic acid, tannin matter, fat, and chlorophyll. The mineral matter consists of alumina, ferric oxide, sodium sulphate and chloride, magnesium and calcium carbonate (Schunck, P. M. [3] 39, 194; A. 61, 64; Kane, Tr. 1840, 273; Heeren, Schweigger's J. Ph. 59, 346). Stenhouse (A. 149, 288) examined a Lima 'weed' in 1848, and found it to contain lecanoric acid, but it is now considered to have been *Roccella tinctoria*, and not identical with the *R. fuciformis*, which constituted the Lima 'weed' examined by him in 1869, and in which he found erythric acid. Compare Hesse (A. 117, 332; 139, 22), who also found Lima 'weed' to contain erythric acid and not lecanoric acid. Stenhouse considers the *Roccella montagnei* from Angola, in which he found erythric acid, to be identical with the *Roccella tinctoria*, var. *fuciformis*, examined by Schunck.

A stunted variety of *Roccella fuciformis* (Valparaiso weed) examined by Menschutkin and Lampater was found to contain β-erythrin, a substance very like erythrin, but having a lower melting-point. In a better-grown specimen ordinary erythrin was obtained (Lampater, A. 134, 243).

A variety of *Roccella fuciformis* growing on rocks, and imported by a Portuguese firm, probably from the West Coast of Africa, contains erythric acid, fat, resinous matter, chlorophyll, and an intensely bitter substance named picro-roccellin (Stenhouse and Groves, A. 185, 14).

Roccella montagnei, Belen.; *v. Roccella fuciformis.*

Roccella tinctoria, Ach. This lichen, used largely for the manufacture of orchil and cudbear, is imported from the Cape of Good Hope, the Cape Verd Islands, Chili (Valparaiso weed). Formerly it seems to have been imported also from Lima (Stenhouse). It contains lecanoric acid (Stenhouse's α- and β-orsellic acid) and roccellinin; the latter is, however, probably a decomposition product of the former (Stenhouse, P. M. [3] 32, 300; A. 68, 55; 149, 288; C. J. 20, 221). Compare also Hesse, A. 139, 22.

Scyphophorus pyxidatus, Hook.; *v. Cladonia pyxidata.*

Scyphophorus bellidiflorus, Hook.; *v. Cladonia bellidiflora.*

Squamaria elegans, Fée. *Squamaria murorum.* Contain chrysophanic acid (Thomson, P. M. 25, 39; N. Edin. Phil. J. 37, 187; J. pr. 33, 210; A. 53, 252).

Squamaria lentigera, Dec. (*Parmelia lentigera*, Ach.) Contains a large quantity of calcium oxalate (Braconnot, A. Ch. [2] 28, 319).

Sticta pulmonacea, Ach. Contains lichenin and a bitter substance (Weppen, Ph. C. 1838, No. 12) very similar to cetraric acid in composition, and named stictic acid by Knop and Schnedermann (J. pr. 39, 363; A. 55, 144). Compare John (Chem. Schr. 6, 39). This lichen is known as 'hazel crottle.'

Urceolaria esculenta, Ach. Contains a large quantity (13 p.c.) of gum (Kirchhoff, Scherer's Am. 3, 218).

Urceolaria scruposa, L. Contains a large quantity of calcium oxalate (Braconnot, A. Ch. [2] 28, 319).

Urceolaria lichens collected in the basalt rock of the Vogelsberg, in Upper Hessia, contain lecanoric and erythric acids and fatty matter (Schunck, Mem. Chem. Soc. 1, 71).

Umbilicaria pustulata, Hoffm.; *v. Gyrophora pustulata.*

Usnea barbata, Fr. (*Lichen barbatus*, *Parmelia barbata.*) Contains usnic acid (Rochleder and Heldt, A. 48, 8; Stenhouse, A. 155, 51), and lichenin (Berzelius, Scherer's A. 3, 205; Hesse, A. 137, 241; B. 10, 1324).

Usnea barbata, var. *plicata*, Fr.; *v. Usnea hirta.*

Usnea florida, Hoffm. (*Usnea barbata*, Fr. var. *florida.*) Contains usnic acid and resinous matters (Knop, A. 49, 103; J. pr. 31, 196), and a small quantity of lichenin (Schmidt, A. 51, 29). (Compare Salkowski, B. 8, 1459; Hesse, A. 137, 241; B. 10, 1324.) Hesse found *Usnea barbata* collected from quinine bark (Bolivian calisaya bark) to contain carbonusnic acid $C_{19}H_{16}O_8$, and a small quantity of usnetinic acid.

Usnea hirta, Hoffm. (*Usnea barbata*, var. *plicata.*) Contains usnic acid (Knop, A. 49, 103; J. pr. 31, 196), a bitter principle, gum-sugar, and a large quantity of lichenin (Berzelius, Scherer's Ann. 3, 203; Schmidt, A. 51, 29).

Variolaria amara, Ach. Contains an intensely bitter colourless crystalline principle named picro-lichenin, also resinous matter and chlorophyll (Alms, Pharm. Zeit. 1832, 2, 17; A. 1, 61. Gregory, J. Ph. 21, 314; Ph. C. 1835, 39. Vogel and Wuth, N. J. P. 8, 201; J. pr. 72, 272). It contains also cellulose, gum-sugar, bitter extractive matter, calcium oxalate, silicic acid, iron (Müller, Ph. C. 1844, 47; Filhol and Bouchardt, J. de Méd. de Toulouse, 7, 201; Ph. C. 1844, 39).

Variolaria communis, Ach. On lime tree. Contains waxy matter, green colouring matter, a bitter and acrid principle, uncrystallisable sugar, calcium oxalate (4·7 p.c.) a substance similar to gelatin, &c. (Braconnot, A. Ch. [2] 6, 132).

Variolaria dealbata, Dec. (*Lichen dealbatus*, Ach.) Contains variolarin (Robiquet, A. Ch. 42, 236; 58, 320). Schunck found crustaceous *Variolaria* collected on the basalt rocks of the Vogelsberg, in Upper Hessia, to contain lecanoric and erythric acids.

J. J. H.

LICHENIN *v.* Gums.

LICKNER'S BLUE. A silicate of cobalt and potassium. A variety of smalt; *v.* Cobalt.

LIEBERMANN'S PHENOL DYES *v.* Phenol and its homologues.

LIEBIGITE. *Calcic uranic carbonate v.* Uranium.

LIÈGE BLACK. *Blue black v.* Pigments.

LIGHT CARBURETTED HYDROGEN. *Marsh gas v.* Methane.

LIGNIN DYNAMITE *v.* Explosives.

LIGNITE *v.* Fuel.

LIGNOCERIC ACID *v.* Fatty acids.

LIGNUM COLUBRINUM *v.* Nux vomica.

LIMA WOOD. A variety of Brazil wood (*q. v.*).

LIME *v.* Calcium; also Cements.

LIME, BISULPHITE OF, *v.* Calcium.

LIME BURNING *v.* Calcium; also Cements.

LIME, HYDRAULIC, *v.* Cements.

LIME, SUPERPHOSPHATE OF, *v.* Calcium; also Manures.

LIME-OIL *v.* Oils, essential.

LIMESTONE *v.* Calcium; also Cements.

LIMESTONE, MAGNESIAN *v.* Calcium and Magnesium.

LIMNITE (λιμνή, a marsh). A hydrated peroxide of iron $Fe_2O_3.3H_2O$.

LIMOGES ENAMELS *v.* Enamels.

LIMONITE (λειμών, a meadow). A hydrated ferric oxide $2Fe_2O_3.3H_2O$ *v.* Iron.

LINNALITE or **LINNÆITE.** Native cobalt sulphide.

LINSEED. The seed of *Linum usitatissimum*, or common flax-plant. The substance of the seed is contained within four outer membranes, of which the *first* is composed of a layer of large hexagonal colourless and lustrous cells, containing the mucilage which is derived from the seed by infusion. The *second* membrane consists of rounded cells inclosed in thick *parietes*, and containing granular matter. The *third* layer consists of narrow fibres, longitudinal and transverse, firmly constructed. The *fourth* coating is of angular cells inclosing a coloured resinous matter easily separated from the inclosing walls. The *interior* of the seed contains cells filled with starch and the characteristic oil. The oil itself may be seen through the microscope in the form of shining spherules.

Its value consists in the oil which is pressed from it, and in the use of the seed or of the residue after pressing (called linseed cake or oil-cake) for the purpose of cattle-feeding.

The mean of the ash of thirty-one samples obtained from Russia, France, India, Chili, Algeria, Danubian Principalities, Roumelia, and European Turkey, showed a percentage composition of: potash 8·45; chlorine 0·43; sulphuric acid 4·45; phosphoric acid 4·60; soda and carbonic acid 3·76 (=24·10 soluble in water); lime 7·30; magnesia 18·00; phosphoric acid 27·00; sulphuric and carbonic acids 23·43 (=71·00 soluble in dilute nitric acid); silica and insoluble matter 4·80.

LINSEED GUM *v.* Gum.

LINSEED OIL *v.* Oils.

LIPPIA MEXICANA. An evergreen creeping shrub growing in Mexico, of which the leaves and flowers contain a volatile oil, lippiol, a body resembling camphor, and a substance allied to quercitin.

LIQUATION. 'When an ore or metallic mixture containing ingredients differing sensibly in fusibility is exposed to a degree of heat sufficient only to melt the most fusible which may flow away from the unmelted mass, this process is termed liquation' (Percy's Metallurgy). In certain cases a mixture of two metals can be roughly separated in this way. For instance, if an alloy of lead and copper be heated to a temperature a little above the melting-point of lead, the lead trickles out, leaving a porous mass behind. The lead contains 2 p.c. to 3 p.c. of copper. The copper contains 25 p.c. of lead. This process is used commercially to separate antimony sulphide from the ore, by heating in earthenware pots with a hole in the bottom, through which the melted sulphide flows.

At the Schemnitz silver works impure lead is purified by melting it on the bed of a furnace, the lower end of which is connected with a large iron pot, heated independently, and into which the lead trickles. Fresh lead is thrown into the furnace from time to time; the melted lead flows into the pot and leaves less fusible alloys behind. The lead in the pot is then made hot, skimmed and poled. The purification of a metal by this means depends upon the formation of less fusible alloys between the metal and the foreign metals present. Pattinson's process (*v.* Lead) for desilverising lead depends on the formation of such alloys, but in that case the solidified alloys are fished out of the melted lead by a ladle, instead of allowing the lead to flow away from them.

LIQUEUR DE FERRAILLE. *Ferric acetate v.* Acetic acid.

LIQUID STORAX *v.* Balsams.

LIQUORICE ROOT. *Radix Glycyrrhizæ.* (*Réglisse*, Fr.; *Süssholzwurzel*, Ger.) The root of the underground stems of the *Glycyrrhiza glabra* (Linn.), a plant inhabiting the south of Europe and Central Asia (*cf.* Bentl. a. T. 74). Liquorice, or its solid aqueous extract, the 'Spanish juice' of commerce, has long been a favourite demulcent in throat affections, and is used as a laxative. It finds also a considerable employment in porter-brewing.

The root was examined chemically by Pfaff (Syst. Mat. Med. 1, 187), Robiquet in 1809 (A. Ch. 72, 143) also by Trommsdorff (Taschenbuch, 1827, 1) and others (*cf.* Gm. 17, 56). It was found to contain *glycyrrhizin* or *liquorice sugar*, the most important constituent, together with an *acrid oil*, *asparagin*, *malic acid*, *starch*, traces of *tannin*, and other subtances common to plants. Glycyrrhizin was further studied by Vogel (J. pr. 28, 1), Lade (A. 59, 224), and Gorup-Besanez (A. 118, 236), who regard it as a glucoside, giving, when treated with dilute acids, sugar and *glycyrretin*. *Cf.* Martin (J. 1860, 551) and Hirsh (Proc. Am. Pharm. Assoc. 1870, 133).

The more recent inquiries of Roussin (J. Ph. 12, 6), Habermann (B. 10, 870; A. 197, 105), and Sestini (G. 8, 454), show that glycyrrhizin is a tribasic acid which exists in liquorice root in combination with ammonium or calcium. In accordance with this view it is called *glycyrrhizic acid.* Habermann assigns to it the formula $H_3C_{44}H_{60}NO_{18}$, and describes numerous acid and neutral salts. The salts, which are soluble like the free acid, impart a marked sweet taste, To obtain the acid the insoluble lead salt is decomposed by sulphuretted hydrogen. The dry product resembles albumen in appearance. It gelatinises with cold water, but dissolves in hot water or boiling glacial acetic acid. It reduces Fehling's solution.

Subsequently Habermann (J. 1880, 1029) studied the decomposition of glycyrrhizic acid in presence of dilute acids (*cf.* Griessmeyer, D. P. J. 209, 228). Glycyrrhetin was obtained as a crystalline nitrogenous compound, having the formula $C_{32}H_{47}NO_4$, melting at 200° and giving reactions with bromine, nitric acid, and acetyl chloride. On fusing glycyrrhetin with potash, contrary to the statement of Weselsky and Benedict (B. 9, 1158), no paraoxybenzoic acid was obtained. In the breaking up of glycyrrhizic acid no sugar is formed, but instead an isomeric saccharic acid, *parasaccharic acid* $C_6H_{10}O_8$. This is a brown gum soluble in water and alcohol, and possessing the power of reducing Fehling's solution. The salts of parasaccharic acid, unlike the corresponding salts of saccharic acid, do not crystallise.

From the mother liquor in the preparation of acid ammonium glycyrrhizate, Habermann isolated an amorphous bitter compound, *glycyramarin.* The same observer separated from the root a *resin* soluble in glacial acetic acid, which, when fused with caustic potash, yields various volatile fatty acids together with paraoxybenzoic acid. A. S.

LITHARGE *v.* Lead.

LITHIA MICA *v.* Lithium.

LITHIUM. Li. At. w. 7·01 (Hagen, Mallet, Troost, Diehl, Stas). This metal occurs in combination with silica, alumina, and the alkali metals in *lepidolite* or *lithia mica*, *petalite* (containing phosphates of lithium, iron, and manganese), *spodumene*, *triphylene*, and *amblygonite*, usually to the extent of 3 to 6 p.c.

Lithium is widely distributed. It occurs as chloride in most spring water and in sea water. A mineral spring at Wheal Clifford, near Redruth, contains 26 grains per gallon (Miller, Brit. Assoc. Trans. 1864, 35); Phillips has found 34 grains per gallon in a salt spring in Huel Seton copper mines in Cornwall. It is found in most plants, especially in the leaves. The ash of tobacco has been found to contain 0·44 p.c. of lithium chloride (Fruehot, C. R. 78, 1022). The presence of lithium in excess appears to be generally injurious to plants.

Lithium was first isolated by Brandes, but first prepared in quantity by Bunsen (P. 94, 107). Pure lithium chloride is first fused, and decomposed by the current from a battery of 4 to 6 Grove's cells, using a small positive pole of gas carbon and a negative pole of iron wire. In two or three minutes the wire may be withdrawn, and the regulus of lithium, the size of a small pea, removed by a spatula, beneath rock oil. In this way an ounce of the metal may soon be reduced. The metal cannot be reduced by ignition of the carbonate with carbon, or of the hydrate with iron.

Properties.—Lithium is a silver-white metal which tarnishes and oxidises less rapidly than potassium or sodium. It is softer than lead, but less tenacious. Its sp.gr. is 0·589 to 0·598 (Bunsen), lower than that of any known solid or liquid. It melts at 180°C. (Bunsen), and volatilises at a bright red heat in a current of hydrogen. At a temperature somewhat above its melting-point it burns with an intense white light. When heated, it burns in chlorine, bromine, iodine, and sulphur vapour, and in carbon dioxide. In water it oxidises, but does not fuse.

By nitric acid it is rapidly oxidised, often with fusion and ignition. In dilute sulphuric acid and in hydrochloric acid it dissolves quickly; solution is slow in strong sulphuric acid. At a temperature below 200°C. it attacks silica, glass, and porcelain. Like other alkaline metals it dissolves with formation of a blue solution in liquefied ammonia gas.

Detection.—Lithium salts produce a fine crimson colour in the blowpipe flame. They are usually colourless, and when in strong solution give a precipitate on addition of carbonates or sodium phosphate, in presence of ammonia.

Estimation.—The estimation usually entails the separation from potassium and sodium. For this separation Mayer's process is most satisfactory (A. 98, 193). The solution containing the alkalis as chlorides is treated with sodium phosphate (*absolutely* free from alkaline earth phosphates), and sufficient sodium hydrate to keep the solution alkaline, and evaporated to dryness. Sufficient water is added to dissolve the soluble salts, the solution heated gently and filtered after 12 hours. The precipitate is washed with a mixture of 1 part of water and 1 part of ammonia (of which liquid 3,920 parts dissolve only 1 part of lithium phosphate); the filtrate and first two washings are evaporated and taken up as before, any residue of lithium phosphate being added to the bulk of precipitate. The precipitate, dried at 100°C., has the composition Li_3PO_4.

Extraction of salts.—Finely powdered lepidolite or petalite 10 parts, is mixed with barium carbonate 10, barium sulphate 5, potassium sulphate 3, and ignited at the highest temperature of a wind furnace. Two layers are thus produced, the lower of barium silicate and sulphate, the upper of white suphate of potassium and lithium. It is lixiviated with water and treated with barium chloride to convert the alkalis into chlorides and precipitate the sulphuric acid as barium sulphate. The solution is evaporated to dryness and digested with a mixture of equal parts of absolute alcohol and ether, in which the lithium chloride dissolves with only a trace of potassium and sodium chloride (Troost, C. R. 43, 921).

According to Müller (A. 85, 251), *triphylene* is dissolved in hydrochloric acid, the iron oxidised to ferric chloride by the addition of nitric acid, the phosphoric acid precipitated by a persalt of iron, the mixture evaporated to dryness, and extracted with water. Manganous and lithium chlorides are thus dissolved; the former is precipitated with barium sulphide, the excess of barium being removed by the addition of ammonium carbonate or sulphuric acid. The solution is evaporated with oxalic acid and the residual oxalate ignited to carbonate.

At Schering's laboratory in Berlin the following method is adopted. The finely-ground and sifted lepidolite is made into a thin paste with concentrated sulphuric acid, in a warm brick trough, and digested and stirred until it commences to agglomerate. It is then calcined in a reverberatory furnace, and, while warm, well lixiviated with water and filtered. The lye is mixed with sufficient potassium sulphate to convert all the alumina into alum, and the solution decanted from the alum meal. The remaining alumina is precipitated by milk of lime, the alkalis are converted into chlorides by addition of barium chloride, and the solution evaporated to dryness. The chlorides of lithium and calcium are extracted with absolute alcohol, the alcohol evaporated, and the calcium precipitated by ammonium oxalate, and any heavy metals removed by a little ammonium sulphide. The solution is evaporated to dryness in a silver basin (*v.* A. W. Hofmann, D. P. J. 219, 183, and Felsinger, D. P. J. 222, 385).

Lithium oxide Li_2O may be prepared by ignition of the metal in air or oxygen; in solution, by precipitation of the sulphate with barium hydrate solution. It is yellowish white and spongy, less soluble than the oxides of potassium and sodium. It melts below redness, and, as it corrodes platinum powerfully, should be fused in a silver vessel. The hydrated oxide may be obtained in small crystalline grains.

Lithium chloride LiCl may be prepared by combination of lithium and chlorine, or by dissolving the carbonate or oxide in hydrochloric acid. When formed at low temperatures the crystals contain two molecules of water; at temperatures above 15°C. anhydrous octahedral crystals are produced. It dissolves in absolute alcohol and in a mixture of alcohol and ether. At 0°C. 100 parts of water dissolve 63·7 parts, and at 100°C. 145 parts of the chloride.

Lithium chloride is more volatile than potassium chloride; less so than sodium chloride. Below a red heat it volatilises, losing a little hydrochloric acid and producing an equivalent amount of lithium oxide.

Lithium sulphate Li_2SO_4 is prepared by dissolving the carbonate or oxide in sulphuric acid. It forms monoclinic plates, soluble in alcohol and water. It produces a double sulphate with potassium sulphate, but does not form an acid sulphate or an alum.

Lithium carbonate Li_2CO_3 is prepared by the addition of a hot concentrated solution of lithium chloride to an ammoniacal solution of ammonium carbonate. It is a white powder, more fusible than the potassium and sodium salts. Its solubility in cold is greater than in hot water. The solubilities given by different observers are not concordant. According to Bevade (Bl. 43, 123), the solubility in 100 parts of water is as follows:—

Temperature	0°	10°	20°	50°	75°	100°
Parts . . .	1·539	1·406	1·329	1·181	0·866	0·728

The solubility increases after continued boiling. *V.* further Draper (C. N. 55, 169) and Flückiger (Ar. Ph. [3] 25, 509).

The commercial salt usually contains about 98·5 p.c. of lithium carbonate. Lithium forms a very soluble *urate*; for this reason the carbonate and citrate are administered to remove uric acid from the blood in gouty affections.

Lithium citrate $Li_3C_6H_5O_7$ is prepared by the addition of 100 parts of lithium carbonate to a solution of 186·5 parts of citric acid (Umney, Year-book of Pharmacy, 1875, 559). It may be produced as a white, anhydrous, neutral, *non-deliquescent* powder, or in crystals containing 4 molecules of water. It is soluble in 25 parts of cold water. The commercial salt usually contains salts of potassium, sodium, and calcium, and frequently lithium carbonate or citric acid, and powdered lepidolite or petalite (C. Thompson, Ph. [3] 13, 783).

LITHOFRACTEUR *v.* EXPLOSIVES.

LITHOMARGE. (*Steinmark*, Ger.). An amorphous substance, resembling clay in composition and in most of its physical properties, but usually having a hardness of 2 to 2·5. It occurs on a large scale in the doleritic series of Antrim, where it is associated with bole, bauxite, and aluminous iron ore. Some of the Irish lithomarge is of lavender colour, with white specks of bauxite, while other varieties are brown or blackish. The substance is known to the workmen as 'marge.' It may have resulted from the alteration of the dolerite, and appears to resemble some of the steatitic laterites of India. Where peaty water comes in contact with the lithomarge, it occasionally deposits manganese oxide in considerable quantity (*v.* P. Argall, Journ. Geol. Soc. Ireland, 16, 1886, 102; G. H. Kinahan, *ibid.* 307). Lithomarge occurs in several Cornish mines; a fine yellowish variety, with purple veins, being found at Cook's Kitchen, near Redruth. Closely allied to lithomarge is the *teratolite* of Saxony, formerly reputed to possess such powerful medicinal qualities that it was described by old writers as *terra miraculosa Saxoniæ*. F. W. R.

LITMUS. *Tournesol en pain.* This colouring matter is well known to the chemist, since white paper impregnated with its solution in a slightly acid or alkaline condition has long been employed, under the name of red and blue litmus-paper, to indicate the presence, in any solution, of alkalis or acids respectively. Alkalis change the colour of red litmus-paper to blue, acids turn blue litmus-paper red. In alkalimetry litmus tincture has, till recently, been the most generally adopted indicator. This use depends upon the fact that the free colouring matter of litmus is red, whereas its alkali salts are blue.

Commercial litmus has the form of small pale blue cubes, composed essentially of gypsum and chalk mixed with but comparatively little colouring matter, which is largely present in the form of a lake.

It is said to be prepared, chiefly in Holland, from various species of lichens, *e.g. Lecanora tartarea*, *Roccella tinctoria*, &c., the same indeed which are used in the manufacture of orchil (*q.v.*). Under the combined influence of ammonia and atmospheric oxygen the proximate principles contained in these lichens yield *orceïn*, the alkali salts of which are purple (orchil); but if potassium or sodium carbonate is present at the same time, the principles are modified in a different manner, and ultimately yield *azolitmin* (the colouring matter of litmus), the alkali salts of which are blue.

According to Gélis (J. Ph. 24, 277; Revue Scient. 6, 50) litmus may be prepared as follows. Orchil-weed is ground and mixed with half its weight of potassium carbonate, and then repeatedly moistened with urine saturated with ammonium carbonate or with an aqueous solution of this salt; the mass soon acquires a brownish-red colour (3 days), which gradually becomes purple (20–25 days), and finally blue (30 days), yielding a litmus of the best quality in 40 days. The pulpy mass is mixed with chalk and gypsum, then moulded in the form of cubes, and dried in the shade.

By modifying the action of air and ammonia upon orcinol, through the addition of sodium carbonate, De Luynes also succeeded in obtaining the colouring matter of litmus (C.R. 59, 49; D. P. J. 174, 61; C. C. 1865, 127; J. 1864, 551). A mixture of 1 part orcinol, 25 parts cryst. sodium carbonate, 5 parts water, and 5 parts ammonia solution, was heated to 60°–80°C. for 4–5 days with frequent agitation. On diluting the blue solution thus obtained and acidifying slightly with hydrochloric acid, the colouring matter was precipitated. On washing and drying, it assumed a metallic lustre. It is sparingly soluble in water, but readily soluble in alcohol and in ether.

In making a litmus solution to be employed as indicator, the commercial litmus is extracted with boiling water, the filtered solution is slightly acidified with acetic acid, then carefully neutralised with ammonia, and boiled to expel any excess of the latter. Kept for any lengthened period in stoppered bottles, the solution becomes decolourised in consequence of a reductive fermentation; on exposure to air, however, the original colour is restored. This defect is prevented by saturating the solution with sodium chloride (Reichelt). A dry litmus-extract may be prepared according to Vogel in the following manner (J. Ph. 45, 64, 70; C. N.

1864, 205). Twenty grams powdered commercial litmus are twice digested, each time with 150 c.c. cold distilled water. The second solution, which is alone employed, is divided into two equal portions, one of which is slightly acidified with nitric acid and then mixed with the other. The purplish solution thus obtained is evaporated to dryness on the water-bath, and the granular amorphous mass is kept in a stoppered bottle ready for dissolving in water when required.

For the characteristics of litmus as an indicator compared with methyl-orange and phenol-phthaleïn *v.* R. T. Thomson (S. C. I. 6, 198); also Vol. 1, Acidimetry, 19.

Litmus exhibits a characteristic absorption spectrum. Ether extracts it from an acid solution, and forms a yellow liquid, which absorbs the more refrangible end of the spectrum to a point midway between D and E. If the solution is coloured blue by adding a drop of ammonia, an absorption-band is formed, commencing at *d*, where it is extremely black, and gradually diminishing to E. A blue aqueous commercial solution shows a well-marked absorption-band at D. Addition of acid changes the colour to red, the band at D disappears, and the spectrum now resembles that of œnolin, the colouring matter of red wine (A. H. Allen, Com. Org. Analysis, 325).

Our knowledge of the chemistry of the colouring matters contained in litmus is very meagre. Gélis (J. Ph. 27, 477) extracted from it several colouring matters in the following manner. After extracting commercial litmus with water, the insoluble residue is boiled with dilute caustic alkali and the filtered solution is precipitated with basic lead acetate. The blue precipitate is washed by decantation until it begins to dissolve and colour the wash-water. It is then decomposed with hydrogen sulphide, exposed to air till free from excess of H_2S, collected on a filter and digested with dilute ammonia to extract the colouring matter. On adding acid to the filtered solution the main portion of the litmus colouring matters is thrown down as a red flocculent precipitate. The filtrate from this contains a very small quantity of colouring matter (α).

On extracting the dried red precipitate with ether and leaving the orange solution to spontaneous evaporation, it yields a bright-red residue (β) containing crystalline needles. This product is insoluble in water, but readily soluble in alcohol, also in alkalis with a violet colour. The portion insoluble in ether is dissolved in alcohol, and on allowing the blood-red solution to evaporate spontaneously it yields a large quantity of a reddish-purple product (γ) having a bronze lustre. This represents the colouring matter most abundant in litmus.

The residue, which is insoluble in water, in alcohol, and in ether, contains another product (δ) which is soluble in alkalis, from which it may be precipitated by acids. The three products β, γ, and δ, appear to contain nitrogen.

A more detailed examination of litmus was made in 1840 by Kane (Tr. 1840, 298; A. Ch. [3] 2, 129; A. 39, 57; Ph. 1841, 569) who isolated from it the chief and characteristic colouring matters *azolitmin* and *erythrolitmin*, together with *erythroleïn* and *spaniolitmin*.

According to Kane, finely powdered commercial litmus is extracted with boiling water. Most of the colouring matter remains in the form of an insoluble lake in the residue, to which hydrochloric acid is added till effervescence ceases and the mixture is strongly acid. The insoluble matter mixed up with liberated colouring-matter is collected on a filter, washed free from acid, dried, and extracted with boiling alcohol. The alcoholic solution is filtered from an insoluble reddish-brown mass (impure azolitmin) and then evaporated to dryness, and the residue is digested with warm ether until it becomes no longer coloured. On distilling the filtered ethereal solution, *erythroleïn* is left as a purple semi-fluid oily substance. That portion of the alcoholic extract which is insoluble in ether consists of *erythrolitmin*.

The above-mentioned impure azolitmin is purified, either by dissolving it in a large quantity of boiling water and evaporating the solution to dryness, or by dissolving it in very dilute ammonia, evaporating the solution to dryness, neutralising any residual ammonia by dilute hydrochloric acid, and washing with alcohol till free from ammonium chloride and excess of hydrochloric acid. The residue represents purified *azolitmin*.

The colouring matter contained in the deeply coloured solution obtained in the first instance by boiling the commercial litmus with water and filtering, is isolated as follows. The solution is precipitated with neutral lead acetate, the purple precipitate thus obtained is well washed, suspended in water, and decomposed with hydrogen sulphide. The mixture of lead sulphide and liberated colouring matter thus obtained is well washed and digested with warm dilute ammonia; the filtered deep-blue solution is evaporated to dryness, the residue is moistened with hydrochloric acid, washed free from ammonium chloride and any excess of hydrochloric acid, with warm alcohol. The residual deep brownish-red powder consists usually of nearly pure azolitmin, more rarely of *spaniolitmin*, a substance very similar to azolitmin, but which does not contain nitrogen.

Since spaniolitmin occurs so rarely in litmus, and erythroleïn is coloured reddish-purple and not blue by alkalis, Kane considers azolitmin and erythrolitmin to be the essential colouring matters of litmus, in which they are combined with ammonia, potash, and lime, and mixed with a considerable quantity of chalk, gypsum, &c.

Azolitmin is a deep brownish-red amorphous powder, insoluble in alcohol and sparingly soluble in water, but readily soluble in alkaline solutions with a pure blue colour. Its ammoniacal solution gives with metallic salt solutions blue or purple precipitates according as they are more or less basic in character. Kane's formula for it is $C_9H_{10}NO_5$, but Gerhardt considers it is best represented by $C_7H_7NO_4$. It differs from all the other colouring matters isolated from litmus by containing nitrogen. It may be considered to be derived from orcinol, possibly in accordance with the following equation:

$$C_7H_8O_2 + NH_3 + O_3 = C_7H_7NO_4 + H_2O$$

or from orceïn thus $C_7H_7NO_3 + O = C_7H_7NO_4$.

If these formulæ and equations are correct, the explanation of the part played by the necessary alkaline carbonate in the manufacture of litmus may be that it facilitates and increases the oxidation of the orcinol, so that any orceïn at first formed is changed into azolitmin (Gerhardt, Ch. Org. 3, 816).

Erythrolitmin, which from its composition and the large quantity existing in litmus, also constitutes one of the most important ingredients, is a bright-red powder, sparingly soluble in water and in ether. It is abundantly soluble in alcohol, from which it may be crystallised in the form of dark-red granular crystals. In strong caustic potash it dissolves with a blue colour. With ammonia it forms a blue compound which curiously enough is totally insoluble in water. With metallic salts it forms lakes of a fine purple colour. According to Kane its formula is $C_{13}H_{22}O_6$, and he considers it to be an oxidation product of his erythroleïc acid ($C_{13}H_{22}O_4$) obtained from orchil.

Erythroleïn forms a crimson semi-fluid mass. almost insoluble in water, soluble in ether and in alcohol with a red colour, and in ammonia with a purple colour. With metallic salts it gives purple lakes. Kane gives its formula as $C_{13}H_{22}O_7$. Its general properties are very similar to those of the above-mentioned erythroleïc acid.

Spaniolitmin occurs but rarely in litmus, hence its name. It is a bright-red substance, insoluble in alcohol and in ether, and very sparingly soluble in water. It dissolves in alkalis with a blue colour and gives lakes very similar to those of azolitmin. Kane's formula for it is $C_9H_7O_8$.

Under the influence of hydrogen sulphide the colouring matters of litmus are decolourised, Kane's idea being, that a colourless hydrogen sulphide is thus formed. (*V.* also Malaguti, A. Ch. [3] 37, 206; Vogel, J. pr. 16, 311; Kuhlmann, A. Ch. 54, 291). Nascent hydrogen, and such other reducing agents as ferrous and stannous oxide, &c., decolourise them by reduction in the ordinary manner. Azolitmin thus yields colourless *leucazolitmin*, which, however, rapidly oxidises and becomes coloured on exposure to air. If stannous chloride is added to an ammoniacal solution of azolitmin, purple-coloured stannous-azolitmin is precipitated; if this is boiled with slightly acidulated water there is formed the colourless compound of stannic oxide with leucazolitmin, which, if exposed to air, changes into the bright scarlet stannic-azolitmin.

Deoxidising agents such as sulphurous acid and sulphites do not decolourise the colouring matters of litmus.

Azolitmin and erythrolitmin, suspended in water and submitted to the action of chlorine gas, are decolourised and give yellow chlorine derivatives, *chlorazolitmin* and *chlorerythrolitmin*, substances insoluble in water, but soluble in alcohol, ether, and in alkalis.

In his earliest memoir Kane (A. 36, 324) mentions that on heating the colouring matters of litmus mixed with chalk or gypsum, a red vapour is given off which condenses in the form of crystalline scales (atmérythrin) soluble in alcohol. When heated alone this substance is not produced. Although Kane makes no subsequent mention of this body it is possible that it was indirubin or even indigotin, since at a later date Wartha (B. 9, 217) states that he found some samples of litmus to contain indigotin, recognisable by the violet vapour given off on heating a few cubes of the commercial product in a test tube. Its presence may have been due to the use of urine containing indican in the preparation of the litmus.

Wartha (*l.c.*) gives the following results of his examination of litmus. The commercial product is well shaken up with alcohol; the filtered purple solution thus obtained has a green fluorescence, and exhibits in the spectroscope a characteristic absorption band in the green with an almost total absorption of the violet end. The colouring matter (*a*) itself is obtained on evaporating the solution.

The litmus residue insoluble in alcohol is digested for twenty-four hours with distilled water, and the filtered deep-coloured solution is evaporated to dryness. The extract thus obtained is repeatedly treated with absolute alcohol containing a little glacial acetic acid and again evaporated, so that all traces of water may be removed, and there finally remains a brown powdery mass. On extracting this with absolute alcohol a large quantity of a scarlet-red substance (*b*) is dissolved. It is similar to orceïn and dissolves in ammonia with a reddish-purple colour. That portion of the brown powder which is insoluble in the acidified alcohol is dissolved in water, the filtered solution is evaporated to dryness, and the residue is repeatedly washed with absolute alcohol and evaporated in order to expel all traces of acetic acid. The residual brown powder, which is very soluble in water, with a reddish-brown colour, but insoluble in alcohol and in ether, is the purified and extremely sensitive colouring matter of litmus (*c*). Its alkaline solution is blue, its aluminium and tin lakes are violet, and its calcium and barium lakes blue. It appears to be very similar to Kane's azolitmin, but it is said not to contain nitrogen. The yield of these various colouring matters is as follows: (*a*) 2·3 p.c., (*b*) 3·4 p.c., (*c*) 5·7 p.c. (Mitchell, C. N. 1876, 140).

The most recent examination of the colouring matters of litmus has been made by Rochleder and Skraup (Wien. Anz. 1874, 118; C. C. 1874, 424).

Other references are Magner, J. Ph. 12, 418; Desfosses, *id.* 14, 487; Peretti, *id.* 14, 539.

A peculiar blue colouring matter similar to litmus, and called *tournesol en drapeaux* has long been manufactured at Grand-Gallargues, Département du Gard, France, from the *Croton tinctorium* belonging to the Euphorbiaceæ. Coarse linen cloth is steeped in the deep bluish-green sap expressed from the berries and the tops of the plant, then dried quickly in the open air, and exposed for 1-1½ hours between layers of straw to the ammoniacal vapours of lant or horse-dung (*aluminadon*), care being taken not to submit them to this influence too long. The cloth thus acquires a deep-blue colour. It is then steeped in the sap a second time and dried in air till it acquires a purple or dull green. These blue cloths are used by the Dutch farmers for making an infusion with which to impart a red colour to the outside of their cheese, the blue being changed to red by the lactic and butyric acids of the cheese.

According to Joly (A. Ch. [3] 6, 111) the colouring matter pervades the entire plant and is readily extracted therefrom by water heated to 50–60°. On being evaporated an azure-blue resinous mass remains. Acids change the blue colour of its aqueous solution red, and this blue is not restored by alkalis, the colour becoming thereby rather greenish. It is, therefore, probably quite distinct from the colouring matter of litmus. Possibly it is identical with the blue colouring matter which can be extracted from another plant belonging to the Euphorbiaceæ, viz. *Mercurialis perennis*. J. J. H.

LIVER OF SULPHUR. *Hepar sulphuri; potassa sulphurata.* This compound consists of a mixture of salts of potassium, chiefly the higher sulphide, and is prepared by fusing in a Hessian crucible a quantity of potassium carbonate with half its weight of flowers of sulphur. The fused mass is poured out on a greased flagstone and allowed to solidify, assuming a liver-brown colour; hence its name. It is alkaline, and acrid to the taste, and when quite dry is inodorous; but when moist it acquires the odour of sulphuretted hydrogen.

It has many applications in medicine, *e.g.* it is given internally in cases of lepra and psoriasis; while externally it is used in the form of lotions, baths; as ointment in chronic skin-diseases, such as eczema, scabies, and pityriasis.

LIXIVIATION. Lixiviation is the application of a liquid, generally water, to solid bodies for the purpose of extracting the soluble part. For instance, the preparation of pearl-ash by dissolving out the potassium carbonate from the wood ashes, and the preparation of sodium nitrate from the crude nitrate, of beet sugar by Schützenbach's process, of alum from effloresced alum schist, of tartaric acid from wine lees, are all applications of water to extract the soluble part.

In carrying out this process on a commercial scale three things are sought to be attained: First, that the residue should be completely exhausted of soluble matter; second, that the solution obtained should be nearly saturated; and, thirdly, that the process should be continuous. A series of tanks is therefore provided, standing at the same level, and provided with false bottoms covered with a filtering bed, and with connecting tubes, pumps, and so on. Each of these tanks contains the substance to be lixiviated, and the water travels from tank to tank, increasing in saturation.

The process is so arranged that at any given moment a nearly saturated liquor is passing over a *fresh* supply of the substance, while clean water is running through the nearly exhausted residue. When the residue in any tank is completely exhausted it is removed, fresh stuff put in, and that tank made the last of the series. In some cases a pump is necessary between each tank to pump the liquid from beneath the false bottom into the next tank.

If the solution formed is of high specific gravity so much pumping is not necessary. One detailed description will suffice. In the preparation of soda by the Leblanc process, the black ash (roughly speaking, soluble sodium carbonate and insoluble calcium sulphide) is lixiviated. For this purpose, four or more iron tanks are used, built side by side, each about 10 feet × 10 feet × 6 feet. Each tank has a false bottom of perforated iron plates, and a large cock in the bottom, by which all the liquor it contains can be run off. It has also an overflow pipe, rising from below the false bottom and communicating with the next tank, and a second overflow pipe which communicates with a trough outside. The first tank is connected with the last by a pipe. Any of these pipes can be closed by plugs or cocks. Suppose the process to be in full working order. Fresh black ash, broken in large lumps, has been placed in tank 4, on a bed of cinders laid over the false bottom. Tanks 3 and 2 contain partially exhausted black ash, and tank 1 completely exhausted black ash (tank waste).

The overflow pipe between 3 and 4 is opened, and a pump connected to 1, which pumps the liquor over into 2. It flows from 2 to 3, from 3 to 4, until 4 is full. Tank 1 is now cut off, emptied, cleaned, and a fresh supply of black ash put in.

While this is going on, fresh water is flowing into 2, and sufficiently saturated liquor flowing away from 4 by the outside overflow pipe. 4 is now connected with 1. The liquor is pumped out of 2 into 3, flows from 3 to 4, from 4 to 1. When 2 is empty of liquor it is in the same way cleaned out, and a fresh charge put in, and so the lixiviation is kept continuous, strong soda solution running off at one end, and exhausted tank waste being removed at the other.

LOADSTONE. A name applied to magnetic iron ore when powerfully magnetic. It crystallises in the cubic system, and contains Fe_3O_4 with theoretically 72·4 p.c. of iron. Specimens frequently exhibit polarity, and were formerly set in steel frames and used as natural magnets. The best loadstones are found in Sweden, Siberia, and Elba; and at Magnet Cove, Arkansas, U.S. On the methods of exploring for magnetic iron-ore by means of the magnetic needle *v.* B. H. Brough, Journ. Iron and Steel Inst. 1887, 289. F. W. R.

LOBELACRIN *v.* Lobelia.

LOBELIA. *Indian tobacco.* (*Lobélie enflée* Fr.; *Lobeliakraut,* Ger.) The official lobelia, *Lobelia inflata*, was described by Linnæus in 1741 (Acta Soc. Reg. Scient. Upsal. 1746) from specimens cultivated by himself, but he does not ascribe to it any medicinal properties. It is an annual herbaceous, somewhat pubescent plant, attaining a height of from 9 to 18 inches, with inconspicuous bluish racemose inflorescence. It is indigenous to the eastern portions of North America, and is cultivated in European gardens (Fl. a. H. 399; Bentl. a. T. 162). According to J. U. and C. G. Lloyd (Ph. [3] 17, 566), the first to employ lobelia in medicine was Thomson, an American herbalist of some notoriety about the end of the last century. The Indians, although they made use of the great lobelia, *L. syphilitica* (Linn.), were not acquainted with the *L. inflata*, as has been commonly supposed and as one of its names would imply. Gradually the drug has come into favour as an article of materia medica, and it now finds a place in the pharmacopœias. The herb should be gathered when, after flowering, some of the capsules have become inflated In physiological action lobelia resembles tobacco.

It is an acrid, narcotic poison, but in small doses is expectorant or emetic, and is largely employed in diseases of the respiratory organs. The seed is more active than the herb, but the latter is almost exclusively employed in medicine. It is generally administered in the form of tincture, made with proof spirit or a mixture of alcohol and ether.

Much uncertainty still exists as to the active constituents of lobelia. Colhoun investigated the plant in 1834 (J. Ph. [2] 20, 545), but the first definite results were obtained by Procter a few years later (Am. J. Pharm. 9, 98; 13, 1). The seed was exhausted with spirit containing a little acetic acid, the solution evaporated, and the residue mixed with magnesia and extracted with ether. On evaporating the ether an acrid alkaloidal liquid, *lobeline*, remained, which, by conversion into acetate and treatment with animal charcoal, was obtained in a purer form. Lobelia was further studied by Pereira (Mat. Med. 2nd ed. 2, 584), Reinsch (Ph. [1] 3, 128), Bastick (Ph. [1] 10, 217), F. F. Mayer (Am. J. Pharm. 37, 209), Richardson (Am. J. Pharm. [4] 2, 293), and, more recently, by Lewis (Ph. [3] 8, 561), Dragendorff and Rosen (C. C. 1886, 873), J. U. and C. G. Lloyd (Ph. [3] 17, 566, 686, a. 1037; 18, 135), and Dresser (Arch. exp. Path. u. Pharm. 26, 237). To obtain lobeline Bastick only slightly modifies the process of Procter; Richardson precipitates an infusion of the drug with potassio-mercuric iodide; Lewis mixes the drug with animal charcoal, extracts with water containing acetic acid, and substitutes, at the end of the process, amylic alcohol for the ether used by Procter. The lobeline of Lewis is of the consistence of honey. Dragendorff and Rosen obtain two active compounds, lobeline and a crystalline substance soluble in chloroform, but difficultly soluble in water. J. U. and C. G. Lloyd also find associated with lobeline—which, however, they describe as an amorphous solid—a second compound *inflatin*, which is crystalline. Taking care to avoid heat, and the contact of free alkaloid with alkalis, these observers follow a process similar to that of Procter. Ether and ammonia are used to separate the alkaloid from its combination, instead of ether and magnesia. The crude product is purified by successive conversion into a salt in aqueous solution, and treatment with ether and ammonia. Finally, the ether is acidified and evaporated, leaving a residue partly amorphous and partly crystalline. From this residue carbon disulphide separates the crystalline portion, inflatin, leaving amorphous lobeline acetate undissolved. The latter, on standing, loses a little adhering volatile oil, and is purified by the method already described (*cf.* M. 11, 131).

Lobeline, according to J. U. and C. G. Lloyd, is an amorphous powder or glassy residue, without colour or odour, and extremely active, a very small quantity of its solution applied to the tongue causing immediate vomiting. It is soluble in alcohol, chloroform, ether, benzene, carbon disulphide, and slightly soluble in water. In a pure state it is very stable. Oxidised by permanganate it yields benzoic acid (Paschkis a. Smita, M. 11, 131). Salts of lobeline are soluble in water and alcohol, but, excepting the acetate, not in carbon disulphide. The aqueous solution is precipitated by alkalis and alkaloidal reagents. According to the recent experiments of Dresser, the only active constituent in lobelia is lobeline. Inflatin, which may also be prepared direct from the herb or seeds, is odourless and tasteless. It possesses neither acid nor basic properties. It melts at 107°, is insoluble in water, but soluble in carbon disulphide, benzene, chloroform, ether, and alcohol.

Lobeline occurs in the plant, according to most observers, in combination with *lobelic acid*, a compound first obtained by Procter. It is precipitated from an aqueous decoction of lobelia by cupric sulphate, and separated from its copper compound by treatment with sulphuretted hydrogen and extraction with ether. When purified, it consists, according to Lewis, of small acicular crystals, non-volatile, and soluble in water, alcohol, and ether. The substance described by Enders (Fl. a. H. 400), which appeared to be a glucoside, 'lobelacrin,' Lewis regards as lobeline lobelate. J. U. and C. G. Lloyd, however, consider it a mixture of several of the plant's constituents. The 'lobeliin' of Reinsch is also not a definite compound.

Lobelia contains traces of a *concrete volatile oil*, the 'lobelianin' of Pereira. It is crystalline, and melts at 71° (Procter, Reinsch, Lewis, Lloyd). Procter found in the seed 30 p.c. of a drying *fixed oil*, and this has to be removed, usually by means of a solvent, before it can be used for the preparation of alkaloid. A. S.

LOBELIANIN *v.* Lobelia.

LOBELIC ACID *v.* Lobelia.

LOBELIN *v.* Lobelia.

LOBELINE *v.* Lobelia.

LOGANETIN *v.* Nux vomica.

LOGANIN *v.* Nux vomica.

LOGWOOD. This important dyestuff is the heart-wood of *Hæmatoxylon campechianum*, a tree belonging to the natural order of the Leguminosæ, and growing abundantly in Central America and the West Indies. The bark and outer sap-wood is chipped off, since these contain little or no colouring matter, and the remaining portion comes into commerce in the form of irregularly shaped logs, hence the name 'logwood.'

It was introduced to European dyers shortly after the discovery of America, and although in the times of Queen Elizabeth and her immediate successors its use was forbidden, because, in comparison with indigo blue, its colours were not permanent, it may be reckoned at the present time as one of the most important dyewoods employed.

The chief varieties of logwood, in general order of merit, are as follows: Campeachy-wood, or Spanish-log, from Yucatan and Mexico; Honduras-wood; St. Domingo; Jamaica; Martinique; Guadaloupe.

Like most other dye-woods, logwood is employed by the dyer in three forms, viz. chipped, rasped or ground, and as an aqueous extract, either liquid or solid.

Logwood liquor and extract are invariably prepared from newly rasped wood, that is, such as has not been submitted to any preliminary treatment, since it then contains the colouring principle in its most soluble condition (hæmatoxylin).

When, however, it is employed in the chipped or rasped forms, it is submitted to a process of 'mastering,' 'maturing,' 'ageing,' or 'oxidation.' This consists in wetting the wood thoroughly with water, then forming it into large heaps, four to five feet high, in large airy chambers. Very soon the mass begins to ferment, which is indicated by a rise of its internal temperature. Care must then be taken to avoid excessive heating, *i.e.* a too vigorous fermentation, by frequently turning over the heap with wooden shovels and admitting plenty of fresh air, otherwise the colouring matter would be more or less destroyed.

With careful treatment and a suitable temperature, the moist wood acquires, at the end of three or four weeks, a dark brownish-red colour; when rubbed in the hands it gives a rich crimson stain, and, if allowed to dry, it assumes a greenish-bronze lustre. In this matured condition, containing about 30 p.c. of moisture, it is sold to the dyer, and is considered to be much stronger in colouring power than it was before the treatment.

The chemistry of this ageing process has been explained differently by various writers. Some have considered that the increase of colouring power points to the existence, in the fresh-cut wood, of a glucoside, which under the influence of the fermentation is decomposed, and yields glucose and useful colouring matter. It is thought, too, that certain accompanying tannin-matters are modified and rendered inert by the fermentation. Others have erroneously supposed that the chief purpose of the process was to soften the wood and thus to facilitate the subsequent extraction of the colouring matter in the dye-bath. Others, again, have formed the opinion—and this is most probably the true one—that the essential feature of the process is one of oxidation, whereby the primitive colouring principle (hæmatoxylin) contained in the fresh-cut wood is changed into the true colouring matter (hæmateïn). This being so, the fermentation which occurs must be regarded, not as an essential element, but merely as an accompaniment, of the ageing process, which, however, it indeed facilitates by furnishing a small amount of ammonia through the decomposition of the nitrogenous matters present in the wood. Direct addition, however, of ammonia or other alkaline agent to the water employed in moistening the ground wood, must be strictly avoided, otherwise excessive oxidation and destruction of the colouring principle rapidly ensues.

Practical dyeing experiments by the writer confirm the above view, and show that the dyeing properties of fresh-cut and aged logwood correspond to those of hæmatoxylin and hæmateïn respectively.

It is practically certain that no real increase in colouring power, due to the decomposition of a glucoside, results from the ageing process, and that the different results observed by the dyer in the use of logwood in the two conditions named must be ascribed rather to the different dyeing properties of the two principles named above.

Hæmatoxylin ($C_{16}H_{14}O_6$), the colouring principle contained in fresh-cut logwood, was first isolated by Chevreul, and named by him hæmatin; but this was afterwards given up, at the suggestion of Erdmann, in favour of the first-mentioned name, in order to avoid confusion with that given to the colouring matter of blood.

It is prepared by extracting with ether, fresh-cut logwood, or dried logwood-extract mixed with sand. After distilling off excess of the solvent, a little hot water is added to the concentrated ethereal extract, and it is allowed to evaporate spontaneously. Crystalline crusts of impure hæmatoxylin are not unfrequently found in logwood-liquor casks which have been stored for some considerable time, and it may be often observed in the form of prismatic crystals in highly concentrated syrupy logwood-extracts. Crude hæmatoxylin is readily purified by recrystallising from water containing a slight addition of sulphurous acid or acid ammonium sulphite.

From an aqueous solution, saturated at 100°C., it separates on cooling as yellow tabular rhombic crystals, containing 1 mol. H_2O; from dilute solutions it crystallises with 3 mols. H_2O in the form of colourless or pale-yellow tetragonal prisms.

Hæmatoxylin dissolves slowly and sparingly in cold water, but readily in hot water, alcohol, and ether. It has a sweet taste, reduces Fehling's liquid, and rotates a polarised ray to the right (=1·85° for 1 gram in 100 gr. solution, length of tube 200 mm.).

It exhibits the characteristics of a phenol and forms compounds with bases, which in the absence of oxygen are colourless or only slightly coloured, but in contact with air they rapidly oxidise, and thus change into the corresponding red, purple, or violet hæmateïn compounds.

Heated with ammonia in a sealed tube to 180°C., it yields an unstable nitrogenous compound, probably an amido- derivative. A concentrated aqueous solution of hæmatoxylin, containing ammonia and exposed to air, rapidly absorbs oxygen and yields a cherry-red solution of ammonia-hæmateïn, which is gradually formed as a crust or deposit. By addition of acetic acid to the oxidised solution the hæmateïn itself is thrown down as a brown precipitate. If excess of ammonia is employed the hæmatoxylin solution assumes a violet colour on oxidation, and by continued exposure further oxidation takes place, the colour changes finally to brown, and a worthless humus-like substance is then precipitated by addition of acid.

Submitted to the action of chlorine, phosphorus pentachloride, potassium chlorate, and hydrochloric acid, hydrobromic and hydriodic acids, hæmatoxylin has not hitherto yielded serviceable substitution products.

Heated with acetyl chloride, or acetic anhydride, it gives pentacetyl-hæmatoxylin

$$C_{16}H_9(C_2H_3O)_5O_6;$$

obtainable as colourless silky needles; m.p. 165–166°.

Heated with caustic potash it yields pyrogallol and formic acid. When it is submitted to dry distillation one obtains a mixture of pyrogallol and resorcinol. The product of the energetic action of nitric acid upon hæmatoxylin is oxalic acid.

By adding bromine to hæmatoxylin, both being in glacial acetic acid solution, a cherry-red solution is obtained, from which deep-red acicular crystals of dibrom-hæmatoxylin ($C_{16}H_{12}Br_2O_6$) separate.

When bromine in glacial acetic acid solution reacts upon pent-acetyl-hæmatoxylin in the cold, a mono-bromine derivative is obtained

$$(C_{16}H_8Br(C_2H_3O)_5O_6);$$

if the reaction is effected at 100° a crystalline tetra-brom-pentacetyl-hæmatoxylin

$$(C_{16}H_5Br_4(C_2H_3O)_5O_6)$$

is produced. Under the influence of alkalis the former yields brom-hæmatoxylin.

Hæmateïn ($C_{16}H_{12}O_6$) is the true colouring matter of logwood, and is derived from hæmatoxylin by oxidation according to the following equation

$$C_{16}H_{14}O_6 + O = C_{16}H_{12}O_6 + H_2O.$$

It may be obtained in small quantity (1 p.c.) by extracting aged logwood with ether, and allowing the thick ethereal extract to stand for some time.

If a few drops of concentrated nitric acid are added to an ethereal solution of hæmatoxylin the yellow solution soon becomes brownish-red, and hæmateïn is deposited in the form of minute lustrous brownish-red crystals.

Hæmateïn may be also obtained as an amorphous brownish-red precipitate by carefully oxidising an ammoniacal solution of hæmatoxylin, and precipitating with acetic acid the purple coloured solution thus obtained. If the precipitate is dissolved in dilute acetic acid, and the filtered solution is evaporated on the water-bath, the hæmateïn frequently separates in an anhydrous form as minute brownish-red rhombic plates in stellate groups, and possessing a brilliant metallic lustre. Similar crystals are also obtainable by precipitating a boiling ammoniacal solution of hæmateïn with acetic acid. Occasionally it is found possible to recrystallise this anhydrous hæmateïn by simply cooling an aqueous solution which has been concentrated at the boiling-point, but usually brownish-red amorphous hæmateïn separates.

Another method of obtaining crystalline hæmateïn is to add 1 mol. finely powdered potassium nitrite to an ice-cold solution of 1 mol. hæmatoxylin in glacial acetic acid, and allowing the mixture to stand for some time.

On cooling a hot concentrated aqueous solution of crystallised hæmateïn it congeals to a gelatinous mass, which, when evaporated under the air pump or at a low temperature, dries up in the form of amorphous scales possessing a green metallic lustre, which represent hæmateïn hydrate ($C_{16}H_{12}O_6 + 3H_2O$). When dried over sulphuric acid this hydrate loses 2 mols. water, and if heated to 130°C. it becomes anhydrous.

The hæmateïn obtained by carefully oxidising an ethereal solution of hæmatoxylin with nitric acid is, according to Reim, readily reduced to hæmatoxylin by means of sulphurous acid, and yields a colourless crystalline acetyl derivative with m.p. 216–219°, whereas the hæmateïn obtained by oxidising an ammoniacal solution of hæmatoxylin yields a similar acetyl derivative with m.p. 165–166°; further, it is, according to Erdmann and Schultz, incapable of reduction to hæmatoxylin, either by zinc and sulphuric acid, sulphurous acid, or stannous chloride and sodium hydrate. Owing to these differences, which seem, however, to require further confirmation, the former has been provisionally termed *β-Hæmateïn.*

Hæmateïn is insoluble in benzene and chloroform, and very sparingly soluble in water, alcohol, and ether. In glacial acetic acid and in concentrated hydrochloric it dissolves more readily, in the former with a deep reddish-brown, and in the latter with a bright-red colour. In an excess of caustic soda it dissolves with a bluish-violet colour, if an insufficiency of alkali is present the colour of the solution is cherry-red; these differences probably point to the existence of two hydroxyl groups in hæmateïn replaceable by metals.

With ammonia hæmateïn forms an unstable violet-black compound ($C_{16}H_{12}O_6.2NH_3$), soluble in water with a purple colour and in alcohol with a brownish-red colour.

Hæmateïn dissolves in cold concentrated sulphuric acid, forming a brown solution, which, on diluting with water, gives an orange-red precipitate of an unstable compound, which dissolves in alkalis with a reddish-purple colour. If the sulphuric acid solution is exposed to the air, so that it may attract moisture slowly, the compound crystallises out near the surface in the form of transparent orange prisms, or, if the solution is diluted with hot glacial acetic acid it is at once thrown down as an orange crystalline powder. This substance is a sulphuric acid derivative of an isomer of hæmateïn, and is named 'acid iso-hæmateïn sulphate'

$$C_{16}H_{11}O_5.HSO_4.$$

In contact with water or alcohol it loses sulphuric acid and yields, in the case of alcohol being used, a dark orange-red crystalline substance possessing a metallic lustre and having apparently the formula

$$(C_{16}H_{12}O_6)_x.C_{16}H_{11}O_5.HSO_4.$$

By heating hæmateïn in sealed tubes with hydrochloric and hydrobromic acids to 100°C. analogous chlorine and bromine derivatives are formed, viz. iso-hæmateïn-chlorhydrin

$$C_{16}H_{11}O_5.Cl$$

and iso-hæmateïn-bromhydrin $C_{16}H_{11}O_5.Br$. By treating these compounds with argentic hydrate, practically the whole of the bromine or chlorine can be removed, and there remains *iso-hæmateïn* $C_{16}H_{12}O_6$ or $(C_{16}H_{12}O_6)_3$ as an amorphous mass possessing a green metallic lustre. It differs from hæmateïn by yielding differently coloured lakes on dyeing mordanted cotton; with alumina it gives a dull brownish-red instead of the dull violet of hæmateïn. Its sodium hydrate solution is reddish-purple instead of violet-blue as in the case of hæmateïn.

The chemical constitution of hæmatoxylin and hæmateïn has not yet been determined. The researches made up to the present seem to indicate, however, that they are probably related to the phthaleïn group, that they contain the quinone oxygen group and hydroxyl groups of an alcoholic as well as of a phenolic character.

Logwood is the dyestuff *par excellence* for producing blacks on silk, wool, and cotton, chiefly in conjunction with iron and chromium mordants. It enters also into the composition of numerous compound shades. The colours thus obtained may be reckoned as only of moderate fastness to light and soap. (For notes on its application in dyeing see article Dyeing, vol. i. p. 708.)

Literature.—Chevreul, A. Ch. [2] 82, 53, 126; Leçons de chim. à la teinture, ii.; Journ. chim. méd. 6, 157; Erdmann, J. pr. 26, 193; A. 44, 292; Hesse, A. 109, 332; J. pr. 75, 219; Rammelsberg, J. 1857, 490; Reim, Ber. 4, 329; R. Meyer, B. 12, 1393; Letts, B. 12, 1652; Halberstadt and Reis, B. 14, 611; Hummel and Perkin, B. 15, 2339; J. Ch. Soc. 41, 367; Erdmann and Schultz, B. 16, 430; A. 216, 234; Buchka, B. 17, 683; Schall and Dralle, B. 23, 1433.

J. J. H.

LOKAÏN *v.* Glucosides.

LÖLINGITE. A native ferric arsenide.

LONDON WHITE. *Flake white v.* Pigments.

LUBAN MATI or **MEYETI** *v.* Oleo-resins.

LUBRICANTS. The purpose of lubricants is to reduce friction between surfaces which move one upon another. The laws of friction determined by experiments upon solids and liquids, which have been formulated as laws of 'rolling,' 'sliding,' and 'fluid' friction, are not entirely applicable to the case of lubricated bearings, because here two or more of these phenomena occur in combination, and exhibit their different methods of variation and resistance in relative degrees varying with the circumstances of the case, as to velocity, pressure, temperature, &c. Thus the friction between a well-oiled shaft and its bearing may be, in the main, 'fluid' friction under a light load, and approximate to the 'sliding friction' of solids when the pressure is increased. By itself, fluid friction varies with the square of the velocity, and is proportioned to the area of the rubbing surfaces, and is probably independent of pressure. Whilst the coefficient of sliding friction, or the ratio of frictional resistance to the total pressure holding two sliding solids in contact, varies directly as some function of the pressure, and is nearly independent of the velocity of motion and of the area of the surfaces in contact. The 'friction of quiescence' or the resistance to starting two bodies into relative motion, is greater than the 'friction of motion,' but is subject to the same laws (Thurston). This statement is limited, on the one hand, as an amount of pressure which shall depress or abrade the rubbing surfaces; and, on the other hand, at the point where pressure is so low that the resistance is principally due to the viscosity of the lubricant itself; and, between these limits, the resistance due to friction between solid *lubricated* surfaces is of a mixed nature (Thurston).

The ordinary methods of measuring friction are fully described in many mechanical and engineering handbooks, the investigations of earlier writers, and especially the extensive inquiries of Morin in 1831–34, having been supplemented by many others, and latterly, almost exclusively with the view of testing the effects of lubricants of various kinds. For the purpose of this article the results of inquiries determining the coefficients of lubricating materials are alone of importance, since frictional resistance is determined by the character of the lubricating material; and with this in view tables of Kirchweger and Thurston are here reprinted. It should, however, be borne in mind that since various conditions are at work which themselves undergo changes during friction, too much importance must not be attached to individual experiments. Nor even should the mean determination be considered as more than an approximation to a fixed truth; the fact being that several modifying considerations have to be taken into account, such as the character of the material composing the contiguous surfaces, the velocity of sliding, and the manner in which pressure is distributed, temperature, &c. Kirchweger's table, although confined to a small number of lubricants, is probably accurate as far as it goes.

Kirchweger's coefficients of friction for lubricants.

Waggon axle, cast steel; diameter of shank, 7 centimetres; length of shank, 14·5 centimetres; journal of slag-lead; supporting surface, 14·3 centimetres; number of revolutions, 180 per minute.

Lubricant	Load 2,035 kilos. = 136 kilos. per sq. centimetre		Load 3,035 kilos. = 203 kilos. per sq. centimetre		Load 4,035 kilos. = 270 kilos. per sq. centimetre		Mean of all the coefficients of a horizontal series
	Coefficients of friction						
	Largest and smallest	Mean of six experiments	Largest and smallest	Mean of six experiments	Largest and smallest	Mean of six experiments	
Colza oil . .	0·0112 0·0099	0·0103	0·0109 0·0094	0·0100	0·0093 0·0084	0·0087	0·0097
Olive oil : .	0·0109 0·0090	0·0096	0·0111 0·0106	0·0109	0·0112 0·0099	0·0105	0·0103
Tallow . . .	0·0130 0·0102	0·0115	0·0098 0·0086	0·0094	0·0105 0·0079	0·0095	0·0101
Palm oil lubricant	0·0113 0·0103	0·0107	0·0109 0·0090	0·0097	0·0101 0·0077	0·0086	0·0097

Thurston, using organic and mineral lubricants under a pressure gradually increasing from 1·758 to 19·335 kilos. per square centimetre, found the following numbers with the apparatus invented by him:—

Thurston's coefficients of friction for lubricants.

Steel pivots in bronze journals.

Lubricant	Pressure per sq. centimetre of surface in kilogrammes				
	1·758	10·546	14·062	17·777	19·335
	Coefficients of friction				
Sperm oil	0·041	0·0090	0·0096	0·0095	0·0091
Tallow oil	0·056	0·0136	0·0127	0·0110	0·0090
West Virginian mineral oil	0·056	0·0120	0·0095	0·0081	0·0100

Steel pivot and cast journal. Pressure 3·515–70·310 kilos.; velocity 0·750 metre per second.

Pressure per sq. centimetre	Sperm oil	Tallow oil	West Virginian mineral oil
3·515 kilos.	0·013 kilos.	0·0200 kilos.	0·203 kilos.
7·031 „	0·008 „	0·0157 „	0·150 „
17·577 „	0·005 „	0·0085 „	0·009 „
36·154 „	0·005 „	0·00525 „	0·0052 „
52·732 „	0·0043 „	0·0066 „	0·0050 „
70·310 „	0·009 „	0·0125 „	0·0100 „

With a larger series of lubricants the following results were arrived at:—

Name of lubricants	Pressure of							
	8 lbs. per square inch; 0·56 kilogrammes per square centimetre		16 lbs. per square inch; 1·12 kilogrammes per square centimetre		32 lbs. per square inch; 2·24 kilogrammes per square centimetre		48 lbs. per square inch; 3·36 kilogrammes per square centimetre	
	Average	Min.	Average	Min.	Average	Min.	Average	Min.
	Coefficient of friction.							
Sperm oil	0·1721	0·1330	0·1627	0·1083	0·1020	0·0833	0·1180	0·1020
Whale oil	0·1866	0·1333	0·1383	0·0916	0·1109	0·0874	0·0881	0·0777
Lard oil	0·2386	0·1666	0·1575	0·1166	0·1405	0·1000	0·1005	0·0750
Olive oil	0·1668	0·1333	0·1575	0·1000	0·1681	0·1000	0·0930	0·0555
Colza oil	0·1817	0·1333	0·1567	0·1250	0·1187	0·0833	0·1063	0·0722
Mineral sperm . . .	0·1875	0·1333	0·1604	0·1416	0·0861	0·0791	0·0944	0·0944
Lubricating white . .	0·1537	0·1500	0·1583	0·1500	0·1277	0·1125	0·1277	0·1277
Lubricating unbleached .	0·2550	0·1500	0·2067	0·1500	0·1275	0·1250	0·1555	0·1444
Paraffin oil	0·2607	0·2000	0·1777	0·1333	0·1343	0·1125	0·2222	0·2222
Cottonseed oil . . .	0·2156	0·1577	0·1757	0·1250	0·1444	0·1083	0·0996	0·0694
Palm oil	0·2826	0·1666	0·2041	0·1250	0·1016	0·0584	0·1013	0·0666
Linseed oil	0·1598	0·1333	0·1215	0·0833	0·1347	0·0750	0·0962	0·0609
Cocoanut oil . . .	0·1750	0·1333	0·1066	0·9160	0·1062	0·0791	0·0794	0·0611
Train oil	0·2475	0·1500	0·1488	0·1250	0·1016	0·0666	0·0805	0·0661
Bone oil	0·1746	0·1500	0·1254	0·1000	0·1198	0·0791	0·1159	0·1000

It is not intended in this article to enter into those questions which more properly belong to a treatise on mechanics, such as friction under varying pressure, friction between various materials, friction of quiescence or resistance to starting, &c. &c. It may, however, serve a useful purpose, as indicating the important part played by such influences, if the effect of some of them at least upon a standard lubricant is shown. The table of Thurston is therefore introduced on p. 477.

The characteristics of good lubricants, as formulated by the same authority, are these:—

1. Enough 'body' or combined capillarity and viscosity to keep the surfaces between which it is interposed from coming in contact with maximum pressure.

2. The greatest fluidity consistent with the preceding requirements, *i.e.* the least fluid friction allowable.

3. The lowest possible coefficient of friction under the conditions of actual use, *i.e.* the sum of the two components, solid and fluid friction, should be a minimum.

4. A maximum capacity for receiving, transmitting, storing, and carrying away heat.

5. Freedom from tendency to decompose or to change in composition by gumming or otherwise, on exposure to the air or while in use.

Coefficients of friction-velocity, pressure and temperature variable.

New journal of steel; bearings of bronze; lubricant, standard sperm oil.

Speed per minute	9 metres or 30 feet					30 metres or 100 feet					76 metres or 250 feet		152 metres or 500 feet		366 metres or 1,200 feet		
Pressure lbs. per square inch	200	150	100	50	4	200	150	100	50	4	200	100	200	100	200	150	100
Kilogrammes per square centimetre	98	68	44	22	1·8	98	68	44	22	1·8	98	44	98	44	98	68	44
Temperature: Cent. 66°, Fahr. 150°	·0500	·0500	·0250	·0125	·125	·0140	·0074	·0025	·0037	·0630	·0047	·0028	·0053	·0037	·0060	·0058	·0061
Cent. 60°, Fahr. 140°	·0250	·0330	·0110	·0087	·125	·0100	·0050	·0025	·0036	·0630	·0047	·0030	·0053	·0037	·0062	·0058	·0070
Cent. 54°, Fahr. 130°	·0160	·0200	·0044	·0075	·125	·0087	·0041	·0019	·0037	·0630	·0047	·0030	·0053	·0037	·0065	·0062	·0075
Cent. 49°, Fahr. 120°	·0110	·0110	·0044	·0075	·125	·0056	·0035	·0019	·0037	·0630	·0047	·0037	·0056	·0037	·0069	·0067	·0080
Cent. 43°, Fahr. 110°	·0100	·0033	·0037	·0067	·094	·0044	·0033	·0019	·0037	·0630	·0050	·0044	·0062	·0050	·0075	·0075	·0087
Cent. 38°, Fahr. 100°	·0075	·0028	·0031	·0056	·094	·0040	·0033	·0019	·0037	·0630	·0056	·0045	·0065	·0061	·0081	·0083	·0094
Cent. 32°, Fahr. 90°	·0056	·0025	·0031	·0037	·094	·0040	·0033	·0019	·0037	·0630	·0070	·0052	·0075	·0061	·0100	·0170	·0150

6. Entire absence of acid or other properties liable to produce injury of materials or metals with which they may be brought into contact.

7. A high temperature of vaporisation and of decomposition, and a low temperature of solidification.

8. Special adaptation to the conditions as to speed and pressure of rubbing surfaces under which the unguent is to be used.

9. Freedom from grit and all foreign matter.

The value, therefore, of a lubricant *per se* is to be measured by its conformity to such requirements as are indicated in the foregoing clauses, and is independent of price. The consumer will, however, take into account both the cost and efficiency of the lubricant for the work it is required to do.

Lubricants are (*a*) solid; (*b*) semisolid; (*c*) fluid.

(*a*) SOLID LUBRICANTS.

Several materials, such as plumbago, soapstone, and 'anti-friction metals' have been introduced, intended either to obviate the use of oils or to form a yielding surface to the shaft or journal working in the bearing. They are either fixed permanently or are applied at intervals like oil. They are for the most part compositions of metallic and non-metallic substances—viz., blacklead, soapstone, asbestos, sulphur, lampblack, and white lead. Of those which are permanently fixed the substance known as 'metalline' and under other names is prepared in the shape of plugs which are inserted in borings made in the bearing; the heat caused by friction is sufficient to soften the material, which then begins to lubricate the journal. Plumbago and soapstone are commonly used in the powdered state and are applied at intervals. Certain 'anti-friction metals,' such as Babbitt-metal, are also used by engineers to act as a cushion in which the shaft may gradually 'bed' itself; in a similar manner lead is used as a lining to brass bearings.

(*b*) SEMI-SOLID LUBRICANTS

comprise tallow, lard, grease of various kinds, palm-oil preparations, lead-soap lubricants, soft-soap lubricants, preparations of caoutchouc, naphthalene, resin, and asphaltum.

Tallow lubricants are very efficient, although somewhat expensive. Since tallow is easily affected by variations of temperature, a corrective expedient is resorted to in the employment of other lubricating agents in admixture with it. For the purpose of railway work in greasing the axles of locomotive and carriage wheels, the management of the Austrian Staats Railway adopts the following different admixtures of tallow and olive oil, as suited to the seasons of winter and summer:—

	Tallow Parts	Olive oil Parts	Old grease Parts
For winter . . .	100	20	13
For spring and autumn.	100	10	10
For summer . . .	100	1	10

('Old grease' is the residue in the boxes from one filling to the next). The fats are melted together, and constantly stirred meanwhile, to 302°F., and then cooled.

Tallow and train-oil lubricant. Purified tallow 2 parts, train-oil 1 part, or in cold climates something more than 1 part. The tallow is only just melted and the oil stirred in.

Sulphur waggon grease. Tallow 2 parts, train-oil 2 parts, powdered sulphur 1 part. Prepared as above; the sulphur being last added.

Booth's patent lubricant, also for railways, is prepared in two ways:—No. 1. Purified tallow 6 parts, palm-oil 12 parts, water 8 parts, soda 1 part. No. 2. Tallow 8 parts, palm-oil 20 parts, water 10 parts, soda 1·5 parts. In both cases the tallow is first heated to about 302°F. and the palm-oil stirred in. The soda having been dissolved in the water is then very gradually added. It is much used on English railways.

Another English railway grease:—

	Summer	Winter
Tallow . .	504 parts	420 parts
Palm-oil. .	280 „	280 „
Sperm oil .	22 „	35 „
Caustic soda .	120 „	126 „
Water . .	1,370 „	1,524 „

Other preparations are made of tallow with colza oil, soda, and water in various proportions; and, for fine machines, of tallow with castor oil &c. &c.

Palm-oil lubricants. Although palm-oil may be used alone, its melting-point is too low for most purposes; to correct this, tallow and other fats are added to the amount of one-third or one-half of the total weight of the lubricant. A small quantity of soda should form a part of these lubricants, as by its use the free fatty acids which are contained in palm-oil are saponified and their action on the metals with which they come in contact is destroyed. Soda also is the medium by which water is introduced into the mixture.

Lead-soap lubricants. Lead salts yield on saponification with fats solid combinations called lead-soaps; they are hard at low temperatures, viscous at ordinary temperatures, but sufficiently fluid on heating by friction. The melting-point of lubricants prepared from these substances is high, and they are therefore less suited for high speeds. So-called 'anti-friction lubricants' are composed of lead-soaps. A basic acetate of lead or sugar of lead is combined with the requisite quantity of fat in the following manner. The lead solution is thus prepared. Sugar of lead 10 parts, litharge 10 parts, and soft water 110 parts, are boiled with frequent stirring for an hour and a half or two hours. The mass is then allowed to rest, and the clear fluid drawn off and restored to 100 parts by the addition of water. It is then heated to from 145°F. to 165°F. and immediately mixed with ordinary fat (colza oil, lard, and sometimes neats-foot oil), as, *e.g.*, solution of sugar of lead 100 parts, colza oil 80 parts, lard 80 parts. The preparation should show a uniform grey colour, and, after melting, congeal at from 100°F. to 122°F. (Brannt).

Soap lubricants. Ordinary soft soap, or fat combined with potash, is serviceable for some purposes, but is liable to have a part of the potash lye not fixed, by which damage is done to metals.

The following are from Brannt:—

Caoutchouc lubricants for belts. Caoutchouc 20 parts, linseed oil 1,000 parts. Melt the caoutchouc together with the same quantity of linseed oil, and as soon as the mixture commences to evolve vapours, stir in 20 parts of linseed oil and afterwards add the remainder of the oil by instalments of 100 parts.

Asphaltum waggon grease. Asphaltum 32 parts, black pitch 8 parts, petroleum 8 parts, litharge 8 parts, water 80 parts.

Naphthalene grease. Naphthalene 100 parts, colza oil 50 to 100 parts. Crude naphthalene is used.

Resin lubricant. Common resin 100 parts, resin oil 50 parts, lard 300 parts.

Graphite waggon grease. Tallow 36 parts, lard 9 parts, palm oil 9 parts, graphite 2 parts.

Graphite lubricants for quick-moving axles. Tallow 100 parts, graphite 100 parts; especially adapted for shafts revolving with great velocity without great load, as circular saws, ventilators, &c.

(*c*) FLUID LUBRICANTS.

These are comprised under the name of oils (*v.* OILS, FIXED).

The oils, which are principally used as lubricants either alone or in combination with each other or with other lubricating bodies, are sperm oil, whale oil, seal oil, fish oils, neats-foot oil, lard oil, bone oils, olive oil, colza and rape-seed oils, cotton-seed oil, linseed oil, castor oil, rosin oil, and mineral oils. Some of these may be mixed according to the purpose for which they are required; and such mixtures are frequently claimed as specialities under various names by oil merchants. Fluid lubricants have the advantage over greases that they are at once applicable to the running surfaces, or, in other words, that they do not require the heat of friction to render them fluid; they are also less affected in consistency by change of temperature, and they are more easily applied to the journals than are greases.

Lubricating oils should not flash below 250°F. (120°C.), nor take fire at a much higher temperature. According to Spon—

1. A mineral oil flashing below 300°F. (149°C.) is unsafe on account of causing fire.
2. A mineral oil evaporating more than 5 p.c. in 10 hours at 140°F. (60°C.) is inadmissible, as the evaporation leaves a viscous residue, or leaves the bearing dry.
3. The most fluid oil that will remain in its place, fulfilling other conditions, is the best for all light bearings at high speeds.
4. The best oil is that which has the greatest adhesion to metallic surfaces and the least cohesion in its own particles; in this respect, fine mineral oils are first, sperm oil second, neatsfoot oil third, lard oil fourth.
5. Consequently the finest mineral oils are best for light bearings and high velocities.
6. The best animal oil to give body to fine mineral oils is sperm oil.
7. Lard and neats-foot oils may replace sperm where greater tenacity is required.
8. The best mineral oil for cylinders has sp.gr. 0·893 at 60°F. (15·5°C.), evaporating-point 550°F. (288°C.), and flashing-point 680°F. (360°C.).

9. The best mineral oil for heavy machinery has sp.gr. 0·880 at 60°F. (15·5°C.), evaporating-point 443°F. (229°C.), and flashing-point (518°F.) (269°C.).

10. The best mineral oil for light bearings and high velocities has sp.gr. 0·871 at 60°F. (15·5°C.), evaporating-point 424°F. (218°C.), and flashing-point 505°F. (262°C.).

11. Mineral oils alone are not suited for the heaviest machinery on account of want of body and higher degree of inflammability.

12. Well-purified animal oils are applicable to very heavy machinery.

13. Olive oil is foremost among vegetable oils, as it can be purified without the aid of mineral acids.

14. The other vegetable oils admissible, but far inferior to olive oil, are, in their order of merit, gingelly, ground-nut, colza and rape, and cotton-seed oils.

15. No oil is admissible which has been purified by means of mineral acids.

The best lubricants under the usual conditions found in practice are (Thurston):—

Under low temperatures. As in rock-drills driven by compressed air, light petroleums.

Under very great pressure with slow speed. Graphite, soap-stone, and other solid lubricants.

Under heavy pressure with slow speed. The above and lard, tallow, and other greases.

Heavy pressures and high speed. Sperm oil, castor oil.

Light pressures and high speed. Sperm, refined petroleum, olive, rape, cotton-seed.

Ordinary machinery. Lard oil, tallow oil, heavy mineral oils, and the heavy vegetable oils.

Steam cylinders. Heavy mineral oils, lard, tallow.

Watches and other delicate mechanism. Clarified sperm, neats-foot, porpoise and olive oils.

For mixture with mineral oils. Sperm oil is best, although lard oil is much used.

V. Oils, fixed. Also Treatise on Friction and Lubrication, Thurston; Treatise on Friction and Lost Work in Machinery and Millwork, Thurston; and a Practical Treatise on Animal and Vegetable Fats and Oils, Brannt.

LUCIFER MATCHES *v.* Matches.

LUMINOUS PAINT *v.* Barium sulphate.

LUNAR CAUSTIC. Silver nitrate fused and cast into rods or sticks.

LUPININE *v.* Vegeto-alkaloids.

LUPULIN *v.* Oleo-resins.

LUPULINE *v.* Vegeto-alkaloids.

LUTECIENNE. A mixture of Fast Red A with Orange II. (β-naphthol orange), the sodium salt of parasulphobenzene-azo-β-naphthol, comes into commerce under this name. Known also as French Red. The name is also given to the alkaline salts of dibromodinitro-fluoresceïn, prepared by simultaneous nitration and bromination of fluoresceïn in alcoholic solution or by nitration of dibromo-fluoresceïn in acetic acid or aqueous solution.

LUTEOLIN. The soda salt of *m*-xylidin-sulphonic-azo-diphenylamine. An orange-yellow dye discovered by Witt in 1883. No longer used. Also the colouring matter of Weld (*q. v.*).

LUTES are used for packing joints, repairing fractures, and coating vessels externally to render them impervious to vapours &c.

Of lutes for joints which are not to be subjected to high temperature may be mentioned: (1) Soaked bladder stretched and tied over a joint or employed to secure another lute on the joint. (2) India-rubber bands, or caoutchouc melted or dissolved in coal tar, naphtha, or other solvent. (3) A solution of 1 part caoutchouc in 2 parts hot linseed oil mixed with 3 parts pipeclay; this mixture remains soft and is very impervious. (4) Linseed or almond meal made into a paste with water, milk, glue, or lime-water. (5) A mixture of white lead and oil spread upon strips of linen or bundles of tow. (6) Quicklime reduced to a dry powder by addition of a small quantity of water, and mixed with white of egg diluted with its own volume of water, is spread on linen strips and rapidly applied to the joint. This lute dries rapidly and adheres strongly to glass. (7) *Lute d'âne*, a very strong cement prepared by mixing strong glue with recently slaked lime, with subsequent addition of white of egg. (8) Chalk and linseed oil (glazier's putty). (9) Plaster of Paris made into a paste with water, gum water, or glue, and coated when dry, if the joint is to be gas-tight, with melted paraffin or oil. (10) *Fat lute*, consisting of a mixture of clay and boiled linseed oil, is applied and retained by bladder or other substance, to hot joints or to prevent escape of corrosive vapours. (11) A mixture of clay with a solution of gelatine in pyroligneous acid. (12) For joints which are to resist considerable internal pressure, a mixture is applied consisting of equal parts of red lead and white lead made into a paste with linseed oil and mixed with tow.

For making permanent joints and closing joints between metal and glass &c., various compositions containing beeswax are used. Beeswax when fused with one-eighth its weight of turpentine becomes less brittle and, when the materials are fused in equal proportions, the product becomes pliant when held in the hand, melts easily, and is known as *soft cement*. *Cap cement* or *hard cement*, for closing the covers &c. of scientific apparatus, is prepared by mixing and melting 1 part beeswax, 5 parts resin, and 1 part dried red ochre or other colouring matter. The mixture is heated to 100°C. until all frothing has ceased and is cooled with frequent stirring to prevent settlement of the pigment.

A waterproof cement, introduced by Edmund Davy, is prepared by melting together two parts by weight of common *pitch* and one part of *gutta percha*, with constant stirring. The resultant homogeneous fluid adheres with great tenacity to metal, stone, wood, &c., if applied to warm surfaces of those substances, and, although hard, is not brittle. It softens when heated and passes through various stages of viscosity until above 100°F. it forms a thin fluid. It appears to be absolutely unaffected by contact with water.

A lute acquiring a hardness equal to that of marble, and known as *oxychloride of zinc cement*, is prepared by dissolving 3 p.c. of borax in a solution of zinc chloride of 1·49 to 1·65 sp.gr. with addition of sufficient recently ignited zinc oxide to produce the proper consistency.

Bruyère's hydraulic cement is prepared by heating to bright redness for three hours a mixture of 3 parts clay and 1 part slaked lime, and powdering the product.

A cement employed for closing leaks in *boilers* &c. is prepared by mixing 6 parts clay and 1 part iron filings to a paste with boiled linseed oil.

Iron cement for permanently closing joints in iron, consists of a mixture of 100 parts iron filings, 3 to 20 parts flowers of sulphur, and 3 to 5 parts ammonium chloride, mixed with water to a paste and applied quickly. The larger proportion of sulphur is required when the iron filings are fine. The mixture soon becomes hot, with evolution of ammonia and sulphuretted hydrogen, and in a short time becomes almost as hard as iron. It is stated that the best iron lute consists of a mixture of 100 parts iron filings with only one or two parts of sal ammoniac and no sulphur. This lute, however, though stronger, requires a considerable time to set.

For coating earthenware, a paste is applied consisting of a mixture of equal parts of zinc white and fine sand, made into a paste with a concentrated solution of zinc chloride. *Willis' lute* for the same purpose consists of a paste made with slaked lime and a solution of 2 oz. borax in 1 pint water. It is applied with a brush, and when dry is covered with a plastic mixture of slaked lime and linseed oil, and is ready for use after a few days.

Among lutes for resisting high temperatures may be mentioned Stourbridge clay made into a paste with water, which withstands a higher temperature than any other lute in general use, and *Windsor loam*, a natural mixture of clay and sand. Both are used for coating vessels and for packing hot joints of metal vessels. With the addition of about one-tenth part of borax these clays are useful for glazing earthenware vessels.

Gas retorts and similar vessels closed temporarily to withstand high temperatures are usually merely luted with mortar.

For luting crucibles, a paste of fireclay and powdered firebrick is useful, preferably with addition of a small proportion of borax to render the lute coherent.

A most valuable mixture for repairing broken furnaces &c. consists of a paste of firebrick and liquid sodium silicate. Even considerable openings, if roughly filled with broken firebricks, may be sealed with this lute (*v.* CEMENTS).

LUTIDINE *v.* BONE OIL.

LUTIDINIC ACID *v.* BONE OIL.

LYCOCTONINE *v.* VEGETO-ALKALOIDS.

LYCOPODINE *v.* VEGETO-ALKALOIDS.

LYDIAN STONE or **LYDITE.** A black jaspideous or cherty substance, which from its hardness and the closeness of its grain has been used as a touchstone for testing the quality of gold, whence its name *basanite*. The metal to be tested is rubbed on the polished surface of the stone, and the streak thus produced is compared with the streaks made by a series of alloys of known composition; the observer judging of the purity of the metal by the colour of the mark and by its behaviour when treated with a drop of acid. Lydite is also used as a hone-stone. Most Lydian stone has a schistose structure, and may be described as a horn-stone slate, or *Kieselschiefer*. The Lydian stone of Devon and East Cornwall is a fine-grained, indurated, carbonaceous shale, belonging to the culm-measures. F. W. R.

LYDIN. A synonym for mauve or aniline purple.

M

MACASSAR OIL. An oil obtained from the reddish-brown seeds of *Schleichera trijuga*, in which it exists to the extent of 36 p.c. The buttery fat has a sp.gr. of 0·924 at 15°, and melts at 28° (21°–22° Thümmel). It has an iodine number of 53, a saponification equivalent of 219 (1 gram requires 230 milligrams of potash for saponification), contains 91 p.c. of insoluble fatty acids, and 6·3 p.c. glycerin. The fatty acids present include acetic, butyric, lauric, arachidic, and oleic (L. v. Itallie, Apoth. Zeit. 1889, 4, 506; S. C. I. 8, 722). According to Thümmel, the oil contains small quantities of hydrocyanic acid and benzaldehyde, due possibly to sophistication with bitter almond oil (*l.c.* 1889, 4, 518; S. C. I. 8, 722).

MACE is the epidermis of the fruit of the *Myristica moschata*, the nutmeg; it is of an orange-brown colour, reticulated and flaky, aromatic and agreeable to the taste, and is more esteemed as a spice than the nutmeg. It contains a thin volatile oil in conjunction with a thick unctuous butter (myristicin). *V.* NUTMEG and NUTMEG OIL.

MACE OIL *v.* NUTMEG OIL.

MACHROMIN *v.* FUSTIC.

MACLURIN *v.* FUSTIC.

MADDER. Although the commercial value of this dyestuff has been reduced to a minimum through the introduction of artificial alizarin, it has still very great historical and scientific interest. Originally a native of, and no doubt first used for dyeing in, India and Central Asia generally, its use dates from the most ancient times. According to Pliny, it was employed by the Hindoos, Persians, and Egyptians. The Greeks and Romans used it for dyeing wool and leather, under the names Erythrodanon and Varantia (later Rubia), whence is derived the French name Garance. About the time of the Crusades the cultivation of madder was introduced into Italy and probably also into France. The Moors cultivated it in Spain, and during the sixteenth century it was brought to Holland. Colbert introduced it into Avignon in 1666, Frantzen into Alsace in 1729, but only towards 1760–1790 did its cultivation become important. During the wars of the Republic its cultivation was largely abandoned, and only after 1815 did it again become regular. In our own day the chief seats of the madder culture have been France, Holland, Italy, Turkey. Attempts to grow it successfully in this country have failed.

The madder plant belongs to the natural family of the Rubiaceæ, the chief species being *Rubia tinctorum* grown in Western Europe, *R. peregrina* in the Levant, and *R. mungista* in India and Japan. The plant is perennial, it has a quadrangular stem with whorls of lanceolate leaves, small flowers, and an underground stem from which spring numerous roots, which are the chief seat of the colouring matter. It flourishes best in a somewhat moist loose sandy soil, and preferably in a warm climate. Old roots are richer in colouring matter than young ones, hence in Europe it is the custom to leave the plants in the ground for two or three years, and in the Levant as long as six years; their length varies from 1–2 feet, and their thickness from ¼–½ inch. The colouring matter is situated chiefly in the thick, fleshy, cortical part of the root which surrounds the fibrous, woody, central portion. The whole root bears in many countries the name 'alizari' or 'lizari,' and only when dried and ground should it be termed madder, but usually this latter name is assigned to it in all conditions. The root is pulled up, dried in the open air or in stoves to prevent rotting, and after beating off loose earth, &c., it is sent into the market, or it is well dried in stoves and ground.

Varieties.

The principal kinds of madder are: Dutch, Alsatian, Avignon, and Turkish.

The *Dutch madder* is coarsely ground and tends to cake together, especially when kept in a somewhat damp atmosphere. It possesses a strong and somewhat disagreeable odour, a bitter-sweet taste, and a colour which varies from orange to reddish-brown, according to the mode of manufacture. Crop-madder, obtained by grinding the inner portion of the root, is reckoned the best quality; Mull-madder, obtained by grinding the outer bark only, is the lowest quality.

Alsatian madder is similar to Dutch madder. Its odour is even still more penetrating, its taste is also bitter, but not so sweet. It is also coarsely ground, and although it does not ferment so readily as the Dutch madder, it still cakes together very firmly. The different qualities of Alsatian madder are known as: mulle (O.), mifine (M.F.), fine-fine (F.F.), surfine (S.F.), and surfine fine (S.F.F.), the F.F. quality being the most used. Both the Dutch and the Alsatian madders require to be stored in casks for about two years, in order to attain their full colouring power. Both are rich in pectic matters, possess an acid reaction, and should be used, in dyeing, with calcareous water.

Of *Avignon madder* there are two varieties, the 'palus' and the 'rosée'; the former is grown in a particular district near Avignon, having a moist light soil, the latter, which is of a pink colour, is grown in calcareous soil. The darker palus madder is preferred. The smell of Avignon madder is agreeable, the taste is sweet and only slightly bitter. It is usually finely ground, dry, and not much caked together, owing to the pectic matters being present only in small quantity. The marks (F.F.), (S.F.), &c., are usually accompanied by P. (Palus), R. (Rosée), or (P.R.) a mixture of both, or (P.P.) 'pure palus.'

Avignon madder may be used while still comparatively fresh, *i.e.* without long storage.

Turkish or *Levant madder*, exported principally from Smyrna, is sold in the unground state, and is highly esteemed because of its richness in colouring matter.

Commercial preparations of Madder.

The principal of these are: Garancine, Garanceux, Flowers of Madder, Commercial Alizarin or Pincoffin, and Madder extract.

Garancine. The preparation of this product results from the observation in 1827 of Robiquet and Colin, that by treating ground madder with an equal weight of concentrated sulphuric acid, the various principles of the madder were destroyed with the exception of the colouring matter alizarin. We now know further that the glucoside of the root is decomposed by the action of the acid. This first product was termed *charbon sulphurique*, but soon the method of its preparation was slightly altered, and it then received the name *garancine*.

Garancine is made by mixing, in a wooden tank with false bottom, 100 kilos. ground madder, 1,000 litres water, and 2 kilos. sulphuric acid, 168°Tw. (sp.gr. 1·84), stirring up and allowing the whole to macerate for about 12 hours. The liquid is then drawn off, the residue is mixed with a little water and 30 kilos. strong sulphuric acid, and the whole is boiled for 2–3 hours. After running off the acid liquor, the garancine remaining is washed with water till free from acid, then drained, pressed, dried and ground.

The colouring power of garancine is 3–4 times that of good madder, it dyes more readily, giving yellower toned reds and pinks, and greyer lilacs. They are not quite so fast to soap as the madder colours, but since, in the case of printed calicoes, the unmordanted white parts are not so much soiled in the dye-bath, the operation of soaping can be omitted.

Garanceux or *Spent Garancine* was introduced in 1843 by L. Schwarz of Mulhouse. It is simply a low quality of garancine prepared in the above manner from the spent madder of the dye-baths, and made by each calico-printer for himself, by way of economy. Its colouring power is about one-fourth that of good garancine.

Flowers of madder was first made in 1851 by Julian and Rogner of Sorgues. It is simply prepared by macerating ground madder for several hours with cold water very slightly acidulated with sulphuric acid (1–2 p.c. on the weight of madder), then washing, draining, pressing, drying, and grinding. In this manner all soluble, mucilaginous, and sugary matter, &c., is removed, decomposition of the glucoside by fermentation occurs, and the residue has nearly double the colouring power of the original madder. The waste liquors are neutralised, allowed to ferment with the addition of yeast, and then distilled to gain the alcohol—100 kilos. madder yield 45–60 kilos. flowers of madder and 10 litres alcohol, suitable for making varnish, &c.

Commercial Alizarin or *Pincoffin* was introduced in 1852 by Schunck and Pincoff, who prepared it by submitting ordinary garancine to the action of high pressure and superheated (150°C.) steam. By this treatment the verantin and rubiretin present in the garancine are destroyed, while the alizarin remains intact, and the product yields in consequence more brilliant purples, and less soaping is required to clear the whites or unmordanted portions of printed calicoes.

Madder extracts. Already in 1826, attempts were made by Gaudin to apply mordants along with the colouring matter of madder in the form of an extract, directly to calico, *i.e.* as a steam-colour, instead of by dyeing, and in 1837 Gastard succeeded in doing this successfully on a large scale by means of a product named *colorine.* The expense, however, of this and other early madder extracts retarded their application, but, their utility having been clearly demonstrated, the endeavours of numerous chemists were directed to their production in a reasonably cheap manner. Madder extracts consist of variable mixtures of the two colouring matters of madder, alizarin and purpurin, or of each separately, in a more or less pure condition. Since the introduction of artificial alizarin, just when their manufacture was about being perfected, they have lost all their importance. The following were the chief methods of production employed.

Leitenberger's method consisted in first extracting all the purpurin from ground madder by water heated to 55°C., and afterwards dissolving out the less soluble alizarin from the dried residual madder by means of wood-spirit. The aqueous solution was precipitated by lime, the washed calcium-purpurin lake was then decomposed with hydrochloric acid, the liberated purpurin collected and washed, when it was ready for use. The alcoholic solution of alizarin was merely precipitated by water, collected and washed. Alizarin and purpurin extracts were thus obtained.

Paraf's method (1868) consisted in extracting madder with superheated water, with or without the addition of a small quantity of alum or sulphuric acid, then collecting and washing the flocculent alizarin precipitate which separated out on cooling.

An important method was that of E. Kopp (1861), which consisted in extracting the glucoside of madder by means of an aqueous solution of sulphurous acid, and then decomposing it by the action of sulphuric acid. Ground madder was thrice macerated for 12–15 hours with a weak solution of sulphurous acid containing a trace of hydrochloric acid, just sufficient to neutralise earthy carbonates existing in the root. The solutions thus obtained were mixed with 3–5 p.c. sulphuric acid, and heated to 60°C., when a red flocculent precipitate of purpurin was thrown down which was collected, washed, dried and sold under the name 'commercial purpurin.' The remaining solution was boiled for 2–3 hours, and allowed to cool, when a dark-green impure alizarin was precipitated, which when washed and dried was known as 'green alizarin.' This product was extracted at 150°C. with petroleum oil, the alizarin was dissolved out from the cooled petroleum solution by agitation with a dilute aqueous solution of sodium hydrate, the separated alkaline solution was acidified with dilute sulphuric acid, and the precipitated alizarin was collected, washed, and sold as 'yellow alizarin.' The madder from which the alizarin and purpurin glucosides had thus been removed still contained colouring matter, this was removed by boiling with dilute caustic soda, precipitated by acid, and, after a further purification by treating with an acid solution of aluminium sulphate, was collected, washed, and sold as 'orange extract of madder.'

Pernod's madder-extract, once largely used, was prepared by extracting garancine with boiling water very slightly acidified with sulphuric acid, collecting and washing the precipitate thrown down on cooling, and extracting the dried precipitate with boiling alcohol. After recovering the major portion of the alcohol by distillation, the remaining solution was mixed with water, and the precipitated alizarin was collected and washed.

CHEMICAL HISTORY.

Robiquet and Colin, as far back as 1826 and 1828, isolated two orange-coloured crystalline colouring matters, alizarin and purpurin, from their *charbon de garance*, by sublimation. Zenneck, however, suggested that these colouring matters did not exist as such in the madder, but were present in combination with sugar or some other substance. About the same time (1823) Kuhlmann extracted a bitter-sweet yellow amorphous compound from the root and named it *xanthin.* Runge, Watt, and others also succeeded in extracting a similar yellow substance from madder. In 1837, Decaisne, on examining sections of fresh madder-root under the microscope, noticed that its cells were filled with a yellow liquid which on exposure to air became pink coloured. His conclusion therefore was, that the fresh madder root contained a yellow principle, which only on oxidation yielded useful red colouring matter.

This view, however, was not universally accepted; some ascribed the change to the action of atmospheric ammonia, and others could not reconcile it with the recognised necessity of storing the madder even though it might be little exposed to air. Moreover, it seemed evident, by the expansion of the madder during this period of storage, even to the bursting of the staves of the casks containing it, that fermentation was in progress.

In 1848, Higgin observed that if a cold aqueous infusion of madder, which has a deep-yellow colour, and an intensely bitter taste, were allowed to stand for some time, or more rapidly if heated to about 50°C., with or without access of air, it lost these characteristics, and a gelatinous or flocculent precipitate was formed in which all the tinctorial power of the original infusion resided. He noticed further that this change was arrested by heating the infusion to the boiling point, or by the addition of alcohol, acids, or acid salts. Higgin concluded therefore that the xanthine of the madder must, during this process, have been converted into alizarin, and that the change was probably brought about by the action of some peculiar ferment contained in madder and extracted along with the xanthin by cold water.

In 1851 and following years appeared the classic researches of Schunck in which he showed Kuhlmann's xanthin to be a mixture of two substances, *chlorogenin* and *rubian*, the latter of which alone furnishes the colouring power of madder. Schunck further succeeded in isolating a peculiar ferment from madder and named it *erythrozym*.

I. *Erythrozym*. Schunck prepared this by extracting madder with water at a low temperature (38°C.), and precipitating the solution with alcohol. When dried it forms a brown amorphous mass. It acts as a ferment towards sugar and also towards rubian, decomposing the latter into glucose and alizarin, together with certain by-products, a property which is not possessed in any considerable degree by other common ferments, except emulsine.

II. *Rubian*, the characteristic glucoside of the madder-root, was first prepared by Schunck, by mixing stannous chloride with a watery extract of madder, passing hydrogen sulphide through the mixture, and dissolving out the rubian from the stannous sulphide along with which it is precipitated, by means of boiling alcohol. Subsequently he made use of the attractive power of animal charcoal for rubian. A filtered infusion of ground madder, made with boiling water, was mixed with animal charcoal (about 1 oz. charcoal to 1 lb. madder) for a short time. After washing the charcoal with cold water to remove chlorogenin, the rubian was dissolved out from it by boiling alcohol. By evaporating the solution to dryness, redissolving the residue in water, and repeating the treatment once or twice with the charcoal already used, an alcoholic solution was ultimately obtained which, after precipitation of some resinous impurity by means of sulphuric acid, yielded pure rubian (about 1·7 grams from 1 kilo. madder).

Rubian forms a dark brownish-yellow, transparent, amorphous, hard mass, very soluble in water and alcohol, but insoluble in ether. Its solutions have an intensely bitter taste, and give with basic lead acetate a pale-red precipitate. Concentrated sulphuric acid and also caustic alkalis dissolve it with a blood-red colour. On boiling the alkaline solution, the colour changes to purple. Rubian is not a dye-stuff, but a glucoside, capable of being decomposed into the colouring matter alizarin and glucose by the action of alkali, acid, or ferment. Other substances are produced at the same time.

When rubian is boiled with alkalis it gives—(*a*) alizarin, *rubiretin*, *verantin*, *rubiadin*, and glucose; when boiled with acids it gives: (*b*) alizarin, rubiretin, verantin, *rubianin*, and glucose; and when decomposed by the action of the ferment erythrozym it yields: (*c*) alizarin, rubiretin, verantin, *rubiafin*, and glucose.

(*a*) *Rubiretin* ($C_{14}H_{12}O_4$) is a brownish-red resinous mass, soluble in concentrated sulphuric acid, alkalis, and alcohol, but almost insoluble even in boiling water. It is not capable of dyeing.

Verantin ($C_{14}H_{10}O_5$) is a resinous reddish-brown powder, having properties similar to those of rubiretin.

Rubiadin is one of the constituents of the yellow flocculent precipitate obtained by boiling rubian with alkali and acidifying with acid. If to a filtered alcoholic solution of this precipitate aluminium acetate is added, and after filtering off the alizarin-lake thrown down, one adds lead acetate to the filtrate, the accompanying rubiretin and verantin are precipitated as purplish-brown flocks, and the filtered liquid contains rubiadin. It is precipitated from the solution by water, in the form of yellow flocks; these are dissolved in a little boiling alcohol. The solution is shaken up with stannous hydrate to remove traces of rubiretin, and on cooling the filtered solution the rubiadin separates out. It forms small yellow needles, capable of sublimation, insoluble in water, more soluble in boiling alcohol than rubianin, soluble in concentrated sulphuric acid with a yellow colour, and in boiling sodium carbonate solution with a blood-red colour. Its alcoholic solution is not precipitated by lead acetate. It is not a dye-stuff.

(*b*) *Rubianin* is contained in the yellow flocculent precipitate obtained by boiling rubian with dilute sulphuric acid. This precipitate is deprived of alizarin, verantin, and rubiretin by treating it repeatedly with boiling alcohol until this no longer acquires a dark-yellow colour. The residue, together with what separates from the alcohol on cooling, consists chiefly of rubianin with a little verantin. It is dissolved in a large quantity of boiling alcohol, the verantin is precipitated by lead acetate, and after filtering, the solution is allowed to cool. The rubianin then crystallises out as lemon-yellow silky needles. It is more soluble in hot water than rubiacin, and less so in alcohol than rubiretin and verantin. It is soluble in concentrated sulphuric acid with a yellow colour; on boiling, the solution becomes black, and sulphur dioxide is given off. Nitric acid, even when concentrated and boiling, dissolves it without effecting any change. Ammonia and alkaline carbonates have no action in the cold, on boiling, they yield a blood-red coloured solution, from which unchanged rubianin separates on cooling. Neutral lead acetate does not precipitate it from its alcoholic solution. It possesses no dyeing power.

(*c*) *Rubiafin* is one of the products contained in the gelatinous precipitate resulting from the action of erythrozym upon rubian. This precipitate is treated with boiling alcohol, and after filtering off the unchanged erythrozym, the solution is successively precipitated with aluminium and lead acetates. These precipitates are decomposed by hydrochloric acid, and the resultant yellow flocks, after washing with cold alcohol to remove rubiretin, are dissolved in boiling alcohol. Rubiafin and verantin are thrown down from the solution by copper acetate, and the purple precipitate is decomposed by hydrochloric acid. The red flocks thus obtained are washed, dissolved in boiling alcohol, the solution is agitated with stannous hydrate, filtered, and allowed to cool. The rubiafin separates as lustrous yellow plates and needles. It is soluble in alcohol, but only slightly soluble in boiling water. Boiling nitric acid and concentrated sulphuric acid dissolve it unchanged. Its alcoholic solution gives with lead acetate a fine crimson precipitate. It dissolves in a solution of ferric nitrate with a dark brownish-purple colour; if this solution is boiled for some time and hydrochloric is then added, a yellow precipitate of rubiacic acid is produced. In all its properties rubiafin resembles rubiacin, from which it appears to differ only in composition.

Rubiagin bears a strong resemblance to rubianin, rubiadin, and rubiafin in properties and composition. It occurs in the dark-yellow alcoholic filtrate from the lead precipitate, alluded to in the preparation of rubiafin, and is precipitated therefrom with water. The precipitate is boiled with sulphuric acid, washed, dissolved in boiling alcohol, and the filtered solution is evaporated to dryness. On treating the residue with cold alcohol, rubiadipin dissolves, and rubiagin remains undissolved. By recrystallisation from alcohol the rubiagin is obtained as lemon-yellow crystalline granules composed of needles. It is not changed into rubiacic acid by the action of ferric salts. It is distinguished from rubianin by its insolubility in water; from rubiadin, by its being incapable of sublimation; and from rubiafin by its not being convertible into rubiacic acid. It differs from all these by its behaviour towards lead acetate with which its concentrated alcoholic solution gives an orange-coloured precipitate.

Rubiadipin, which is a characteristic product of the fermentation of rubian, being always present among the bodies formed, is a yellowish-brown. soft, and viscid mass, somewhat similar, both in appearance and general properties, to rubiretin. Its preparation is referred to under rubiagin.

Glucose was obtained as a decomposition product of rubian with acids, as a yellow syrup, having no tendency to crystallise, but having apparently the same composition as grape sugar.

III. *Rubianic acid* ($C_{26}H_{28}O_{14}$) is, according to Schunck, an oxidation product of rubian, and proves to be the special glucoside of alizarin. It is identical with the *ruberythric acid* of Rochleder.

It is prepared by mixing an aqueous solution of rubian with baryta water in excess, leading carbon dioxide through the solution until a large quantity of barium carbonate has been formed, and exposing the filtered solution in a shallow vessel to the air. A crystalline scarlet film consisting of the barium compounds of rubianic acid and of rubidehydran, is formed on the surface, and a further quantity separates as red flocks on evaporation, while the liquid contains rubihydran. The film and red precipitate are added together, and decomposed with cold dilute sulphuric acid; excess of acid is neutralised with lead carbonate, and the filtered yellow solution is evaporated to dryness. Cold water dissolves rubidehydran from the brownish-yellow residue, and leaves the rubianic acid as a yellow powder. It is purified by crystallisation from boiling water.

To prepare rubianic acid direct from madder, the ground root is extracted with boiling water. Add lead acetate to the extract, and filter off the brownish-purple precipitate (alizarin, &c.); add ammonia to the yellow filtrate, and filter off the bulky precipitate (rubian, &c.). Decompose this precipitate with cold dilute sulphuric acid and filter. Add barium hydrate to the solution till it is alkaline; pass carbon dioxide through the liquid till a clear yellow solution is obtained, and filter; expose the filtrate in shallow vessels to the air. Filter off the scarlet crust which forms on the surface, stirring up the liquid several times in order to expose all the solution to the air and thus to obtain as much of the crust as possible. Collect and wash the crust slightly with cold water, and dissolve it in acetic acid; evaporate the yellow solution to dryness, and crystallise the washed residue from boiling water, to which a little animal charcoal has been added and then filtered off.

Rubianic or ruberythric acid crystallises from water in silky needles of a pure lemon-yellow colour; m.p. 258-260°C. Its solution has a slightly acid reaction and a bitter taste, though not so intensely bitter as that of rubian. It is soluble in alcohol, but not in ether. On sublimation it decomposes and yields alizarin. Cold concentrated sulphuric acid dissolves it with a dark-red colour. When boiled with dilute sulphuric acid it gives orange-coloured flocks of alizarin, and the solution contains glucose. Heated with nitric acid it yields oxalic acid and a brown syrup. In caustic potash or soda it dissolves with a cherry-red colour, which on boiling changes to purple and finally to violet, from which solution acids precipitate alizarin. With potassium carbonate solution it gives dark-red needles of potassium rubianate. Baryta hydrate precipitates it as a flocculent crimson precipitate. Neutral lead acetate colours its aqueous solution red, but produces no precipitate; basic lead acetate, however, gives a red flocculent precipitate. Under the influence of erythrozym it splits up into alizarin and glucose. It possesses no dyeing power.

Rubidehydran occurs as a by-product during the preparation of rubianic acid. Its cold aqueous solution, referred to above, is evaporated to dryness, the residue is dissolved in cold water, and the solution is precipitated by alcohol. It forms a reddish-yellow, transparent, brittle, gum-like mass, soluble in water, and possessing a bitter taste; it is indeed very similar to rubian in appearance and properties, with the exception that it is incapable of yielding rubianic acid.

Rubihydran is prepared from the yellow liquid filtered from the scarlet film and red flocks referred to above in the preparation of rubianic acid. After adding baryta water in order to precipitate unchanged rubian, filter, precipitate excess of barium by carbon dioxide, filter, and precipitate with lead acetate. Decompose the washed precipitate with cold dilute sulphuric acid, add lead carbonate, filter, remove excess of lead by hydrogen sulphide, filter, and evaporate.

Rubihydran forms a brownish-yellow, transparent, gummy mass, having a bitter taste. It bears a strong resemblance, in appearance and properties, to rubian, from which it differs by being very hygroscopic; also by its behaviour towards the action of boiling caustic alkali, when it yields only very few purple flocks; and by its inability to yield rubianic acid.

IV. *Rubiacin* (Runge's *madder-orange*) is a yellow crystalline substance, obtainable directly from the madder root, and is formed, according to Schunck, by the decomposition of a glucoside. It crystallises in small quantity from an aqueous infusion of madder, made with only a small quantity of cold water, after it has become sour by twelve hours' standing. It may also be prepared by treating rubiacic acid with alkaline reducing agents. Schunck also prepared it from the waste liquor of the madder dye-bath. The liquor is mixed with hydrochloric acid; the precipitate formed is treated with boiling alcohol; the orange-yellow powder, which separates from the solution on cooling, is re-dissolved in boiling alcohol; hydrated stannous oxide is then added, and the filtered liquid on cooling yields rubiacin. It crystallises in the form of plates and needles, having a strong reddish-green lustre. Hot concentrated sulphuric acid dissolves it unchanged. Alkalis dissolve it with a purple colour.

Rubiacic acid is prepared by boiling rubiafin, rubiacin, or the brown flocks precipitated from waste madder dye-bath liquors by hydrochloric acid, with ferric chloride or nitrate. Precipitate the dark reddish-brown filtrate with hydrochloric acid; dissolve the precipitate in a boiling solution of alkali carbonate, and precipitate the filtered solution with hydrochloric acid.

Pure rubiacic acid is an amorphous yellow powder, little soluble in boiling water. Its potassium salt forms brick-red silky needles.

V. *Chlorogenin* (Rochleder's *rubichloric acid*) is an amorphous substance, the characteristic property of which is, that it is converted into a dark-green insoluble substance (*chlororubin*) by boiling with dilute hydrochloric or sulphuric acid. To obtain it in a relatively pure state, a decoction of madder is precipitated with oxalic acid, the filtrate is neutralised with lime, filtered, and evaporated to dryness. The residue is dissolved in water, filtered, and the solution precipitated with basic lead acetate. After removing excess of lead from the filtrate by hydrogen sulphide and filtering, the solution is evaporated over sulphuric acid, when the chlorogenin is left as a brownish-yellow, honey-like residue. It still contains glucose and potassium, calcium, and magnesium acetates. It is soluble in water and in alcohol, insoluble in ether.

About the same period when Schunck was engaged in his researches on madder, of which the foregoing is a brief résumé, Rochleder was also busy with a similar investigation, and succeeded, already in 1851, in isolating for the first time the special glucoside of alizarin, viz. ruberythric acid (Schunck's rubianic acid) in a pure condition.

Rochleder extracted ground madder completely with boiling water, and treated the filtered decoction as follows:—

(*a*) An addition of neutral lead acetate produced a dark purplish precipitate containing the ready formed colouring matters alizarin and purpurin, also citric, sulphuric, and phosphoric acids, also traces of ruberythric (rubianic) and rubichloric acids (chlorogenin).

(*b*) On the addition of basic lead acetate to the filtrate from the foregoing, a pink or flesh-coloured precipitate is produced, composed almost entirely of the lead compound of ruberythric acid.

(*c*) The filtrate from this last precipitate yields, on the addition of ammonia, a precipitate containing glucose and rubichloric acid (chlorogenin). The method of preparing the ruberythric acid will alone be considered here.

To obtain the ruberythric acid, the pink precipitate alluded to is well washed, then suspended in water and decomposed with hydrogen sulphide. The lead sulphide (which contains also the ruberythric acid) is collected and washed with cold water, whereby phosphoric, citric, rubichloric, and also a small quantity of ruberythric acid, are removed, the latter imparting to it a yellow colour. The ruberythric acid is removed from the washed lead sulphide by repeated boiling with alcohol, the filtered yellow solution is evaporated somewhat, water and a small quantity of barium hydrate solution are added, and after filtering off a white precipitate, the filtrate is thoroughly decomposed by adding a further and larger quantity of barium hydrate. The dark cherry-red precipitate of barium ruberythrate is dissolved in acetic acid, the solution is filtered, barely neutralised with ammonia, and tribasic lead acetate is added. The red precipitate thus produced is washed with alcohol, suspended in alcohol and decomposed by hydrogen sulphide, the liquid and precipitate together are heated to the boil and filtered hot. On cooling, the amber-coloured solution yields pale-yellow needles of ruberythric acid, which are recrystallised from hot water.

Liebermann and Bergami have recently improved upon Rochleder's method, by extracting the madder with absolute alcohol (8–9 litres per 1 kilo. madder) instead of with water, in order to prevent decomposition of the glucoside and thus obtain a larger yield. The root is boiled with alcohol 2–4 hours and filtered hot. On evaporating the solution to ⅓–¼ of its volume and cooling, a yellowish-brown crystalline substance separates, which represents the impure glucoside. After filtering and evaporating the filtrate still further, pale-yellow tinted crystals of cane sugar crystallise out. Finally, by adding water to the remaining alcoholic solution, impure colouring matter (alizarin, &c.) is precipitated. Treated by this method 1 kilo. madder gave

Impure glucoside	50–60 grams	(5–6 p.c.)
„ sugar	15-30 „	(1·5–3 „)
„ colouring-matter	30–40 „	(3–4 „).

Since the impure glucoside becomes resinous when dried, or exposed to air, it must be at once purified. For this purpose it is dissolved in 5-6 times its volume of water, the solution is precipitated with lead acetate and basic lead acetate successively, and the latter precipitate is treated according to Rochleder's method.

The formula of ruberythric acid is considered as $C_{14}H_6O_2\left\{\begin{array}{l}OH\\ O.C_{12}H_{14}O_3(OH)_7\end{array}\right.$ and its decomposition by acids is represented thus:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

By treating with acetic anhydride and sodium acetate it yields an octacetyl derivative,

$$C_{26}H_{20}O_6(C_2H_3O_2)_8$$

m.p. 230°.

USE OF MADDER IN DYEING.

Previous to 1870 madder and its derivative garancine were the dyestuffs *par excellence* of the calico-printer and Turkey-red dyer.

By the former, it was used because of its characteristic property of yielding a variety of colours with the mordants aluminium, tin, and iron, viz. red and pink, orange, lilac and black;

also brown or chocolate, by employing a mixture of aluminium and iron mordants. Further, all these colours are fast to soap and light. To the calico-printer both the alizarin and the purpurin of the madder were of use, though undoubtedly the alizarin would, in most styles of work, be the essential colouring matter. The Turkey-red dyer employed madder, and afterwards garancine, because they yielded, by his peculiar process, the most brilliant and most permanent red on cotton which was known. In this case the alizarin was the all-important colouring matter, since the purpurin, although fixed on the fibre at first, was modified and more or less removed during the operations of clearing, no doubt chiefly by the action of the stannous salts employed. Alizarin, in conjunction with aluminium and iron mordants, gives a bluish-red and a comparatively bright lilac, purpurin, a yellowish-red and a greyish-lilac, respectively. It is interesting to know that, during the dyeing process itself, a certain amount of colouring matter was generated from the glucoside by fermentation, and it was the invariable custom of the madder dyer to begin dyeing at a low temperature, and to raise it to the boiling-point very slowly, say in the course of one or two hours; he thus promoted and prolonged the fermentation, and obtained richer colours.

The method of applying madder in Turkey-red dyeing was similar to that now employed in the case of alizarin (*v.* vol. i. p. 712).

Another interesting feature in connection with the application of this dyestuff is that, if the madder was deficient in lime, it was necessary to add a given proportion of chalk to the dye-bath; it now appears that calcium is a normal constituent of the madder colours, especially those obtained with aluminium and iron mordants.

Madder has also been used in the past, and is even now employed to a small extent, by the indigo dyer and the woollen dyer.

(For further notes on the application of madder as a dyestuff, *v.* the article DYEING, vol. i. p. 709).

Literature.—Robiquet and Colin, A. Ch. [2] 34, 225; Robiquet, A. Ch. 63, 311; A. 20, 196; Kuhlmann, J. Ph. 14, 354; Zenneck, P. 13, 261; Decaisne, J. Ph. 24, 424; Gaulthier de Claubry and Persoz, A. 2, 31; Runge, J. pr. 5, 362, 374; Higgin, P. M. 33, 232, 282; J. pr. 46, 1; Schunck, Tr. 141, 433; 142, 67; 145, 389; A. 66, 174; 81, 151, 344; 87, 345, 351; Débus, A. 66, 351; Wolff and Strecker, A. 75, 3; K. Moy, A. 54, 346; H. Koechlin, A. 59, 344; Schiel, A. 60, 79; E. Kopp, Bull. Soc. Ind. Mulh. (1861) 31, 9; (1867) 37, 437; Rochleder, A. 80, 323; 82, 207; Schwarz, A. 80, 333; Willigk, A. 82, 339; Stenhouse, A. 130, 341, 343; Bolley and Rosa, D. P. J. 171, 446; Strecker, J. (1868) 479; Liebermann and Bergami, B. 25, 2241; Gmelin, Handb. 16, 32; 14, 129.

J. J. H.

MADDER CAMPHOR *v.* CAMPHORS.

MADDER LAKE *v.* LAKES.

MAGDALA RED *v.* AZINES.

MAGENTA *v.* TRIPHENYLMETHANE COLOURING MATTERS.

MAGENTA BRONZE *v.* TUNGSTEN.

MAGISTERY. The term magistery was employed by the older chemists to denote the white precipitates which form on the addition of water to the strongly acidified solutions of certain metals.

MAGISTRAL. An old medical term signifying a sovereign remedy, employed by the Spanish smelters of Mexico and South America to the roasted and powdered copper pyrites, which is added to the stamped silver ores in the *torta* or magma obtained in the *patio* process of decomposing horn silver (*v.* SILVER).

MAGMA. A pasty or semi-fluid mixture. Applied in medicine to the residuum obtained after expressing certain substances to extract the fluid parts of them, or after treating a substance with some menstruum; a thick ointment or confection (Dunglison).

MAGNESIA ALBA (a hydrated basic magnesium carbonate) *v.* MAGNESIUM.

MAGNESIA NIGRA (an old name for native manganese dioxide) *v.* MANGANESE.

MAGNESITE. Native magnesium carbonate *v.* MAGNESIUM.

MAGNESIUM. Mg. At.w. 24·37 (Marignac, A. Ch. [6] 1, 289). The compounds of magnesium most widely occurring in nature are *magnesite* $MgCO_3$, *kieserite* $MgSO_4.H_2O$, *kainite* $MgSO_4.KCl.6H_2O$, *carnallite* $MgCl_2.KCl.6H_2O$, and the many silicates, as *enstatite*, *talc*, *meerschaum*, *augite*, *olivine*, and *serpentine*. Together with calcium it frequently occurs in huge mountain masses as *dolomite* $(MgCa)CO_3$. The sulphate $MgSO_4.7H_2O$ is one of the principal saline constituents of many springs, and the chloride occurs in sea water.

Preparation of the metal.—Magnesium was first obtained by Davy in 1808 by electrolysis, and also by reducing the oxide in a current of the vapour of potassium. In 1830 Bussy obtained it in larger quantity and in a purer form by heating anhydrous magnesium chloride to redness with potassium. On dissolving out the residual chlorides the metal was obtained as a powder which could readily be fused into globules. Bunsen subsequently prepared it by electrolysis of the fused chloride, using a battery of ten zinc-carbon cells. The operation was conducted in a porcelain crucible, of which the upper part was divided by a vertical partition, ground to the right size out of an ordinary crucible lid. The crucible was fitted with a tile cover, through which the poles of gas carbon were inserted, one on each side of the partition. The negative carbon pole was cut like a saw, in such a manner as to form overhanging ledges, under which the light magnesium collected, and was thus prevented from floating to the surface and burning at the high temperature employed.

As the anhydrous chloride is difficult to prepare, Matthiessen improved the process by substituting a mixture of three equivalents of potassium chloride with four of magnesium chloride. A little ammonium chloride is added, the mixture fused and electrolysed in Bunsen's apparatus; it is, however, unnecessary to cut the negative pole, as the magnesium is heavier than the fused mixture. In small quantities the metal may be readily obtained by electrolysing this mixture in a clay tobacco pipe heated over a lamp, the negative pole being formed by an iron wire inserted down the stem, and the positive by a piece of gas-carbon just touching the surface to the fused mass.

Manufacture.—The first steps towards the preparation of magnesium on an industrial scale were taken by Deville and Caron, whose process essentially consisted in heating a mixture of anhydrous magnesium chloride, fluorspar, and sodium. In the earlier experiments 600 grams of the fused chloride, 480 grams of finely-powdered fluorspar, and 230 grams of sodium in small pieces were employed. The fused magnesium chloride is obtained by evaporating to dryness a mixed solution of magnesium and ammonium chlorides, and fusion of the residue. Magnesium chloride alone cannot be fused without decomposition, hence the use of the ammonium chloride, which prevents this.

The finely-powdered fluorspar requires to be free from silica and phosphoric acid. The dry mixture, in the proportions mentioned, is then introduced into a red-hot earthen crucible and the cover pressed down by a weight while the violent reaction occurs. When all action ceases, the contents are stirred with an iron rod, which causes the minute globules of metal to coalesce into larger ones. After being left to cool for a short time, small quantities of the dry fluorspar are from time to time added, and the mass again stirred till it becomes pasty. By careful manipulation all the magnesium may be collected as a ball upon the rod before the melt becomes solid. The metal is then hammered to free it from slag, and should amount to about three-fourths of the theoretical equivalent of the sodium used.

Wöhler subsequently showed that the troublesome preparation of the anhydrous chloride may be avoided by using instead a mixture of magnesium chloride with one-sixth of its weight of sodium chloride, or of a mixture of sodium and potassium chlorides.

Deville and Caron also showed that the metal may be distilled at nearly the same temperature as zinc, in carbon-lined vessels, in an atmosphere of hydrogen, and were thus enabled to obtain it in a very pure form, free from carbon, silicon, and nitrogen.

Sonstadt, in 1863, introduced a few improvements in the process of Deville and Caron. An iron crucible was substituted for the earthen one, and the mixture used consisted of magnesium and sodium chlorides with one-fifth its weight of sodium. An excess of sodium should be avoided, as it causes troublesome explosions on the subsequent treatment with water, and it is best to powder the chloride before mixing with sodium. A layer of mixed chlorides is first laid at the bottom of the crucible, then the greater part of the sodium in large pieces, the rest of the crucible being filled up with the remainder of the chlorides, interspersed with small fragments of sodium. If the heat be raised above full redness magnesium vapour escapes and burns brilliantly in the air. The heat is continued for about half an hour after the whole crucible has been raised to full redness.

In a later patent Sonstadt extends the whole process to a manufacturing scale, and adopts an enlargement of Deville and Caron's method of purification by distillation. The 'magnesium still' consists of two wrought-iron vessels placed vertically over each other; the upper one serves as the crucible, and is connected with the lower one, which acts as receiver, by means of an iron condensing tube, which projects upwards into the crucible to within an inch of the lid. The whole apparatus can be rendered air-tight. The crucible filled with crude magnesium to the level of the top of the tube is fixed in a furnace and surrounded by fuel; the receiver is fitted into a recess of the fire grating, and projects below. Before commencing the distillation, the wrought-iron lid is screwed down, and the air displaced by a current of hydrogen or coal-gas driven in through an entrance tube attached to the lid, and escaping by a hole in the receiver. When the last traces of air have been removed, the openings are filled up by steel plugs, that of the lower one being bored by a fine orifice so as to permit of expansion on heating. When the fire has been lighted, the escaping hydrogen or coal-gas is allowed to burn as long as it will, and when the jet becomes extinguished the hole is closed by a tightly-fitting wire. The receiver is cooled by external application of water. The crucible is maintained at an almost white heat until the operation is complete. The whole apparatus is then removed from the furnace and cooled; on taking to pieces, the magnesium is found as a solid mass in the receiver. This may then be remelted and cast into ingots.

Magnesium is prepared on a large scale in this country by the Magnesium Metal Company, at Patricroft, near Manchester.

Von Püttner (Eng. Pat. 1031, Jan. 24, 1885) prepares the metal by a process very like the reduction of zinc, which metal magnesium very nearly resembles. The magnesium mineral is first treated so that the metal is present entirely as oxide. This is then intimately mixed with carbonaceous matter, to which may advantageously be added oxide of iron, and heated to whiteness in retorts. The vaporised metal is condensed and collected in receivers similar to those used in the zinc manufacture. A reducing or neutral gas may with advantage be passed through the retorts during the distillation. The retorts must be very refractory, and are preferably made from highly aluminous bauxite, or clay and dolomite, or magnesite.

Gerhard and Smith (Eng. Pat. 16,651, Dec. 19, 1884) describe a process for the electrolytic deposition of magnesium as follows. Magnesium ammonium sulphate is prepared by crystallising together 228 parts of magnesium sulphate and 132 parts of ammonium sulphate. This is dissolved in 35,000 parts of water, and the electro-deposition is effected in this solution at a temperature from 150° to 212°F. If a white metal is desired, a nickel anode is employed; for magnesium bronze, a copper anode. In the latter case the most suitable bath is formed by dissolving 360 parts of magnesium ammonium sulphate, 550 parts of potassium cyanide, and 550 parts of ammonium carbonate in 35,000 parts of water.

Properties.—Magnesium is a brilliant white metal resembling silver. When heated *in vacuo* to the temperature of the softening of porcelain it sublimes, and deposits itself upon the cooler parts of the vessel in beautiful silver-white crystals (Dumas, C. R. 90, 1027). During the heating it gives off about one and a half times its volume of gas; 20 grams of the metal yielded 12·3 c.c. of hydrogen and 4·1 c.c. of carbon monoxide. The faces of the crystals are often curved and the edges rounded; the usual form is a regular hexagonal prism, the basal planes being less brilliant than the prism faces. The angle of the corresponding rhombohedron is 80° 3′, and is intermediate between those of zinc and arsenic (Des Cloizeaux, C. R. 90, 1101). Its specific gravity is 1·74–1·75. It melts at a temperature just below 800°C. (V. Meyer, B. 20, 497), and boils a little higher than zinc. It preserves its silvery lustre in dry air, but soon tarnishes in moist air owing to the formation of a film of hydrated oxide. It is readily malleable, but only ductile at high temperatures. On the large scale it is usually pressed into wire while in a state of semi-fluidity. This is then flattened into ribbon, in which form it is most employed. It burns when heated in a flame in air with an intense white light, very rich in the chemically active violet rays; hence its use in photography. According to Roscoe, a burning magnesium wire of 0·297 mm. thickness evolves as much light as 74 stearin candles of which five go to the pound. The light of burning magnesium is also employed in signalling and pyrotechny. For the production of the so-called 'Bengal lights,' the following mixtures are recommended. For white fire, 1 part shellac is fused with 6 parts barium nitrate, the fused mixture ground and mixed with 2·5 p.c. of powdered magnesium. For red fire, 1 part shellac is fused with 5 parts strontium nitrate, and the ground mass mixed with 2·5 p.c. of magnesium. These mixtures may either be made into ribbons about a finger's breadth or may be charged into thin zinc tubes so as to serve as torches. On burning the zinc case burns along with the mixture.

The strength of magnesium has been determined at the mechanical experimental station at Charlottenburg, and shown to be very considerable. Its breaking coefficient for tensile strain per square mm. is 23·2 kilos.; specific resistance to compression, 27·2 kilos. per square mm.; bending strength, 17·4 kilos. At a temperature of 450°C. it can be rolled, pressed, worked, and brought into complicated forms. Screws and threads of magnesium are considerably sharper and more exact than those of aluminium (S. C. I. 6, 730).

Magnesium has no action on pure water, but in presence of a trace of platinum chloride it decomposes water rather quickly, evolving hydrogen and forming magnesium hydroxide. Platinised magnesium constitutes a good deoxidising agent; it reduces nitrobenzene, for instance, completely to aniline (Ballo, B. 16, 694). Dilute acids rapidly dissolve it with violent evolution of hydrogen; with dilute hydrochloric acid it inflames when first thrown in. Strong sulphuric acid acts slowly, and a mixture of this acid with fuming nitric acid has no action upon it at ordinary temperatures. Solutions of caustic alkalis have no action upon it, but, heated with solutions of ammonium salts, it evolves hydrogen and dissolves, forming a double salt of ammonium and magnesium. Aqueous solutions, however, of bicarbonates of soda or potash, as well as solutions of carbonic acid, dissolve the metal with evolution of hydrogen (Ballo, B. 15, 3003). Magnesium burns when heated in chlorine gas or bromine vapour, and especially brilliantly in the vapours of sulphur and iodine. It combines at determinate temperatures, when in a finely-divided state, with sulphur, phosphorus, and arsenic, and at a red heat decomposes oxides of carbon, sulphurous anhydride, and many hydrocarbons. Silica and boric acid are readily reduced by it. It combines directly with nitrogen, forming a crystalline nitride Mg_3N_2. It precipitates nearly all the metals from their neutral solutions in the metallic state, aluminium, uranium, and chromium as oxides.

Magnesium may be advantageously employed in place of zinc in toxicological investigations, owing to its freedom from arsenic. It may likewise be used instead of zinc in voltaic batteries, owing to its higher electromotive force (Roussin, J. Ph. [4] 3, 413).

Alloys.—Magnesium forms malleable alloys with potassium and sodium, which decompose water at ordinary temperatures. 15 parts of magnesium form with 85 parts of tin a brittle lavender-coloured alloy, which also decomposes water. An alloy with 5 p.c. of thallium is stable and more malleable than pure magnesium. With mercury it does not appear to form an amalgam at ordinary temperatures. Alloys with aluminium, zinc, cadmium, lead, bismuth, antimony, silver, gold, and platinum have also been prepared (Parkinson, C. J. [2] 5, 125) by fusing the metals together in a current of hydrogen, or by fusion in an earthen crucible under a flux of equal parts fluorspar and cryolite, or one part fluorspar with two parts of common salt. The magnesium was attached to the end of an iron rod and well stirred among the other metal, otherwise, being so light, it would float to the top. Triple alloys were also obtained with bismuth and copper, copper and gold, and with copper and nickel. All these alloys are brittle, showing a granular fracture, and are unfortunately too easily alterable for use in the arts.

Magnesium oxide. Magnesia. MgO. This is the product of the combustion of magnesium in air or oxygen. It is also formed when the carbonate or nitrate is ignited in the air. As thus obtained, it is a white amorphous powder, but may be obtained crystallised in cubes and octahedrons by ignition of the amorphous form in a current of hydrochloric acid gas. If ferric oxide be mixed with the magnesia, brilliant black octahedrons of magnoferrite $MgO.F_2O_3$ are formed, together with octahedrons of MgO, slightly yellow in colour, due to oxide of iron, and identical with those of periclase, a mineral found at Monte Somma, near Vesuvius. Ordinary magnesia is known in commerce as magnesia usta or calcined magnesia, and is much used for medicinal purposes. It is a fine bulky powder of sp.gr. 3·07 to 3·2. The sp.gr. is increased by heating in a pottery furnace to 3·61.

It is only fusible at the temperature of the oxyhydrogen blowpipe flame, and on again solidifying forms a hard enamel, which scratches glass like the diamond. It is alkaline to litmus, but is not caustic. It is almost insoluble in water; according to Fresenius, it requires 55,368 parts of either cold or boiling water to effect solution. This solution has an alkaline reaction.

Manufacture.—Magnesia is generally obtained commercially by gentle but prolonged ignition of the carbonate or by ignition of the hydrate. Since the discovery, however, of the immense stores of carnallite, the double chloride of potassium and magnesium, in the saline deposits of Stassfurt, several processes have been patented for utilising the waste magnesium chloride liquor obtained as by-product in the manufacture of potassium chloride.

Schlœsing, in 1881 (C. R. 93, 156, and 215), describes the following process for obtaining cheap magnesia. When dry slaked lime is moistened with solution of magnesium chloride it sets hard, and a fragment of the hardened mass suspended in a solution of magnesium chloride is entirely converted after a time into magnesium hydrate, the lime being removed as chloride. In actual practice, a paste of slaked lime and water containing 34-36 p.c. of calcium oxide is allowed to run through perforations in a metallic plate into a solution of magnesium chloride containing 60-95 grams per litre. As soon as the lime paste reaches the solution it becomes coated with a layer of magnesium hydrate, which acts like a shell, causing it to form long threads, which are entirely converted into magnesium hydrate in about six days. The hydrate thus obtained may be washed by diffusion, and, when triturated with water and dried, gives a compact, friable powder, which can of course be converted into calcined magnesia by ignition in a suitable furnace. Presence of common salt has no effect on the value of the process, but if soluble sulphates are present, they must be removed by adding some of the calcium chloride solution from a previous operation, allowing to settle, and decanting from the more insoluble calcium sulphate.

Wünsche (Ger. Pat. 18,722, July 1881) converts the chloride into carbonate in the following manner. From the solution of magnesium chloride, ammonium magnesium carbonate is precipitated in the form of a coarse crystalline powder by treatment with ammonium chloride and ammonia and passing a current of carbonic acid gas. The precipitate is washed with ammonia, and the moist double salt is then mixed with magnesia, when the whole of the magnesium present is converted to carbonate $Mg(NH_4)_2(CO_3)_2 + MgO = 2MgCO_3 + 2NH_3 + H_2O$. The magnesium carbonate is then calcined to oxide. The evolved ammonia and carbon dioxide in the two latter stages are recovered and used again.

Ramdohr, Blumenthal, & Co. in 1881 patented the following process (Ger. Pat. 19,259, Sept. 1881). A solution of magnesium chloride is evaporated until it consists approximately of $MgCl_2.6H_2O$. About 4-10 p.c. of magnesite is added, and the mixture heated to redness in a current of air until the evolution of hydrochloric acid gas ceases. Magnesium oxychloride is left, which, on heating with water, splits up into magnesium hydrate and chloride.

The United Chemical Works Joint Stock Co., Leopoldshall, in 1882, patented the following process (Ger. Pat. 20,277, Feb. 1882). Burnt lime is treated with a solution of calcium chloride. After removal of the clear liquid, the paste is washed with a fresh solution of calcium chloride, while the clear solution in turn is repeatedly digested with fresh lime. A small portion of this solution is then mixed with the magnesium chloride solution in order to precipitate all the iron and sulphuric acid which it contains. The purified magnesium solution is then added to the bulk of the clear calcium solution, which contains oxychloride of calcium $3CaOCaCl_2.16H_2O$, when pure hydrated magnesium oxide separates out.

Magnesia is now largely used on account of its infusibility in the manufacture of crucibles, cupels, firebricks, &c. For the preparation of magnesia crucibles, Johnson (Eng. Pat. 9,917, July 1884) roasts cakes of magnesite, gisbertite, periclase, or other magnesium minerals. If the crucible is required to be free from silica, magnesia obtained from sea-water is employed. Whatever the source, the product of the calcination is ground, mixed with 10-40 p.c. of caustic magnesia (the hydrate), and moistened with water containing starch, flour, or other binding material, and well rammed into moulds. The crucibles thus prepared, when dry, are ready for use for most purposes. If desirable, they may be exposed to a high temperature in a furnace.

Maxwell-Lyte (Eng. Pat. 4,889, April 1885) employs a process differing from the above in a few details. The oxide, as before, is first calcined at a strong white heat in order to prevent subsequent cracking of the manufactured article. This operation should be repeated two or three times, the material being recrushed and sieved after each roasting. It is then mixed either with water alone, with a solution of any soluble magnesium salt but the sulphate, or with 6-10 p.c. of 'heavy' magnesium hydroxide or 10-15 p.c. of lightly-burnt magnesia and water, and fashioned into the required article, which may then be fired for use. Addition of sawdust or flour to the mixture increases the porosity, and of powdered carbon the refractoriness. If it is required to be used in contact with fused metallic oxides it should first be well glazed.

For the preparation of magnesia tests and cupels the same patentee employs highly calcined magnesite. This is treated either with dilute hydrochloric acid or magnesium chloride solution, recalcined and sifted. It is then mixed with lightly-calcined magnesia or bone-ash, or with a metallic oxide or clay to impart strength, or with sawdust or flour to increase the porosity. Whilst the cupels are setting they should be kept moist to prevent cracking. After setting they may be fired.

For the manufacture of infusible bricks, Schlœsing (C. R. 101, 131) employs magnesium hydroxide obtained from sea-water. The sodium chloride present may be removed by repeated treatment with fresh water. Heated to redness, it loses its water and contracts, and at a white heat contracts still further, but if kept at this temperature for a short time it undergoes no further change on again heating. To convert the powdered product into bricks, 4 parts by weight are mixed with one part of magnesia which has only been heated to redness, and the mixture submitted to a pressure of 10,000 kilos. per square decimetre. The compressed bricks are then heated for a short time at a white heat in a circulatory furnace, burning gas or some liquid fuel.

Magnesium oxide prepared from the sulphate when mixed with 0·1 p.c. of chromic oxide shows a brilliant red fluorescence (Boisbaudran, C. R. 104, 330).

Magnesium suboxide. A substance of this nature appears to be formed when a solution of sodium or ammonium chlorides is electrolysed, using poles of magnesium wire, the positive pole becoming covered with a black deposit (Beetz, J. 1866, 172). The same substance is also obtained when magnesium is immersed in solutions of chlorides of the alkalis and alkaline earths, common salt giving the largest deposit. In a few days it disappears, being replaced by the ordinary white oxide. It turns white when heated just below redness. It dissolves in nitric acid with partial reduction of the acid. It readily dissolves in hydrochloric and sulphuric acids with effervescence, forming the ordinary chloride and sulphate (Gore, C. N. 50, 157).

Magnesium hydrate $Mg(OH)_2$ occurs native as the mineral *brucite*, crystallising in the rhombohedral section of the hexagonal system. The hydrate is precipitated as a white powder when hydrate of potash or soda is added to the solution of a magnesium salt. De Schulten (C. R. 101, 72) obtained it in the form of flattened hexagonal prisms, of sp.gr. 2·36 at 15°, by heating a mixture of 12 grams crystallised magnesium chloride $MgCl_2.6H_2O$, 340 grams of potash, and 60 c.c. of water, to 210-220°. The solid residue, after washing away the alkali, consisted of these small crystals of the hydrate. They were readily soluble in acids and in a warm solution of ammonium chloride.

Magnesium hydrate slowly absorbs carbon dioxide from the air. At a low red heat it loses its water, becoming converted into the oxide. This calcined magnesia is again capable of taking up water, with evolution of heat, to reform the hydrate.

Magnesium hydrate is much used upon the Continent for extracting sugar from molasses; it forms an insoluble granular crystalline magnesium saccharate, which when decomposed by carbon dioxide yields pure sugar.

In order to meet this demand the Consolidated Alkali Company of Stassfurt manufacture large quantities of magnesium hydrate by the following process. The 3 p.c. of sulphates contained in the last mother liquor from the extraction of potassium chloride from carnallite is first removed by means of a solution of calcium chloride. A quantity of milk of lime is then added rather less than sufficient to decompose the whole of the magnesium chloride; the precipitated magnesia is allowed to settle and then passed through filter presses, in which it is thoroughly washed. The magnesium hydrate thus obtained contains only 0·1 p.c. of calcium sulphate, and is eminently suitable for the purpose of the sugar refiner (Hake, S. C. I. 2, 149).

Magnesia prepared by ignition of the nitrate is converted by prolonged immersion in water into a form of the hydrate having the density of marble, but harder and more translucent. A similar form, but contaminated with oxide of iron and aluminium, magnesium carbonate and sand, is also obtained by action of water upon the product of the ignition of commercial magnesium chloride. This singular property of hardening is only possessed by magnesia prepared by ignition of the nitrate or chloride at a moderate red heat. After heating to whiteness it appears to lose it. Ignition of native magnesite at the lowest possible temperature also yields a product possessing the same hydraulic property, but the basic carbonates of commerce yield a hydrate perfectly soft. The paste prepared from calcined magnesite and water hardens in about half a day, and afterwards not only withstands the action of water, but actually acquires in contact with it the hardness of the best Portland cement.

A mixture of magnesia with a concentrated solution of magnesium chloride of sp.gr. 1·16–1·26 hardens in a short time to a compact mass of basic chloride, which resists the action of water. The pasty mixture is very plastic, and is capable of binding more than twenty times its weight of sand.

Magnesium chloride $MgCl_2$ is one of the salts present in sea-water and the water of many springs. It also occurs combined with potassium chloride in large quantities as the mineral *carnallite* $MgCl_2.KCl.6H_2O$ in the Stassfurt deposits. It is formed when magnesium burns in chlorine, or when a stream of chlorine is passed over a heated mixture of magnesium and carbon. It is also produced by dissolving the metal, oxide, or carbonate, in hydrochloric acid. On concentration of the solution monoclinic crystals of the composition $MgCl_2.6H_2O$ separate out. Crystals of this composition have also been discovered, associated with carnallite and rock salt, at Stassfurt, and named *bischofite*. On attempting to obtain the anhydrous chloride by ignition of these crystals, hydrochloric acid is evolved in addition to water, and a portion of the chloride becomes converted to oxide. If, however, the crystals be heated in a current of hydrochloric acid gas, the anhydrous chloride is obtained without the formation of any basic salt (Hempel, B. 21, 897). Another method of obtaining the anhydrous chloride is to add ammonium chloride to the solution, evaporate to dryness, and ignite in a platinum dish. The double chloride of ammonium and magnesium formed loses its water without any decomposition of the magnesium chloride, and the ammonium chloride can then be sublimed out, leaving the anhydrous magnesium chloride as a clear fused mass, which on cooling solidifies to a crystalline solid. 100 parts of water at 0° dissolve 52·2 parts of the anhydrous chloride, with considerable evolution of heat, forming a solution of sp.gr. 1·3619 at 15° (Engel, Bl. 47, 318). At the ordinary temperature 100 parts of water dissolve about 130 parts, and at 100° about 366 parts. This solution on cooling again deposits the crystals. Magnesium chloride solution possesses a bitter taste. The solid, either anhydrous or crystals, is very deliquescent. It combines directly, with evolution of heat, with methyl and ethyl alcohols, the solutions yielding, on cooling with ice, crystals of $MgCl_2.6CH_3OH$ and $MgCl_2.6C_2H_5OH$.

Commercial preparation.—The last mother liquor obtained in the process of preparing potassium chloride from the carnallite at Stassfurt supplies as by-product large quantities of magnesium chloride. The liquor has a sp.gr. of 1·32, and contains no less than 35 p.c. of the chloride. It is first evaporated to sp.gr. 1·34, when potassium and sodium chlorides and magnesium sulphate separate out. The hot concentrated liquor is then run into casks, where on cooling it solidifies to a white translucent mass containing 50 p.c. of magnesium chloride. In this state it is largely exported to this country, being used by cotton-spinners as a thread lubricator (Hake, S. C. I. 2, 149).

Lanquetin, in 1881, patented (Ger. Pat. 20,396) a process for preparing magnesium chloride by introducing burnt magnesite or dolomite into a solution of waste calcium chloride, and driving carbon dioxide through the mixture, when carbonate of lime separates out and magnesium chloride remains in solution.

Cochrane and Bramley, of Middlesbrough (Eng. Pat. 15,498, Nov. 1886), charge hydrated magnesium carbonate into a series of closed vessels through which a solution of calcium chloride is circulated, carbon dioxide being at the same time injected. Magnesium chloride is in this case also gradually formed in solution and carbonate of lime precipitated.

Magnesium chloride may also be extracted from the mother liquor of the potassium chlorate manufacture (Muspratt and Eschellmann, Widnes, Eng. Pat. 1,900, Feb. 1885).

Magnesium chloride unites with the alkaline chlorides to form crystalline double salts.

Magnesium potassium chloride

$MgCl_2.KCl.6H_2O$,

the carnallite of Stassfurt, crystallises in colourless deliquescent rhombic prisms. On heating, the water is driven off without loss of chlorine, the anhydrous mixture fusing at a red heat. The native carnallite used at Stassfurt for the extraction of potassium and magnesium chlorides has the following average composition (Hake, S. C. I. 2, 149):

KCl	16·2	$CaCl_2$	0·2
$MgCl_2$	24·3	Clay and $CaCO_3$	2·1
$MgSO_4$	9·7	H_2O	28·8
NaCl	18·7		

Magnesium ammonium chloride

$MgCl_2.NH_4Cl.6H_2O$

is deposited from mixed solutions of magnesium and ammonium chlorides in small rhombic crystals.

The corresponding sodium salt appears to contain only one molecule of water (Poggiale, C. R. 20, 1130).

Magnesium calcium chloride, *Tachydrite*, $2MgCl_2.CaCl_2.12H_2O$, is also found at Stassfurt in deliquescent yellowish masses.

Magnesium oxychlorides. When highly calcined magnesia is treated with a strong solution of magnesium chloride, it dries in a few hours to a hard mass of oxychloride, capable of receiving a polish. A sample prepared in this manner, and hardened by six months' exposure in the air, was found to consist of a mixture of $MgCO_3$ with a compound $MgCl_2.5MgO.17H_2O$. On heating to 180° it was converted into $MgCl_2.5MgO.6H_2O$. By prolonged treatment with water the whole of the magnesium chloride was extracted, and the compound $2MgO.3H_2O$ left. This residual hydrate is a compact solid as hard as sandstone, possessing a brilliant surface, and taking a high polish; its cohesive power is not impaired by either cold or hot water (Bender, A. Ch. 159, 341).

The crystalline deposit frequently found in bottles containing magnesia mixture (magnesium sulphate or chloride, ammonia, and ammonium chloride) consists of a hydrated oxychloride $MgCl_2.5MgO.13H_2O$. On washing the crystals with a large quantity of water the whole of the chloride may be removed, the residue consisting of hydrated oxide (Davis, C. N. 25, 258).

By mixing freshly calcined magnesia with a solution of magnesium chloride in a flask well corked and nearly filled with the liquid, and heating on a water-bath with frequent agitation, needle-shaped crystals of an oxychloride are formed. When washed and dried at 110° they consist of $MgCl_2.10MgO.14H_2O$. The dry crystals are not attacked by carbon dioxide, but when moist are decomposed (Krause, A. 165, 38).

When 20 grams of calcined magnesia are boiled with a solution of 400 grams magnesium chloride in 500 grams of water and the solution filtered, the filtrate deposits needles of $MgCl_2.MgO.16H_2O$. When dried *in vacuo* they are converted into $MgCl_2.MgO.6H_2O$. Both salts are decomposed by water and alcohol (André, C. R. 94, 444).

When crystallised magnesium chloride is heated in air, an oxychloride of variable composition appears to be left, a portion of the chlorine passing away in the form of hydrochloric acid. If the chloride be heated to a sufficiently high temperature in a current of air a certain amount of free chlorine is evolved; and if a mixture of hydrochloric acid gas and air is passed over the heated chloride, especially in presence of a little free magnesia, a larger quantity of chlorine is obtained in the free state. This reaction forms the basis of the Weldon-Pechiney process of manufacturing chlorine, as worked at Salindres (Weldon, Eng. Pats. 9,307, June 1884, and 11,036, Aug. 1884). A solution of magnesium chloride is first evaporated down until it approximately consists of $MgCl_2.6H_2O$. This is then converted to oxychloride by addition of 1½ equivalents of calcined magnesia. This oxychloride is crushed and sifted, solid pieces free from dust being eventually chosen not larger than the size of a walnut. It is next heated to remove a portion of its water, and finally decomposed by heating to a high temperature in a current of air. The furnace employed for the latter process is constructed upon the principle of a baker's oven. It consists of a series of vertical chambers, the thickness of the dividing walls of which is greater than the width of the spaces between them. Before charging these spaces with the small lumps of oxychloride, products of combustion are passed through them until the dividing walls are raised to a high temperature. After charging, the oxychloride becomes heated by contact with the walls, and a mixture of chlorine, nitrogen, excess of air, and hydrochloric acid is evolved. The hydrochloric acid is condensed in ordinary towers, and the remaining gases pass on to the bleaching powder chambers. The magnesium remains as oxide, the oxygen being furnished by a regulated supply of air, and is afterwards partly dissolved in the condensed hydrochloric acid for preparation of more oxychloride (Weldon, S. C. I. 4, 175). The reactions occurring in the process are probably as follows:

(1) $H_2O + MgCl_2 = MgO + 2HCl$.
(2) $2HCl + O = H_2O + Cl_2$.
(3) $MgCl_2 + O = MgO + Cl_2$.
(Kingzett, S. C. I. 7, 286.)

Nithack (Ger. Pat. May 29, 1884) decomposes magnesium chloride for the preparation of chlorine by injecting a fine spray of the solution into heated chambers, when the same reactions occur.

Hermite (S. C. I. 7, 726 and 737) prepares chlorine for bleaching purposes by the electrolysis of a solution of magnesium chloride.

Magnesium bromide $MgBr_2$ occurs in sea-water and many salt springs. It very much resembles the chloride, being deposited from a solution of magnesia in hydrobromic acid in needles of $MgBr_2.6H_2O$, which behave like the chloride on heating.

Magnesium iodide MgI_2 also occurs in sea-water and saline springs, and may be obtained by dissolving magnesia in hydriodic acid, when deliquescent crystals separate, which readily evolve iodine on warming.

Magnesium fluoride MgF_2 occurs native in the mineral *sellaïte* in colourless quadratic crystals, and may be prepared in an amorphous form by evaporating magnesia with excess of hydrofluoric acid. When the amorphous form is fused with sodium chloride and gradually cooled, it is obtained, after washing with water, in crystals resembling those of sellaïte.

Feldmann (Eng. Pat. 15,295, Nov. 1887) patents a process for an industrial preparation of this salt. Magnesium chloride is treated with calcium fluoride in either the dry or the wet way. In the former the fluorspar is mixed with the anhydrous chloride in excess, and the mixture fused at a red heat, when $CaCl_2$ and MgF_2 are formed. After cooling, the mass is lixiviated, when the magnesium fluoride remains behind. In the wet method powdered fluorspar is suspended in a concentrated solution of magnesium chloride and heated till double decomposition occurs, water being added to make up the loss by evaporation. It is then allowed to cool, when the mass solidifies and is lixiviated as before. Any undecomposed calcium fluoride may be removed by elutriation from the specifically lighter magnesium fluoride.

A double fluoride of magnesium and sodium $MgF_2.NaF$ is obtained in insoluble cubical crystals by fusing magnesium chloride with a large excess of sodium fluoride and chloride and allowing to cool slowly. · Also in amorphous state by boiling a solution of sodium fluoride with magnesia.

Magnesium carbonate $MgCO_3$ occurs native as *magnesite* in rhombohedral crystals isomorphous with those of calcite. It is also found in large compact or granular masses, and, combined with calcium carbonate, as dolomite $(MgCa)CO_3$, in immense quantities all over the world. The amorphous precipitate formed when an alkaline carbonate is added to a solution of a magnesium salt has the composition $MgCO_3.2H_2O$, but after standing an hour or two at a temperature below 16°, it becomes converted into tabular crystals of $MgCO_3.5H_2O$. If the temperature exceeds 22° it becomes converted into prismatic crystals of $MgCO_3.3H_2O$. Between 16° and 22° both these salts are formed. The amorphous precipitate is decomposed by water into a basic carbonate of the composition

$$5MgO.4CO_2.11H_2O$$

or $5(MgCO_3.2H_2O)$, in which one molecule of $MgCO_3$ has been converted into $Mg(OH)_2$. This basic carbonate absorbs carbon dioxide from the air, and becomes $MgCO_3.2H_2O$ again (Engel, C. R. 100, 911). According to Marignac, normal magnesium carbonate is also formed by the action of magnesium chloride on calcium carbonate.

When the precipitated carbonate is suspended in water and dissolved by the passage of a current of carbon dioxide, on evaporation of the solution the anhydrous carbonate is precipitated in minute crystals isomorphous with arragonite, the rhombic form of calcium carbonate. On the other hand, when mixed solutions of a soluble magnesium salt and an alkaline bicarbonate supersaturated with carbon dioxide are inclosed in a strong vessel closed by a cork, through which the carbon dioxide is slowly allowed to escape, microscopic rhombohedrons of the anhydrous carbonate resembling those of native magnesite and calcite are deposited.

Both the natural and artificial varieties of magnesium carbonate give an alkaline reaction with litmus solution. They dissolve slowly in acids with but little effervescence.

Magnesium carbonate dissolves in water saturated with carbon dioxide. According to Engel (C. R. 100, 444, and 1224) the solubility at constant temperature is proportional to the cube-root of the pressure of the carbon dioxide. The results of a large number of experiments agreed with those calculated from the general formula $x^{\cdot 333} = ky$ or $y = \frac{1}{k}\sqrt[3]{x}$, where x represents the pressure of carbon dioxide, y the quantity dissolved, and k a constant $= 0{\cdot}03814$. At different temperatures under atmospheric pressure the amount of magnesium carbonate dissolved is proportional to the coefficient of solubility of carbon dioxide at the particular temperature. The following table is given by Engel and Ville (C. R. 93, 340) showing the solubility first at constant temperature and second at constant pressure:

Atmospheres pressure	Temperature	$MgCO_3$ dissolved in a litre of water
	°	
1	19·5	25·79
2·1	19·5	33·11
3·2	19·7	37·30
4·7	19·0	43·50
5·6	19·2	46 20
6·2	19·2	48·51
7·5	19·5	51·20
9·0	18·7	56·59
mm. pressure		
751	13·4	28·45
763	19·5	25·79
762	29·3	21·94
764	46·0	15·70
764	62·0	10·35
765	70·0	8·10
765	82·0	4·90
765	90·0	2·40
765	100·0	0·00

When the solution in carbonic acid is left to evaporate spontaneously, or kept in a partially closed flask for some time at 50°C., it deposits small hexagonal prisms of $MgCO_3.3H_2O$, which effloresce in air, becoming opaque. At a winter temperature the same solution deposits monoclinic prisms of $MgCO_3.5H_2O$. Warmed with water at 50°C., they are converted into the triaquate, while on boiling with water they lose carbonic acid and become converted eventually into the basic carbonate $2MgCO_3.Mg(OH)_2.2H_2O$.

Basic carbonates. A basic carbonate of the composition $3MgCO_3.Mg(HO)_2.3H_2O$ occurs native as hydromagnesite in small white monoclinic crystals of sp.gr. 2·14-2·18. A salt of the same composition is also obtained by mixing magnesium sulphate with excess of a hot solution of potassium carbonate and boiling the precipitate with fresh quantities of water so long as acid carbonate dissolves out. Also by boiling a saturated solution of the acid carbonate, and twice boiling the precipitate produced with fresh quantities of water. When dried at 100° in the air it absorbs carbon dioxide, and is converted into $5MgO.4CO_2.5H_2O$.

Another basic carbonate of the composition $2MgCO_3.Mg(OH)_2.2H_2O$ is obtained as above from the solution of the normal carbonate in carbonic acid. Also, according to Fritzsche (P. 37, 310), by precipitating magnesium sulphate with a very large excess of sodium carbonate and boiling till granular, then washing rapidly three times with fresh boiling water.

Commercial carbonates. The commercial preparation known as *magnesia alba* is a basic carbonate of slightly varying composition, according to the conditions of production. It is usually prepared by precipitation of either the commercial sulphate or chloride of magnesium with sodium carbonate. As thus obtained it is a very light bulky powder, and is distinguished as *magnesia alba levis*. If the precipitation is carried on at a higher temperature by the addition of one volume of a cold saturated solution of sodium carbonate to a boiling mixture of one volume of a saturated solution of magnesium sulphate with thirty volumes of water, the precipitate washed with hot water and dried at 100°, a denser form is obtained known as *magnesia alba ponderosa*. The composition of the light variety is generally given as the same as that of hydromagnesite $3MgCO_3.Mg(OH)_2.3H_2O$. Beckurts (Ar. Ph. [3] 18, 429; 19, 13), however, deduces the formula $5MgCO_3.2Mg(OH)_2.7H_2O$, but also found several specimens of the hydromagnesite formula, but containing $4H_2O$. Kraut (Ar. Ph. [3] 20, 180) gives $4MgCO_3.Mg(OH)_2$ as the correct formula. Hence it appears likely that different samples vary somewhat in composition. As representing the composition of the heavy variety, Beckurts (*l.c.*) gives the formula $3MgCO_3.Mg(OH)_2.4H_2O$, which only differs from that of hydromagnesite by one molecule of water.

Magnesia alba levis and *ponderosa* yield upon calcination corresponding light and heavy varieties of the oxide, known in commerce as *magnesia usta levis* and *magnesia usta ponderosa*.

Another method of preparing magnesia alba was patented by Pattinson. This consists in treating slightly-ignited dolomite with water and carbon dioxide under a pressure of 5–6 atmospheres. So long as any magnesium carbonate remains undissolved, the calcium carbonate remains unattacked, the acid carbonate of magnesium being much more readily formed. This solution of hydrogen magnesium carbonate is decanted from the carbonate of lime and heated by injection of steam, when *magnesia alba* is precipitated as a white bulky powder of loose texture. Unignited dolomite does not yield any acid carbonate with carbonic acid.

Bramley and Cochrane, of Middlesbrough, have patented a process (Eng. Pat. 13,762, Oct. 1886) in which magnesia is added to the solution of an alkaline bicarbonate or sesquicarbonate and the mixture heated and agitated. The alkaline carbonate is converted to a normal carbonate, and hydrated magnesium carbonate formed. The operation is performed in closed vessels to prevent loss of carbon dioxide.

Magnesia alba can also be profitably prepared from sea-water (Gutzkow, D. P. J. 270, 30). The mother-liquor (bittern) obtained after extraction of common salt (bay-salt) is treated with milk of lime; the precipitated magnesium hydrate is allowed to settle, the supernatant liquid removed by decantation, and the precipitate stirred up with water through which a stream of carbon dioxide is passed. The hydrate is dissolved as acid carbonate. The clear solution is then heated rapidly to 70°C., and afterwards more gradually to the boiling-point. The precipitated *magnesia alba* is filtered off and dried on plates heated by steam. If necessary, the original mother-liquor may first be freed from organic matter by treatment with alum.

Magnesia alba is almost insoluble in water, but dissolves readily in solutions of ammonium salts owing to the formation of soluble double salts of magnesium and ammonium and carbonate of ammonia.

Magnesium ammonium carbonate

$$MgCO_3.(NH_4)_2CO_3.4H_2O$$

separates in rhombohedral crystals from a mixture of cold aqueous solutions of sulphate or chloride of magnesium and excess of ammonium carbonate and free ammonia.

Magnesium potassium carbonate

$$MgCO_3.K_2CO_34H_2O$$

is obtained in small rhombic prisms when *magnesia alba* is digested with a solution of bicarbonate of potash for fifteen hours at 60–70°C.

A salt of the composition

$$MgCO_3.HKCO_3.4H_2O$$

is obtained in large crystals from a cold aqueous mixture of chloride or nitrate of magnesium with excess of bicarbonate of potash. Engel (C. R. 100, 1224) obtained the same salt by decomposing a solution of the acid carbonate of magnesium with potassium bicarbonate, and also by direct action of the bicarbonate of potash upon normal magnesium carbonate.

Magnesium sodium carbonate $MgCO_3.Na_2CO_3$ is similarly obtained in small anhydrous crystals by digesting *magnesia alba* with sodium bicarbonate.

Magnesium nitrate $Mg(NO_3)_2$ occurs in the mother-liquors of the saltpetre manufacture, and also frequently in well-water. It may readily be prepared by dissolving *magnesia alba* in nitric acid and evaporating to small bulk, when monoclinic prisms and needles of the hydrated salt $Mg(NO_3)_2.6H_2O$ separate out. These are soluble in half their weight of cold water, and also in nine times their weight of alcohol of sp.gr. 0·84, with which magnesium nitrate forms an alcoholate of the composition $Mg(NO_3)_2.6C_2H_6O$. When dried over sulphuric acid the crystals lose four molecules of their water, and at the temperature of melting lead another molecule is evolved, leaving the salt $Mg(NO_3)_2.H_2O$. When this latter salt is heated to a still higher temperature the last molecule of water is given off, together with part of the nitric acid, and a tri-magnesium nitrate $Mg_3(NO_4)_2$, analogous to the tri-orthophosphate, is left.

Magnesium sulphite $MgSO_3$. When water containing magnesium hydrate in suspension is saturated with sulphur dioxide, the solution concentrated *in vacuo* at a temperature below 100° and then allowed to cool, rhombohedral crystals of $MgSO_3.6H_2O$ are deposited (Hartog, C. R. 104, 1793).

A basic magnesium sulphite of the composition $MgSO_3.2Mg(OH)_2$, similarly prepared by passing sulphur dioxide into water holding magnesia in suspension, is used in sugar factories (Bergreen and Licht, B. C. 1884, 201).

Magnesium sulphate (*Epsom salts*) $MgSO_4$ occurs in the mineral *kieserite* $MgSO_4.H_2O$, in the Stassfurt salt beds; and as *epsomite* $MgSO_4 7H_2O$ in the gypsum quarries of Montmartre, in Spain, Chili, and in the Mammoth Cave, Kentucky. Kieserite is occasionally found in rhombic prisms, but more generally occurs in granular masses. Epsomite is found both in the massive state and in silky fibrous crystals. Natural crystals of epsomite more than a centimetre long have also been found coating the walls of a gypsum quarry in the Department of Hérault, France. The sulphate was in a constant state of exudation, and as it solidified formed a lustrous coating of crystals upon the surface of the gypsum (De Rouville, C. R. 87, 703).

Magnesium sulphate forms the purgative principle of bitter spring waters (hence its name of Bitter salt) such as those of Epsom in Surrey, and Seidlitz, Saidschütz, and Püllna in Bohemia. At the three latter places it is obtained by digging pits into which the bitter water runs, and allowing the solution thus collected to evaporate in shallow pans.

The magnesium sulphate of commerce is now chiefly obtained from the kieserite of Stassfurt.

The crude kieserite obtained from the upper layers (Abraumsalz) of the Stassfurt beds is first freed from magnesium and sodium chlorides by being placed in large sieves, standing in tanks of water. The two salts mentioned dissolve out, whilst the kieserite, which is very sparingly soluble in water, falls through the meshes of the sieves in a state of fine powder. Any gangue or other impurities such as anhydrite or larger lumps of rock salt remain behind in the sieves. The kieserite powder is then packed into conical wooden moulds, where it sets to a compact solid, owing to its combining with six more molecules of water to form epsomite. This solid 'stone' is then dried and afterwards powdered. In this condition it contains from 80 to 90 p.c. of $MgSO_4$ and about 1 to 2 p.c. of sodium chloride. A large quantity is brought into the market in this form. The rest is crystallised from water and brought into commerce as Epsom salts.

Another mode of manufacturing magnesium sulphate, which was almost universally employed before the working of the Stassfurt beds, consists in decomposing dolomite, magnesian limestone $(CaMg)CO_3$, with oil of vitriol. As calcium sulphate is only sparingly, while magnesium sulphate is readily soluble, the separation affords no difficulty.

The dolomite is first calcined, when on treatment of the hot mass with a small quantity of water it is readily broken up into powder. This powder is then suspended in water in large digesters constructed of wood lined inside with lead and Yorkshire flags. For a digester 6 feet square and 7 feet deep, about 3 tons of dolomite would form a convenient charge. Into this emulsion are then poured the contents of twelve carboys of sulphuric acid, and water added until the specific gravity becomes 1·125 to 1·150. At the end of an hour, when the contents begin to cool down, steam is injected by a leaden pipe which completes the action. Excess of acid must be carefully avoided, as it causes loss in crystallising. The liquor is then run off into a settler made of lead or flags, but not of iron; after settling the clear solution is siphoned over into an iron evaporating pan, where it is evaporated down to 66° of Twaddell's hydrometer. The clear concentrated liquor is allowed to stand an hour or two to allow any suspended matter to settle, after which it is conveyed to the coolers, which are made of wood, flags, or, best of all, slate, where it is agitated so as to cause the salt to fall in small crystals. The crystals are then drained and finally dried on shelves in a stove room at a temperature not exceeding 80°F.

Magnesium sulphate is largely used in the Lancashire cotton trade in the process of warp-sizing; it is also employed for medicinal and agricultural purposes and for dyeing with the aniline colours.

The crystals have the composition of epsomite $MgSO_4.7H_2O$, and form right rhombic prisms, resembling those of the sulphates of zinc and nickel. They have a specific gravity of 1·676 (Thorpe and Watts, C. J. 37, 106). On heating they melt in their water of crystallisation, lose 6 molecules of water at 150° and the seventh at 200°.

A salt also having the composition $MgSO_4.7H_2O$ is occasionally deposited from cold supersaturated solutions in monoclinic prisms isomorphous with those of ferrous sulphate $FeSO_4.7H_2O$. By crystallisation of the ordinary salt above 40° monoclinic prisms of a hydrate $MgSO_4.6H_2O$, of sp.gr. 1·734, are obtained. By drying the heptahydrate over oil of vitriol to constant weight, $MgSO_4.5H_2O$, of sp.gr. 1·869, is obtained. A salt of the composition $MgSO_4.2H_2O$ may also be prepared by boiling finely powdered Epsom salts with absolute alcohol, sp.gr. 2·373. The specific gravity of the monohydrate $MgSO_4.H_2O$ is 2·445 and that of the anhydrous salt 2·709 (Thorpe and Watts, *l.c.*).

Magnesium sulphate is readily soluble in water. According to Gay-Lussac 100 parts of water dissolve 25·76 parts of the anhydrous salt at 0° and 0·47816 parts for every degree beyond. One part of Epsom salts dissolves in 0·79 parts of water at 18°·75, forming a liquid of sp.gr. 1·2932.

The following table, as determined by Schiff (A. 108, 336), shows the amounts of the sulphate in solutions of different specific gravities:—

Sp.gr. at 23°	Per cent. of $MgSO_4.7H_2O$	Per cent. of $MgSO_4$
1·0048	1	0·488
1·0096	2	0·975
1·0193	4	1·951
1·0290	6	2·928
1·0387	8	3·904
1·0487	10	4·878
1·0587	12	5·854
1·0688	14	6·830
1·0790	16	7·806
1·0894	18	8·782
1·0997	20	9·756
1·1103	22	10·732
1·1209	24	11·708
1·1316	26	12·684
1·1426	28	13·660
1·1536	30	14·634
1·1648	32	15·610
1·1760	34	16·586
1·1875	36	17·562
1·1991	38	18·538
1·2108	40	19·512
1·2228	42	20·488
1·2349	44	21·464
1·2472	46	22·440
1·2596	48	23·416
1·2722	50	24·390
1·2850	52	25·366
1·2980	54	26·341

Magnesium sulphate also dissolves in dilute alcohol, but is insoluble in absolute alcohol.

Magnesium hydrogen sulphate $MgH_2(SO_4)_2$. If 2 parts of anhydrous magnesium sulphate are dissolved in 100 parts of boiling sulphuric acid of sp.gr. 1·7 and the solution evaporated at the boiling-point, $MgH_2(SO_4)_2$ is deposited in prisms. On cooling, an acid salt of the composition $MgSO_4.3H_2SO_4$ crystallises out in small shining tables which fuse and decompose when heated.

Magnesium sulphate forms an isomorphous series of double salts with the sulphates of the alkali metals, of the general formula

$$MgSO_4.M_2SO_4.6H_2O,$$

which crystallise in monoclinic prisms. The potassium salt is found native in the Stassfurt deposits as *schönite*, and the ammonium salt together with a smaller quantity of the potassium salt has been found in the boric acid lagoons of Tuscany at Sasso and Acquaviva, which are poorest in boric acid.

Magnesium citrate $Mg_3(C_6H_5O_7)_2.14H_2O$ is obtained as a crystalline crust when magnesia is dissolved in slightly more than an equivalent quantity of a solution of citric acid, and the solution evaporated at about 50°. It is very soluble in water, and is often preferred as a mild purgative to Epsom salts on account of its pleasanter taste.

The citrate of magnesia of the shops, so popular as an effervescent salt, may be prepared by mixing 16 parts of sodium bicarbonate, 10½ of tartaric acid, 4 of citric acid, about 12 of sugar, ½ part of Epsom salts, and 2 parts of crystallised sodium bisulphate, and heating on an enamelled iron plate until it becomes spongy from the escape of carbon dioxide. The cooled mass is then put through sieves of four to six meshes per square inch. In this granular form it is again heated until quite dry. The solution of the granules in water, after the liberation of the carbon dioxide, contains principally citrate and tartrate of soda and sugar.

It may also be prepared by making a mixture of magnesium citrate, prepared by dissolving magnesia in citric acid solution and crystallising, with sodium bicarbonate, citric acid and sugar, and rendering granular by moistening with alcohol and drying.

The magnesia preparation called *sinodor*, used for removing unpleasant odours and for disinfecting and preserving purposes, is obtained by heating neutral magnesium acetate with magnesium oxide until the mass assumes a pasty consistency. It consists of basic magnesium acetate containing excess of magnesium hydrate (Kubel, Pat. 18,090, Nov. 1881).

A. E. T.

MAGNETIC PYRITES, known also as *Pyrrhotine* or *Pyrrhotite*, occurs occasionally in six-sided crystals, belonging apparently to the hexagonal system; but is usually found in granular or compact masses, with a platy structure sometimes mistaken for cleavage. From ordinary pyrites it is distinguished by its colour, which is bronze-yellow or tombac brown, and by its magnetic properties which are sometimes feeble though in rare cases the mineral exhibits polarity. It is readily scratched by the knife (hardness 3·5 to 4·5), giving a greyish streak, whence it may be distinguished from the much harder iron-pyrites. Sp.gr. 4·5–4·6. In chemical composition pyrrhotite comes very near to FeS (which requires 63·6 Fe, 36·4 S); but there is always a slight excess of sulphur, generally suggesting Fe_7S_8 (or 60·5 Fe, 39·5 S). Habermehl gives Fe_7S_8 as the formula for the variety from Bodenmais; while Lindström regards Fe_8S_9 as representing the commonest type. According to Rammelsberg the general formula may be written Fe_nS_{n+1}, where n varies from 6–11. Some mineralogists regard pyrrhotite as a mixture of FeS and Fe_2S_3, in variable proportions. It is notable that nickel is very commonly present in magnetic pyrites, in some cases up to 5 or 6 p.c., and the mineral is often worked for the sake of this metal. Cobalt may also be present. It is said that those varieties which are richest in nickel are generally feeblest in magnetic properties. The principal localities are Bodenmais, in Bavaria; Waldenstein, Carinthia; Falun, Sweden; Modum and Kongsberg, Norway; and Minas Geraes in Brazil. A similar, if not identical, mineral is found in certain meteorites.

F. W. R.

MAGNETIC IRON ORE *v.* Iron.

MAGNETITE *v.* Iron; also *v.* Lodestone.

MAGNOFERRITE *v.* Iron.

MAIROGALLOL *v. Pyrogallol*, art. PHENOL AND ITS HOMOLOGUES.

MAIZE *v.* CEREALS.

MAIZE *v.* AZOXY- COLOURING MATTERS.

MALACHITE. An ore of copper, crystallising in the monoclinic system, but usually occurring in mammillated and botryoidal forms, or in fibrous, compact or earthy masses. It is a basic copper carbonate, containing $H_2Cu_2CO_5$ (or $CuCO_3 + H_2CuO_2$), having a sp.gr. of 3·7 to 4·1, and hardness 3·5 to 4. Heated in a tube, it evolves water and turns black, while on charcoal it yields metallic copper. Malachite is frequently found as an alteration-product of other copper ores, and occurs as a pseudomorph after cuprite. If derived from copper-pyrites it is generally accompanied by limonite. Malachite is not only important as an ore of copper, but is valued as an ornamental stone, since its vivid colours are frequently arranged in regular zones due to its stalagmitic origin. It is chiefly used for vases and small boxes, but its comparative softness stands in the way of its extensive use in jewellery. Large slabs are not generally attainable, but small pieces are skilfully joined together, the interstices being filled in with powdered malachite, and the whole polished; in this way it becomes easy to employ it for inlaid and incrusted furniture, especially for table-tops of considerable size. Malachite is also used to a limited extent as a green pigment, but the term 'malachite green' has been extended to certain organic dyestuffs. Malachite is widely distributed as a mineral, being found in greater or less quantity in most copper-deposits, but the finest examples occur near Nischne Tagilsk, in Siberia, and in South Australia. F. W. R.

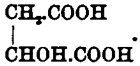
MALACHITE GREEN *v.* TRIPHENYLMETHANE COLOURING MATTERS.

MALAYAN CAMPHOR *v.* CAMPHORS.

MALAY FERN *v.* FILIX-MAS.

MALEIC ACID *v.* FUMARIC ACID.

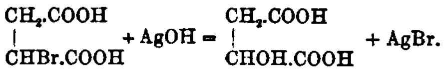
MALIC ACID (*Acide malique*, Fr.; *Aepfelsäure*, Ger.)



$$\begin{array}{l}CH_2.COOH\\ |\\ CHOH.COOH\end{array}$$

This acid, which occurs widely distributed in the juices of plants, was discovered by Scheele, in 1785, in sour apples. At the present day it is generally prepared from the unripe berries of the rowan (*Sorbus aucuparia*). The expressed juice is evaporated, filtered, heated to boiling, and saturated with milk of lime. The calcium malate which separates is dissolved in hot dilute nitric acid (1 : 10); on cooling, the solution deposits the acid malate, which is purified by recrystallisation from water. In order to obtain malic acid from it, its solution is precipitated with lead acetate and the lead salt is decomposed with sulphuretted hydrogen.

It has been obtained artificially by boiling a solution of bromosuccinic acid with moist silver oxide:

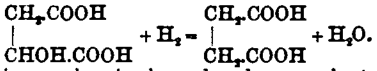


$$\begin{array}{l}CH_2.COOH\\ |\\ CHBr.COOH\end{array} + AgOH = \begin{array}{l}CH_2.COOH\\ |\\ CHOH.COOH\end{array} + AgBr.$$

Also by the action of nitrous acid on asparagine and aspartic acid; by the partial reduction of tartaric acid with hydriodic acid; and by heating fumaric acid with caustic soda at 100°.

Crystallises with difficulty, in deliquescent needles. Very soluble in water and in alcohol. The natural product is optically active; in concentrated solutions it is dextrorotatory, in dilute solutions lævorotatory; the addition of acids, thus of sulphuric acid, also causes a dextrorotatory solution to become lævorotatory. The artificial acid from bromosuccinic acid or from fumaric acid is inactive.

By reduction with hydriodic acid it yields succinic acid



$$\begin{array}{l}CH_2.COOH\\ |\\ CHOH.COOH\end{array} + H_2 = \begin{array}{l}CH_2.COOH\\ |\\ CH_2.COOH\end{array} + H_2O.$$

Calcium malate is also reduced to succinate by fermentation with yeast. Hydrobromic acid converts it into bromo-succinic acid. When heated with water at 180° it breaks up into fumaric acid and water. By destructive distillation it yields fumaric acid, maleic acid, maleic anhydride, and water.

The normal malates of the alkalis are deliquescent and crystallise with difficulty, but the corresponding acid salts crystallise well; thus *hydrogen ammonium malate* $C_4H_5O_5(NH_4)$ forms rhombic prisms. *Calcium malate* $C_4H_4O_5Ca.H_2O$ separates as a crystalline powder on boiling a solution of malic acid which has been neutralised with lime; the acid salt $(C_4H_5O_5)_2Ca,6H_2O$ crystallises in sparingly soluble rhombic octahedra.

Free malic acid gives with lead acetate a bulky precipitate which, on boiling, cakes together as a resinous mass and partly dissolves. A concentrated solution of an alkaline malate gives with calcium chloride on boiling a precipitate of calcium malate. Ammonium salts prevent the precipitation, addition of alcohol aids it. F. R. J.

MALLEABLE CAST IRON *v.* IRON.

MALLOTOXIN *v.* RESINS.

MALT *v.* BREWING.

MALTHA. A variety of 'mineral tallow' or wax, soluble in alcohol, naphtha, and oil of turpentine, said to be originally found on the coast of Finland, sp.gr. 0·77. It is white, brittle, and stains paper like oil, melts at a moderate heat, and burns with a smoky flame. A similar hydrocarbon is met with in the oil-fields of California.

MALTOSE, *Maltobiose*, *Amylon*, $C_{12}H_{22}O_{11}$; $C_{12}H_{22}O_{11}.H_2O$. De Saussure (Bibl. Brittanique, 56, 1814, 333; P. 1819, 29, 58) may have obtained this sugar when studying the products of the spontaneous decomposition of starch paste, when exposed to the air at 20–25°. Guérin-Varry (A. Ch. 60, 32; 61, 66) described accurately how the body could be prepared in the crystallised state and some of its properties, but failed to recognise it as a distinct substance; Jacquelain (A. Ch. 63, 167) added nothing to Varry's work; Dubrunfaut (A. Ch. [3] 21, 78) prepared the body according to Varry's method, observed that it was less soluble in alcohol than dextrose, and had an optical activity three times as great, *i.e.* $[\alpha]_j = 58 \times 3 = 174$, a figure so high as to lead one to believe that he had not a pure body in his hands; he recognised it as a distinct body and called it *maltose*; he, however, looked upon it as a glucose, *triglucose*; O'Sullivan (C. J. 1872, 576; 1876, 478) showed that it was not a glucose but a saccharose, and from this and a fuller description of its characters gave it a place among chemical entities.

Occurrence.—It is present in some commercial glucoses and in beer (Valentin, J. S. A. 24, 404); probably in bread; in *amé*, a rice-extract prepared in Japan (Yoshida, C. N. 43, 29), and in germinated cereals to the extent of 1–2 p.c. (O'Sullivan, C. J. 49, 58). After feeding with amylaceous substances it is found in the intestinal canal, but the blood of the mesenteries contains only dextrose. If injected into a vein, it is found in the urine; if injected subcutaneously, it is partially converted into dextrose (Phillips, B. C. 1882, 127). Some of the reducing sugars of blood may be maltose.

Formation.—Diastase converts starch and the dextrins into maltose (O'Sullivan, *l.c.*). The ferment of saliva, ptyalin, of the pancreas, and of the liver, act in the same way (Nasse, Jb. f. Thie. Chem. 1877, 62; Musculus a. v. Mering, Z. 2, 403). The same ferments act on glycogen, maltose being amongst the products; dextrose is present when saliva is employed (Kütz, Pfh. Archiv, 24, 8). All mineral acids and many organic acids act on starch and glycogen; maltose is amongst the products.

Preparation.—100 grams purified starch are mixed as completely as possible with 300 c.c. water at 40°, and then poured with continuous stirring into 2 litres of boiling water. The paste is cooled to 60° and the extract from 20 grams pale malt added to it; the mixture is kept at 60–63° for four or five hours, and the solution may be allowed to cool and stand for a few days. At the end of that time it is evaporated, best in a vacuum, to 200 c.c., and then boiled with two litres alcohol, sp.gr. ·820. On cooling and standing, the clear liquid is decanted off the undissolved syrup and put aside in a corked flask; at the end of six days the sides of the flask will be found to be covered with a crystalline crust of maltose. Or the undissolved syrup may be treated with strong alcohol as long as any matter is taken up, the whole of the clear alcoholic solutions are mixed, the alcohol distilled off and the residue concentrated to a syrup; this on standing in a cool place becomes filled with crystals of maltose, especially if a few crystals from a previous preparation be stirred in. These may be washed with dry methyl alcohol; if this is used hot, a portion of the crystals dissolves and the solution soon yields much sugar. The crystallisation is hastened by adding half a volume of ethyl alcohol (·810 sp.gr.) or a little ether with some crystals of a previous preparation (O'Sullivan, *l.c.*; Schulze, B. 7, 1047; Soxhlet, Cit. B. 236, 277; Herzfeld, A. Ch. 220, 209; Cuisinier, J. 1884, 1803). The body may be purified by recrystallisation from methyl alcohol.

Properties.—Maltose crystallises out of water in plates which contain $C_{12}H_{22}O_{11}.H_2O$; out of alcohol (sp.gr. ·810) it crystallises in crusts and at times in cauliflower-like or warty aggregations which contain $C_{12}H_{22}O_{11}$. The hydrous body easily parts with its water at 100° in a current of dry air. The anhydrous body is but slightly soluble in strong ethyl alcohol; it is more soluble in methyl alcohol. The hydrous body dissolves more freely in both solvents. Both bodies are very soluble in water, but less so than dextrose. The solution is optically active, and the activity for a solution containing 10 grams in 100 c.c. is 15–20° less when freshly prepared than after standing. The activity becomes constant in 10–12 hours in the cold or immediately on boiling (Meissel, J. pr. Ch. [2] 25, 120).

The specific rotatory power for dry maltose is $[\alpha]_j = 154\text{–}155°$, $[\alpha]_D = 189\text{–}140°$ at 15·5° in solutions containing 10 grams per 100 c.c. and under (O'Sullivan, C. J. 35, 771 and 45, 5); Meissel (J. pr. [2] 25, 114) gives the formula

$$[\alpha]_D = 140{\cdot}375 - {\cdot}01837\ P - {\cdot}095\ T$$

to represent the specific rotatory power of dry maltose at 0°, in which P = percentage of maltose in solution and T the temperature of observation. On calculating the value of the sugar in a 10-gram solution at 15·5° from this formula we get $[\alpha]_D = 138{\cdot}9$ (*v.* also Soxhlet, *l.c.* and Herzfeld, A. 220, 206). A solution of maltose containing 10 grams dry substance in 100 c.c. at 15·5° has a sp.gr. $\frac{15{\cdot}5°}{15{\cdot}5°} = 1{\cdot}0395$. Maltose reduces alkaline copper solution. O'Sullivan (C. J. 35, 771) gives its reducing power K = 62·5, *i.e.* 62·5 parts dextrose reduce as much copper oxide as 100 parts of maltose. Soxhlet (J. pr. 21, 227–317) says 0·5 gram maltose in 1 p.c. solution = 64·2 c.c. undiluted Fehling solution (1 c.c. = ·005 gram dextrose), *i.e.* K = 64·2, and 67·5 c.c. if the solution is diluted with four times its volume of water, *i.e.* K = 67·5. He further states that 100 parts of dry maltose = 113 parts Cu, hence 141 parts CuO; from this, we have K = 63·94. There appears to be fair evidence that the K varies within certain limits according to the mode of manipulation, but when we see that the K should be 63·17 if it be supposed that 1 molecule maltose reduces 6 molecules CuO, and that the observed numbers closely approach this, we may take it that this is the true number when errors of manipulation are avoided. If the Cu_2O be separated, the filtrate treated with acid gives a further reduction with Fehling's solution which if added to the first equals the reduction of dextrose (Herzfeld, A. B. 589, 220). Alkaline mercuric cyanide solutions are also reduced by maltose. Copper acetate is not reduced by it (Barfoed, Org. Analysis, 214); dextrose reduces this reagent. When maltose reduces copper oxide, glycollic and a mixture of acids of unknown composition are produced (Habermann and Hönig, M. 5, 208).

Maltose is hydrolysed to dextrose according to the equation $C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$ by the following reagents:—the mineral acids and many organic ones; pancreatic secretion and portions of the small intestine (Brown and Heron, C. N. 42, 63; Bourquelot, C. R. 97, 1000 and 1322); a ferment developed in *Aspergillus niger* and in *Mucor mucedo*; the former contains also a ferment capable of inverting sucrose, the latter yields only the one (Bourquelot, *l.c.*).

Maltose withstands the hydrolytic action of sulphuric acid with five times the power of sucrose; 3 hours' digestion with a 3 p.c. solution gives complete hydrolysis (Meissel, *l.c.*). 0·5 p.c. solution of lactic acid does not hydrolyse it, even at 110°; 1 p.c. oxalic acid acts at that temperature; carbonic acid at 100°, and under a pressure of six atmospheres, is without action (Bourquelot, J. de l'Anat. et de la Physiol. 22, 161–204). *V.* also Urich (B. 18, 3074).

Under the influence of yeast, maltose ferments, yielding the usual products of alcoholic fermentation.

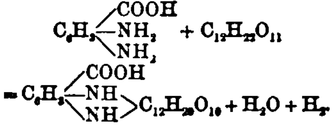
Nitric acid converts maltose into saccharic acid and finally oxalic acid. Chlorine does not act on it as energetically as it does on dextrose or sucrose; the product is identical neither with gluconic or glycollic acids (Meissel, *l.c.*). Herzfeld (Bd. Clb. 1883) obtained an acid which he called maltonic acid, by the action of bromine on maltose; this is probably identical with Fischer and Meyer's (B. 22, 194) *maltobionic acid* $C_{12}H_{22}O_{12}$, which they prepared by acting on maltose in aqueous solution with bromine in the cold for two or three days. This acid is broken down into dextrose and gluconic acid by digestion with sulphuric acid. Treated at 110° with acetic anhydride and acetic acid, maltose yields *monacetyl maltose* $C_{12}H_{21}(C_2H_3O)O_{11}$ (Yoshida, *l.c.*, and Steiner, C. N. 43, 52); with sodium acetate and acetic anhydride the *octacetyl* derivative $C_{12}H_{14}(C_2H_3O)_8O_{11}$ is produced, the optical activity of which is $[\alpha]_D = 81{\cdot}18°$ (Herzfeld, A. 220, 206).

Sodium $C_{12}H_{21}NaO_{11}$, calcium $C_{12}H_{20}CaO_{11}.H_2O$, strontium $C_{12}H_{20}SrO_{11}H_2O$, and barium $C_{12}H_{20}BaO_{11}.H_2O$ maltose are prepared as easily decomposable amorphous precipitates when alcoholic solutions of maltose and the corresponding bases are mixed (Herzfeld, *l.c.*). Compounds with the alkaline chlorides or bromides have not been prepared.

When 1 part maltose, 2 parts phenyl hydrazine hydrochloride, 3 parts sodium acetate, and 15 parts of water are heated together for 1½ hours, *phenylmaltosazone* crystallises out on cooling in fine yellow needles, m.p. 190–191°. The equation

$$C_{12}H_{22}O_{11} + 2N_2H_3.C_6H_5 = C_{24}H_{32}N_4O_9 + 2H_2O + H_2$$

represents the reaction. Only 30 p.c. of the maltose employed is obtained as *osazone* (Fisher, B. 17, 583). With γ-diamido-benzoic acid, maltose yields *malto-γ-diamido-benzoic acid* according to the equation



$$C_6H_3\begin{cases}COOH\\NH_2\\NH_2\end{cases} + C_{12}H_{22}O_{11} = C_6H_3\begin{cases}COOH\\NH\\NH\end{cases}\!\!\!>C_{12}H_{20}O_{10} + H_2O + H_2$$

The body crystallises in white microscopic needles or narrow plates, its barium salt is a gummy mass (Griess and Harrow, B. 20, 2212). For estimation *v.* SACCHARIMETRY. O'S.

MANCHESTER BROWN *v.* AZO- COLOURING MATTERS.

MANCHESTER YELLOW. *Dinitronaphthol v.* NAPHTHALENE. Dinitronaphthol-yellow has lately been used to artificially colour natural saffron. To detect the adulteration, an infusion of the matter is prepared, to which some tartaric acid is added. A hank of wool is then dyed in the solution, which is kept on the boil during that time. The wool thus dyed is washed in very dilute sulphuric acid, and the acid afterwards neutralised with ammonia. If the saffron contained any dinitronaphthol at all, the wool or the solution will be coloured yellow, whereas wool dyed with a decoction of genuine saffron and treated in the same manner becomes colourless (Cazeneuve and G. Ginnossier, S. C. I. 5, 437).

MANDARIN *v.* AZO- COLOURING MATTERS.

MANDARIN ORANGE *v.* AZO- COLOURING MATTERS.

MANDRAGORIN $C_{17}H_{23}NO_3$. An alkaloid isomeric with atropin, and possessing similar physiological properties, obtained by Ahrens from *Mandragora* root (F. B. Ahrens, A. 251, 312). To extract it the roots are powdered, macerated with alcohol, and pressed, and the solution is evaporated to dryness, the residue extracted with very dilute acid, and after neutralisation with potassium carbonate, treated with ether. On distilling off the ether the alkaloid remains as a brittle deliquescent gum, m.p. 77° to 79°, possessing an alkaline reaction. The sulphate forms white deliquescent plates; the gold chloride double salt $C_{17}H_{23}NO_3HClAuCl_3$ melts at 153°–155°; forms shining plates, sparingly soluble in water. The chloro-platinate melts at 194°–196°; the mercuric chloride double salt melts at 160°–161°, and crystallises from water in white needles. Mandragorin is not converted intro atropin by the action of alkalis. Mandragora root would appear to possess another alkaloid isomeric with mandragorin and atropin.

MANGANATES *v.* MANGANESE.

MANGANESE. Mn. (Fr. *Manganèse*; Ger. *Mangan.*) At. w. 54·8 (Turner, Berzelius, v. Hauer, Dumas; 55·07 Marignac; 55·038 Dewar and Scott). Manganese is not found in the metallic state. In combination, especially as oxide, it is widely distributed. The most important ores are those corresponding to the peroxide MnO_2. It occurs as sulphide in *alabamite*, MnS, and in *hauerite*, MnS_2; as arsenide in *kaneite*. As carbonate it is found in *dialogite* or *rhodocrosite*, in rose or brownish-coloured rhombohedral crystals in various British localities, at Freiberg, in Newfoundland, and in the United States. As silicate it occurs in *rhodonite* or *manganese spar*, SiO_2MnO. The peculiar pinkish colour of many silicates is due to the presence of this mineral. Manganese is present in soils, and frequently in mineral, particularly chalybeate, waters. It occurs in many plants, especially in tea and tobacco.

Preparation.—Metallic manganese is not used in the arts except when alloyed with other metals. It may be prepared by reduction of the oxide with carbon. Finely-powdered manganese carbonate is ignited in a covered crucible, and the resultant oxide is mixed with oil and ignited in a crucible to convert the oil into charcoal. The mass is again mixed with oil and re-ignited, and the treatment repeated until sufficient charcoal has been reduced in contact with the oxide. The carbonaceous mass is then made into a solid paste with oil, placed in a crucible lined with carbon, covered with charcoal, heated to redness for half an hour to decompose the oil, and cooled. The lid is then luted down, and the whole exposed for one and a half hours in an air furnace to as high a temperature as the crucible will stand, with occasional shaking. The button of metal so obtained contains carbon and silicon. After a second ignition in a similarly coated crucible, under a layer of salt containing one-tenth its weight of nitre, it becomes more fusible and brilliant, and leaves no carbon on solution in acid (John, Gehlen's J. für Chem. Phys. 3, 452). Brunner (A. 102, 330) prepares the metal by the action of sodium on manganese chloride or fluoride. Two parts of the anhydrous fluoride or an equal quantity of the chloride mixed with its own weight of fluorspar, is arranged in alternate thin layers with one part of sodium, well pressed and covered by a layer of salt, and the whole covered by small pieces of fluorspar. The crucible is covered and heated, at first gently and finally to bright redness, in a blast furnace for about 15 minutes. The metal so produced always contains considerable quantities of silicon. The metal may be readily obtained by the reduction of the anhydrous chloride by magnesium. The finely-powdered anhydrous salt is intimately mixed with twice its weight of well-dried potassium chloride. The mixture is then fused in a Hessian crucible at the lowest possible temperature, and a quantity of metallic magnesium is introduced in small portions at a time, the total quantity necessary being about one-sixth of the weight of the manganous chloride employed. Provided the crucible has not been heated too much above the melting-point of the mixture of chlorides the action is regular, the magnesium dissolving quickly. When the action has ceased the contents of the crucible are again strongly heated. On breaking the crucible when cold, a regulus of metallic manganese is obtained in quantity equal to about 1½ times the weight of the magnesium employed (E. Glatzel, B. 22, 2857). Deville has prepared pure manganese by reduction of the pure oxide with a quantity of sugar charcoal insufficient to reduce the whole.

Valenciennes (C. R. 70, 907) has produced it hard and brittle, easily split, and quickly oxidised by reduction of the pure oxide with carbon in a magnesia-lined crucible.

Oxides of manganese are reduced to the protoxide but not to metal by ignition in hydrogen. Hugo Tamm (C. N. 26, 111) recommends the following process for the preparation on the large scale. Two fluxes are prepared. (1) A fusible 'white' flux of ground glass (free from lead) 63, quicklime 18½, and fluorspar 18½. (2) Flux No. 1 34 parts, lampblack 5½, native manganese peroxide of good quality 60½.

The crucibles used should be very refractory, lined with a mixture of 3 parts plumbago and 1 part fireclay, made into a paste with water. This casing resists the action of the flux for a considerable time. In such a crucible flux No. 2 is ignited at the highest temperature of a wind furnace with the production of 17½ parts of 'Cort manganese' and a green slag saturated with protoxide of manganese. Of this flux 635 parts are thoroughly mixed with 91 parts of lampblack (charcoal cannot be used), and then mixed with 1,000 parts of rich manganese ore. The whole is made into a paste with oil, pressed into the crucible, covered with a piece of wood to prevent oxidation, and luted down, leaving an aperture for the escape of gases.

The crucible is next heated in a blast furnace, at first gently, until fumes cease to escape, and finally to whiteness, for several hours. On cooling, the manganese is found as a coherent mass. The green slag may be again used several times with the addition of a little white flux to increase the fluidity, provided too much gangue be not present in the ore.

Operating with an ore containing 79·5 p.c. manganese dioxide, 6·5 p.c. ferric oxide, and 10·5 p.c. gangue, manganese obtained showed the following composition: Mn 96·9, Fe 1·05, Al 0·10, Ca 0·05, P 0·05, S 0·05, Si 0·85, C 0·95. This metal, when fused with one-eighth part of manganous carbonate, contained Mn 99·91, Fe 0·05, Si 0·015, C 0·025.

Properties.—The properties of this metal vary considerably according to the method of preparation. That produced by the reduction of the oxide with charcoal is greyish-white and brittle, of finely-grained structure, sp.gr. 8·013. It oxidises quickly in the air and requires to be preserved under benzene. It dissolves rapidly with evolution of hydrogen, in cold dilute hydrochloric and sulphuric acids, and decomposes water slowly at the ordinary temperatures.

That obtained from the chloride resembles cast iron, is brittle, of a whitish-grey colour, and non-magnetic, harder than steel and capable of taking a high polish. It is so hard that a file makes no impression on it. On heating, it passes, like steel, through various shades of colour. Its sp.gr. is 7·138 to 7·206 (7·329 at 22° Glatzel), but may be raised to 8·0 by repeated heating with carbon. It rusts in moist air; readily soluble in cold dilute sulphuric acid, evolving hydrogen; in the hot concentrated acid it dissolves with evolution of sulphurous oxide. Soluble in hydrochloric, nitric, and acetic acids. The powdered metal takes fire in chlorine gas, and dissolves readily in heated bromine.

According to Deville (C. R. 44, 673) the presence of silicon causes the difference between this metal and that prepared with carbon, but Brunner has lowered the proportion of silicon to 0·1 p.c. by fusion of the metal under a layer of salt containing 1 p.c. of potassium chlorate, without perceptibly altering the properties. According to Sefström, manganese containing 6 or 7 p.c. of silicon does not oxidise even at a red heat. Manganese is slightly volatile at the high temperatures of a blast furnace (Jordan, C. R., 86, 1376).

Detection.—All compounds of manganese, if strongly ignited, impart an amethyst-red colour to the borax bead in the oxidising flame; it can be rendered colourless by careful heating in the reducing flame. When heated with soda and a little nitre on platinum foil a very small quantity of manganese produces a green colour.

A very delicate test, in the absence of chlorides, consists in heating the substance or solution with dilute nitric acid and a little lead peroxide. The manganese is thus oxidised and imparts to the solution the pink colour of permanganic acid (Crum).

When manganese is present in its usual form, as a protosalt, sulphuretted hydrogen produces a flesh-coloured precipitate from alkaline, but not from acid or neutral solutions.

Potassium and sodium hydrates precipitate white hydrated protoxide which rapidly becomes brown from absorption of oxygen. Ammonia produces the same precipitate, soluble in excess, especially in presence of ammonium chloride, slowly precipitated as the brown oxide.

Where the manganese exists as the acid oxide, as in manganates and permanganates, the reactions are different. Alkaline manganates produce green solutions which slowly become red on exposure to air, more rapidly on addition of an acid, from production of the permanganate. Both these compounds are rapidly reduced and rendered colourless by the addition of sulphurous acid, ferrous salts, or other reducing agent. The manganese then exists as a base and shows the usual reactions. All manganates and permanganates oxidise hydrochloric acid, especially when heated, with evolution of chlorine.

Estimation.—Manganese is usually precipitated as carbonate. To the nearly boiling solution, sodium carbonate is added drop by drop, until precipitation is complete, and the solution boiled for a few minutes and allowed to subside. The precipitate is washed by decantation three times and finally well washed on the filter. The dried precipitate is strongly ignited in a platinum crucible and weighed as Mn_3O_4, which contains 72·05 p.c. of manganese. The ignited mass should show no alkaline reaction with test paper.

A very delicate method of estimating small quantities of manganese, as in limestones, &c., has been devised by Chatard. The process, as modified by Thorpe and Hambly (C. J. 1888, 182), is as follows. The solution should contain no chlorides, between 0·004 and 0·008 grams of manganese, and should occupy about 25 c.c. To it is added 5 c.c. concentrated nitric acid, 2 or 3 grams of lead peroxide, and 10 to 20 c.c. dilute sulphuric acid (1 acid to 2 water), and the solution gently boiled for four minutes. The sides of the flask are washed down to destroy any organic matter, and the liquid boiled for half a minute longer. The lead sulphate and excess of lead peroxide are allowed to subside and the solution is at once filtered (with the aid of a filter pump if possible) through a plug of asbestos recently ignited and washed with dilute sulphuric acid. The filtrate is heated to 60°C. and titrated with a weak solution of ammonium oxalate, freshly standardised by a standard solution of permanganate.

The separation from other metals is not difficult. From the alkaline earths it may be separated by addition of hydrated ammonium sulphide to the nearly neutral solution; the sulphide so precipitated is washed well, redissolved in hydrochloric acid, and precipitated as above with sodium carbonate.

From iron, chromium, uranium, and aluminium, it may be separated by digesting the dilute solution with freshly precipitated barium carbonate. These metals are thus deposited as hydrates. The barium is removed from the solution by the addition of sulphuric acid, and the manganese precipitated as usual.

When manganese occurs together with a large proportion of iron, as in iron ores, iron, steel, &c., the following separation is useful. The nearly boiling solution of the substance in hydrochloric acid or aqua regia, which must be absolutely free from organic matter, is treated with ammonia, with constant stirring, until it becomes much darkened; weaker ammonia is then cautiously added until the liquid has become of a mahogany colour but still without any permanent precipitate. A hot solution of ammonium acetate is then added. The precipitate of basic ferric acetate should be brick-red; if it be dark red, more ammonium acetate must be added. The solution is boiled for a few minutes only, and the granular precipitate filtered through a large filter paper. The filter with the precipitate is replaced in the beaker which still contains the remaining portions of the precipitate and is redissolved in hydrochloric acid, reprecipitated as before and filtered into the beaker containing the first filtrate. In this way the small portion of manganese contained by the first iron precipitate is separated. A portion of the second ferric acetate precipitate should, in important cases, be boiled with lead peroxide and nitric acid, when, if a trace of manganese be present, the liquid will acquire a pink colour.

The liquid containing the manganese may be concentrated by evaporation, filtered if necessary, and cooled. Sufficient bromine is added, with frequent shaking, to render it brown, and the whole rendered alkaline by ammonia. The manganese is thus precipitated as black hydrated peroxide.

The liquid is heated to boiling, filtered, and the precipitate washed and ignited as usual to Mn_3O_4. If a trace of organic matter be present in the solution, a portion of the iron will not be precipitated as acetate and will come down with the manganese. If this is the case the ignited oxide is redissolved and the iron precipitated as acetate, ignited, and weighed as Fe_2O_3 and its weight deducted from that of the manganese oxide obtained.

ALLOYS.

Iron alloys with manganese in all proportions. The presence of manganese in iron and steel much increases their elasticity and hardness; even 1 p.c. of that metal renders cast steel more tenacious. Its presence is said to increase the rusting action of water (Gruner, C. R. 96, 195). For a memoir by Hadfield on alloys of iron and steel with *considerable* proportions of manganese (upwards of 7 p.c.), *v.* Proc. Inst. Civil Engineers, 1888, vol. 93, p. 1–126.

Copper possesses a considerable affinity for manganese. The alloys resemble those of copper and tin; they are strong, sonorous and fusible; they acquire a greenish tarnish. Those containing 5 to 30 p.c. of manganese are both malleable and ductile when cold. With 25 p.c. of manganese, the alloy is brittle when hot, malleable when cold.

They may be produced by ignition of a mixture of copper and manganese oxide with charcoal in a plumbago crucible at a white heat. The addition of *zinc* produces alloys resembling nickel silver, easily worked both hot and cold. Useful alloys are also produced by the addition of tin and lead (*v.* J. F. Allen, C. N. 22, 194). An alloy known as 'manganese bronze' is hard and of the colour of gun metal. It is said to consist of ordinary bronze containing manganese, to be thoroughly workable at a red heat, and to possess a tenacity equal to that of bar iron (D. P. J. 221, 334).

According to Mewburn (C. C. 13, 416) useful alloys are produced by mixing ferromanganese of suitable composition with copper, and melting in a reverberatory furnace. If the alloy is required to be rolled into sheets, zinc is added. For a forgeable alloy the protoxides of manganese and iron are mixed with sufficient coal to reduce them, the proper quantity of copper is added, and the mixture strongly ignited. This alloy is said to resemble aluminium bronze.

Aluminium forms alloys with manganese, from which the former metal may be removed by the action of alkaline solutions. An alloy corresponding to $MnAl_3$ has been prepared by Wöhler (A. 115, 102). Terreil (Bl. [2] 21, 289) has obtained an alloy of the composition $AlMn_3$ hard enough to scratch glass, by igniting aluminium with anhydrous manganous chloride. The corresponding alloy with *magnesium* was less hard. *Zinc* reduced the chloride with explosion.

By reduction of an acidulated solution of manganous chloride with sodium amalgam, an amalgam of manganese and mercury is obtained, from which the mercury may be volatilised by heating in a current of hydrogen.

The addition of manganese is said to increase the malleability of cobalt and nickel.

Manganese oxides. The compounds of manganese with oxygen are numerous. The lower or protoxide of manganese MnO is powerfully basic; the sequioxide Mn_2O_3 is less basic, the tetroxide Mn_3O_4 and the dioxide MnO_2 are practically neutral; the higher oxides, however, MnO_3 and Mn_2O_7 have decided acid-forming properties and produce well-marked series of salts.

Manganous oxide MnO is prepared by ignition of any other oxide, or of the carbonate, in a current of hydrogen. It is of an olive-green colour and absorbs oxygen from the air with formation of a brown oxide. In solution in acids it forms manganous salts.

Manganese sesquioxide Mn_2O_3 occurs in nature as *braunite* in brownish black, anhydrous, acute octahedra frequently containing silica. In the hydrated form it occurs as *manganite* in brilliant, black or steel-grey, rhombic prisms.

It may be prepared by passing chlorine, not to saturation, through water in which manganese carbonate is suspended, and removing the excess of carbonate by dilute nitric acid. It dissolves slowly in sulphuric or hydrochloric acid, with formation of manganic salts isomorphous with those of aluminium and iron. The colour of the amethyst is attributed to the presence of this oxide.

Manganese tetroxide. Red oxide of manganese M_3O_4 occurs as *hausmannite* in brownish black octahedra, and in massive forms. It is produced by heating any oxide of manganese in the air.

Manganese dioxide. Peroxide or black oxide of manganese, frequently known as 'manganese,' MnO_2.

This important oxide occurs as *pyrolusite* in very pure iron-black or steel-grey, rectangular rhombic prisms of sp.gr. 4·8 to 5, and frequently massive or reniform, in radiating fibrous masses, usually brittle. Its hardness varies within wide limits.

A hydrated variety occurs largely as *psilomelane* in amorphous, massive, stalactitic, and frequently in botryoidal masses, but never in crystals. Its composition is very variable. It usually occurs in the same localities as pyrolusite, frequently in alternate layers with that mineral. *Varvicite* and *newkirkite* are also hydrated varieties of pyrolusite.

Wad is an important earthy variety produced by the decomposition of other manganese minerals. It occurs, generally in low-lying districts, in amorphous, earthy, dull black or brownish pieces of very variable composition and hardness. It frequently contains oxide of cobalt; one variety known as *Asbolane* or *earthy cobalt* sometimes contains as much as 32 p.c. of cobalt. Another variety, *lampadite*, contains 18 p.c. of copper oxide. In addition to its employment as a chlorine producer, wad is used as an 'umber' paint.

Of these oxides pyrolusite is the purest and contains the highest percentage of oxygen; it has therefore the greatest commercial value.

It is used for the preparation of oxygen on the large scale. At a red heat it evolves one-third of its oxygen, leaving the red tetroxide.

When heated with concentrated sulphuric acid, it dissolves with formation of manganous sulphate and evolution of half its oxygen. If organic matter be present the oxygen decomposes it with evolution of carbon dioxide.

Its action on hydrochloric acid is of great importance. The hydrogen of this acid is oxidised, a portion of the chlorine thus liberated combines with the manganese, while the remainder is set free;

$$MnO_2 + 4HCl = MnCl_2 + 2OH_2 + Cl_2.$$

By this reaction chlorine is prepared on the large scale.

Nitric acid has but slight action upon it. Pyrolusite is a good conductor of electricity and is strongly electronegative: it is used as the negative plate of the Leclanché battery. It is used to destroy the injurious tint produced in glass by the presence of protosalts of iron. The oxygen converts the greenish protosalt into the nearly colourless persalt, while the slight pink tint imparted by the manganese still further counteracts the bluish colour. It seems probable that the effect is due principally to the latter cause, as red lead and other oxidising agents have not this decolourising power.

Pyrolusite is also used in the preparation of black enamel for pottery.

(For further information regarding these oxides *v.* CHLORINE.) Manganese dioxide may be prepared artificially by moderately igniting the nitrate, boiling the residue with nitric acid, washing and gently heating (Berthier). The hydrated oxide has been used for the removal of iron from aluminium sulphate.

According to Fremy (C. R. 82, 1231) it forms a definite sulphate on solution in sulphuric acid.

Manganese trioxide. Franke (J. pr. 1887, 14) has described a trioxide MnO_3; its existence has been confirmed by Thorpe and Hambly (C. J. 1888, 177). This oxide appears to form a sulphate $(MnO_3)_2SO_4$.

Manganese heptoxide Mn_2O_7 is a highly hygroscopic, non-volatile, reddish-brown liquid, which gradually decomposes on exposure to the air. Its composition was determined by Aschoff (P. 3, 217). These two oxides are of interest, as they form the acid radicles of manganates and permanganates; thus, MnO_3K_2O, $Mn_2O_7.K_2O$.

SALTS OF MANGANESE.

Of the salts corresponding to these various oxides, only two series are of practical importance, manganous salts, corresponding to the protoxide, and manganates and permanganates, in which manganese acts as an acid corresponding to the tri- and hept-oxides.

Manganous chloride $MnCl_2$ is produced by the action of chlorine gas on metallic manganese, or of hydrochloric acid gas on the heated carbonate. In solution, it is obtained by dissolving the oxide or carbonate in hydrochloric acid.

On the large scale it is usually produced from the residual solutions from the chlorine manufactures. This is first evaporated to remove excess of hydrochloric acid, and one-fourth of the solution is removed and precipitated by sodium carbonate. The precipitate, which contains manganous carbonate and ferric hydrate, is washed and boiled with the remainder of the solution. The iron in solution is thus precipitated as hydrate, being replaced by an equivalent quantity of manganese from the carbonate. Copper, if present, is precipitated by the addition of sulphuretted hydrogen, leaving in solution manganese, and usually calcium and other alkaline earthy metals. Cobalt and nickel may be removed by the addition of freshly-precipitated manganous sulphide,. as long as it becomes darkened; those metals are then precipitated as sulphides.

The manganese is precipitated by means of ammonium sulphide, washed, dissolved in hydrochloric acid, evaporated, and crystallised.

According to Kolbe, it may be obtained pure by evaporating the crude solution of the ore in acid to dryness, igniting gently in a crucible, exhausting the residue with water, concentrating and crystallising. It forms pink deliquescent crystals, containing 4 molecules of water, soluble in two-thirds their weight of water at 60°C., soluble in alcohol.

In commerce it usually occurs as a rose-red, very deliquescent mass, obtained by evaporating the solution to dryness. It is used for the production of a brown colour in calico printing.

Manganous sulphate $MnSO_4$ may be prepared by dissolving the carbonate or oxide in sulphuric acid. On the large scale it is usually obtained from the black oxide. This is ignited with about one-tenth part of powdered coal, and thus reduced to the protoxide. The mass is dissolved in sulphuric acid, evaporated, gently ignited to decompose the ferrous sulphate, and the manganous sulphate dissolved out by water. By another process the peroxide is first digested with dilute sulphuric acid to remove carbonates, and made into a paste with strong sulphuric acid, heated until the evolution of oxygen has ceased, and then to strong redness, cooled, digested in water, and the solution evaporated and crystallised. If iron be still present, it may be removed as in the case of the chloride by boiling with manganous carbonate. Manganous sulphate forms pink crystals very soluble in water, insoluble in absolute alcohol. It is used in calico-printing.

Potassium manganate K_2MnO_4. This compound is produced when equal weights of finely-powdered oxide of manganese and caustic potash are fused together, a sesquioxide of manganese being produced at the same time. By the addition of potassium nitrate or by performing the ignition in a flat vessel, a portion of this oxide is reoxidised, and increases the yield of manganate.

It dissolves in water, forming a fine green solution which, on evaporation *in vacuo*, produces green crystals isomorphous with sulphate and chromate of potassium. The solution, especially if dilute, when exposed to the air becomes converted into the permanganate with precipitation of hydrated manganese dioxide; the liquid passes through various shades from green to pink, whence its name of 'mineral chameleon.' In presence of excess of alkali this change does not take place. On the addition of free acid, especially sulphuric acid, the change is immediate, the alkali and manganese, instead of being liberated as hydrates, being at once converted into sulphates, and thus losing their tendency to reproduce the manganate. Potassium manganate is a powerful oxidising agent. Its general action in this respect resembles that of the permanganate.

Sodium manganate Na_2MnO_4 is largely manufactured for disinfecting purposes on account of its greater cheapness.

For the preparation of Condy's fluid 30 cwt. of soda ash are causticised with lime, mixed with 7 cwt. manganese dioxide, and ignited in a shallow vessel at a dull red heat for about forty-eight hours. The mass is treated with water, decanted, and the solution evaporated to the required concentration. When the product is required to consist only of permanganate the solution is treated with sulphuric acid, and evaporated until crystals of sodium sulphate separate. Sodium permanganate is, however, much more difficult to purify by crystallisation than the potassium salt (*v.* Hofmann, Reports on Chem. Processes at the Exhibition of 1862, 109).

According to Desclabissac (D. P. J. 201, 58), the following methods are used for the preparation of sodium manganate and permanganate on the large scale. (1) 500 parts of soda lye (45°B.) are evaporated with 100 parts potassium chlorate mixed with 180 parts of the finely-powdered oxide, and ignited in iron pots until quietly fused, cooled, with constant stirring, again heated to redness, cooled, and extracted with water. (2) 12 parts of caustic soda, dissolved in 58 parts of water is heated with 12 parts potassium chlorate and 18 parts manganese dioxide, until it begins to crumble; the heat is then increased to redness, and the mass, after cooling, is extracted with 200 to 220 parts of water. (3) To a fused mixture of 10 parts caustic soda and 1 part nitre is added 6 parts strongly heated manganese dioxide; the cooled mass is ladled out and extracted as before.

Potassium permanganate $KMnO_4$ or $K_2Mn_2O_8$. This salt may be prepared directly by the addition of 10 parts of potash dissolved in the minimum of water to a mixture of 8 parts manganese dioxide and 7 parts potassium chlorate. The solution is evaporated to dryness, finely powdered, and ignited at a dull red heat for about one hour, until the chlorate has become decomposed. The mass is boiled with water, decanted, evaporated rapidly to a small bulk until crystals form on its surface, decanted from the precipitate which has fallen, and allowed to crystallise; 1 part of permanganate is produced from 3 parts of the oxide (Gregory, J. Pharm. 21, 312).

It is, however, usually prepared by the action of an acid on the manganate.

According to Städeler (J. pr. 103, 107), 90 p.c. of the oxide may be converted into permanganate by first preparing the manganate and converting it into permanganate by the addition of chlorine instead of acid

$$2K_2MnO_4 + Cl_2 = 2KCl + Mn_2K_2O_8.$$

The solution is evaporated and the permanganate crystallised, leaving the potassium chloride in solution.

Tessié du Mothay and Maréchal prepare it by addition of magnesium sulphate to the manganate, according to the equation

$$3K_2MnO_4 + 2MgSO_4 + 2H_2O$$
$$= K_2Mn_2O_8 + 2K_2SO_4 + 2Mg(HO)_2 + MnO_2.$$

Potassium permanganate forms fine dark purple prismatic crystals of greenish metallic lustre, soluble in 16 parts of water at 15°C. When heated they decompose, evolving oxygen, and leaving a mixture of manganate and manganese dioxide. Heated in hydrogen they ignite and leave a green mass containing protoxide of manganese and potash.

It is an extremely powerful oxidising agent; each molecule contains five atoms of 'available' oxygen, more than any other salt.

When triturated with sulphur or phosphorus it detonates; when mixed with carbonaceous matters and many other reducing agents, and heated, it burns. Mixtures containing permanganates and organic substances are very liable to spontaneous decomposition.

The crystals oxidise strong hydrochloric acid in the cold, with evolution of chlorine; in solution the same effect is produced on heating.

A solution of the salt is rapidly reduced by the addition of sulphurous acid, ferrous salts, and most other reducing agents, less rapidly by organic matter. The solution is therefore used as a test for such substances, and to estimate their amount.

Solutions of the salt can only be filtered through asbestos or glass wool, as they quickly destroy filter-paper.

Zinc, iron, lead, mercury, and many other metals are oxidised more or less rapidly by the solution. Pure potash has no action on permanganate, even when heated, but in presence of organic matter it is rapidly reduced to the green manganate (Mohr, Z. 9, 43).

It is largely used as a local disinfectant. On mixing concentrated solutions of this salt and of silver nitrate, a red crystalline precipitate of *silver permanganate* $Ag_2Mn_2O_8$ is produced. It may be used for the preparation of other permanganates. On mixing with a solution of barium chloride, silver chloride is precipitated, and *barium permanganate* remains in solution, from which *permanganic acid* may be produced by the addition of dilute sulphuric as long as a precipitate falls. On evaporation of the solution the acid is obtained as a brown, crystalline, very soluble mass, easily decomposed by heat.

Sodium permanganate $Na_2Mn_2O_8$ resembles in its properties the potassium salt (*v.* Sodium manganate).

Aluminium permanganate. Condy (Eng. Pat. 1884, 10,015) has patented a method of preparing this salt for disinfecting purposes. It is said to give up five-sevenths of its total oxygen to reducing agents. The alumina present would also assist in the precipitation of impurities in water &c. To 1,000 parts of a solution of aluminium sulphate, containing one-third its weight of the sulphate, is added 53 parts of potassium permanganate, which is dissolved by the aid of heat. On cooling, potassium alum crystallises out, and the decanted solution, which contains the whole of the permanganate and a considerable amount of aluminium sulphate, is ready for use.

MANGANESE BRONZE *v.* Tin.

MANGANESE SPAR or **MANGANESE SILICATE** *v.* Manganese.

MANGANITE. *Manganese sesquioxide v.* Manganese.

MANILA ELEMI *v.* Oleo-resins.

MANIOT or **MANIHOT** is the farina of *Manihot utilissima*, formerly known as *Jatropha manihot*, the plant which furnishes tapioca. Indigenous to America, but also cultivated in Africa and tropical climates generally. Maniot is occasionally imported under the name of 'Brazilian arrowroot.'

MANNA is the concrete saccharine exudation of *Fraxinus ornus*, or flowering ash, obtained from incisions in the bark. The manna of commerce is procured from Sicily, and is used as an aperient medicine.

The chief constituent of manna is *mannite* or manna sugar, a hexatomic alcohol $C_6H_8(OH)_6$ (*q. v.*), which constitutes 70 or 80 p.c. of the best kinds.

A large number of varieties of manna are used in other localities, none of which contains the characteristic mannite. Amongst these are the Persian and Turkestan manna, derived from *Alhagi maurorum* or *camelorum*; the tamarisk manna, also of Persian origin, from the *Tamarix gallica*; oak manna, procured from *Quercus valonia* and *Quercus persicus* in Kurdistan; Australian manna, *Eucalyptus viminalis*, &c. &c.

MANNHEIM GOLD *v.* Gold, Mannheim.

MANNITOL or **MANNITE** $C_6H_8(OH)_6$, a hexatomic alcohol, isomeric with dulcitol or dulcite, first found in manna, the dried exudation from the manna ash *Fraxinus ornus*, by Proust in 1806. It is contained also in the sap of the larch, in monkshood, in *Viburnum opulus*, in the leaves of *Syringa vulgaris*, in celery, sugar-cane, in the fungus *Agaricus integer*, and in rye bread, &c. It can be obtained from dextrose by treatment with sodium amalgam

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

The addition of the hydrogen takes place only in alkaline solution, and the conversion does not exceed 10 p.c. of the dextrose employed (Linnemann, A. 123, 136). Mannite crystallises in white rhombic prisms, which are anhydrous, readily soluble in cold water; m.p. 166°. On heating, mannite is converted by loss of water into *mannitan* $C_6H_{12}O_5$ and *mannide* $C_6H_{10}O_4$. By oxidising agents it yields *mannose* and *lævulose*. Nitric acid transforms it into *saccharic acid*, and ultimately into *oxalic acid.* With a mixture of nitric and sulphuric acids it gives *nitro-mannite* or *hexone hexinitrate* $C_6H_8(NO_3)_6$, crystallising in white acicular crystals, m.p. 112–113°, which explode violently on being struck or when suddenly heated. Mannitol has only a slight sweet taste, is optically inactive, and is not fermentable with yeast, and does not reduce Fehling's solution.

Although the aqueous solution is optically inactive, on the addition of borax it becomes strongly dextrorotatory; with caustic soda it becomes lævorotatory.

MANNOSE $C_6H_{12}O_6$, a carbohydrate belonging to the group of the glucoses obtained by the hydrolysis of salep-juice, but best prepared by the action of nitric acid upon mannitol. For details of mode of preparation *v.* E. Fischer and Hirschberger, B. 21, 1805, 22, 365. On adding ether to the alcoholic solution, mannose is precipitated in the form of flocks which gradually become hard on standing under absolute alcohol. It is highly deliquescent, reduces Fehling's solution, and ferments with yeast like dextrose and levulose. Specific rotatory power +13. With phenyl hydrazine gives an insoluble hydrazone, and when treated with an excess of the reagent yields an osazone identical with phenyl glucosazone. Is reduced by sodium amalgam forming mannitol. By the action of bromine and water forms the lactone of mannonic acid. With hydroxylamine forms *mannosoxime* $C_6H_{12}O_5(NOH)$ m.p. 184°. For the relations of mannose to levulose *v.* Levulose.

MANQUETA or **MAQUATA.** The African names of a fossil gum resin, resembling copal gum, found in Angola, below the surface of a ferruginous hard clay or soil, at a depth of a few inches to a couple of feet, often in pieces weighing several pounds.

MANURE, ARTIFICIAL. The object of manuring is to enrich the soil with plant-food. The constituents of plant-food which are naturally derived from the soil are nitrogen, phosphorus, sulphur, potassium, calcium, magnesium, iron, together with the less important constituents silicon, chlorine, and sodium. A manure will always contain one or more of these substances. Nitrogen, phosphorus, and to a less extent potassium, are by far the most important constituents to be applied as manure, as they are those in which the soil is most generally deficient. In an efficient manure the constituents must be in a condition suitable for immediate assimilation by the plant, or at least speedily acquire this condition after mixing with the soil. By the term 'artificial manures' is understood all manures save the excrements of animals and the residues of crops, which form the natural manure of a farm. In the present article we shall consider – 1. The substances employed as manure; 2. The relative value of manures; 3. Special methods employed for their analysis.

I. The Substances Employed as Manure.

Manures are sometimes classed as *general* and *special.* The former division embraces those which supply many of the requirements of a crop; they can thus be used alone, and admit of pretty general application. Special manures, on the other hand, supply few, occasionally but one, of the elements of plant-food, and are thus applied in certain cases only, and are frequently used in mixture with other manures. The principal artificial manures having a claim to be considered *general* are seaweed, fish manure, guano, and oilcakes.

Seaweed. This is largely used in some localities near the sea. When quite fresh, seaweed contains about 80 p.c. of water. Its composition varies a good deal. The nitrogen may be 1–3 p.c. of the dry matter. The average percentage of potash in 20 analyses of *Fucus* and *Laminaria* was 3 p.c., and of phosphoric acid 0·5 p.c. of the dry matter. The proportion of nitrogen and potash in fresh seaweed is thus very similar to that in farmyard manure, while the phosphoric acid is deficient.

Fish manure. Whole fish are employed as manure in places near the sea. Way found in fresh sprats 63·7 p.c. water, 1·94 p.c. nitrogen, and 2·1 p.c. ash, including 0·43 potash and 0·90 phosphoric acid.

Fish manure is made on a considerable scale from various kinds of fish refuse. The Norwegian fish guano is prepared from cod. It contains about 9·8 p.c. of water, 8·5 p.c. of nitrogen, 13·8 p.c. of phosphoric acid, and 0·3 p.c. of potash. Other foreign fish manures have a similar composition. The amount imported from Sweden and Norway was in 1886 3,188 tons, and in 1887 1,749 tons.

In the United Kingdom fish manure has been prepared in considerable quantity during recent years; the yearly make is perhaps somewhere about 7,000 tons. The manufacture is chiefly carried on in London, and along the east coast of England and Scotland. The fish offal is simply dried and powdered. The manure generally contains 7–8·5 p.c. nitrogen, and 6–8·5 p.c. phosphoric anhydride[1] existing as calcium phosphate, and a considerable amount of alkali salts. The practical value of the manure depends to some extent on the quantity of oil present, the smaller the quantity of oil the more readily does the manure decompose in the soil.

Guano. This manure was introduced into England in 1839: for many years it occupied the first place among our artificial manures. The best and largest deposits are now exhausted, although a considerable quantity yet remains.

Guano has been formed from the excrement and carcases of sea-fowl. The fresh excrements are highly nitrogenous, and consist chiefly of uric acid and calcium phosphate. If the climate is hot and dry, the excrements are quickly desiccated, and the nitrogenous matter preserved. This has been the case on the rainless coast of Peru. In a moist climate the nitrogenous matter is quickly converted into ammonia, and dissipated by evaporation or drainage, a phosphatic guano, practically destitute of nitrogen, remaining. We will first mention the nitrogenous guanos.

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[1] In analyses of British manure the nitrogen is usually stated as ammonia, and phosphoric acid as tricalcic phosphate. It may be useful, therefore, to note that 1 part of nitrogen is equivalent to 1·214 of ammonia, and 1 of ammonia to 0·8235 of nitrogen. Also 1 of phosphoric anhydride is equivalent to 2·183 of tricalcic phosphate, and 1 of tricalcic phosphate to 0·4581 of phosphoric anhydride.

1. *Nitrogenous guanos.* The main supply of Peruvian guano for thirty years was from the Chincha Islands, which yielded in all about ten million tons. This guano was a dry, excellent manure, containing 13–14 p.c. nitrogen, and 13–14 p.c. phosphoric anhydride. On its exhaustion, about 1868, guano was imported from the Guanape and Macabi Islands; this was a damp guano, containing 9–11 p.c. nitrogen, and 12–14 p.c. phosphoric anhydride. This was succeeded by importations from the Ballestas Islands. The Ballestas guano was of better quality, containing 12–13 p.c. nitrogen, and 12–14 p.c. phosphoric anhydride. These deposits are now exhausted. The present importations are from deposits on the mainland coast at Pabellon de Pica, Punta de Lobos, and Huanillos, and from the islands of Lobos de Afuera.

The mainland deposits are on the base of the Cordilleras, below the sodium nitrate zone, in the district of Tarapacá. The guano is covered by a layer of sand or conglomerate, from 2-150 feet in thickness. The guano is most deeply covered at Pabellon de Pica, and is here best preserved, containing the largest amount of nitrogen (7·5 p.c.). The more southern deposits, at Punta de Lobos and Huanillos, are less nitrogenous. The guano from the Lobos Islands is still less nitrogenous (3·5 p.c.); it contains a considerable amount of potash. Analyses of average cargoes are given in the adjoining table. A mixed 'equalised' guano is now prepared by the importers, the Anglo-Continental Company, containing 6·5–7·5 p.c. nitrogen, 30–35 p.c. phosphates, and 3–4 p.c. potassium sulphate.

The imports of Peruvian (now Chilian) guano into the United Kingdom amounted in 1888 to 16,446 tons, in 1889 to 17,000 tons. These amounts are much smaller than formerly. About five million tons have in all been imported into the United Kingdom.

In a dry nitrogenous Peruvian guano the nitrogen chiefly occurs as uric acid and urates, and a smaller proportion as ammonium salts. A damp guano contains more ammonia, and smells strongly of ammonium carbonate. Some of the Peruvian guanos contain distinct amounts of nitrate. The phosphoric acid exists chiefly as finely divided calcium phosphate; besides this, some is present as ammonium phosphate, and as phosphates of other alkalis; a portion of the phosphates is thus readily soluble in water. Guano is an extremely valuable manure, supplying in larger or smaller quantity all the essential constituents of plant-food in a condition readily assimilated by the plant, or acquiring that condition very quickly after admixture with the soil.

Dissolved Peruvian guano was introduced by Messrs. Ohlendorff in 1864. Guano is treated with 25–30 p.c. of sulphuric acid, sp.gr. 1·73, by which means the ammonium carbonate is neutralised, the urates to a considerable extent converted into ammonium salts (Vogel), and the calcium phosphate rendered soluble. This process is of considerable advantage in the case of damp guanos.

Besides Peruvian, the only other nitrogenous guanos imported are from South Africa, and Patagonia. The South African guanos originally found were phosphatic; these have been removed, and the fresh deposit of the birds is now annually collected from Ichaboe, Bird, and other Islands, opposite the west and south coast of Africa, and from Saldanha Bay on the mainland. These guanos, being fresh deposits, are generally rich in nitrogen, and comparatively poor in phosphates. The nitrogen in the Ichaboe guano varies from 9–14 p.c.; the phosphoric anhydride from 8–12 p.c. It should be recollected that a considerable part of the nitrogen is in the form of feathers, and cannot therefore have as high a value assigned to it as the nitrogen in Peruvian guano. The deposits in Saldanha Bay, and on the Islands opposite the Cape, are inferior to that from Ichaboe. The imports of South African guano were in 1885, 4,076 tons, and in 1886, 1,673 tons.

Patagonian guano is a recent deposit collected from the mainland; only a few cargoes reach this country. A similar guano is obtained from the Falkland Islands. These guanos are much contaminated with sand.

The small deposits found on the islands off the Californian coast may be considered as intermediate between the two classes of nitrogenous and phosphatic guanos; they are now apparently exhausted.

2. *Phosphatic guanos.*—The ancient deposits of guano occurring in climates in which rain is frequent have lost almost the whole of their nitrogenous matter; they are, when free from sand or rock, of great value as phosphatic manures, and have been much used for the manufacture of high-class superphosphates. Some of these guanos have been considerably altered by the action of water, and other natural chemical agents. One common result of this action is the formation of 'crusts,' consisting largely of calcium phosphate containing considerably less calcium than tricalcic phosphate, and therefore of special value as manure. Gypsum is also present in some cases to a considerable extent.

The principal places from which phosphatic guanos have been obtained are as follows: an asterisk denotes that the deposit is now apparently exhausted. (1) *Bolivian Coast.* Mejillones* guano. This was an immense deposit of excellent quality, containing about 33 p.c. phosphoric anhydride, and 0·9 p.c. nitrogen. (2) *Caribbean Sea.* Valuable deposits have been found on the islands of Tortola,* Aves, and Mona. The deposit at Aves is large and of good quality, containing about 33 p.c. phosphoric anhydride. Mona guano contains about 30 p.c. Deposits on other islands, which though possibly originally guano have been much altered, will be described under the head of phosphatic materials. (3) *Arabian Sea.* The islands of Kuria Muria.* (4) *Australia.* Abrolhos Islands, on the west coast, opposite Champion Bay. About 6,000 tons are annually exported; the composition is given below. Guano has also been exported from Sharks Bay, and from Lacepede,* Browse, and Timor on the north-west. (5) *New Caledonia.* Chesterfield and Huon Islands. This is of inferior quality and is not exported to Europe. (6) *Mid-Pacific Ocean.* Deposits, some of very considerable amount, have been worked on Jarvis,* Howland,* Starbuck,* Flint,* Phœnix, and Enderbury islands. From Baker's, Malden, and Sydney islands some guano is still shipped. Average analyses of Baker and Malden guano are given in the following table.

Analyses representing the now exhausted deposits of guano will be found in the papers of Way (J. Roy. Agri. Soc. 1849, 196), Nesbit, and Voelcker (*ibid.* 1860, 350; 1872, 217; 1874, 54; 1875, 399; 1876, 440).

Percentage composition of Guanos.

—	Nitrogenous Guanos					Phosphatic Guanos		
	Peruvian				African	Australian	Pacific Ocean	
	Pabellon de Pica	Punta de Lobos	Huanillos	Lobos d'Afuera	Ichaboe	Abrolhos	Baker	Malden
Water	14·9	17·3	14·2	15·7	16·4	3·5	11·0	5·1
Organic matter and ammonium salts	37·2	28·7	20·4	17·0	48·4	7·6	7·0	6·9
Phosphoric anhydride	14·5	17·7	22·5	21·5	9·7	33·6	34·8	35·6
Lime	12·4	15·8	19·0	16·5	9·1	44·0	40·0	46·5
Alkalis, magnesia, chlorine, sulphuric anhydride, &c.	15·4	15·9	12·4	15·7	6·5	9·5	6·6	5·8
Siliceous matter	5·6	4·6	11·5	13·6	9·9	1·8	0·6	0·1
Nitrogen	7·5	5·9	4·8	3·5	12·4	1·0	0·5	0·4
Phosphoric anhydride	14·5	17·7	22·5	21·5	9·7	33·6	34·8	35·6
Potash	3·4	2·7	1·6	4·3	1·5	—	0·1	0·2

Oilcakes. Cheap or damaged oilcakes, or cakes unfit for food (as castor), are employed to a small extent as manure. They will contain 4–7 p.c. of nitrogen, 1·5–3·0 p.c. phosphoric anhydride, and 1–2 p.c. potash.

Sodium nitrate and ammonium sulphate. These salts have in recent years largely taken the place previously occupied by Peruvian guano, and are now the most powerful nitrogenous manures at the farmers' disposal. Information regarding them will be found under their respective heads in this dictionary.

Hoof and horn. The powdered horn obtained in making combs, and other articles, is used to a considerable extent by manure manufacturers; it is extremely rich in nitrogen, containing about 15 p.c.

Dried blood. This is a very valuable manure, its nitrogenous matter becoming readily available to the crop after mixing with the soil. Perfectly dry blood will contain about 15 p.c. nitrogen, and 4 p.c. ash, of which one half is common salt. The commercial article contains 9–12 p.c. nitrogen, 10·3 p.c. is about the average.

Meat meal, meat guano. The residue from the manufacture of meat extract is exported as manure from South America, and from Queensland and New Zealand. The amount reaching this country probably does not exceed 3–4,000 tons per annum. The composition varies much, chiefly according to the proportion of bone ground up with the meat. The nitrogenous samples contain 11–13 p.c. nitrogen, and 0·6–3·0 p.c. phosphoric anhydride. The phosphatic samples contain 6–7 p.c. nitrogen, and 14–17 p.c. phosphoric anhydride.

Shoddy and wool waste. These are useful nitrogenous manures, but much less active than those previously enumerated, being only slowly decomposed in the soil. They are much less used than formerly, owing to the cheapness of ammonium salts. Pure dry wool and hair would contain about 17 p.c. nitrogen, and 2 p.c. ash. The percentage of nitrogen, in ordinary shoddy varies from 5–8, the general average being about 7. Shoddy is apt to contain a good deal of water; the other impurities are cotton, oil, and mineral dust.

Leather. The percentage of nitrogen is 4–6. This is the least active form of nitrogenous matter used as manure.

Soot. House soot is used by farmers as a top-dressing for spring corn. It contains on an average about 3·5 p.c. nitrogen, but the amount varies a good deal; the nitrogen is partly present as ammonium sulphate.

Bones. These are seldom used in their fresh state, they have generally been first steamed to extract the fat. A more perfect method of extracting the fat by means of benzene has been recently introduced (S. C. I., 1884, 375, 490, 575), but not much employed. Less nitrogenous matter is removed from the bone when benzene is used. A third form of bone is that left after extracting the greater part of the gelatinous matter by boiling under pressure. These three descriptions of bone will contain about the following percentages of nitrogen and phosphoric anhydride.

	Nitrogen	Phosphoric anhydride
Fresh bone	3·7	19
Steamed bone	3·7	23
Boiled bone	1·4	29

Bones are either applied to the land directly as half-inch bones, or as bone-dust or bone-flour; or they are employed for the manufacture of superphosphate. The soft parts of bone are more nitrogenous than the hard parts, bone-dust is therefore generally more nitrogenous than coarse bones. Bone-flour is a still finer powder, prepared from boiled bones.

The amount of bone and bone-ash imported into the United Kingdom in 1887 was 51,883 tons; this is a smaller amount than formerly. The amount of bone annually collected at home for the use of the manure manufacturer is estimated by Mr. Voss as 60,000 tons.

Bone ash. This is imported from South America. It was formerly much used for preparing high-class superphosphates, but is now less employed, owing to the abundance of cheaper phosphates. Pure ox bone ash will contain nearly 40 p.c. phosphoric anhydride. The commercial article is usually sold on a basis of 75 p.c. tricalcic phosphate, equal to 34·4 p.c. phosphoric anhydride.

Phosphatic slag. By the process patented by Thomas (1877–79) the phosphorus is removed from pig-iron. The melted iron is placed in a Bessemer converter lined with lime, a large dose of lime is added, and the blast applied. At the high temperature reached the impurities in the iron are oxidised by the air introduced, the phosphorus becomes phosphoric pentoxide and unites with the lime. A slag is formed containing about 50 p.c. lime, 4 p.c. magnesia, 2 p.c. alumina, 14 p.c. iron oxide, 5 p.c. manganese oxide, 10–25 p.c. phosphoric pentoxide (average 17 p.c.), and 8 p.c. silica. The process has been adopted to a very large extent. The quantity of phosphatic slag produced in Europe in 1887 was about 532,550 tons; of this amount about 116,400 tons were produced in the United Kingdom, and 303,780 tons in Germany and Luxemburg. By introducing only a portion of the lime at first, a slag rich in phosphates can be prepared.

For several years the slag was regarded as valueless, the large amount of iron present leading agricultural chemists to believe that the phosphoric anhydride would not prove available to plants, while the ferrous oxide would probably be injurious. It is now known that the phosphoric anhydride in the slag is almost wholly combined with calcium, and that this calcium phosphate is easily disintegrated and rendered soluble in the soil, and that no ill effects arise from the presence of the ferrous oxide. Tetracalcic phosphate is apparently the combination in which most of the phosphorus occurs (Hilgenstock, D. P. J. 250, 330; Otto, Z. 11, 255; Bücking u. Zinck, Stahl u. Eisen, 7, 245). About 1·5 p.c. of the total phosphorus exists as iron phosphide, which is changed into phosphate in the soil (Jensch, Z. 10, 820). The phosphate in the slag is not soluble in water; it is dissolved to a considerable extent by a solution of ammonium citrate.

At first attempts were made to dissolve the phosphates in the slag, and then reprecipitate them for use as manure; this was afterwards found to be unnecessary. Field experiments with finely ground, untreated slag, commenced in 1882, and soon became very numerous, as it was found to produce an excellent effect. The Germans were the first to realise the importance of the new manure, and they succeeded in purchasing a large proportion of the English make before Englishmen had become alive to its value.

To be effective the slag must be very finely ground; it should pass through a sieve having 100 meshes to the linear inch. The grinding requires special machinery. It is advisable, according to Horn (S. C. I. 1886, 242), to break first under stamps, to further reduce between rollers, then to separate pieces of iron by passing over slanting sieves, and finally to grind between millstones.

According to Wagner's trials, 2 parts of phosphoric anhydride in powdered slag (of which 80 p.c. passed a sieve with meshes 0·2 mm. diameter), are equal in manuring power to 1 part of soluble phosphoric anhydride in superphosphate; the effect will, however, vary in different soils.

Precipitated phosphate. Phosphatic minerals which are unsuitable for the manufacture of superphosphate, either from their poverty in phosphate, or from the presence of an objectionable amount of iron oxide or alumina, are sometimes treated with acid, the calcium phosphate dissolved out, and then recovered by precipitation. By a previous calcination, the ferric oxide and alumina of the mineral may frequently be rendered more insoluble, and again by the use of cold or weak acid much of these objectionable ingredients may be left undissolved. The solution in acid is then precipitated with lime, chalk, or solution of calcium sulphydrate, prepared by acting on alkali waste with a solution of hydrogen sulphide. If the addition of the neutralising base is stopped while the solution is still acid, the precipitate will consist chiefly of dicalcic phosphate. Solution of calcium sulphydrate is the best precipitant; its addition should cease as soon as a dark colour indicates the formation of some iron sulphide (De Bouquet, S. C. I. 1884, 526; Lombard, *ibid.* 259, 1885, 173; also Twynam, *ibid.* 1883, 476).

The phosphoric anhydride in precipitated phosphate stands next in value to that existing as monocalcic phosphate. Commercial dicalcic phosphate may contain as much as 40 p.c. P_2O_5; it is thus a very concentrated manure, and especially suitable for use where manure must be conveyed a long distance. It is employed on the Continent, but not in England.

Superphosphates. The phosphates previously mentioned may be applied directly to the soil with good effect, if in the condition of fine powder. Many phosphatic deposits are, however, too hard and insoluble to be economically used in this manner; these are treated with sulphuric acid, and converted into superphosphates.

The treatment of bone with sulphuric acid was originally recommended by Liebig. The treatment of mineral phosphates with sulphuric acid originated with Lawes, who took out a patent for this process in 1842, and founded a manufacture which has since reached enormous dimensions. The annual production of superphosphates in the United Kingdom probably exceeds 600,000 tons; in France the phosphatic manures employed are about 250,000 tons; in Germany and Austria, 800,000 tons; in the United States probably about 1,000,000 tons per annum.

Phosphatic materials used.

Superphosphate was prepared by Lawes in the first instance from spent animal charcoal; Suffolk (tertiary) coprolite, and Estremadura phosphorite were also early employed. The Suffolk coprolite was for 15 years the principal material made use of. The far superior Cambridge (greensand) coprolite then became for many years the chief material; this is now scarcely used, other phosphates being much cheaper. Deposits rich in calcium phosphate have been found all over the world; many of these have been exhausted, and others given up as of inferior quality, or as being at present prices too expensive to work. We shall give some account of those at present in use, with their average composition, and then enumerate the principal deposits which have become matters of history, or the use of which is at present in abeyance from the effect of competition.

South Carolina or Charleston phosphate. This is apparently a converted eocene marl. It occurs in rough masses, largely perforated by boring mollusca, and associated with fossil bones and teeth. It is classed as 'land' and 'river' phosphate; the latter is obtained by dredging the Bull, Soosaw, and Stono rivers. This phosphate came first into use in 1867, and soon became the chief material for the manufacture of superphosphate. The quantity exported to the United Kingdom in 1887 was 165,275 tons (principally river phosphate); in the same year 430,549 tons were used in the United States. There are three grades, containing phosphoric anhydride equal to 50–52, 55–56, and 58–60 p.c. tricalcic phosphate; they differ simply in the proportion of siliceous matter present. South Carolina phosphate is not rich enough for the preparation of high-class superphosphates, but it is an admirable material for the production of an ordinary superphosphate, containing, according to the quality of the phosphate used, from 11–14 p.c. soluble phosphoric anhydride, or in commercial language 24–30 p.c. soluble phosphate.[1]

Belgian and Somme phosphate. In the north of France (departments Somme and Pas de Calais), and in the adjoining districts of Belgium, there exists an enormous deposit of a friable phosphatic rock, 'craie grise,' extending over seven million acres. This deposit lies on ordinary white chalk; it consists of yellowish grains embedded in a chalky matrix. The rock contains 20–30 p.c. of calcium phosphate, occurring in the crystalline grains above mentioned. In the upper layer of this deposit are pockets, chiefly developed in France, which contain a sand far richer in phosphate and poorer in carbonate than the underlying rock, the proportion of phosphate in this sand being 50–80 p.c. The sand has probably been formed from the original rock by the action of water. This phosphatic sand is known as 'Somme phosphate'; it has come into use during the last three years.

Of Somme phosphate about 150,000 tons were raised during 1888. The supply is far more limited than that of the poorer rock, and will in a few years be exhausted. There are four grades in the market, containing 55–60, 60–65, 70–75, and 75–80 p.c. of calcium phosphate. The higher grades of this phosphate form the chief material at the present time for the manufacture of high-class superphosphate.

The Belgian phosphatic rock is, as already mentioned, generally of low quality. By washing and blowing, a material containing 40–45 p.c. calcium phosphate is produced. Many schemes have been tried for removing the calcium carbonate, and thus raising the value of the material; none has yet become a commercial success. Belgian phosphate is used with other phosphates as a diluent: the carbonate it contains produces much gypsum when acted on by the sulphuric acid, and considerably improves the porosity and dryness of the manure. The export from Belgium to the United Kingdom was 45,322 tons in 1887.

One practical advantage possessed by the Belgian and Somme phosphates is that they require no grinding. Somme phosphate as imported goes entirely through a sieve of 60 wires to the inch.

Phosphorites. Large deposits of apatite, or of phosphates having an apatite character, occur in many places; those most worked have been the Estremadura, the Canadian, and the Norwegian; the latter is not now brought to this country.

1. *Estremadura phosphorite.*—An immense deposit occurs at Caceres. In composition it is a fluor-apatite, but mixed with much quartz, and with more or less calcium carbonate. Three qualities are sold, containing about 50, 60, and 70 p.c. tricalcic phosphate; the bulk of the exports consists of the lowest quality. The calcium carbonate varies from 6–16 p.c. The exports have in former years been very large, amounting sometimes to 60,000 tons per annum; in 1887 the export to the United Kingdom was 15,612 tons.

2. *Canadian phosphorite.*—This is much richer than the Estremadura phosphorite, containing 70–80 p.c. tricalcic phosphate. The lower qualities contain much mica. The amount exported to the United Kingdom in 1887 was 19,194 tons.

Caribbean phosphates. Under this head we group the rock phosphates found on many of the West India Islands, some of which are often classed as phosphatic guanos.

1. *Aruba.*—This is one of the Dutch islands. The deposit has been worked about seven years. The quantity raised is about 20,000 tons annually. In 1887, 9,505 tons were imported into the United Kingdom. The phosphate is of high quality, containing 75–80 p.c. tricalcic phosphate.

2. *Curaçao.*—Another Dutch island. This is one of the finest phosphates available, containing about 85 p.c. tricalcic phosphate. With this phosphate superphosphate may be made containing 44–45 p.c. soluble phosphate (20–20½ p.c. soluble P_2O_5). This deposit is not at present worked, though not exhausted.

3. *Sombrero.*—This valuable deposit is nearly exhausted. It contains 70–78 p.c. tricalcic phosphate.

4. *Monk* and St. Martin's* Islands.*—Both deposits are now exhausted; the former was of very high quality.

5. *Great Cayman.*—This deposit contains phosphoric acid equal to 52–65 p.c. tricalcic phosphate, with a good deal of alumina and some iron. It is employed to some extent in the United States.

6. *Navassa.*—The deposit on this island has a well-marked pisolitic structure. The phosphoric anhydride is equivalent to 60–70 p.c. tricalcic phosphate. The use of Navassa phos-

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[1] By 'soluble phosphate' the English manufacturer understands the amount of tricalcic phosphate rendered soluble.

phate is limited by the considerable amount of alumina and ferric oxide present, which makes it unsuitable for the preparation of high-class superphosphates.

7. *Redonda and Alta Vela.*—The phosphates of these islands consist chiefly of aluminium phosphate. They are quite unsuitable for the manufacture of superphosphate. They have been dissolved in sulphuric acid, and the alumina separated as alum. It has also been found possible to obtain a large proportion of the phosphoric acid as sodium phosphate by heating with sodium chloride in superheated steam, or by firing with sodium sulphate and carbon (S. C. I. 1886, 570).

Bordeaux phosphate. Raised in the departments of Lot, and Tarn-et-Garonne. This is now little used in England, as it is not rich in phosphate, and contains a good deal of ferric oxide and alumina.

Nassau or Lahn phosphate. This is still used locally, but the exports to this country have ceased. It varies much in composition; the higher qualities are suitable for the manufacture of superphosphate, but the lower qualities contain much iron. This phosphate is remarkable as containing a distinct amount of iodine.

Coprolites. The phosphatic nodules commonly known as coprolites are at present less used than formerly, richer and cheaper phosphates being now available. The Cambridge (Upper Greensand) coprolite is the best of the English sorts; it contains 55–60 p.c. tricalcic phosphate, without an admixture of ingredients prejudicial to the production of soluble phosphate. About 20,000 tons were raised in 1887. The Suffolk coprolite (tertiary) contains less phosphate (55 p.c.), and more ferric oxide. The Bedfordshire coprolite (Lower Greensand) is still more inferior, the ferric oxide being present in increased proportion.

In France there are considerable deposits of coprolite in the Upper Greensand in the departments of Pas de Calais, Meuse, and Ardennes; those from Pas de Calais are shipped to England from Boulogne. These coprolites generally contain a low proportion of phosphate, and much siliceous matter.

Deposits of coprolite have also been found in Russia.

The composition of the principal phosphates employed by English manufacturers is shown in the following table; the figures are in most cases the means of many analyses. The smaller constituents are frequently unavoidably omitted, as they are not determined for commercial purposes.

Percentage composition of Mineral Phosphates employed in the Manufacture of Superphosphate.

—	South Carolina		Belgian	Somme		Estramadura	Canadian		West Indian			Coprolites		
	River	Land	Ordinary quality	First quality	Second quality	Ordinary	First quality	Lower quality	Aruba	Curaçao	Navassa	Cambridge	Bedfordshire	Pas de Calais
Water	2·3	1·3	0·4	1·3	1·5	2·7	0·4	0 9	2·5	0·6	5·0	4·0	3·4	1·1
Phosphoric anhydride	25·8	25·7	18·9	34·9	32 7	23·4	39·8	33·2	35·5	40·2	32·0	26·6	24·9	20·4
Lime	41·0	40·0	50·9	51·1	49·1	33·3	54·7	45·5	47·5	50·1	36·5	43·3	33·6	32·5
Magnesia	0·6	0·6	—	·4	—	—	—	—	—	1·2	0·6	1·0	0·2	0·5
Potash and soda	0·7	—	—	—	—	—	—	—	—	0·7	0·9	1·2	—	—
Ferric and ferrous oxide	2·2	3·0	1·2	1·2	1·5	—	—	—	2·0	0·3	4·4	2·2	5·8	3·2
Alumina	1·3	2·6	0·4	0·5	0·6	—	—	—	2·1	0·0	8·9	2·0	3·5	3·2
Carbonic anhydride	4·6	4·2	20·0	4·0	—	3·5	—	—	—	3·0	2·5	6·8	—	4·4
Sulphuric anhydride	1·0	1·8	—	0·8	—	—	—	—	—	1·1	0·2	0·9	—	1·0
Chlorine	3·4	—	—	—	—	—	3·2	—	—	0·1	0·2	—	—	—
Fluorine		—	—	1·8	—	—		—	—	0·5	0·0	—	—	1·7
Siliceous matter	14·0	14·0	2·7	1·1	2·4	32·5	1·0	10·1	2·1	0·9	3·2	8·2	15·3	26·4
Phosphates reckoned as tricalcic phosphate	56·3	56·0	41·3	76·2	71·4	51·1	86·9	72·5	77·5	87·8	69·9	58·1	54·4	44·5
Excess of lime over tricalcic phosphate	10·5	9·6	28·5	9·8	10·5	5·6	7·6	6·2	5·5	2·6	nil	11·9	4·2	8·4

Process of Manufacture.

The phosphate to be employed is first thoroughly dried, and then reduced to an extremely fine powder. Considerable improvements have lately been effected both in the economy of the grinding, and in the degree of fineness attained. When the material is in considerable masses it is first broken into small pieces by Blake's stone-crusher. It may then be transferred to a Morris' mill, and ground by edge stones on a revolving bed. The dust may then be separated from the product by a fan, and the grit fed to ordinary horizontal millstones. A Mumford's separator is of great use in removing the fine dust from partly ground products, thus enabling the remaining grit to be reduced to powder with a smaller consumption of power. The Sturtevant (centrifugal) mill is also sometimes employed for reducing phosphates to powder. The finer the powder obtained, the more complete will be the decomposition by the sulphuric acid. For first-class work the powder should pass a sieve of eighty wires to the inch.

The sulphuric acid employed is ordinary chamber acid, sp.gr. 1·57. Acid of this strength is of course preferred on the ground of economy; it is essential, however, that the acid contain water, as the dryness of the product is determined by the formation of gypsum ($CaSO_4,2H_2O$). The proportion of water necessary must depend on the composition of the materials, and the nature of the reaction. If free phosphoric acid (H_3PO_4) and gypsum are the result of the reaction, the sulphuric acid used should have 1·65 as its maximum sp.gr. If hydrated monocalcic phosphate ($CaH_4P_2O_8,2H_2O$) is the product formed, the maximum sp.gr. of the sulphuric acid will be 1·55. If the material contains calcium carbonate or fluoride, these constituents will require acid of 1·78 sp.gr. for their conversion into gypsum. Practically the weak chamber acid answers well. Some water is lost as steam during the mixing, and a certain proportion of moisture does not injure the texture of the superphosphate when it contains a sufficient amount of gypsum. It is clear, however, that when dealing with a phosphate containing much carbonate or fluoride, an acid somewhat stronger than ordinary chamber acid is to be preferred.

The proportion of sulphuric acid to be used depends of course on the composition of the phosphatic material. Theoretically, 100 of tricalcic phosphate will require 94 of sulphuric acid sp.gr. 1·6 (55 p.c. SO_3), or 100 of sulphuric acid sp.gr. 1·55 (51·5 p.c. SO_3), if monocalcic phosphate is to be produced, and one half more if phosphoric acid is to be the result. The proportion of sulphuric acid used in practice is usually as large as can be employed without endangering the dryness of the product; it is generally somewhat in excess of that needed to produce monocalcic phosphate, but is considerably below that required to yield only phosphoric acid. For South Carolina river phosphate (the phosphate most largely used), the ordinary proportion is 90 p.c. of sulphuric acid, sp.gr. 1·57.

The excess of lime present in the material (as carbonate or fluoride) is a principal factor in determining the quantity of sulphuric acid to be employed: 100 of lime will require 260 of acid sp.gr. 1·6, or 277 of acid sp.gr. 1·55 to produce calcium sulphate. At the foot of the table previously given will be found the excess of lime (over that required to form tricalcic phosphate) present in each of the mineral phosphates commonly employed. Phosphates containing a considerable excess of lime will yield a poorer superphosphate than their percentage of phosphoric acid would seem to warrant, owing to the large proportion of sulphuric acid which they require. Siliceous matter is the least harmful impurity in a mineral phosphate, as it consumes no sulphuric acid.

To prepare a 'mineral superphosphate' the only ingredients are the powdered phosphate and sulphuric acid. When turnip manures, or other manures containing a little nitrogen, are prepared, crushed bones, powdered hoof and horn, shoddy, or ammonium salts, are added when the ingredients are mixed. Superphosphate is very seldom made from bone alone, as it is difficult to obtain a dry product, and the proportion of soluble phosphate yielded is but small. So-called 'dissolved bones' are usually prepared from a mixture of mineral phosphate, bone, and some concentrated nitrogenous matter.

The mixer in which the reaction takes place stands on a platform, over an empty chamber known as the 'pit.' It consists of a wooden cylinder, sometimes nearly horizontal, sometimes vertical, furnished in the centre with a revolving shaft, carrying arms set on screw-wise. Into this mixer the charge of weighed 'dust' is emptied, bag by bag, while at the same time a measured quantity of sulphuric acid is run in from a tank. When the charge is completed, agitation is continued for two minutes; a valve is then opened, and the whole contents of the mixer (about 16 cwt.) allowed to fall into the pit below. Ten charges can be easily worked in one hour. The pit below is built of brick or concrete on three sides, the fourth side consists of a wooden hoarding which is taken down when the pit is being emptied. A pit will hold about 140 tons. The fluid material which enters the pit rapidly reaches a temperature considerably exceeding 100°, and then becomes solid. In a day or two it will be dug out with pickaxes.

The gases given off during the reaction, both from the mixer and pit, are of a particularly unpleasant description, especially when the phosphate contains fluorides. Both mixer and pit are provided with flues in connection with a fan, by which all the gases are removed; these are purified in a scrubber, and then conducted to a tall chimney.

Well-made superphosphate is a porous mass, the cavities being due to imprisoned gas. It is reduced to powder by passing through Carr's disintegrator. If mixed manures are to be made, the other ingredients are added while passing through the disintegrator. By adding ammonium sulphate or other nitrogenous material, with or without potash salts, 'corn,' 'grass,' 'mangel,' and 'potato' manures are produced. Sodium nitrate cannot safely be added to superphosphate unless the latter is very dry; if this precaution is neglected free nitric acid is produced, the manure bags are destroyed, and serious mischief may occur. To employ ammonium sulphate and sodium nitrate together is still more objectionable, as ammonium nitrate is formed, and even when it does not suffer decomposition it ruins the manure by its deliquescence.

Having sketched the process of manufacture, we must say a few words on some of the chemical reactions involved. It was formerly supposed that the soluble phosphate produced consisted almost entirely of monocalcic phosphate; it is now recognised that a part, and often a large part, of the soluble phosphate consists of free phosphoric acid (Ruffle, S. C. I. 1887, 327; Mellon, *ib.* 803). In the first stage of the reaction phosphoric acid alone is probably produced, and this afterwards reacts on the remaining undecomposed phosphate. The proportion of free phosphoric acid in the resulting manure is greater when strong sulphuric acid has been employed, the total soluble phosphoric acid being at the same time diminished (Mellon, *l.c.*). When superphosphates are dried at 100° a loss of soluble phosphoric acid also occurs, and this loss becomes much greater when a higher temperature is employed (Ruffle). Monocalcic phosphate can, in fact, exist only when in union with water.

A further reaction which is of great practical moment to the manufacturer of superphosphate is the disappearance of soluble phosphate by keeping. The regenerated insoluble phosphate is known as 'reverted phosphate.' This deterioration during storage is not observed in the case of well-made superphosphate prepared from finely ground mineral phosphate containing no appreciable quantity of iron or aluminium, but it is observed when ferric oxide or alumina is present. In few of the phosphates employed by the manufacturer, excepting Navassa, is any considerable amount of the phosphoric acid combined with iron or aluminium. In some phosphates, as Cambridge coprolite and Carolina river phosphate, the iron is apparently present as pyrites, or as ferrous silicate, and exercises no injurious influence; but in many other phosphates the iron exists as ferric oxide. When a red-coloured phosphate of this description, as Lahn or Navassa phosphate, is treated with sulphuric acid, and the *temperature kept low* during the reaction, the red colour remains unchanged, and nearly all the phosphoric acid is found to have become soluble. If, however, the superphosphate is made in bulk in the usual way, and a high temperature is consequently attained, the manure loses its red colour in a few hours, and the soluble phosphate is found to be greatly diminished. In two comparative experiments with Lahn phosphate, the superphosphate was in one case broken up, and cooled as soon as it became solid: it yielded 23·8 p.c. soluble phosphate, the greater part of its red colour remaining. In the other case, the bulk remained eighteen hours untouched; the red colour had then disappeared, and the soluble phosphate was reduced to 13·6 p.c. It appears that, at a high temperature, free phosphoric acid readily attacks ferric oxide and alumina, and combines with them. The same action proceeds, though at a far slower rate, in the cold, unless the superphosphate is very dry, and made with a minimum of sulphuric acid. So long as superphosphate is valued on the basis of its contents in soluble phosphate, ferruginous and aluminous phosphates will be avoided by the manufacturer. On the Continent, however, and in the United States, reverted phosphate has a considerable money value, and mineral phosphates containing iron and aluminium consequently find employment.

Ordinary superphosphate is made from a mixture of phosphates, and contains 25-27 p.c. of dissolved phosphate (11·5–12·4 P_2O_5), and 2–3 p.c. of undissolved phosphate. The turnip manures containing bone have generally rather less of dissolved phosphate, more of undissolved, and nearly 1 p.c. of nitrogen. Special manures of greater strength are also prepared. From good Carolina phosphate, superphosphate containing 30–31 p.c. dissolved phosphate (13·7–14·2 P_2O_5) may be obtained. Somme phosphate of 76 p.c. will yield manures containing 38 p.c. dissolved phosphate (17·4–17·9 P_2O_5). From Curaçao phosphate, superphosphate with 44–45 p.c. dissolved phosphate (20·2–20·6 P_2O_5) may be prepared.

Far richer superphosphates are obtained by the process patented by Packard (Eng. Pat. 6,176, 6,750–6,752). Superphosphate, prepared so as to be rich in free phosphoric acid, is extracted with water, the solution evaporated to sp.gr. 1·125–1·300, and sufficient calcium phosphate, carbonate, or hydrate added so as to leave one-third of the phosphoric acid in the free state. The solution is then filtered, and the filtrate evaporated to dryness. The product contains about 40 p.c. of soluble phosphoric acid, equal to 87 p.c. of so-called 'soluble phosphate.' This superphosphate has a special value where manure has to be conveyed a long distance.

There is a considerable export trade in English-made superphosphate.

Gypsum. This has in most cases a very small value as a manure. Where superphosphate is employed, it is applied in this manure. Massive gypsum is imported from the South of France. It was formerly used as a diluent in making the lower class of superphosphates, but this place is now taken by Belgian phosphate. It is an excellent drier for mixing with damp manure.

Lime, chalk, and marl. These can hardly be classed as artificial manures, as they are not generally applied as plant foods, but for the sake of the considerable amelioration of the soil which they effect.

Potassium salts. These will be found described under their own head.

II. The Relative Value of Manures.

We have described as briefly as possible the various nitrogenous and phosphatic manures at present used. The important question remains, have the nitrogen and phosphoric acid the same value in all these manures? and, if not, what is the difference of value? This question may be answered from (1) a trade point of view. We can calculate from the market price of various manures what is the money value of their chief constituents. If the prices given for manures were determined by an accurate knowledge of their effect in the field, these prices would really show us their average relative value. As a fact, market prices do generally indicate, though sometimes very imperfectly, the relative manuring value of different manures. We may also attack the subject from (2) the data afforded by actual investigation. In this case we soon find that the number of available investigations is insufficient, and that the relative value of the same manures differs more or less with differences in the soil, crop, and season. Notwithstanding the difficulties of the subject, it is too important to be passed over. We will confine ourselves to the best-ascertained facts.

The trade values of nitrogen and phosphoric acid in various forms are annually calculated both in Germany and America. We give below Wolff's figures for 1888, and the Connecticut, New Jersey, and Massachusetts figures for 1888. Instead of affixing money values, the highest value is here taken as 100.

Relative trade values of nitrogen in different manures.

1. *Wolff.* 1888.

Ammonium salts, nitrates, dry powdered blood, meat flour, Peruvian guano	100–87
Finest steamed bone-dust, fish guano, oilcakes, poudrette	87–73
Coarser bone-dust, horn-meal, wool-dust	80–66
Coarse fragments of bone, horn shavings, woollen lumps, farmyard manure	60–53

2. *American.* 1888.

Ammonium salts	100
Finely ground fish, meat, blood, bone and oilcake	94
Nitrates	91
Fine-medium bone	74
Medium bone	60
Coarse bone	49
Hair, horn shavings, and coarse fish scrap	46

Relative trade values of phosphoric acid in different manures.

1. *Wolff.* 1888.

Phosphate soluble in water	100
Precipitated phosphate, Peruvian guano	92
Reverted phosphate, finest steamed bone-dust, fish guano, poudrette	83
Phosphatic guanos	75
Coarser bone-dust, powdered animal charcoal, bone-ash	67
Coarse fragments of bone, powdered phosphorite and coprolite, Thomas's slag, farmyard manure	33

2. *American.* 1888.

Phosphate soluble in water	100
Phosphate soluble in ammonium citrate	94
Fine bone-dust, powdered fish . .	88
Fine medium bone	75
Medium bone	62
Coarse bone	50
Finely-ground rock phosphate . .	25

We turn next to the facts taught by actual trials with crops.

Nitrates are, in a large majority of cases, the most active, and therefore the most valuable form of nitrogen. Comparisons between sodium nitrate and ammonium salts, containing similar amounts of nitrogen, have been made for many years at Rothamsted, and also at Woburn. With cereal crops the nitrate, on an average, yields distinctly more corn and considerably more straw than the ammonia. The produce by the nitrate is most in excess in dry seasons; in a wet season the ammonia may be superior. On pasture the relative superiority of the nitrate is about the same as with cereals. With potatoes ammonia apparently is equal to nitrate. With mangel-wurzel, or sugar beet, the nitrate is far superior. A good result with ammonium salts is much more dependent on the presence of abundance of phosphates and potash in the soil than is the case with nitrates. Nitrates and ammonium salts give all their effect in the first year of their application.

The effect of organic nitrogenous manures differs in different soils. In a clay soil bones decompose so slowly as to be of little value. Organic manures, as shoddy, oilcake, bones, and farmyard manure, yield only a small portion of their nitrogen to the crop during the first year, and several years will elapse before the supply is exhausted. The continued use of such manures increases the proportion of nitrogen in the soil. The proportion of the nitrogen in the manure that is recovered in the crop is frequently smaller than that obtained under favourable circumstances in one season from the application of sodium nitrate, the slowly-acting manures being, in the case of arable land, subject to an annual loss of nitrogen as nitrates by drainage. Organic nitrogenous manures are more active in proportion as they are finely divided, and when applied to a well-aerated soil. They are best applied in autumn, while nitrates and ammonium salts should be applied in spring.

The relative value of different forms of phosphates has been a subject of much controversy. Some mineral phosphates (as apatite) having been found almost useless as manure, it was too hastily concluded that (with the exception of bone and guano phosphates) only phosphates soluble in water were effective. Latterly it has been maintained by some, that very fine grinding will render any phosphate as available as soluble phosphate.

In considering the subject we should bear in mind that the phosphates in the soil, on which plants feed, are not soluble in water, drainage waters being free from phosphoric acid. Soluble phosphate when applied to a fertile soil is quickly precipitated, and is generally finally converted into a hydrated ferric or aluminic phosphate. The practically insoluble phosphates of the soil are dissolved by the acid sap of the root-hairs immediately before absorption by a crop.

One great advantage possessed by a phosphate soluble in water consists in its diffusibility. When rain falls after an application of superphosphate, the phosphoric acid is distributed in the soil more perfectly than can be achieved by any other mode of application, and consequently a greater number of root-hairs may come in contact with it. Superphosphate is thus more immediately effective than any other form of phosphate. The superiority of superphosphate is, however, not shown in the case of some soils very poor in lime, and in which any additional supply of acid matter is hurtful to the plant; in such cases an assimilable undissolved phosphate may produce a better result.

Numerous experiments have been made regarding the assimilability of mineral phosphates when finely ground. It appears that apatites, and other crystalline phosphates not disintegrated in the soil, have a very small effect as manure even when finely ground. The small crystalline grains of the Somme phosphate lie in this category. The majority of mineral phosphates are, however, effective as manure when very finely ground, but to a different extent on different soils. In 1857 a very extensive trial of ground French coprolite was made in many parts of France. M. de Molon reported (C. R. 46, 233)—1. On clay, schistous, granitic, and siliceous soils rich in organic matter, the coprolite may be used with advantage. 2. On the same soils if poor in organic matter, especially when they have been long under cultivation or have recently received a dressing of lime, the coprolite powder must be mixed with animal manure. 3. On limestone soils, especially chalk, the coprolite is applied with most advantage in the state of superphosphate. This judgment has not been altered by any subsequent experience. The conditions favourable to the use of undissolved phosphates are presence of humus, and absence of lime. On the moor soils of Germany, where such conditions prevail, Thomas' slag has had its greatest success. A calcareous soil is the one most unsuitable for the use of undissolved phosphates, calcium carbonate offering a great resistance to the solution of calcium phosphate (C. J. 1866, 313).

It is generally admitted that precipitated dicalcic phosphate is nearly equal in effect to soluble phosphate. Phosphates that are soluble in ammonium citrate (including the reverted phosphate of superphosphate) may be safely regarded as assimilable by plants; in America they are regarded as of about equal value with water-soluble phosphate; that they are so always is certainly open to doubt. Phosphates that are insoluble in ammonium citrate are often effective as manure. Ammonium citrate gives thus no safe distinction between assimilable and non-assimilable phosphates.

We may quote in conclusion the average results obtained by Wagner in 1886, in numerous experiments with two soils in pots, as an example of the relative value of different phosphates as shown by the crops (wheat, barley, and flax) which they produced. The phosphoric acid in the various manures had the following relative values in the first year of their application:—

Superphosphate	100
Thomas' slag (finest powder) .	61
,, ,, (fine powder) . .	58
,, ,, (coarse powder) .	13
Peruvian guano	30
Bone-dust (steamed) . . .	10
Coprolite powder	9

The residue of the less soluble phosphates remaining in the soil is of course larger, and produces in subsequent years a greater effect than the residue remaining from the application of superphosphate. Thus Wagner found the relative results in one and two years of a single application as follows:—

Phosphoric acid applied		Relative result in crop	
Quantity	Form	First year	Two years
1	Superphosphate	100	100
2	Thomas' slag	100	120
2	Bone-dust	10	22

3. Special Methods of Analysis.

The enormous quantity of artificial manures bought and sold upon the results of analysis has led to great attention being paid to the acquisition of accurate and speedy analytical methods. Latterly committees of agricultural chemists have studied the subject with the object of selecting methods to be adopted by all, and thus prevent as far as possible divergencies in the results of analysis. We refer especially to the 'Rapport fait au Comité des Stations agronomiques' (A. a. 1887, 274), which deals in detail with determinations of nitrogen, phosphoric acid, and potash under various forms. Also to 'Methods of analysis of commercial fertilisers, cattle foods, dairy products, sugar, and fermented liquors' (Bulletin 19, United States Depart. Agri. 1888). For general methods we must refer to the article on 'Analysis' in this Dictionary; we shall here only describe a few methods peculiar to the analysis of manures.

Water.—In preparing a finely ground sample for analysis water is frequently lost, and sometimes to a large extent. It is thus often indispensable to determine water both in a large quantity of the coarse original material, and in the fine powder prepared for analysis, and after the analysis to find by calculation the composition of the original material.

Superphosphates contain combined water which is given off at 100°. To ascertain the true hygroscopic water, Ruffle recommends to expose the superphosphate in its original powdery condition in a vacuum over calcium chloride for 18–24 hours, at the ordinary temperature, after which time very little loss occurs. Results thus obtained are much lower than those yielded at 100°, but they agree with the hygroscopic water theoretically present in superphosphates of known history (S. C. I. 1887, 327).

Phosphoric acid.—1. *Total.* A simple and effective method is recommended by the 'Verband landwirthschaftlicher Versuchs-Stationen im deutschen Reiche' for the analysis of Thomas' slag; the method is applicable to many phosphates (Landw. Versuchs-Stat. 35, 439). 10 grams are heated with 50 c.c. concentrated sulphuric acid for $\frac{1}{4}$ hour in $\frac{1}{2}$ litre flask, at a temperature at which white fumes are developed. Water is then added to 500 c.c. and the whole filtered. To 50 c.c. of the filtrate are added 20 c.c. of citric acid solution (500 grams per litre), and the whole nearly neutralised with 10 p.c. ammonia. 25 c.c. of the usual magnesium chloride mixture are then added, and finally one-third the volume of 10 p.c. ammonia. The ammonio-magnesium phosphate is collected in the usual way.

In the French method (*l.c.*) 1 gram of powdered phosphate is boiled for 10 minutes with 10 c.c. hydrochloric acid in a 200 c.c. flask; there is then added 50 c.c. water, 20 c.c. of alkaline ammonium citrate (400 grams citric acid, and ammonia 22° (Baumé ?) to 1 litre), and 10 c.c. acetic acid 8°; the solution should be freely acid. The whole is boiled, 1·5 gram ammonium oxalate added in crystals (this should be an excess), and the clear liquid decanted through a filter. The precipitate after a few washings receives 2 c.c. ammonium citrate, and washing with hot water is continued till the bulk of the filtrate is 2[illegible]0 c.c. When cold 10 c.c. magnesium chloride solution (150 grams magnesium chloride, and 150 grams ammonium chloride per litre; 5 c.c. = ·5 gram P_2O_5), and afterwards 50 c.c. ammonia are added. The rest proceeds as usual.

In the method recommended in America, 2 grams of the phosphate are boiled with 30 c.c. hydrochloric acid, and 0·5 gram potassium chlorate cautiously added in small quantities till all organic matter is destroyed; the whole diluted to 200 c.c. and filtered. 50 c.c. of the filtrate then receive 15 grams ammonium nitrate, and are neutralised with ammonia. To the hot solution, 50 c.c. of molybdic solution (100 grams molybdic acid in 417 c.c. ammonia sp.gr. ·96, poured into 1,250 c.c. nitric acid sp.gr. 1·2) are added for every decigram P_2O_5 supposed to be present. Digestion at 65° continued for one hour, the precipitate collected, washed with plain water, dissolved in ammonia and hot water, not exceeding 100 c.c., nearly neutralised with hydrochloric acid, magnesium mixture (110 grams crystallised mag. chlor., 280 grams amm. chlor., 700 c.c. ammonia sp.gr. ·96, water to 2 litres) added drop by drop, with stirring; after fifteen minutes 30 c.c. ammonia sp.gr. ·95 is added, and after standing two hours the precipitate is collected, washed with ammonia, ignited intensely ten minutes, and weighed.

2. *Soluble phosphoric acid.*—The amount of soluble phosphoric acid found in superphosphate depends to some extent on the manner in which the extraction is made. (A) 10 grams of superphosphate are placed in a mortar, a little water added from a litre flask, the whole rubbed to a thin paste, more water added, the turbid liquid decanted into a bottle, and the process repeated till only fine grit remains in the mortar. The residue is then transferred to the bottle, the rest of the litre added, and the whole shaken at intervals during one or more hours. The analysis is made in 100 c.c. (B) 2 grams of superphosphate are quickly washed, either on a filter, or in a beaker by decantation. In method A, the free acid of the superphosphate remains long in contact with the partially-insoluble phosphates in the manure, and brings a part into solution. If, therefore, the original material were pretty free from iron, method A will show the largest amount of soluble phosphoric acid. If, on the other hand, the superphosphate contains ferric compounds unsatisfied with phosphoric acid, method B will give the larger amount of soluble phosphate, as on this plan the soluble phosphoric acid more quickly escapes contact with the iron. Method B is the one now generally preferred.

The French and American methods are quite similar. 2 grams of superphosphate are placed in a glass mortar, washed four or five times by decantation, using 10-15 c.c. of water each time, and the turbid solution is filtered through a small filter. The residue of superphosphate is then rubbed smooth with a caoutchouc-covered pestle, washed again four or five times, transferred to the filter, and washed till the bulk of the filtrate reaches 200 or 250 c.c. Solution corresponding to 1 gram of superphosphate is then taken for the determination of phosphoric acid by the French method (*v. ante*), or half that quantity for the American (molybdic) method.

3. *Reverted phosphate.*—The amount of reverted phosphate in a superphosphate is determined from its being insoluble in water, but soluble in a solution of ammonium citrate. The citrate is employed in a neutral or alkaline condition. The citrate employed by the American chemists contains 370 grams citric acid in 2 litres (sp.gr. 1·09 at 20°); it is neutral to an alcoholic solution of coralline. The citrate employed by the French chemists is the alkaline citrate already described.

The French chemists place the filter paper containing the part of the superphosphate undissolved by water in a flask, add ammonium citrate solution (80 c.c. if 2 grams of superphosphate taken), and leave it in contact one hour with agitation, and twelve hours at rest; then make the volume to 200 c.c., and filter. If only the reverted phosphate, or rather the citrate-soluble phosphate, is required, it is precipitated from this solution by the magnesium mixture, as already directed; but if it is required to know the total soluble phosphoric acid (the water-soluble *plus* the citrate-soluble), then a portion of the watery extract of the superphosphate is mixed with a portion of the citrate extract so as to represent 1 gram of superphosphate, and one determination made in the mixed solution.

In the method adopted in America there is no direct determination of phosphate soluble in ammonium citrate; the total phosphoric acid is determined, that soluble in water, and that insoluble in ammonium citrate; the part soluble in ammonium citrate is then found by difference. The part of the superphosphate undissolved by water is treated with 100 c.c. of the neutral ammonium citrate in a closed flask, quickly brought to 65°, and maintained at this temperature for half an hour with frequent agitation, then filtered quickly, the residue washed, ignited, dissolved in concentrated hydrochloric or nitric acid, and the phosphoric acid determined.

Potash. The French committee recommend Schloesing's perchlorate method. 1 gram of the potassium salt is converted into nitrate by successive treatment with barium nitrate and ammonium carbonate, and concentration of the filtrate, first with repeated portions of nitro-hydrochloric acid (one-fifth hydrochloric) to destroy ammonia, and finally with nitric acid alone. To the dry residue is added 10 c.c. of perchloric acid (1·6 grams of acid), evaporation to dryness is repeated, and the residue heated till no more fumes of perchloric acid appear. The residue is then washed with successive portions of alcohol (95 p.c.), saturated with potassium perchlorate, the washings being passed through a small Swedish filter. To ensure the perfect washing of the residue it is heated with 5 c.c. water, again taken to dryness, and again washed with alcohol. The washed residue is finally dissolved in a little boiling water, the solution passed through the filter and evaporated to dryness in a weighed capsule, a drop of perchloric acid being added to prevent the salt creeping over the edge. The weight of potassium perchlorate × 0·339 = potash.

When potash has to be determined in a mixed manure, 5 grams of the manure are mixed with 1 gram of calcium hydrate and a little water, and calcined at a low red heat. The mass is extracted with a little hot water, the solution precipitated with baryta water, the excess of barium removed by treating with ammonium carbonate, and the filtrate then treated as described above.

The American committee employ platinum. Of potassium salts ·5 gram is taken (if the salt is not the commercial chloride, with ·25 gram of sodium chloride), a few drops of hydrochloric acid added, with 15 c.c. of platinum solution (1 gram platinum in 10 c.c.), evaporated to dryness, the residue treated with water, and strong alcohol added. The precipitate is collected on a filter, and washed with strong alcohol. The washing is then continued with a solution of ammonium chloride (200 grams per litre saturated with K_2PtCl_6), 25 c.c. being six times passed through. The washing is completed with alcohol, the precipitate dried and weighed.

Of superphosphate 10 grams are taken, boiled with water, a little ammonium oxalate and excess of ammonia added, and the whole brought to 500 c.c. and filtered. 50 c.c. of the filtrate are evaporated to dryness, and ignited. The residue is dissolved in dilute hydrochloric acid, ·1 gram sodium chloride added, and 4 c.c. platinum solution, the rest of the operation being conducted as above.

Nitrogen. The well-known soda-lime and Dumas' methods have been already described under 'Analysis.' The determinations of ammonia and of nitric acid are also made by familiar methods. It should be recollected that if nitrogenous organic matter be present, ammonia should always be separated by distillation with magnesia only. In the presence of organic matter nitric acid must generally be determined as nitric oxide gas by Schloesing's method (Trans. Chem. Soc. 1880, 468; 1882, 345). A solution of indigo is often employed with fallacious results. The presence of many kinds of organic matter is fatal to accuracy with indigo. The indigo solution must also be standardised with solutions of nitre of a wide range of strength, under conditions exactly similar to those in which the actual analysis is to be made, as large and small quantities of nitre do not under similar conditions oxidise the same relative proportion of indigo (C. J. 1879, 578).

The method of determining nitrogen due to Kjeldahl is recommended by the German, French, and American committees. We will describe the method as pursued in the most complex case—namely, where nitrates, as well as ammonia and organic nitrogen, are present.

The German committee mix in a mortar 5 grams sodium nitrate with five times its weight of gypsum, or 1 gram of a mixed manure with twice its weight of gypsum, and place the mixture in a rather long-necked flask of 350 c.c. capacity, with 25 c.c. of phenolsulphuric acid (40 grams phenol dissolved to 1 litre in sulphuric acid sp.gr. 1·77). After mixing for five minutes, 3 grams of zinc-dust are very gradually added, the flask being kept cold, and two drops of metallic mercury. The contents of the flask are now boiled till all colour has disappeared.

The Americans bring ·7–1·4 gram of substance into the boiling flask, add 30 c.c. of sulphuric acid (sp.gr. 1·83) containing 2 grams salicylic acid, then add very gradually 3 grams of zinc-dust, heat gently till white fumes no longer appear, then add ·7 gram mercuric oxide (precipitated), and boil till the contents are nearly colourless. If the contents tend to become solid, 10 c.c. more sulphuric acid are added. The oxidation is completed by dropping in small quantities of powdered potassium permanganate into the hot liquid (removed from the flame) till it remains of a green or purple colour.

When no nitrates are present, ·5–2·5 grams of substance are taken, according to its richness in nitrogen, and 20 c.c. of strong sulphuric acid. A flask 9 inches long and of 250 c.c. capacity is employed. The phenol or salicylic acid, and the zinc-dust are omitted. If much frothing takes place a small piece of paraffin is added.

After the treatment with permanganate all the nitrogen exists as ammonia. The acid mass is then transferred to a large flask, using 200 c.c. of water, a few small pieces of zinc are added, and then 50 c.c. of a saturated solution of sodium hydrate, and 25 c.c. of potassium sulphide solution (40 grams per litre). The last two additions are best made through a funnel tube after the flask is closed. The flask is connected with a suitable condenser, best a tin worm; 150 c.c. are distilled. The distillate is received in a flask containing a known volume of standard sulphuric acid; the amount of ammonia is determined from the extent to which the acid is neutralised. The apparatus must be so arranged that no spray of soda is carried into the distillate.

Ruffle's modification of the ordinary soda-lime method, so as to admit of the determination of nitrogen in manures containing nitrates (C. J. 1881, 87), is thus employed by the American committee. The combustion tube receives first 1½ inch of a mixture of equal parts soda-lime and sodium thiosulphate. The substance is intimately mixed with 5–10 grams of equal parts powdered sugar and flowers of sulphur, and then with soda-lime and thiosulphate mixture sufficient to fill 10 inches of the tube; this forms the next zone. In front come 5–6 inches of ordinary soda-lime. In burning, heat the soda-lime in front to full redness before proceeding backward. The rest is conducted as usual. R. W.

MAQUI. The maqui is a small evergreen shrub, common in Chili along the course of torrents, and in shady mountainous woods. It is not cultivated, but grows wild, and the berries, which in Chili are eaten either fresh or preserved, are now exported largely to Europe for the purpose of colouring wines. In the three years ending 1887 the exports were respectively as follows, in kilos.: 26,592, 136,026, and 431,392. To France alone the exports during the same years were 500, 115,000, and 315,774 kilos.

MARBLE. Although this term should strictly be limited to those varieties of limestone which are sufficiently compact to receive a polish, it is loosely applied in trade to a great range of ornamental stones, including many which, like serpentine and alabaster, are not true limestones. Typical marble, such as that used for statuary, has a crystallo-granular texture, resembling that of loaf sugar, whence it is termed 'saccharoidal.' Under the microscope it commonly shows an aggregation of grains of calcite, exhibiting twin lamellæ. The development of such a structure appears to be due to that kind of metamorphic action which A. Geikie has termed *marmorosis*. That an ordinary limestone may be converted by the operation of heat and pressure into a crystalline marble is known to every field geologist, while the fact has been confirmed experimentally by Sir J. Hall and others. Metamorphic limestones, such as statuary marbles, are often rich in various crystallised silicates, such as garnet, zoisite, actinolite, and mica, which are supposed to have resulted from the alteration of the foreign materials originally associated with the limestone.

Of ancient marbles, the most renowned for the purposes of sculpture was the *Parian*, obtained from the isle of Paros, one of the Cyclades, in the Ægean sea. The finest kind, known as *lychnitis*, had a peculiar sparkling grain and a warm surface, which enabled the sculptor to render the texture of skin with great effect. The old quarries have been described by R. Swan (Brit. Ass. Rep. Newcastle, 1889). The famous *Pentelic* marble, largely used in Athenian architecture in the age of Pericles, was a coarser material, adapted for bold sculpture rather than for delicate statuary. *Carrara* marble, extensively employed in Rome under the name of *Luna* marble, and used by Michael Angelo and Raphael, is a very fine-grained saccharoidal limestone, still worked with other varieties at Carrara, Massa, and Serravezza in the province of Æmilia. According to the geological survey of Italy it is of triassic age.

The ancient marbles used in Italy have been studied by Corsi and other antiquaries. *Giallo antico* was a fine yellow marble from Numidia, while *rosso antico* was a homogeneous red marble, probably from Greece, sometimes confounded with *porfido rosso antico*, a hard red porphyry with white felspar crystals, from Jebel Dokhan in Egypt, the quarries of which have been described by W. Brindley. *Verde antico*, or *verde antique*, is a mixture of serpentine and limestone from near Atrax, on the Peneus, in Sicily, quite distinct from the *porfido verde antico*, or Lacedæmonian stone, a felspathic porphyry from Mount Taygetus. Many marbles are known by fanciful names derived from colour, locality, or a superficial resemblance to natural objects: thus, *bardiglio* is a grey or bluish marble with white veins, while *cipollino* is a white marble with green veins of mica or talc. (For Italian marbles *v.* Jervis, I Tesori Sotterranei dell' Italia, vol. 4, 1889.)

The marbles of Great Britain are derived mainly from the Devonian and carboniferous formations. *Plymouth* marble occurs in the Upper Devonian, while the Great Devon limestone, of Middle Devonian age, has been worked as a marble at Babbacombe and St. Mary Church. The *madrepore marbles* of Torquay are largely used for trivial ornaments. The carboniferous limestone of Derbyshire has long been famous for the beauty and variety of its marbles, the best known being the *encrinital* marbles, which owe their characteristics to the embedded remains of crinoids or 'stone lilies.' Similar encrinitic marble occurs at Dent in Yorkshire and in King's Co., Ireland. *Rosewood* marble is a beautiful brown variety from Ashford in Derbyshire. *Black* marble, such as is worked in Derbyshire, Galway, and Kilkenny, usually emits a fetid odour when struck, and loses its colour on calcination. W. N. Hartley found 1·48 p.c. of carbon and ·01 of sulphur in the black marble of Kilkenny (Proc. R. Dub. Soc. 5, 486). The black carboniferous limestone of Belgium and France, with small white sections of encrinites, is termed locally *petit granit*.

Lumachella is an Italian name for any shelly marble, but is specially applied by mineralogists to a Liassic limestone from Bleiberg, in Carinthia, containing the remains of ammonites, which by their brilliant play of colour resemble precious opal. An argillaceous limestone, remarkably rich in dendritic markings, occurs in irregular masses in the Rhætic series, near Bristol, and has been polished under the name of *landscape marble*. The *ruin marble* of Tuscany is a soft argillaceous material, found near Pisa, and sometimes described as a kind of lithomarge. The *ammonite* marble, found near Yeovil, is a brown Liassic limestone, rich in the remains of ammonites. The oolitic formation known as *Forest marble* takes its name from Wychwood Forest in Oxfordshire, which yields a coarse shelly limestone, occasionally polished as an ornamental stone. The famous *Purbeck* marble, extensively used in Gothic architecture, especially for slender clustered shafts, is a grey fresh-water limestone of upper oolitic age, crowded with *paludinæ*; whilst the *Sussex* marble is a similar shelly limestone, of fresh-water origin, occurring in bands in the Weald clay. (For English marbles *v.* H. B. Woodward, Geology of England and Wales, 2nd ed. 1887.)

Among foreign marbles those of the Pyrenees and of Numidia deserve special mention. The so-called *Algerian onyx* is a beautiful stalagmitic form of calcium carbonate, formerly called alabaster and now known as 'Oriental alabaster,' the adjective being used to distinguish it from true alabaster, which is a native form of calcium sulphate. The *Mexican onyx-marble* is a similar stalagmitic material, used as an ornamental stone. (For American marbles *v.* S. M. Burnham's Limestones and Marbles, Boston, 1883, and Rep. of U.S. Tenth Census, 10, 1884).

Ophicalcite is a name applied to serpentinous limestones, which generally display clouded patterns, due to the interblending of a white limestone or dolomite with a green serpentinous mineral. The 'Irish green' of architects is a rock of this character from Connemara in Western Galway. Of a similar nature are the serpentinous marbles of Anglesey, the eozoonal marble of Canada, and the verde antique previously mentioned. As the two constituents of an ophicalcite are unequally attacked by atmospheric agents, such a rock is unsuited for use in exposed situations, since it soon weathers to a rough surface. In fact, marble generally is hardly suitable for out-door work in large towns. The atmosphere of a city becomes charged with the products of the combustion of coal, including acid compounds of sulphur, and must sooner or later attack all marble monuments. It has been shown by A. Geikie that marble slabs exposed in the churchyards of Edinburgh suffer total destruction in less than a century (Proc. R. Soc. Ed. 10, 1880, 518).

A minor use of marble is for the production of carbon dioxide in soda-water manufacture. In the United States about 25,000 tons of scrap marble are annually ground into dust for this purpose. F. W. R.

MARC BRANDY OIL *v.* Fusel oil.

MARCASITE. White iron pyrites or ferric sulphide. The term is also occasionally applied to bismuth.

MARGARIC ACID *v.* Fatty acids.

MARGARINE. *Oleomargarine, Butterine, Butter surrogate, Dutch butter—Bosch, Suine, Beurre de margarine, Kunstbutter.* This substance was first prepared by M. Mège Mouriès while endeavouring to make a real butter from animal fat by processes analogous to those occurring in the body. By his process 1,000 kilos. of ground fat from freshly slaughtered cattle is mixed with 300 kilos. of water, 1 kilo. of potassium carbonate, and two sheep or pig stomachs cut into pieces, and is heated at 45°C. by steam for two hours. The pepsine aids the separation of the fat, which rises to the top, and, after being skimmed, is run off and heated to 30–40°C. with 2 p.c. of salt, and the clear fat is poured from the sediment and cooled at 20° to 25°C. The granular, solid product is cut into cakes, packed in linen, and exposed to hydraulic pressure at about 25°C. with the production of a solid cake of *stearin* amounting to nearly one half the total fat, and melting at 50-59°C., and the liquid *oleomargarine*, which is passed through cylinders and washed by a shower of water.

Of the melted oleomargarine, 50 kilos. is mixed with 25 litres of cows' milk and 25 kilos. of water, in which has been macerated 100 grams of the finely-ground mammary gland of the cow; annatto is added, the whole is churned for about two hours, and the product is kneaded and well washed. *V.* further J. de Pharm. et de Chim. June 1872; Am. Ch. 4, 370; Report made to the Board of Health of the Department of the Seine on Artificial Butter by Mège Mouriès; and U.S. Patent Specifications, 1873, No. 146,012.

In the United States, and at Vienna, Munich, and other centres, pepsine is not used. The Commercial Manufacturing Company of New York employ a modification of the above process introduced by Mott. The selected fat is ground to a creamy consistency, and is heated to a temperature below 50°C. by steam or hot water, in large wooden vats, and the liquid portion is run off into jacketed vats and allowed to cool slowly. When sufficiently solid it is wrapped in small portions in cloths, and compressed at about 100 tons pressure, the solid residue of stearin being used for candle-making &c.

A mixture of 100 lbs. of the oleomargarine with 14 to 20 lbs. of sour milk, ¼ to ½ ounce of sodium bicarbonate, and a sufficient quantity of annatto, is churned for 10 to 15 minutes, and is placed in a trough containing broken ice. After 2 or 3 hours it is placed on an inclined table, and is kneaded to eliminate water. The mass is again churned with 20 to 25 lbs. of sour milk for every 80 lbs. of the oleo., and is then put up for sale.

The greater proportion of the oleomargarine extracted in America and elsewhere is, however, exported direct to Holland, to be there converted into margarine. The supremacy of Holland above all other countries in this manufacture is well shown in the following table referring to the margarine trade of England (S. C. I. 1889, 834):—

—	1886		1887		1888	
	Cwt.	£	Cwt.	£	Cwt.	£
Total imported . .	886,573	2,958,300	1,273,095	3,869,948	1,138,174	3,263,826
Imported from Holland .	833,957	2,767,599	1,172,074	3,546,591	1,043,401	2,951,522
Re-exported . . .	17,549	48,533	22,180	53,482	20,457	50,614

Out of a total exportation of 39,321,000 lbs. of oleomargarine from America in 1884, Holland received 33,173,849 lbs. in addition to 39,600,000 lbs. from European countries, principally from Austria-Hungary, France, and Prussia.

The largest factory in Holland is that of Oss, which in 1884 exported about 150 tons of margarine weekly to England. The process of manufacture is as follows:—

The oleomargarine is melted at about 50°C., and is mixed with the requisite proportions of milk and of the best Kampen butter and earthnut (*arachis*) or other oil to lower the melting-point to that of butter, and is churned and washed with ice-cold water. The Kampen butter is prepared specially for this manufacture from an unskimmed mixture of milk and cream, and is preferred on account of its powerful flavour, which, though unpleasant alone, imparts a pleasant flavour to the margarine. About 12 tons of butter and 12,000 gallons of milk were used weekly at that factory in 1884 (*v.* Jurgens, Journ. Soc. Arts, 33, 82; Riche, J. Ph. [5] 2, 125, and 193; Journ. Roy. Agric. Soc. 1881, 434.)

The British Customs returns do not distinguish between butter and margarine, but in 1884 nearly 125,000,000 lbs. of one or other—nearly one half our total import of butter—was received from Holland, and we may safely assume that considerably over 50,000,000 lbs. was margarine. The rendered and unrefined fat received in New York for this manufacture represents one third to one half the fat of the animals slaughtered for that market.

Good beef fat when rendered as described yields:

Oleomargarine	32
Stearin	12
Tallow	20
Residue used for manure . .	6
Loss by volatilisation . . .	30
	100

The following shows the average composition of dry margarine fat and of commercial margarine:—

—	Margarine fat	Commercial margarine
Water	—	12·01
Palmitin	22·3	18·31
Stearin	46·9	38·50
Olein	30·4	24·95
Butyrin, caproin, and caprylin	0·4	0·26
Casein	—	0·74
Salts	—	5·22
	100·0	99·99

Dry butter fat contains:

Stearin and palmitin	50·00
Olein	42·21
Butyrin	7·69
Caproin, caprylin, and rutin	0·10
	100·00

In this manufacture, as practised at the large factories, there is nothing in any way objectionable. The low temperature used in the expression of the oleomargarine is not sufficient to destroy germs or parasites, so that the use of the fat of pigs, or of any animals which are not perfectly healthy, should be avoided.

Numerous oils have been used in addition to the oleomargarine, the principal being *arachis* (*earthnut*), *cotton-seed*, *sesame*, *cocoanut*, and *palm oils*. Horse and bone fat, and, for flavouring, butyric acid and artificial butyrin, are also said to be used. The addition of soapstone as a weighting material is doubtful.

A clarified butter, largely made and used—principally for cooking purposes—in Eastern countries, and known as *ghee*, is said to be frequently adulterated with cotton-seed oil. The various terms used for margarine are somewhat confusing. The term 'oleomargarine' should be confined to the animal oil used in making margarine. The name 'bosch' was formerly applied to an inferior butter made in Holland. Its manufacture has been entirely discontinued, and the term is now synonymous with 'margarine.' 'Suine' is margarine made from pig's fat.

V. further, British Consular Reports, 1881, 651; United States Consular Reports [3] 148; [18] (1886), 99; [22] (1887), 556 and 769; Consular Reports of the U.S. regarding Dairy Farming [1] 1887, pp. 14 and others; also La Margarine et le Beurre Artificiel, by Girard and Brevans (Paris, 1889). Concerning legislation regarding margarine, *v.* Times, April 2, 1881; the Parliamentary Blue Book of Reports on Foreign Legislation on Oleomargarine [9] 1885, and the above work by Girard and Brevans.

Analysis.—Before commencing the analysis of butter or margarine it is necessary to separate it from water, curd, salt, &c., by heating about 50 grams in a dry beaker at 50–60°C., but not above, with occasional careful stirring. The clear fat is filtered, and if not perfectly clear is reheated and again filtered.

The determination of the *melting-point* is of no value, as vegetable oil is invariably added in the manufacture to bring the melting-point to that of butter. The *specific gravity* is of importance, but should not be relied upon, especially when the butter is old. The density of margarine is sensibly higher than that of butter, but is increased by the addition of cotton-seed or cocoanut oil.

The behaviour with glacial acetic acid appears to be an important indication: 3 c.c. of the melted fat is treated with exactly 3 c.c. of *glacial* acetic acid and heated until complete admixture occurs on agitation. The solution is cooled spontaneously, and the point at which it becomes turbid is noted. Pure butter appears to produce turbidity at 56–61·5°C., while for margarine the temperature is 98–100°C. The presence of much cocoanut oil in margarine lowers the turbidity point considerably.

Reichert's distillation process is of great value. Saponify 2·5 grams of the fat with 25 c.c. of semi-normal alcoholic potash solution, and evaporate over the water-bath until quite free from alcohol. Dissolve in water, acidulate slightly with sulphuric acid, dilute with water to 75 c.c., add a few fragments of pipe stem or platinum to prevent succussion, and distil off 50 c.c. Occasionally, the distillate contains solid particles of lauric acid, in which case it requires filtration. It is then titrated with decinormal potash, using phenol-phthaleïn as an indicator; 2·5 grams of cows' butter requires 12·5–15·2 c.c. of decinormal potash, while that weight of margarine requires only 0·2 to 1·6 c.c.

By determining the 'saponification equivalent' as proposed by Koetstorfer, butter fat may be distinguished from all fats except cocoanut and palm oils. This equivalent represents the number of grams of an oil which is decomposed by a litre of a normal solution of potash or soda, and is found by saponifying a known weight of oil with a known volume of semi-normal alcoholic potash solution free from water, and determining the amount of unaltered potash by titration with hydrochloric acid and phenolphthaleïn. The average saponification equivalent of butter is 247, and that of cocoanut or palm-nut oil 209–255, while those of other possible oils are above 277 and average 285.

Good results are obtained by determining the proportions of fatty acids soluble and insoluble in water obtained by saponification. In butter the soluble acids calculated as butyric acid should be at least 4·5 p.c (Bell), but frequently reach 7 p.c., while margarine gives but little soluble acid.

The examination of margarine by these methods requires considerable attention to details, a description of which will be found in Allen's Commercial Organic Analysis [2] 145–160, and in Blyth's Foods, 287–304.

MARINE ACID. *Syn.* for hydrochloric acid (*q. v.*).

MARJORAM, *Origanum majorana*, of the family *labiatæ.* cultivated as a seasoning herb, and furnishing oil of marjoram by distillation. The essence so prepared is composed of a terpene $C_{10}H_{16}$, b.p. 178°, sp.gr. $\frac{18\cdot5}{}$ 0·8463 together with a sesquiterpene hydrate $C_{15}H_{26}O$ (Beilstein and Wigand, B. 15, 2854).

MARL (Ger. *Mergel*), a name properly restricted to calcareous clays, but frequently extended so as to include any clay which, when dry, is readily friable. Thus the Keuper or New Red Marls, of triassic age, often contain little or no calcareous matter. An analysis of a red keuper marl, from Worcester, by Dr. Voelcker, yielded 4·85 per cent. of lime. Marls have been used for ages by agriculturists for the purpose of improving certain lands, the material for 'marling' being systematically dug from 'marl pits.' Since a marl is a calcareous clay, it may obviously pass into an argillaceous limestone: the *chalk marl* is a rock of this kind. When a marl becomes indurated it is often known as *marlstone* or *marl-rock*, and the hard beds of the middle lias, which in Yorkshire yield the Cleveland iron ore, are recognised by geologists as the 'marlstone.' A laminated variety of hardened marl is termed *marl-slate*, which readily passes into a calcareous shale. The marl-slate occurring in the Permian series in the north of England is equivalent to the German *Kupferschiefer*, a bituminous marly shale, containing copper-ore. The *shell-marl* found at the bottom of certain lakes, especially in Scotland, is a calcareous ooze, consisting largely of organic remains. F. W. R.

MARRUBIIN v. Marrubium.

MARRUBIUM, *Horehound, hoarhound; Marrube blanc*, Fr.; *Andornkraut*, Ger. Horehound has been employed for its mild tonic, stimulant, and laxative properties, especially in domestic medicine, for a long period. It consists of the leaves and tops of the *Marrubium vulgare* (Linn.), a perennial herb growing throughout most parts of Europe, Asia, and America (Bentl. a. T. 210). The only constituent which has been examined, except a trace of *volatile oil*, is the bitter neutral *marrubiin*.

Marrubiin was discovered by Mein (Gm. 18, 234), and further studied by Harms (Ar. Ph. [2] 83, 144; 116, 141) and Kromayer (Ar. Ph. [2] 108, 257). The dried plant is exhausted with hot water, the solution evaporated to a syrup, the syrup extracted with alcohol, and the extractive obtained, after distilling off the alcohol, is mixed with sodium chloride and treated with ether. On spontaneous evaporation of the ether the marrubiin remains (Harms). Kromayer takes advantage of the power of animal charcoal to absorb marrubiin from the juice of the plant or an infusion, and to yield it again when the charcoal is treated with alcohol. An alcoholic extractive is thus obtained from which ether removes the marrubiin.

From ether marrubiin crystallises in plates and from alcohol in needles. It has a bitter and somewhat acrid taste. It melts at 148° (H.) or 160° (K.). It is insoluble in cold, very slightly in hot water; but dissolves in alcohol or ether. It is not affected by alkalis, and is not precipitated by tannic acid nor by metallic salts. A. S.

MARSH GAS. *Methane or methyl hydride* v. Methyl compounds.

MARSH-MALLOW GUM v. Gums.

MARSH ROSEMARY. *Andromeda polifolia*; also an American name for *Statice caroliniana*. *Andromeda polifolia*, belonging to the *Ericaceæ*, is the only British species of the genus; it is found also in peat-bogs throughout the north of Europe, Asia, and America. It is an acrid narcotic and is fatal to sheep pasturing off it.

Statice caroliniana is found in marshy situations from Maine to Florida. According to Parrish, it contains 12 p.c. of tannin and has been used in the manufacture of leather.

MARTIUS'S YELLOW. A synonym for Naphthalene yellow; known also as *Jaune d'or, naphthol yellow, Manchester yellow.* The sodium or lime salt of dinitro-α-naphthol v. Naphthalene.

MASOPIN RESIN v. Resins.

MASSICOT v. Lead.

MASTIC CEMENT v. Cements.

MASTIC RESIN v. Resins.

MASTIC VARNISH v. Varnish.

MATAZIETTE. A name given to an explosive made in Switzerland, formed of nitroglycerine, sand, and chalk, coloured with ochre.

MATCHES. (Ger. *Zündhölzer, Zündhölzchen*; Fr. *Allumette*; Sw. *Tändsticka*, pl. *Tändstickor.*)

Definition.—An instantaneous fire-producer, consisting of a short stem, rod, or tube, tipped at one or both ends with a composition or paste, inflammable by friction.

History and development.—The lucifer match belongs to a late era of civilisation. Its development from fire-producing appliances of a primitive type has been accomplished within the past fifty years, but as a simple technical application of scientific principles, it has already reached a high degree of perfection. According to a tradition enshrined in the writings of Æschylus, the human race derived a knowledge of the use of fire from Prometheus, who stole it, hidden in a hollow tube, from the gods; and it is certain that the production of fire by the friction of two stones, or of flint against steel, was a familiar operation at a very early period. The ancient Greeks were also acquainted with the properties of the burning glass and concave mirror. The Romans rubbed decayed wood between two stones with a thin roll of sulphur, and ignited dry leaves by the friction of two pieces of hard wood (Pliny recommended laurel and ivy woods). Carefully tended fires were kept continually burning in the temples and other public buildings, and the sanctuary-lamps of many modern churches are probably a survival of this custom, which originated in necessity. The North American Indians still obtain fire by the friction of two pieces of wood; the Polynesians rapidly rotate a pointed rod of dry soft wood (the fire drill) against a block of harder wood; and wood-turners in civilised countries frequently carbonise wood, for ornamental purposes, by friction. Such methods as these, but chiefly the friction of flint and steel, were used exclusively throughout the middle ages. The tinder-box became known in the fourteenth century, and thenceforth this malodorous, inconvenient, and aggravating apparatus, with the accompanying paraphernalia of steel, flint, and sulphur-tipped splinters or 'spunks' of wood, reigned supreme for four hundred years. No other appliance was in general use before 1820; and in 1840 the tinder-box was still to be found in many kitchens. Amadou or German tinder (the pileus of two species of the fungus *Polyporus*, *P. igniarius* and *P. fomentarius*, treated with a solution of nitre and dried) was often used instead of ordinary tinder; and iron pyrites (Gr. πυρίτης, a stone from which fire may be struck) sometimes replaced the flint. Since the discovery of phosphorus in 1673 by Brand, of Hamburg, many attempts had been made to expeditiously obtain light and heat by its aid; one of the earliest consisting in rubbing a particle of phosphorus between folds of coarse brown paper, the flame produced igniting a sulphur-tipped splinter of wood. This plan was found to be inconvenient and dangerous, and phosphorus gradually fell into disuse. After the element had been, in a technological sense, left severely alone for more than a century, renewed attempts were made to utilise it, among the later contrivances being the rather impracticable '*phosphoric taper*' (made of wax, inclosed in a sealed glass tube, and provided with a phosphorus-coated wick, which spontaneously inflamed when that end of the tube was cut off with a file), and the '*phosphorus bottle*,' which was suggested by Cagniard de la Tour, and contained partially oxidised phosphorus, some of which was withdrawn by a brimstone match, dipped into the phial, and then ignited by friction. Appliances of other kinds for quickly producing fire were Homberg's '*pyrophorus*' (an oxidisable powder, free from phosphorus, prepared by roasting alum with flour, honey, or sugar, and inflamed by exposure to air), and J. W. Dōbereiner's pyrophorus, of similar character; '*pneumatic tinder-boxes*,' containing amadou or ordinary tinder, ignited by the heat generated when air was compressed by a piston, such as Mollet's Pump, and R. Lorentz's '*light syringe*'; '*electropneumatic fire-producers*' (invented by Brander, of Augsburg, 1778, and by Fürstenberger, of Basle, 1780), in which a jet of hydrogen gas was kindled by an electric spark—to which category M. J. Mayer's apparatus (Eng. pat. 3,470, 1811) belonged; Volta's '*inflammable air lamp*' and Fyfe's '*hydropneumatic lamp*'; and, lastly, Dōbereiner's '*platinum lamp*' (in which contact with spongy platinum—or iridium, as afterwards proposed by the inventor—ignited hydrogen gas), with Eisenlohr's, L. von Babo's, S. von Rōmer's, J. Palkl's, Hare's, Schiele's, and Bōttger's modifications of the same.

The principal stages in the evolution of the lucifer match will now be referred to in chronological sequence (Table I. p. 535—*Chronological Summary*). In 1805, Chancel, assistant to Thenard, of Paris, applying the principle discovered by Berthollet, of the oxidation of combustible bodies by chlorates in the presence of a strong acid, invented the '*oxymuriate matches*,' strips of wood tipped with a mixture of potassium chlorate, sugar, and gum, and ignited by contact with sulphuric acid. In the same year also, according to Nicklés, *friction matches* containing the element phosphorus were made and used in Paris. In 1806 various improvements in the tinder-box were suggested by J. Phillips (Eng. pat. 2,907, 1806), who was followed, in 1807, by R. Lorentz (Eng. pat. 3,007, 1807), with an apparatus for igniting hydrogen gas by the aid of an electrophorus, and with the 'light syringe' already mentioned (same patent). Derepas proposed, in 1809, to render phosphorus more manageable and less inflammable by intimately mixing it with magnesia; and, during the year 1812, '*chemical matches*,' manufactured according to Chancel's invention, began to be largely sold, a hundred for a florin, in Vienna. The sticks were tipped with potassium chlorate, sugar, and gum, or with potassium chlorate, sugar, lycopodium, and gum; colophony, gum benzoin, &c., were also used. These matches, packed in suitable cases, together with little phials containing (in accordance with a proposal made in 1812 by S. von Rōmer, of Vienna) asbestos soaked in sulphuric acid, were more widely sold on the Continent than any others, up to the year 1844. Among the makers were v. Rōmer, H. Peters, A. Wagner, J. Siegel, R. Ehrlich, and G. E. Merckel (*v.* Table IX. p. 552—*Foreign Patents*). The cases were known as 'tunkfeuerzeugen,' 'briquets phosphoriques,' 'inflammable matchboxes,' 'phosphorus boxes,' &c.; and one form was prominently sold in this country as Heurtner's '*Eupyrion*.' Almost explosive violence of combustion, and a liability of the acid to be spirted about, were the chief objections to these matches. In 1816, friction matches tipped with a composition containing phosphorus were manufactured in Paris by Dérosne, who, *pace* Nicklés, is by W. F. Gintl and others regarded as the first maker of the phosphorus friction-match. The year 1823 is marked by the invention of the Dōbereiner lamp, already referred to. About this time, too, were used, at Erfurt, in Prussia, small glass tubes containing equal quantities of phosphorus and sulphur carefully fused together, into which thin sticks or splints of wood were introduced, easily inflamed afterwards by friction. In April 1827, John Walker, of Stockton-on-Tees, invented the original '*lucifer matches*' or '*congreves*' (named after Sir W. Congreve, Bart., the inventor of the Congreve life-rocket), described in the 'Atlas' newspaper of January 10, 1830. These were undoubtedly the first English friction-matches, as Faraday pointed out, but they contained no phosphorus, consisting of wooden splints, or strips of cardboard, tipped with a mixture of sulphide of antimony, potassium chlorate, gum, and starch. Though non-phosphoric, Walker's matches ignited by simple friction on a rubber of glass or sand paper. In this respect, and in name, they were the immediate ancestors of the matches of the present day. In the following year, S. Jones, of London, patented the '*prometheans*' (Eng. pat. 3,732, 1828; Table VIII. p. 549—*English Patents for Compositions, Stems, &c.*), a return to the principle of the oxymuriate match. On the Continent, friction-matches of Walker's type were made at this period by Savaresse and Merckel (Paris), the igniting composition being a mixture of potassium chlorate, antimony sulphide, sulphur, and gum, and the rubbing surface consisting of potassium chlorate, minium, pumice, and gum. Similar non-phosphoric friction-matches were patented in 1832 by J. Siegel, an Austrian manufacturer. Efforts were being made meanwhile to produce *a really practicable and satisfactory friction match*, in which *phosphorus* should take the place of antimony sulphide, and this important result appears to have been simultaneously achieved in several different places during or about the year 1833.

In 1834, S. von Römer, L. Preschel, and J. Siegel, in Vienna, and F. Moldenhauer, at Darmstadt, were manufacturing wooden friction-matches containing phosphorus. The date of v. Römer's patent was Jan. 4, 1834. Other pioneer makers of that time, associates or otherwise of the above, were Pollak and Kreutz (Vienna); Anthon (Darmstadt); and Amüller (Waiblingen), who sold his matches as 'congreves.' In South Germany the invention of the phosphorus friction-match is attributed to J. F. Kammerer, of Ludwigsburg. The oxidising agent used was at first potassium chlorate only, but in 1835 Trévany partly replaced it, as being too violent in its action, by a mixture of minium and manganese dioxide. In the United States of America the first patent for the invention of phosphorus friction-matches was granted on October 24, 1836, to A. D. Phillips, whose igniting composition was a mixture of phosphorus, sulphur, chalk, and glue. In 1837 v. Römer substituted lead peroxide for potassium chlorate; in 1838 Preschel and Kreutz patented a composition consisting of phosphorus, manganese dioxide, nitre, and gum arabic (Table II. p. 536—*Matches with Vitreous Phosphorus*); Beyer (Vienna, 1838, *l.c.*) and Riess (Vienna, 1843) used as their oxidising agent a mixture of minium and nitric acid; and in 1842-3, Dr. R. Böttger, of Frankfort, recommended the employment, in place of potassium chlorate, of mixtures of minium and saltpetre, or of lead peroxide and lead nitrate. Moldenhauer, about the year 1838, introduced the use of calcined magnesia in order to counteract the effects of the formation of hygroscopic oxidation-products of the phosphorus; and chalk also (introduced in 1836 by Ehrlich, of Prague, into a composition for non-phosphoric matches) was used for the purpose. Preschel, and Klug (Fr. pat. 1837) endeavoured to accomplish the same end by coating the match-heads with resinous spirit-varnishes. Between 1820 and 1840 various machines (Tables VII. and IX., pp. 546 and 552), for cutting the wooden stems or 'splints' rapidly and in large quantities, were introduced, and the match industry has since developed in country after country until it is now of enormous magnitude and great importance. Although there have been manifold improvements in the methods of manufacture, in the composition of the igniting pastes, and in the quality of the finished goods, the ordinary phosphorus friction-match of to-day is not *essentially* different from the 'lucifer' of 1833. The use of machinery has been greatly extended, however, and there has been a gradual diminution in the proportion of phosphorus added to the compositions. In 1855, Dr. J. R. Wagner (J. C. T. 1855, 502–505) recommended that less phosphorus should be used, and to this end proposed that the phosphorus should be added to the dipping compositions in a finely divided state, dissolved in carbon bisulphide; but this plan was not very generally adopted. Wagner considered the most suitable proportion of phosphorus in a match-composition to be from one-tenth to one-twelfth. Experience has since shown, however, that considerably less phosphorus will yield good results. Wagner experimented also with barium nitrate and potassium bichromate, as oxidising agents. The latter salt he considered too expensive, and he remarked that lead dioxide, though more costly and no better, had then largely replaced the mixture of minium and manganese dioxide. In 1860, C. Puscher, of Nuremberg, introduced the use of phosphorus sulphide instead of phosphorus, but he found few followers. For making matches *waterproof*, J. Zimmermann (1864) used collodion, as an improvement on the resinous varnishes of Preschel, Klug, Winterfeld (1842), and Krutzler. C. M. Barker (1845), and, after him, Gaillard, applied a coating of sulphur over the friction composition, such matches being found by Abel (Tr. 4th ser. 26, 1863, 356) to be perfectly waterproof, but somewhat difficult to ignite. *Scenting ingredients*, such as gum benzoin, frankincense, &c., were often added to the varnishes; and in 1854 S. Krakowitzer, of Pottenstein, Austria, introduced a process by which a metallic lustre was imparted to the heads of matches '*de luxe*' (containing lead compounds), by exposing them to sulphuretted hydrogen gas. This process was modified by J. Ginzky in 1860, and again by Schindler, in 1867.

A later improvement (A. Kielmeyer, C. I. 2, 1879, 430) was to varnish over the silvered heads with an alcoholic solution of colophony, shellac, &c., to which an aniline or other dye was added. Thus, to obtain a greenish bronze, Kielmeyer used fuchsine or methyl violet; other colours employed are methyl green, aniline orange, and the like.

A considerable number of match compositions, containing ordinary phosphorus, will be found in Table II. p. 536).

Great as was the improvement effected by the substitution of phosphorus for the less easily oxidisable antimony sulphide, there were certain disadvantages attending its use. The poisonous nature of phosphorus, the somewhat too ready inflammability of the igniting compositions made with it, and especially the 'phosphorus disease' (a carious affection of the lower jaw-bone, leading to necrosis, to which the workers—more especially the 'dippers'—in match-factories were found to be subject), attracted much attention, and led to great discussion, between 1840–1865 [*vide* Th. Roussel, Sédillot, Dupasquier and others (C. R. 22, 292, 437; 23, 454, 635; 24, 618); Le Technol., Aug. and Sept. 1846; Harrison (Dubl. Quart. J. M. S. Aug. 1852; Poggiale, Chevallier, and Duvergie, J. Ph. C. 3rd ser. 37, 1860, 180; Children's Employment Comm. Gt. Brit. 1st Report, 1862]. Good ventilation, impregnation of the air of the factories with the vapour of oil of turpentine, and scrupulous cleanliness on the part of the operatives, were found to have the effect of greatly diminishing the number of cases of necrosis; and at the present time the 'phosphorus disease' is not very prevalent among English lucifer-match makers. It has been surmised (C. J. 58, 1890, 545, Thorpe and Tutton) that the disease in question is not due to the effect of the phosphorus after absorption, but that it is caused by the direct action of the vapour of phosphorous oxide, P_4O_6, on the bone itself, and that the characteristic smell always noticeable in the dipping-room of a match-factory is due, not to the vapour of the element phosphorus, but to the fumes of phosphorous oxide. Further, only those workers with carious teeth suffer from necrosis of the jaw (T. L. Brunton, Pharmacology, &c., 771). A director of one of the largest lucifer-match manufactories in Great Britain has informed the writer of this article that, according to his experience, the phosphorus disease is of very rare occurrence, that those attacked by it are mostly of dirty habits, that the health of the workers is, for the most part, decidedly good, and that thorough ventilation, combined with strict attention to personal cleanliness on the part of the employés, is a sufficient protection against this evil. W. Jettel calculated (C. I. 3, 1880, 82) that the cases of illness from necrosis of the jaw among German phosphorus-match makers, during the years 1850-77, amounted to about 3 p.c., though Frief (*ibid.* 237) considered the proportion to be more than 12 p.c. In the annual report of the German inspectors of factories for 1879 it was stated that, in that year, among 5,724 workmen coming in contact with phosphorus vapours, only nine cases of necrosis were observed, six of illness, and three of death (Jettel, C. Z. 1883, 7, 89). In 1884, however, stringent regulations were put into force in Germany with regard to the arrangements in match-factories, especial stress being laid upon the efficient ventilation of the separate rooms in which the operations of mixing the igniting compositions, dipping, drying, and removal of the splints from the dipping frames, were to be conducted.

In Denmark and Switzerland, the use of matches containing ordinary phosphorus was forbidden in 1875 and 1879 respectively; and only the so-called Swedish safety matches have been permitted to be used in Denmark since 1875.

Between 1879 and 1882 the use of matches free from phosphorus and inflammable on any surface was allowed in Switzerland; but a committee appointed by the Department of Commerce found that these matches were unreliable and often dangerous; and in 1882 the Swiss Government also passed an Act, prohibiting the use of any but safety matches.

Efforts had been made to use red phosphorus, discovered by A. v. Schrötter in 1845, and matches tipped with compositions prepared with red phosphorus were manufactured in Germany in 1850, and in England (by Dixon & Co., of Manchester, and Bell & Black, London), Austria (Foster & Wawra, Vienna), and France (Coignet & Co., Paris), in 1851; but they were not successful; and, although improved matches of this description were patented by Albright, of Birmingham, in 1856, and matches made with red phosphorus were again to be seen at the Paris Exhibition of 1867, and the Vienna Exhibition of 1873, they never came into general use. Doubtless the higher cost of red phosphorus had much to do with this; moreover, the mixtures used were unstable and dangerous. Some of the earlier igniting compositions containing red phosphorus (Camaille, Hermann, and others), will be found in Table III., p. 538—*Matches with Red Phosphorus*; and later receipts, of Sudheim & Koppen (Cassel), R. Dimock (London), and L. Horst (C. Z. 1880, 273), are also given. Other igniting compositions containing red phosphorus (Leonard, 1876, and Bell, 1885) are included in Table V., p. 544—*Vestas, Vesuvians*, &c. Jettel (D. P. J. 195, 1870, 369) criticised the impracticably large proportions of red phosphorus in Camaille's compositions, and recommended a mixture (*l.c.*) containing only 6·25 p.c. of this variety of phosphorus. But in 1883 the same writer (C. Z. 7, 89) had arrived at the conclusion that all mixtures of red phosphorus and potassium chlorate are absolutely impracticable.

In 1855 Lundström, of Jönköping, Sweden, acting on Böttger's suggestion that friction-matches might be made so as to be capable of igniting only on an especially prepared surface, manufactured the first true '*safety matches*,' by putting the oxidising mixture on the *splints*, and red phosphorus on the *box*. Here, then, was a use for the non-poisonous and not easily inflammable red phosphorus. Such matches only ignited when rubbed on the specially prepared surface, or 'rubber,' on the side of the box. Lundström's process was patented in England in 1855 by F. May (Table III., p. 538), and safety matches on the same principle were immediately after manufactured by Fürth, of Schuttenhofen, Coignet & Co., Paris, and Foster & Wawra, Vienna. In the closely allied 'allumettes androgynes' of Bombes Devilliers and Dalemagne (Le Technol. 1859, 140), the red phosphorus composition was at one end of the splint and the potassium chlorate at the other (Table III., p. 538). The splints were broken, and the ends rubbed together. Field (1882) adopted a similar plan. The Swedish safety matches, now so largely imported into this country (Table VI., p. 545—*Statistics*), are on Lundström's principle. According to the Zeitschr. für Zündwaaren Fabrikation (1884, Nos. 152 and 153), it appears that, in 1881, 204½ millions of safety matches were made at Jönköping alone; and there are other factories at Gothenburg, Westervik, &c. Various analyses, by Jettel and others, of Swedish safety matches are given in Table III., together with several compositions, patented in England, for matches of this class (*vide* Mennons, 1857, Mearing, 1861, and Palmer, 1868); and a formula published in C. Z. 1881, 196 (A. Rossel). Some safety matches can be ignited, without the aid of an especial rubber, by friction—with a swift, sweeping movement—against a smooth, even surface, such as glass, polished oak or ebony, slate, &c. (Kriwanek, Deutsch. Industriezeit., No. 34, 1871).

A further step was taken in 1857 by G. Canouil (Eng. pat. 2,817, 1857; Fr. P. March 26, 1857, and Oct. 7, 1857; *v.* Le Génie Industriel, 17, 1859, 51), and by H. Hochstätter, of Darmstadt (Eng. pat. 1,190, 1857; Fr. P. Ap. 29, 1857; *v.* Le Génie Indust. 15, 1858, 124), in the production of '*non-poisonous safety matches*,' neither the igniting nor the friction compositions of which contained any variety of phosphorus. In Hochstätter's matches the oxygen compounds used were potassium chlorate, potassium bichromate, lead dioxide, &c., and the phosphorus was replaced by a mixture of antimony oxysulphide and flowers of sulphur. The oxidisable ingredients of Canouil's compositions, where stated, consisted of sulphur, iron pyrites, lead 'sub-sulpho-cyanide' (thiocyanate ?), and lead 'sub-sulpho-ferro-cyanide' ('sous-sulfo-cyano-ferrique de plomb': ferrocyanide and thiocyanate ?), used singly or together. Thirteen formulæ, some given by Canouil in his specifications and others attributed to him by Payen, will be found in Table IV., p. 542—*Matches without Phosphorus*: in three cases the oxidisable bodies are not specifically named. It is probable that some of the earlier so-called non-phosphoric matches were not altogether free from phosphorus, secretly added in very small quantities by the makers, to render their compositions more easily inflammable (Der Vollständige Feuerzeugprakt., C. H. Schmidt, 1861). Hochstätter's recipes, and Vaudaux and Paignon's improvements upon Canouil's pastes, are given in Table IV. Two compositions for non-phosphoric matches, of F. L. Lutz (Gewerbebl. aus Württemb. 43, 1858); and a mixture used by Kummer and Günther (Königswalde, near Annaberg, Saxony, 1861), analysed by Dr. G. Wiederhold, of Cassel, follow. In 1861, Wiederhold made many experiments (D. P. J. 161, 221, 268; 163, 203, 296; and 169, 158) in connection with the production of non-phosphoric matches, and suggested a number of compositions (*vide* table), the most satisfactory of which contained potassium chlorate and *lead thiosulphate*; and matches were made, with the latter salt as the principal oxidisable ingredient of the igniting pastes, by G. Kalliwoda & Co., of Ortenburg, Germany, W. Schnell, London, 1861, Palmer, London, 1868, and others. Mayer (Knapp's Lehrb. d. Chem. Techn. 1865), C. Liebig (*op. cit.*), and Palmer, 1869, also produced non-phosphoric friction matches, containing, respectively, antimony sulphide and lead cyanide (Mayer), antimony sulphide and nitromannite (C. Liebig), and iron thiosulphate (Palmer), in place of lead thiosulphate. Jettel, in 1869 (D. P. J. 191, 369), suggested the use of basic picrate of lead. [Wiederhold had already tried potassium picrate (Table IV., p. 542).] Later, in 1879, L. Wagner, of Mühlheim, patented in Germany and England a non-phosphoric friction match (Table IV.), in which the oxidisable components of the dipping paste were lead thiosulphate, antimony sulphide, sulphur, and finely powdered charcoal. Again, in 1881 and 1884, H. Schwarz, of Gratz, took out German patents for compositions containing lead thiocyanate, and lead sulphide in place—partly or entirely—of antimony sulphide. Lastly, a non-phosphoric match was not long since described in the Polyt. Notizbl. (1888, 120; *vide* also Table IV.—P. Garber) as being non-hygroscopic, safe, and characterised by slow and quiet combustion. Among other substances which have been proposed as ingredients of non-phosphoric safety match compositions are the thiosulphates of copper and sodium (R. Peltzer); copper thiocyanate, lead chlorate, and even finely divided metallic sodium (H. Fleck, Wagn. Jahresb. d. Chem. Techn. 1868, 220).

Most of the compositions for non-phosphoric matches have been described by their inventors as 'ignitable by friction on *ordinary* surfaces'; in some instances, however, a special rubber was necessary, and where this was the case the ingredients of the rubber also are given in Table IV. Many of these non-phosphoric friction matches inflamed on ordinary surfaces with great difficulty; others, again, ignited with almost explosive violence, and most of them were very hygroscopic. The vapours of lead, cyanogen, and thiocyanogen compounds evolved during the manufacture and ignition of such matches cannot but be considered at least as highly injurious as the fumes of phosphorous oxide. A practical trial of matches belonging to this category failed in Switzerland (see p. 522); and there does not appear to be substantial ground for widely dissenting from the conclusions of Jettel (C. Z. 7, 1883, 89), who, after pointing out the impracticability of Wiederhold's proposals, strongly condemning the use of lead compounds (and especially of the thiocyanates of lead and copper), and stating that the number of workmen engaged in this manufacture affected with lead sickness is 1,000 times as great as the number suffering from phosphorus necrosis, expresses the opinion that, apart from the ordinary phosphorus matches and so-called Swedish safety matches, there is in the present state of the match industry no kind of match of practically any value whatever. In fact, a really safe, non-phosphoric, non-hygroscopic, non-poisonous match, which can be readily yet quietly inflamed by moderate friction on any surface, without liberating noxious or unpleasant products of combustion, has yet to be invented.

Various substitutes for the wooden splints generally used for the stems of lucifer matches have been suggested at different times, such as earthenware, pipeclay, bass, cotton or linen stiffened with chalk and gum (Bell, 1859); bone (Letchford, 1867); cardboard and stiffened calico (Cribb and Rackham, 1874); asbestos (Hynam, 1874); jute and glue in a double wire spiral (Byrt, 1882); wood pulp and paraffin (Molyneux, 1889), &c. &c.

The treatment of the wooden stems has also varied greatly. In the early days of match-making the splints were usually dipped in melted sulphur (by v. Römer and others), to ensure ready inflammability of the stems; and hot tallow, resin, and wax were sometimes used for the same purpose. Sulphur-dipping is now rarely resorted to, and the 'brimstone match' is fortunately almost a thing of the past. Sulphur-coated splints are, however, still to be seen occasionally in certain matches of the cheapest and worst qualities, and mostly of continental manufacture. Of the above-named substitutes for sulphur, Böttger (1843) preferred and recommended wax, which was used by Mennons (1857) and others. Later (1861), Letchford introduced the use of melted paraffin or petroleum, also a mixture of paraffin with stearine and Japan wax. Bruce (1863) saturated the stems with potassium nitrate by immersing them in a boiling solution of that salt. Match-stems have occasionally been impregnated with camphor. In 1867 resin was again applied by Letchford, and Grawitz (1873) used naphthalene instead of sulphur. Mapple (1881) preferred oil or tallow. Paraffin and stearine are now very generally used.

Another method of treating the stems has been followed of late years, and is widely adopted at the present time, especially by the makers of Belgian and Swedish safety matches. It consists in impregnating the stems, or the greater part of their length, with solutions which have the effect of preventing the wood from burning or remaining red-hot. Stems so prepared become cool almost instantaneously, and do not readily break; there is thus less chance of the heads and fragments of the splints falling and giving rise to fires—a risk commonly present with the thin badly-cut splints (not so treated) of the cheaper sorts of foreign matches. To render the stems uninflammable, solutions of sodium phosphate (C. C. 1887, 205), sodium tungstate, zinc sulphate (Hynam and Dixon, Eng. pat. 1,865, 1870), alum, ammonium sulphate, and magnesium sulphate have been used (*v.* Table VIII.; Howse, 1868, and others). Field (1879) employed solutions of phosphoric acid, ammonium phosphate, borax and ammonium phosphate together, or boracic acid and ammonium phosphate; and Percival (1887) proposed the use of 'cyanite' for the end held in the hand, the body of the match being impregnated with a 'weak gummy varnish' to prevent the embers from falling about.

F. Gerken and G. Goliasch (agent, v. Nawrocki, Eng. pat. 834, 1883) affixed small friction-tablets to the stems, so that when a match was taken from the case its head should come in contact with the roughened surface on the stem of an adjacent match, and in this manner be inflamed by the act of withdrawal.

To render match-stems waterproof has been an object with many inventors. Collodion and resinous varnishes—used, as has been stated (p. 521), for the purpose of protecting the igniting compositions from moisture—have been also applied to the stems. Caoutchouc solutions have been employed for this purpose.

The development of the machinery used in match-making has kept pace with the many improvements in the compositions and in the treatment of the stems. Some of the later machines will be described in the portion of this article devoted to details of the manufacturing operations.

A few remarks may now be made about vestas and fusees.

Vestas.—The earliest account of the *wax-taper* as a match stem is in the specification of an English patent (No. 6,295), taken out by W. Newton in 1832; and, according to Payen, matches of this description were first made in France in 1836 by Savaresse and Merckel, of Paris. Wax, however, in conjunction with colophony, was used in 1832 by Siegel, of Vienna, as an easily inflammable coating (in place of sulphur) for the previously carbonised splints of the oxymuriate matches manufactured by him. In 1862 J. Childs recommended a mixture, of high melting-point, of one part of Carnaüba wax with nine parts of paraffin; in 1866 Letchford substituted jute for cotton in the tapers; and J. G. Gomez and P. Franco (1889—*v.* Table V.) use strips of Bristol board, immersed in a mixture of resin, stearine, zinc white, &c., for the stems, which are tipped as usual, and are said to burn throughout their whole length, after the ignition of the heads. Some wax vestas are sold at the present time, packed in metal cases containing sand-paper so folded that, on the withdrawal of a vesta, its head is inflamed by friction against the sand-paper, the act of withdrawal thus igniting the match.

Fusees, &c.—Cigar lighters—of brown paper, cardboard, German tinder and the like—impregnated with a solution of nitre, often scented, and tipped with various igniting compositions, mostly phosphoric, were made by Siegel (1832, 1835), v. Römer, and others (*v.* patent of Bardet and Collette, 1854, Table VIII.). Abel states that some fusees examined by him contained sodium chloride as well as nitre, the object perhaps being to yield, by semi-fusion of the first-named salt, a firmer ash. Of the newer kinds of cigar-lighters, variously known as 'flaming vesuvians,' 'etnas,' 'fixed stars,' 'braided lights,' &c., consisting generally of three parts—a stem of wood or glass, a head or ball of 'pastille' composition, and a tip of igniting composition—one of the first was described in 1849 by J. Palmer (Eng. pat. 12, 469, 1849). Grimes (1859) introduced wires into the composition-ends of his splints to prevent the heads from falling off when pressed against the cigar or pipe. Bell & Black (1859) made the stems of wire, coated with a non-conducting composition, such as gum and whiting, or glue and whiting or flour. Simlick (1862) put the composition on a tube fitted on to the end of the splint, and preferred glass. He also (1863) tried stems of slag and powdered oyster-shell, mixed into a paste and calcined; and wire covered with thread or cotton, dipped in coloured liquid gum. Battcock (1863) made stems of stone and slate; and Barker, in the same year, used pipeclay stems, tipped at each end. Ford (1878) softened the splints by treatment with caustic potash or soda, and then subjected them to the action of a solution containing 10 parts of nitre, 1 part of potassium chlorate, and 1 part of sugar in 12 parts of water: this process of course rendered the wood highly combustible. Evans (1882), on the other hand, rendered the stems of his vesuvians incombustible, by the use either of asbestos paint or of sodium tungstate solution. G. A. Sweetser (1884) formed his stems of plastic material moulded into the required shape and size round a core. In the 'braided' lights, manufactured by Bryant & May, Limited, and others, the composition is retained in position by pieces of thin wire, over which strands of cotton are twisted by the braiding machine. T. J. Clanchy had, in 1868, obtained provisional protection for a combined match and fusee, consisting of a shaft or stem with a fusee-head at one end and a match-head at the other. In 1885 R. Bell, proceeding on closely similar lines, introduced the 'fusee vestas,' or wax-stemmed vesuvians, in which the essential parts (tip, head, and stem) of a vesuvian are present, but the stem is of jute, hemp, flax, cotton, or a mixture of some of these fibres, coated with paraffin, wax, or stearine. According to another patent of the same year, the same inventor introduced a wire core into these stems; and in 1886, C. R. E. Bell devised a hollow cylinder or bead of combustible material, to be sold separately, for application to a match or vesta, for use in a light wind (fig. 1). Salts of strontium and barium are sometimes introduced into the compositions of vesuvians, which then burn with coloured flames. Cigar lights of this kind are now sold in the streets of London.

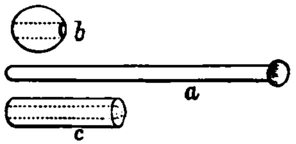

FIG. 1.

Repeating or continuous matches have been invented, but have never had much sale. The earliest English patent of this kind was that of Dove (Eng. pat. 1,137, 1862), in which the igniting composition was attached at intervals to a continuous band or strip of material, inclosed in a box. Later devices of similar nature were those of Tylor (agent, W. E. Newton, Eng. pat. 3,383, 1865); Rogers (agent, Newton, 1869); Perkins (1869), who mixed the igniting composition with collodion, a strip so composed fitting into a case like a pencil case, from which it could be withdrawn at will; Samuel (1871); Jonas (agent, Pollet, 1878); and Klein, same year (*v.* Table VIII. p. 549).

Cigar-lighting appliances of a special kind. Many instantaneous igniters, not matches, have been invented during recent years—chiefly for the convenience of smokers. These contrivances, though numerous, have not interfered with the steady development and increase of the match industry; and as their use is not general, a few types only of such inventions will be mentioned. Some are applications of an alloy of the metals sodium and potassium. A small quantity of the alloy is withdrawn from a case or tube by a wire, which is then rubbed across, and ignites a charred wick (Eng. pat. 17,112, 1887, and 4,557, 1888). Another appliance is simply a pocket edition of the old flint, steel, and tinder-box, and is to be seen in many tobacconists' shops. A third device (W. D. Borland, Eng. pat. 5,771, 1889) consists of an attachment to cigars or cigarettes, by which they can easily be lighted, even in a high wind. Several attempts have been made to attach to cigars and cigarettes a composition or material capable of igniting by friction either upon an ordinary rough surface or on a prepared surface, as in the case of safety matches, but there are many obvious objections to such arrangements, and Borland has merely aimed in his invention at *assisting* the lighting of the cigarette or cigar by a spark, or by contact with any body heated to about 170°C. A minute portion of nitrocellulose fabric, forming a ring round the cigarette, is inserted under the paper, and on applying a spark the material takes fire and slowly smoulders till the whole end is glowing. Numerous details have to be observed in preparing the nitrocellulose insertion, in order to obtain sufficient ease of ignition without undue quickness of burning.

Statistics.—The average daily consumption of lucifer matches was in 1877 estimated as, in England 8, in Belgium 9, and in Europe and North America 6, per head of the total population. The figures are no doubt now much higher. It is to be wished that the *production* of English matches had increased in like ratio, but this is far from being the case, for on a glance at the annexed table (Table VI. p. 545) it will be seen that Great Britain has steadily lost ground in this respect. Her exports of home manufacture to foreign countries have dwindled down from the respectable total of twenty years ago to about one-fourth, and even her Colonial trade has to some extent diminished. On the other hand, the imports have gone up of late years by leaps and bounds, by far the largest being from Sweden, Norway, and Belgium. Many of the matches imported are mainly for export again. It will be observed that the exports of British manufacture to foreign countries are now insignificant in amount, while the supplies of our Colonies are to a large extent matches of *foreign* production which have passed through Great Britain. The chief cause of this deplorable state of things is the great competition of the Scandinavian, Belgian, and Danish match-trades. Considerable quantities of matches also find their way into England from Germany and Holland; and of wax vestas from Italy. In Sweden and Norway there were in 1880, 43 large factories, and some idea of the immense scale on which safety matches especially are there made may be gathered from the fact that, as already stated, 204,500,000 of phosphorus-free safety matches were made in 1881 at the Jönköping factory alone (Zeitschr. f. Zündwaarenfabrik., 1884, No. 152 and 153); and the annual exports from Sweden and Norway increased fourfold between 1870 and 1883. When it is remembered that in Scandinavia the workers only earn 1*d.* the gross of boxes, while in Great Britain they get 2½*d.* per gross (and are not satisfied with that), it is hardly to be wondered at that, although twelve small boxes of Swedish 'Säkerhets-tändstickor' can be bought here for 1½*d.*, a penny will only purchase a single moderate-sized box of English safety matches, the quality of which, it is fair to add, is very decidedly better. Nor, under these circumstances, is it surprising that the match-trade of England with other countries is far from making the progress so desirable from a national point of view. The home trade is, nevertheless, very large, and the industry a most important one. The value of ordinary lucifer matches, safety matches, and vesuvians produced annually by one English firm of manufacturers alone is about 350,000*l.*; and of vestas, inclusive of boxes, 150,000*l.* The total annual value of the English match manufacture has been estimated (S. C. I. 4, 1887, 772) to be from 1,500,000*l.* to 2,000,000*l.* sterling, one half of that amount being spent in raw materials. Probably the makers turn out, altogether, 300,000,000 to 350,000,000 matches daily. The following particulars, furnished the writer by one of the directors of Bryant & May, Limited (the largest English manufacturers) give an idea of the magnitude of the operations in a front-rank match factory. Quantity of *wooden matches* manufactured annually, 2½ million gross of boxes, or 360,000,000 boxes containing 90 to 100 matches each = 36 billions of matches per annum. *Safety matches*: quantity = 15·5 p.c., or one-seventh of the above, *in addition*. *Vesuvians*: 52,000 gross of boxes per annum. This quantity was formerly larger, but wax vestas are rapidly superseding vesuvians. *Wax vestas*: production 35,000,000 per diem = about 10,500,000,000 per annum, requiring 3 tons of wax per diem = 750 tons per annum, and 250 tons of cotton per annum. Taking the population of the entire world as one billion (1,000,000,000), this production of wax vestas is equal to about 10 vestas per head per annum, and 1,700 men, working 10 hours daily, and striking 34 vestas per minute, would be required to use up the above quantity of vestas! Length of wax taper used daily about 850 miles = 255,000 miles per annum. Quantity of vitreous phosphorus annually used, about 30 tons; of red phosphorus, about 1½ ton. Number of employés, 2,000, of whom 10 p.c. are men, the rest being women and boys. The wages of the men range from 26*s*. to 30*s*. weekly, of the women from 13*s*. to 15*s*., and of the boys from 7*s*. to 12*s*., according to skill and regularity of attendance at the factory.

There are at present about a dozen match factories of greater or less importance in or near London. In Germany there were, in 1883, 212 factories, producing matches at the rate of about 60,000,000,000 per annum. Austria-Hungary (originally the chief centre of the European match industry) has about 150 factories, two of which use 20 tons of phosphorus and make nearly 45,000,000,000 matches annually; and in Italy, in 1882, there were flourishing 202 establishments yielding 18 milliards (= 18,000,000,000) of lucifer matches, and 630 millions of vestas, many of which are exported to Greece, Turkey, Egypt, and France (Allgem. Deutsch. Polyt. Zeit. 10. 1882, 225). In France, the manufacture of matches was, until the end of 1889, a monopoly granted by the Government, for an annual tribute, to the Compagnie Générale des Allumettes Chimiques, constituted in October, 1872, and possessing twelve principal establishments, the largest being at Marseilles. The company had an annual sale = 80,000,000 francs, employed many thousands of workers, and consumed 30,000 kilos. of phosphorus, 1,500,000 kilos. of sulphur, and 45,000 cubic metres of wood (Nouv. Dict. de Chim. Appliq., E. Bouant, 1889). The French Government has now taken over this monopoly, and much of the match manufacture is put under the tobacco *régie*, the directors of the tobacco factories undertaking the supervision of the match establishments at Marseilles and elsewhere (The Manufacturer and Inventor, 4, 94, 1890; Moniteur Industriel, 16, 346, 1889, and 17, 83, 1890). The effect of the monopoly is that matches are expensive in France, and that they are used there more economically than in other countries. In the United States the match-trade is in the hands of a comparatively small number of firms; it is thus a great monopoly, and there is a very heavy duty on all imported matches, as well as a tax on the matches manufactured in the country. In 1881, the revenue from the internal tax amounted to $3,272,258, and from the customs duty on imported matches to $6,186. Guatemala imports annually 115,000 gross of wooden safety matches of Swedish, Danish, and German manufacture; Belgium and the United States also contribute to the supply, while 15,000 gross of wax matches are imported into Guatemala, chiefly from Italy. The Ottoman Minister of Commerce and Public Works recently had under consideration the formation of a State monopoly for the manufacture and sale of matches, made in factories to be constructed for that purpose at Constantinople, Salonica, Smyrna, and Alexandria (Board of Trade Journ. Ap. 1889).

As regards the quantities of phosphorus used in the European lucifer match manufacture, there are no complete official returns and few trustworthy figures. The writer has, however, received information from a particularly authoritative and well-informed source, that many of the figures published in foreign technological works and copied into English papers are very wide of the mark, being *greatly* in excess of what the total amount of phosphorus used can possibly be; and, as regards the consumption of phosphorus in the British Isles, in the match trade, the writer's informant would estimate the quantity used as from 40–50 tons per annum, over the last 15 years. The fact that it does not to his knowledge exceed the latter figure is attributable to the largely increased economy practised by match manufacturers. On a fair computation, 1 lb. of phosphorus should be sufficient for about 1,000,000 matches. Nearly all the phosphorus required for European consumption is supplied by two firms, those of Albright and Wilson, Oldbury, near Birmingham, and Coignet et Fils, Lyons. The German Imperial statistics show that in 1889 the English makers maintained the field against their French competitors; but Russian competition is becoming somewhat more perceptible. In 1889 Germany imported 212,500 kilos. of white and red phosphorus from England, 38,300 kilos. from Russia, and 2,100 kilos. from France.

Manufacture.

a. Wooden matches. The manufacture of these matches as ordinarily carried on in England comprises the following operations: 1. 'Scurfing'; 2. Cross-cutting; 3. Steaming; 4. Splint Cutting; 5. Drying the Splints; 6. Filling the Dipping Frames; 7. Paraffining (formerly Sulphuring); 8. Dipping; 9. Drying the dipped splints; 10. 'Laying out,' or 'Racking off'; 11. Halving (sometimes also called 'cross-cutting'); 12. 'Boxing.' The three main operations are splint-cutting, dipping, and drying, but a summary of the whole process will be given here. [The larger makers as a rule cut their own splints, but splint-cutting often constitutes a separate industry, the smaller manufacturers buying their splints already cut and made up into bundles.]

Nature of the wood.—The material almost exclusively used in this country is a very straight-grained white Canadian pine, though soft yellow deal is occasionally employed. Other woods used abroad are poplar, linden, beech, willow, birch, and aspen, the last-named especially in Sweden. Cedar-wood, too, has been used. The planks of wood, usually 12-13 feet long, and 3 inches thick by 11 inches wide, are first of all freed from irregularities and roughnesses of surface by the operation called *scurfing*, knives or cutters, rotary or otherwise, cleaning and smoothing the surface. A machine for effecting this operation is shown in fig. 2. The planks are then *cross-cut* by such a machine as that seen in fig. 3, into blocks or lengths 4¾ in. long × 3 in. thick × 11 in. wide. An ordinary English match-splint, which will yield two match-stems, 2⅜ in. long, is 4¾ in. long, so that the pieces cut off from the plank, measured in the direction of the grain of the wood, have just the length of a splint. Unless the wood is newly felled, and therefore sappy, these blocks must next be *steamed* (third operation) for about twenty minutes. They are then taken to the *splint-cutting* machine (fourth operation). Very many forms of such machines have been invented (Table VII. p. 546) but only three kinds have been of late years at all generally used in the United Kingdom. The two earlier types of splint-cutting machine were the *toothing* machine (fig. 4), and the *flaking* machine (fig. 5). In the toothing machine (one form of which—adapted for pine splints only—is shown in fig. 4), cutters, consisting of vertically-arranged lancet-points or teeth, first score or groove the wood in the direction of the grain and to the depth of a splint, and a horizontal knife or plane then slices off the grooved portions, which fall as match-splints, rectangular in section, and of the above-mentioned length, 4¾ in., beneath the machine, and are collected by an attendant. This kind of machine answers well for 'clean' wood, such as pine-wood, but is not adapted for poplar, aspen, &c. The 'vertical flaking' machine, represented in fig. 5, is suitable for coarse-grained and even knotty wood, and requires little skill in working.

FIG. 2.

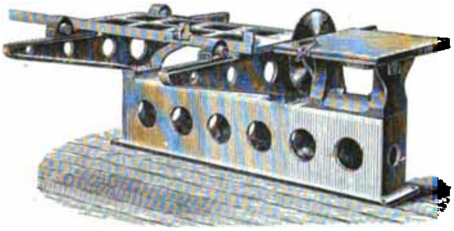

FIG. 3.

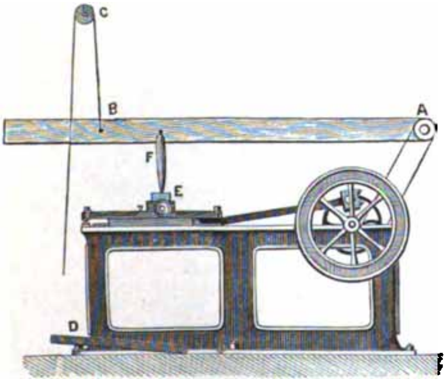

FIG. 4.

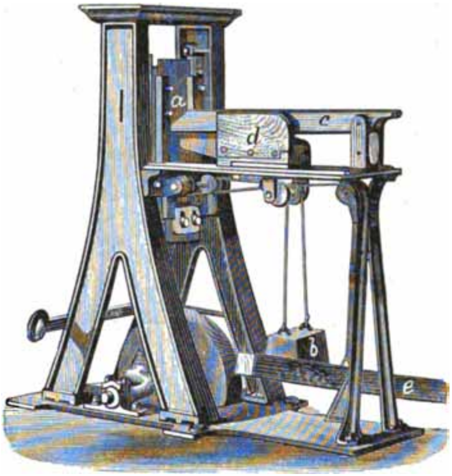

FIG. 5.

In this machine there are no 'teeth,' but a vertical slicing-knife or plane, *a*, cuts flakes from the block of wood, which is kept up to the plane by the weight *b*. The wood is held down by the lever *c*; and the feeder block, *d*, can be withdrawn from the plane by a treadle, *e*. When a quantity of these flakes has been cut, they are placed again in the machine and divided by the plane into splints. This machine therefore forms the splints by two operations, first 'flaking,' and then 'matching,' and it is capable of cutting 650 bundles of splints per day. The earliest machine belonging to the third class, or combined '*toothing and flaking*' machines, was the invention of F. Tillett (1859). A machine, which for London work, has to a great extent superseded the foregoing kinds, has been invented by Pace and Howard (Eng. pat. 1,285, 1872; and further patents, 3,272, 1873, and 802, 1881), and is on the same principle as, but an improvement upon Tillett's invention. In this machine, the cut splints are guided by an indiarubber band so as to pass through a trough, at the lower end of which they are delivered on a table ready for collection and removal. For drawings of Tillett's, and Pace and Howard's machines, the reader is referred to the several specifications. Many other machines, of a special character, in which cutters of various sections, circular, semicircular, rectangular, &c., cut into, or descended upon the surface of the wood, have been employed: to this category belonged the machines of Mayer

(1839), Partridge (1842), Cook (1857), Grimes (1862), and others; also those of v. Römer, Neukrantz (1845), Krutzch (1848), and Bamberger (1851). For later English patents referring to splint-cutting machinery, see Mills, 3,355, 1874; McC. Young, 1,317, 1875; Holms and Saunders, 3,653, 1877; Long, 1,992, 1878, and others, in Table VII. All English, and (at the present time) nearly all foreign match-splints are square or rhombic in section. Round splints, such as were yielded by the old machines of v. Römer, Partridge, Krutzch, Neukrantz, and Bamberger, are now comparatively rarely seen, excepting in Vienna. This statement does not, of course, apply to vesuvians.

In Sweden, and to a considerable extent in Germany, the difference in the nature of the wood used is the cause of a difference in the process by which the splints are cut. A thin veneer of wood is separated from a revolving block, 14 inches (=7 matches) long, and 12–20 inches in diameter, by a fixed plane or knife, with an advance proportionate to the thickness removed from the block, eight other knives, at right angles, or nearly so, cutting the veneer into seven long bands, each the thickness of a match, and having a width equal to its length. These bands are broken into pieces about 6 feet long, freed from knots, and fed into a machine provided with a guillotine knife, which cuts them transversely into splints. Worked by hand, this machine can deliver about 5,000,000 splints *per diem*; and by employing steam-power the manufacturer can obtain double that yield. The disadvantage of some splint-cutting machines constructed upon this principle is that the cutting tool which separates the veneer sometimes cuts slightly *across* the growth-rings of the wood, instead of making an incision parallel to the axis of growth. The result is that the splints produced break very easily; a fact which everyone who has used the cheap Swedish matches must have observed. Several of the machines latterly patented in Great Britain have been on this principle. [*V.* Table VII., p. 546:—Nielsen (agent, Mills), 1874; Bartlett and Read (agent, Clark), 1879; Sebold (agent, Wirth), 1882; Norris and Hagan, 1885; Zappert, 1887; and Ellis, 1888 and 1890. (For foreign patents consult Table IX., p. 552).]

The next (and fifth) operation is the *drying of the cut splints* as they come from the ordinary splint-cutting machine. The splints were formerly always made into *bundles* and then dried. Now they are sometimes thrown loosely into large trays and dried by exposure to warm dry air. (Swedish splints are dried in wire-gauze cylinders revolving within a brick stove.) The dried splints are ready for the operation of *filling the dipping clamps or frames.* Prior to the introduction and general use of dipping clamps, the bundles of dried splints were loosened, the ends dexterously shaken apart and dipped, first into the melted sulphur, and afterwards into the igniting composition; or the ends of the splints were bevelled off or sharpened (Bell & Black, 1855; Bell & Grimes, 1856; H. Higgin, 1859), so that each splint received its coating, non-adherent to the heads of adjacent splints; or the splints were so cut as to be parts of a block, and separated by spaces from one another while dipped (H. Baker, 1861). These were the so-called 'bundle-dipped' and 'block-dipped' matches. In the earlier days of match-making, 'dipping-boards' were sometimes employed, the splints or waxen stems being pushed into perforations in plates, previous to the dipping. 'Frame-' or 'clamp-dipping' was introduced in 1849, and its adoption, which by degrees became general, effected a great saving of time and labour. The dipping clamps are square frames with sides consisting of iron rods, on to which slip 60 boards or laths, each having about 65 grooves on its upper surface, and being lined with felt below. The match-splints are firmly held in the grooves by the pressure of the felt. Each groove thus contains a full-length (*i.e.* 4¾-inch) splint; each lath holds 65 such splints, and each frame 3,900 splints, which, dipped at each end and halved, will yield 7,800 matches. Wire frames have been tried, but unsuccessfully. The dipping frames were at first filled by hand, but Hynam (1850) and Bell and Grimes (1854) invented machines for the purpose. Improvements by Hynam, Muck, Bell, Higgins, Whines, Pace, and Grimes followed (*v.* Table VII.), and in 1865 Simlick introduced self-acting machinery, driven by steam power, to produce the various movements of these frame-filling machines with greater rapidity and economy of labour. The essential parts of all these machines are the same: the splints are put into a wooden case or box, to which an oscillating or jogging motion can be given by the aid of a treadle or otherwise, and are thus shaken on to a plate with grooves cut in it, corresponding in number, size, and distance apart to the grooves on a lath of the dipping

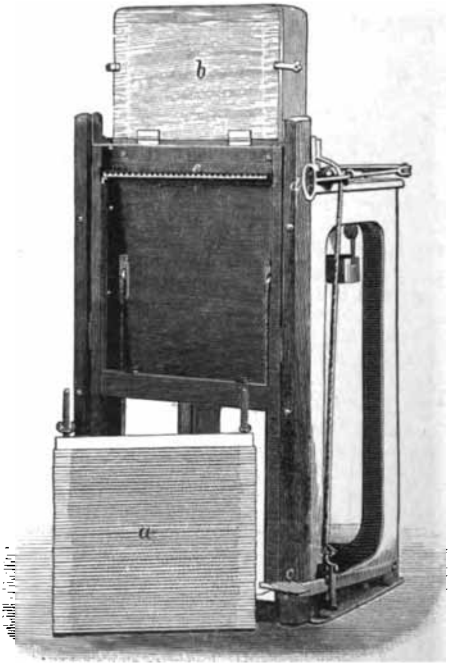

Fig. 6.

clamp. Plungers, working in the grooves and pushed forward by means of a second treadle, drive a row of splints into the grooves on the lath; the frame is then slightly lowered, so that an empty lath now becomes opposite to the grooves in the plate; the plungers come forward and push a new row of splints into the empty lath: and so on, until the frame is filled. The cross-piece at the top is then clamped on with screws and nuts, and the frame is ready to be taken to the dipping-room. One of these machines, commonly used at the present time, is represented in fig. 6. At *a* is shown an unfilled dipping clamp. The splint case, *b*, is shaken or jogged by the treadle, *c*, and the handle, *d*, produces the movements of the plungers backwards and forwards along the grooves in the plate, *e*.

In 1876, E. Beecher, of New Haven, Connecticut, invented and patented in England machinery by which the old-fashioned bundle-dipping, and the later frame- or clamp-dipping, were replaced by what may be called 'coil-' or 'band'-dipping; later patents have been taken out by other inventors, and it is not improbable that this system of working, which has already been introduced into some of the largest English match-works, will effect a general revolution in the method of manufacture, and that coil-dipping will—for wooden matches—eventually entirely supersede frame-dipping.

In Beecher's original machine (Eng. pat. 4,293, 1876, agent W. R. Lake) the splints were so delivered from a hopper as to be set at regular intervals between the coils of a long, flexible tape, band, or belt of cotton webbing, about the thickness of a splint, but considerably narrower than its length; this belt was continuously wound upon a short cylinder or drum adapted to a rotating mandril or axis, until a coil, or bundle, or frame, of the desired size was completed. The end of the binding tape was then secured to the preceding coil by a pin or otherwise, the drum and coil of match-splints thus bound upon it being now ready for removal from the mandril for dipping. By this plan of working, the splints are disposed round the drum in a continuous spiral between the coils of the binder, parallel with each other and with the axis of the drum. Being separated from each other by the thickness of the webbing, and by an interval the width of a splint between every two splints, the splints individually receive the proper proportion of composition when dipped, and can be conveniently dried in the coil. In an improved form of the machine (Eng. pat. 2,506, 1877, G. Evans, patentee) Beecher employs an auxiliary or secondary band in connection with the first, for the purpose of holding the match-splints more securely. This form of the machine is shown in section in fig. 7, A being the coil of the main belt, B the coil of the secondary belt, C the hopper, D a receiving cylinder, E a count wheel, F a setting wheel, and G the mandril or axis for the drum H, on to which is wound the coil I. Other machines for similarly arranging match-splints, preparatory to dipping, between coils of tape, &c., wound upon revolving spindles, drums, and the like, have been invented by W. H. H. Sisum (Eng. pat. 3,524, 1883, agent W. R. Lake), J. Frazer (Eng. pat. 3,554, 1887), C. J. Donnelly (Eng. pat. 5,390, 1887), H. C. Zappert (Eng. pat. 14,813 and 16,353, 1887), and E. Paul (14,111, 1889). In Donnelly's machine (figs. 8 and 9) the splints are fed from a hopper E, provided with a vibrating feed device F F′, connected with the crank wheel G, on to a 'pocketed drum' C, from which they are delivered on to webs M M′, unwound from the reels K K′, and wound on to the two reels L L′ in coils.

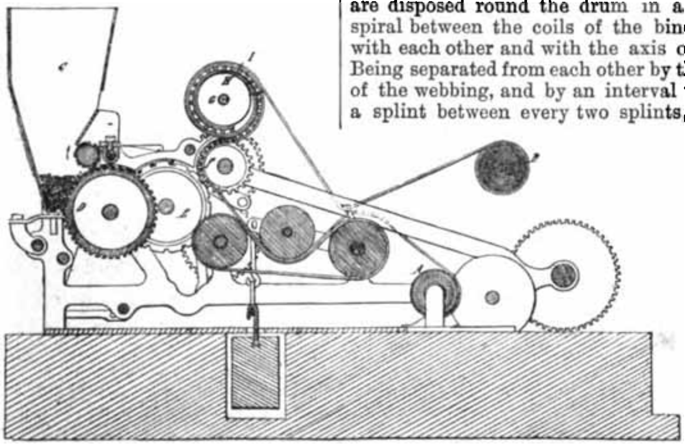

Fig. 7.

7. *Paraffining.*—The match-splints, having been arranged for dipping in one or other of the ways described (in bundle, dipping board, dipping plate, dipping clamp, or coil—now generally either clamp or coil), are ready for paraffining, or 'the first dipping,' as it is sometimes called. The frames or coils are put on a table, and the splint-ends are levelled, if necessary, by taps with a piece of wood: they are afterwards heated (to facilitate their absorption of the paraffin) by application of, or to, a hot iron-plate (hot sand and fusible metal have been used—J. J. Long, Eng. pat. 1,401, 1868), and then immersed in a melted mixture of paraffin and stearine, contained in a shallow, flat- and double-bottomed iron tank, kept at the required temperature by steam or hot water. Both ends of the double-length splints are, of course, thus treated. Sometimes the operation is effected in a brick stove, on the top of which

are three shallow, flat-bottomed, square pans, one serving for the preliminary heating of the splint-ends, the second for the paraffining, and the third for the subsequent dipping in the igniting composition. Another method by which the paraffin mixture is occasionally applied involves the use of a cloth- or felt-covered cylinder, roller, or drum, fitted and revolving in the vessel of melted paraffin. In this case, a series of filled clamps or coils is automatically carried by chains, endless bands, &c., over the roller (v. J. J. Long, *l.c.*).

Formerly the splints were dipped in melted brimstone, or dusted over with sublimed sulphur, but in all but the most inferior matches paraffining has entirely superseded treatment with sulphur. Beeswax, stearic acid, tallow, resin oil, turpentine, petroleum, and mixtures of stearine and colophony have been used by various makers, instead of or in admixture with paraffin. Dussauce (1864) stated that one part of stearic acid is as efficacious in increasing the inflammability of the stems as ten parts of sulphur.

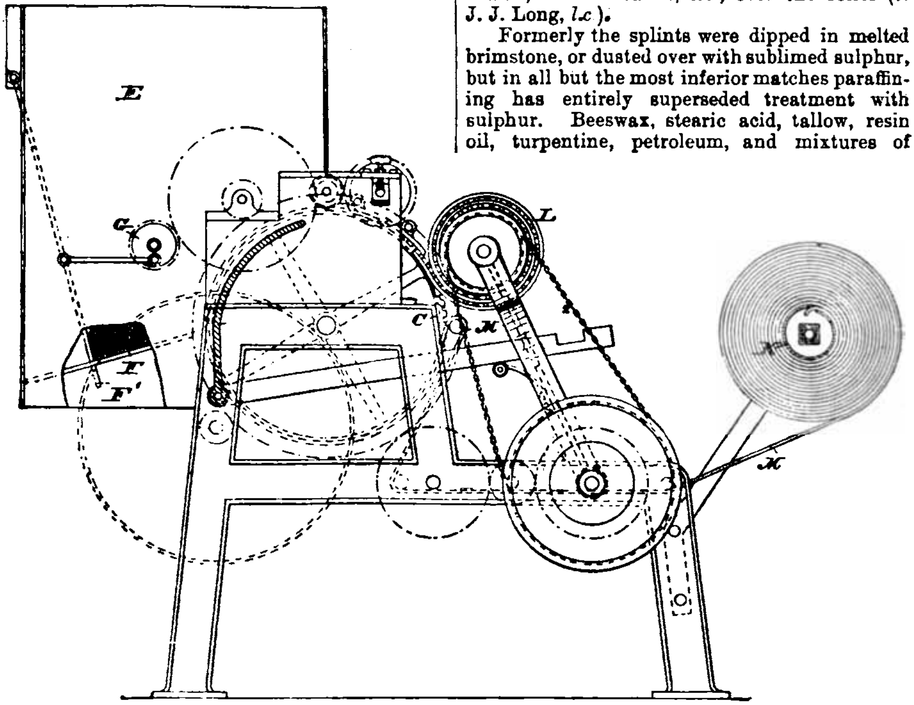

FIG. 8.

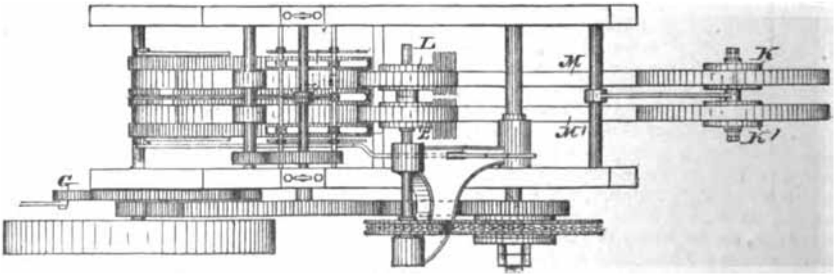

FIG. 9.

8. *Dipping.*—In connection with this important operation, the ingredients of the compositions used first claim attention. Almost every maker has his own especial composition and way of preparing it. But the mixtures in use for ordinary matches invariably contain—(1) the oxidisable body, vitreous phosphorus, in a fine state of division, and intimately mixed with (2) oxidising agents; (3) cementing or binding materials; (4) certain chemically inert bodies added to increase friction; and (5) colouring-matters. The oxidising agents principally employed are potassium chlorate, potassium nitrate, plumbic nitrate, minium, manganese peroxide and lead peroxide: potassium bichromate, 'oxidised minium' (made by heating minium with nitric acid), ferric oxide, and litharge must also be mentioned. In English matches, potassium chlorate is the customary oxidising agent, used alone or with manganese peroxide, &c. German makers prefer lead nitrate, alone or in conjunction mostly with minium, lead peroxide, and

sometimes litharge; and potassium nitrate is frequently present in continental matches, which in general strike more silently than the English matches prepared with potassium chlorate. Glue, gum, gelatine, and dextrine are the binding media mostly used: in Great Britain, glue is almost exclusively employed. Very much depends on the quality of the glue, and its drying properties. Powdered glass and fine sand are the indifferent bodies generally added, and Prussian blue, ultramarine, smalt, magenta, vermilion, and chrome yellow are commonly used to colour the mixtures. The foregoing is not in any respect an exhaustive list of the ingredients which have been, and are, added to the dipping pastes of ordinary matches: but further particulars, and proportions of the components of various igniting compositions, will be found in the tables appended to this article (for ordinary match compositions, *v.* Table II.; also Table VII.). It will be observed that the quantities of phosphorus in some of the later and better compositions are very small. Although Wagner, in 1857, wrote of $\frac{1}{10}$th–$\frac{1}{12}$th as a suitable quantity, experience has amply shown that, if the phosphorus be in a sufficiently finely-divided condition, and thoroughly incorporated with the other ingredients of the igniting paste, far smaller proportions answer very satisfactorily.

The ingredients of a dipping composition are usually mixed in the following manner. The glue and potassium chlorate or nitrate are dissolved in warm water, and the phosphorus is then added to and stirred in the liquid (which should be of a syrupy consistence and at a temperature of about 38°C.), until a perfect emulsion is obtained. The rest of the constituents, powdered glass or sand, colouring matters, and metallic oxides, if present, having been previously ground together in a mill, are now added, and thoroughly mixed with the emulsion.

For the operation of dipping, which is always performed by workmen in a separate apartment called the dipping-room, the emulsion is ladled from a steam-jacketed iron pan on to the dipping plate or table—formerly a marble slab, now generally a shallow, flat-topped, iron box (A, fig. 10), kept hot by steam admitted to its interior. The composition is spread over the plate, and levelled to the required depth by the striking-gauge or 'strickle,' B; and the ends of the splints in the filled frames or coils are then dipped in the thin layer of igniting composition. In matches of the best quality, after the splint-ends on one side have been dipped, the frames or coils are placed in racks, the tipped ends downwards, for about twenty minutes. The tips are thus rounded and improved, the 'hung dip' or 'big head' (preferred by British consumers) being the result. In the commoner sorts of matches, one side is dipped; the frame is then turned over, and the other side is at once immersed in the composition. Where the arrangement consisting of three stove-heated shallow pans is adopted, in the place of the ordinary dipping table, the splints are heated in the first pan, paraffined in the second, and dipped in the third.

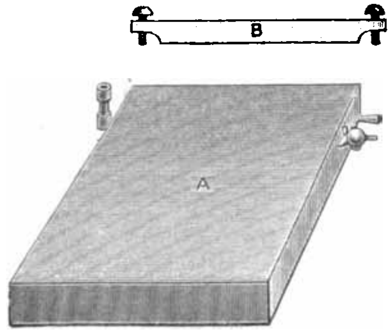

Fig. 10.

Dipping by hand, as already described, is most usual; but the igniting composition is sometimes applied by the aid of india-rubber- or similarly coated cylinders or rollers, partly rotating in hot-water jacketed cases, receptacles, or boxes containing the mixture, endless chains conveying the frames, clamps, or coils, over the rollers (W. E. Newton, Eng. pat. 1,428, 1853; S. A. Bell a. T. Higgins, Eng. pat. 2,311, 1862; H. Arlow, Germ. pat. c. 78, No. 22,308, 1882; W. Holmström, Eng. pat. 3,196, 1883, F. H. F. Engel, patentee; H. C. Zappert, Eng. pat. 16,353, 1887; C. R. E. Bell, Eng. pat. 5,208, 1889). Bevelled wheels (E. Fitch, Eng. pat. 14,992, 1884, J. A. Elliott, patentee) and other devices (L. Urion, Eng. pat. 2,594, 1856; J. H. Mitchell, Eng. pat. 11,686, 1884, S. Pitt, patentee) have also been used for the purpose. According to a recent invention of L. Cobbaert (Eng. pat. 6,595, 1889), the paraffin and striking composition are contained in troughs, to which an intermittent and alternately ascending and descending motion is given by eccentrics, as the clamped splints are carried over them by endless chains.

9. *Drying.*—This operation immediately succeeds the dipping. The frames or coils of double-tipped splints are placed on supports or racks, either in the open air (and this is the most satisfactory plan in dry, windy weather—in March or October, for instance), or in the drying-room—an apartment maintained during the summer at a suitable temperature by fans or otherwise, and in damp weather and winter kept warm and dry by pipes conveying steam or hot air. S. A. Bell (1865) proposed to admit streams of air, impelled by any suitable fan or blower, and previously cooled or heated according to necessity, through pierced pipes fixed around the chamber at the same level as the pendent stems. Fitch (1884) and others direct a blast of air—cool or otherwise—on to the splints, directly they have passed the dipping rollers.

10. *Laying out;* 11. *Halving;* and 12. *Boxing.*—The 'headed' and dried splints have next to be taken out of the dipping clamps or coils, as the case may be. In the first case the operation is termed 'laying out' or 'racking off,' and is always, or nearly always, in England effected by hand. The nuts and crosspiece at the top of a clamp are removed, and then lath after lath is lifted and the row of double-tipped splints beneath deftly withdrawn. The women who do this receive from 1*s.* 1*d.* for each 100 frames laid out. On the Continent, laying out is performed mechanically, the machines of C. Beck (Germ. pat. 696, 1877, and 9,126, 1879) and G. Sebold (Germ. pat. 12,113, 1880, 17,857, 1881,

and 41,994, 1887; also Eng. pat. 4,058, 1880, F. Wirth, patentee) being much employed. Other laying out machines are those of J. Schnetzer (Germ. pat. 38,569, 1886) and O. Walch (Germ. pat. 36,905, 1886). In the case of coil-dipped splints the process is called 'unwinding,' and differs, of course, materially from the methods applicable to dipping clamps. E. B. Beecher (Eng. pat. 3,649, 1877, G. Evans, patentee) has invented a machine which simultaneously performs this operation and the next, 'halving,' 'cutting-down,' or 'cross-cutting.' The circular coil of double-headed splints (*v.* p. 529) is put on a shaft fixed to the framework of the machine, and the ends of the bands or webs are placed by the operative round two other shafts, on to which the bands are wound from the coil, the splints being left between endless straps, carried between two revolving discs covered with caoutchouc, and led forward under a rotating cutter, by which they are divided in the centre. Each splint thus yields two matches. Donnelly's machine (Eng. pat. 5,390, 1887) is also provided with a revolving cutting-blade, by which the splints are divided.

Reverting to clamp-dipped matches, handfuls of the laid-out, double-headed splints are divided, 'halved,' or 'cross-cut,' usually by the pivoted or 'lever' cutting-knife, shown in fig. 11, and the resulting matches are at once *boxed* (*i.e.* put into boxes) by hand. The women, who become exceedingly dexterous in taking up handfuls of splints of just the required size to fill two boxes, receive about 2*d.* per gross of boxes, for halving and boxing, and 35–40 gross of boxes can be filled by hand per diem. There is more loss occasioned by 'firing,' during the operation of boxing, than at any other stage of the match manufacture; in fact, the loss has been known to reach 10 p.c. With the object of diminishing this loss, H. Higgin (Eng. pat. 10,714, 1889) has recently invented a machine (shown in figs. 12 and 13, in front and side elevation), in which a vertically-working knife with a diagonal edge, *d*, is substituted for a lever knife. The block for holding the bundles of splints has the bed, *i*, set at an angle, other than a right angle, with the plane in which the knife works. The result is stated to be that the knife passes gently and easily through the bundle. Although boxing is generally, as has been stated, performed by hand, some of the machines from time to time introduced for the automatic and continuous manufacture of matches have been so constructed as to carry out every operation, from splint-cutting to boxing (*v.* C. R. E. Bell, Eng. pat. 5,208, 1889; L. Cobbaert, Eng. pat. 6,595, 1889: for boxing especially, O. Walch, Eng. pat. 4,861, 1879, W. P. Thompson, patentee; H. H. Lake, Eng. pat. 17,062, 1886; N. M. Ström, Germ. pat. 45,622, 1888; F. Lundgren, 4,768, 1890; Casey, Mantion and Millen, Amer. pat. 418,887, 1890); and in other continuous machines the ready-cut splints are fed into a hopper, all the subsequent processes being carried out automatically (J. H. Mitchell, Eng. pat. 11,686, 1884, S. Pitt, patentee; E. Fitch, Eng. pat. 14,992, 1884, J. A. Elliott, patentee; H. Arlow, Germ. pat. cl. 78, 22,308, 1882).

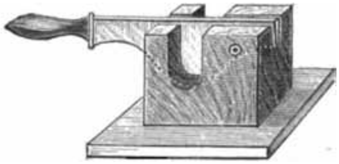

FIG. 11.

Continuous machines cannot be more than mentioned here, and the reader is referred to the several patent-specifications under the names and numbers given; in addition, for Arlow's machinery, to S. C. I. 3, 378, and D. P. J. 251, 536. Reference may also be made, in this connection, to the specifications of Urion (1856), Newton (1858), Bell and Higgins (1862), Holmström (1883), and Zappert (1887), all of whose machines carry out at least several of the operations continuously.

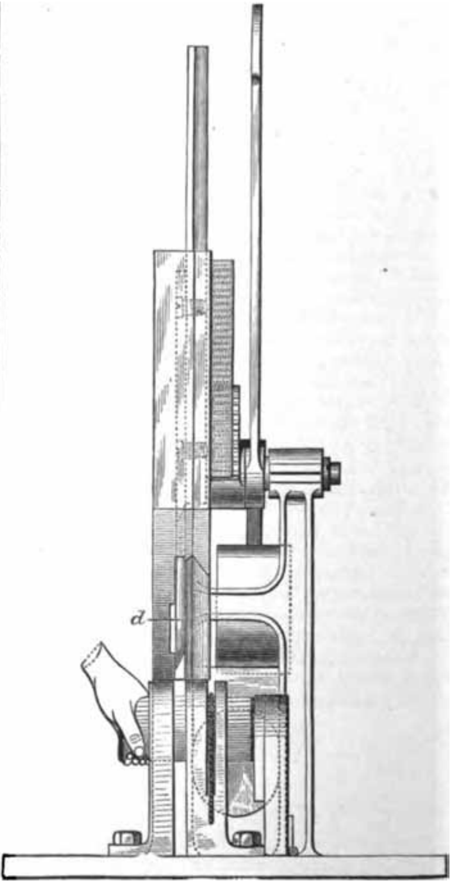

FIG. 12.

Match-boxes are made from thin veneers or squelettes (*Anglice*, 'skillets') of wood, cut by a vertical flaking or 'scribing' machine, such as that shown in fig. 14. The veneers are then scored along the lines in which they must be bent into box-form; moulds are sometimes used. (For box-making machinery, *v.* J. T. Connolly, 237, 1880, A. M. Clark, patentee; M. Wiberg, 2,911, 1880; and W. Ellis [veneer cutting], 8,031, 1888, and 1,074, 1890).

β. **Safety matches.** All that has been stated, with regard to the processes of manufacture of ordinary matches, applies to safety matches, excepting the section on dipping compositions. Many more ingredients have been and are used for safety match compositions than are added to ordinary match pastes; and vitreous phosphorus is almost invariably absent from the first-named, red phosphorus being employed instead. Safety matches have been made—(1) with red phosphorus in the igniting pastes only (*v.* Table III.); (2) in the rubbers only (*l.c.*); (3) in both heads and rubbers (*ibid.*); and (4) without phosphorus, either in the heads or rubbers (Table IV.). Matches of the second class—to which the best-known English, Swedish, and Belgian safety matches belong—are alone largely manufactured: matches of the first and third classes have hitherto failed to answer to requirements; and although very many makers have put on the market matches of the fourth class, it is doubtful if any entirely satisfactory safety matches, without red phosphorus either in the heads or rubbers, are at present to be met with (*v. ante*, p. 523). The igniting compositions of ordinary safety matches (class 2) usually contain, as an oxidisable ingredient—apart, of course, from the red phosphorus in the rubbers—grey antimony sulphide, with or without sulphur; charcoal, too, is occasionally added. Potassium chlorate, potassium bichromate, and minium are the ordinary sources of oxygen, but manganese peroxide and nitre are also used; glue is the usual binding medium. Colouring matters are seldom added to safety match pastes, which are usually black. (For proportions, &c., *v.* Table III.) Certain Swedish safety matches, much sold in this country, and bearing on their boxes the conspicuous legend '*Utan swafel och phosphor*' (without sulphur and phosphorus), have been analysed in the writer's laboratory and found to contain a considerable quantity of sulphur, easily extracted by carbon disulphide.

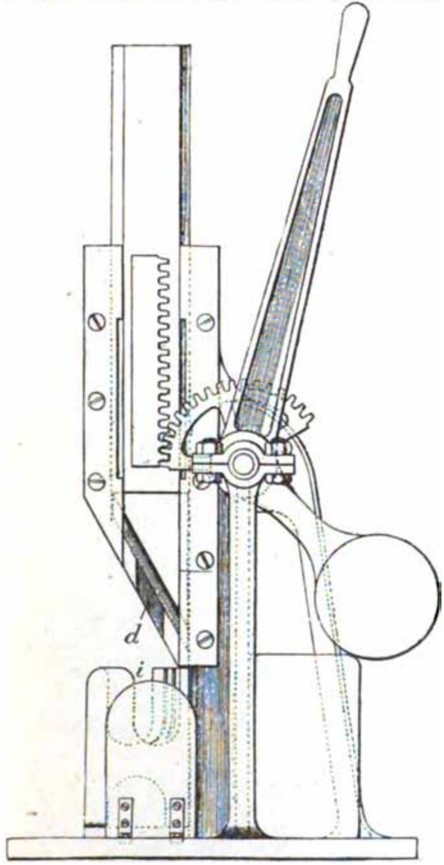

FIG. 13.

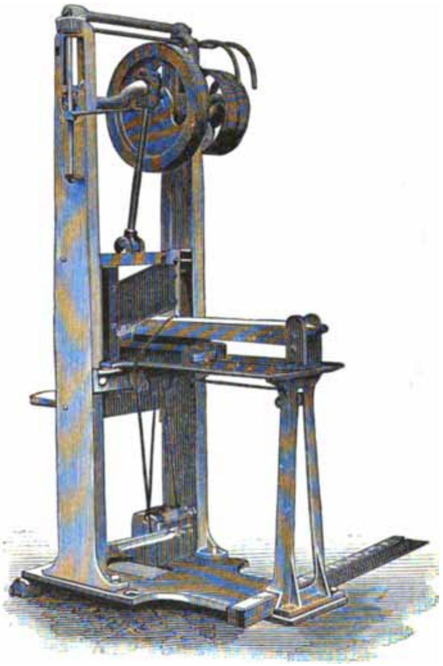

FIG. 14.

γ. **Vesuvians.** The manufacturing processes for cigar lights, fixed stars, braided lights, *et hoc genus omne*, differ but little from the methods in use for ordinary matches. The stems, however, are generally of alder or other hard wood (when not of glass, &c.), circular in section, often braided and wired, and shorter than ordinary match sticks. The round splints employed are imported into England in considerable quantities from Austria. The dipping clamps are smaller, usually filled by hand, and contain from 1,600 (40 × 40) to 2,000 short splints, which are dipped at one or both ends. Coil-dipping is not adapted for this manufacture. Two distinct compositions are used: the pastille or burning composition, used for the head or ball; and the igniting or striking paste, with which the head is tipped. The pastille composition is a mixture of nitre with charcoal (or coal- or coke-dust), glass-powder, gum or glue, and some scenting ingredient, such as cascarilla bark, satinwood, gum benzoin, lignum vitæ, &c. The stems are dipped more than once in this composition, until the heads are of the required size, and a final dip in any ordinary striking composition is given to the heads after they have been dried. The old-fashioned 'fusees' (of brown paper or cardboard, impregnated with nitre, tipped with sulphur, &c.) have given place to vesuvians, which in their turn are being rapidly superseded by vestas and fusee-vestas.

δ. **Vestas.** For the production of the tapers, from 60–100 strands of cotton, of about 20 threads each, are led from a bale, through guides arranged at a convenient height, into a steam-jacketed tank containing stearine, or a mixture of stearine and paraffin, and thence through perforations in a draw plate, and afterwards over a 'drawing drum' (fig. 15), 6–10 feet in diameter, revolving on an axis, by hand or steam power. From this drum the tapers are led back again through the bath to a similar drum on the opposite side of the tank, and by winding alternately from one drum to the other, they are made to pass 6–7 times through the bath, until the cotton has a coating of fat just sufficient to allow it to pass through holes in a suitable gauge plate. The taper is then either cut into lengths, which are bundled together and cut into vesta stems by a pivoted knife, the stems being afterwards filled into dipping frames by a small filling machine, worked by hand or steam, or 60–100 strands of it are wound upon a small drum, and passed from it through guides to a 'cutting and filling' machine of the kind indicated in fig. 16. In this class of machine the tapers are caused to advance between two feed rollers covered with caoutchouc or other elastic material, and having an intermittent motion, their rotation at each revolution of the driving shaft, or movement of the treadles, being through such an angle as to advance the tapers the required distance under a cutter or cutters working in a vertical plane in front of the feed rollers. The dipping frame (which will hold 6,400 stems (80 × 80) is held immediately in front of a perforated plate through which (when the machine is worked) the cut stems are pushed, so as to rest on a lath of the frame; the frame is now lowered, and the next lath is dropped into position, to receive a row of cut stems, immediately the treadles have been pressed down. When the frame is filled, the stems are dipped, on one side only, in the striking composition, in which the proportion of vitreous phosphorus is somewhat larger than that used for ordinary matches; the greater flexibility of the stems rendering it necessary that the composition should inflame with but slight friction. The manufacture of fusee-vestas is similar, the application of the striking paste being preceded by dipping in a scented pastille composition, such as is employed for vesuvians. The remaining processes, drying, laying out, &c., require no especial description.

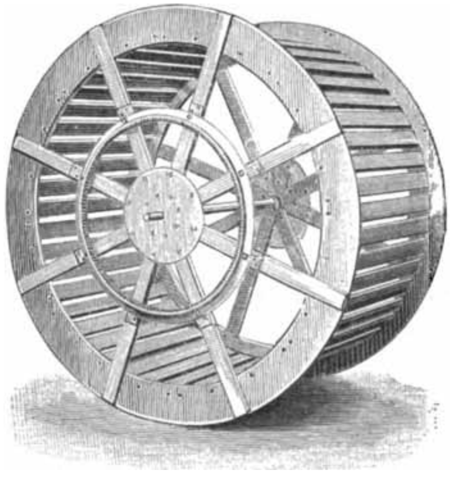

Fig. 15.

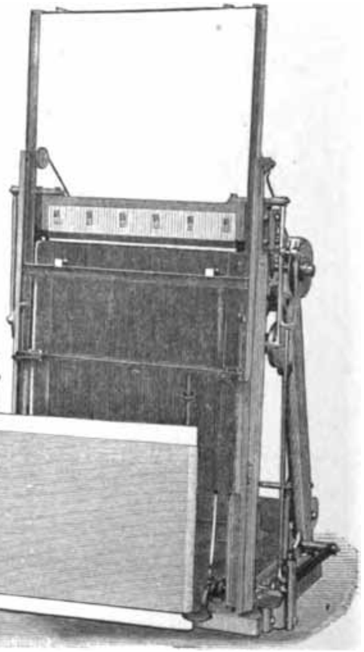

Fig. 16.

(For wax vesta machinery, *v.* E. Zulzer, Eng. pat. 418, 1854, J. H. Johnson, patentee; J. Birch, Eng. pat. 2,231, 1867; C. R. E. Bell, Eng. pat. 278, 1881: for fusee-vestas, *v.* T. J. Clanchy, 455, 1868; R. Bell, 1,965 and 13,938, 1885; and C. R. E. Bell, 16,079, 1886).

ε. **Rubbers.** For ordinary matches, mixtures of sand, glass, emery, and the like, with glue or gum, spread on the paper with which the sides of the match-boxes are coated, form convenient friction surfaces; metal gratings, tablets of unglazed porcelain, and porcelain or metal plates with parallel ridges very close together, are frequently employed; and practically any rough or uneven surface—even cloth—can be made to answer. The compositions used for the special rubbing surfaces are very various; but the ingredients chiefly present are red phosphorus, antimony sulphide, and powdered glass, made into a paste with glue. The antimony sulphide is sometimes omitted, and manganese peroxide is not infrequently added to safety rubbers.

[*Partial list of books and journals consulted.*—Leuchs' Allgem. Polyt. Zeit. 1825–48; Annal. d. Chem. u. Pharm. 47, 334; 49, 349; J. Ph. 1811, 188; 1860, 180; D. P. J. 59–278; particularly Winterfeld, 83, 75, 248; 96, 281; Wagner, 141, 450; 145, 387; 146, 399; Wiederhold, 161, 221, 268; 163, 203, 296; 169, 158; 200, 243; Jettel, 191, 369; 193, 278, 368; 194, 26, 250; 195, 369; 203, 75; Gentele, 209, 369; Gintl, 215, 188; 218, 169; Schwarz, 219, 243; Grothe's Allgem. Deutsch. Polyt. Zeit. 1, 261, 295; 10, 225; Fischer's Zeitschrift f. d. Chem. Ind. 1, 21; 2, 259; Rev. Industrielle, 1877, 418; Polyt. Notizbl. 1888, 120; Die Chem. Indust. 1, 10, 93; 2, 204, 430; 3, 82, 237; 4, 25, 56; 5, 255, 293; 6, 270, 348; 7, 95, 133, 225, 270; 9, 361; 11, 310; J. C. T. 1855, *et seq.*; Chem. Zeit. 1880, *et seq.*; C. C. 1887, 205; Biederm. Techn.-Chem. Jahrb. 1880–88; Zeitschr. f. Zündwaar.-Fabrik. 1882, 126; 1884, 152, 153; 1887, 154; C. H. Schmidt, Der Vollständige Feuerzeugpraktikant, Weimar, 1861; H. Dussauce, A Practical Treatise on the Fabrication of Matches, 1864; J. Freitag, Die Zündwaaren-Fabrikation, Leipzig, 1876; J. Kellner, Handbuch der Zündwaaren-Fabrikation, 1886; F. Abel, P. M. 1863, 356; H. Greeley and others, Great Industries of the United States, 1872; W. G. Crory, East End Industries, 1876; J. Garver, Matches, Scient. Amer. suppl. 84, Aug. 11, 1877; E. G. Clayton, Ex Luce Lucellum, Health, 1887; Journ. Soc. Arts, 1, 200; 4, 641; 12, 46, 115; 14, 561, 667; 20, 59; 21, 129, &c.; J. S. C. I. 1, 338, 425; 2, 363; 3, 378; 4, 365, 417, 418; 6, 522, 772; 7, 768; 8, 649, 930, 1,010; 9, 414, 429, 547, 561, 567, 764, 822, 1,064; Journ. Franklin Inst. 24, 211; 56, 138; 79, 109, &c.; Le Gén. Industriel, 15, 124; 17, 51, &c.; C. R. 22, 292, 437; 23, 454, 635; 24, 618, &c.; Tomlinson's Cyclop. 1866; Cooley's Encycl. (Tuson), 1880; Encycl. Brit. 9th ed.; Spon's Encycl. 1881; Bouant's Nouv. Dict. d. Chim. appliq. 1889; Le Technologiste, 1859, 140; Payen's Chim. Indust. 1867; Paul's ed. of same, 1878; Richardson and Watts, Chem. Technol. 1865; Knapp's Lehrb. d. Chem. Technol. 1865; Wagner and Gautier's Chim. Indust. 1879; Wagner and Crookes' Handb. Chem. Technol., 1872; Echo du Monde Savant, No. 46; Brit. Journ. Comm. Feb. 1887; The Pract. Mechanic, 1854, 154; Hoffman's Reports, 3, 61, 84; Dubl. Quart. Journ. Med. Sci. Aug. 1852; Child Empl. Commiss. 1862, 1st report; The Atlas, Jan. 10, 1830; Chambers's Journ. June 30, 1883; Aug. 13, 1887; Board of Trade Returns; &c. &c.].

TABLE I.—CHRONOLOGICAL SUMMARY.

Year	
1673.	Brand's discovery of phosphorus.
1805.	Chancel's 'oxymuriate matches.'
1809.	Derepas' proposal—addition of magnesia to diminish inflammability of phosphorus.
1812.	'Chemical matches,' on Chancel's principle, sold in Vienna.
1816.	Dérosne's manufacture of phosphoric friction matches in Paris.
1827.	John Walker's 'lucifer matches'—the first friction matches made in England.
1828.	Jones's 'Prometheans' (Chancel's principle).
1832.	General introduction of non-phosphoric friction matches.
„	Invention of wax stems for matches (Newton's patent).
1834.	V. Römer's patent for phosphoric friction-matches. General introduction of phosphoric matches, and beginning of their manufacture on a large scale.
1835.	Trévany's substitution of minium and manganese dioxide for potassium chlorate, in phosphoric friction-matches.
1836.	First American patent for phosphoric friction matches.
1837.	V. Romer's use of lead peroxide.
1842.	Böttger's recommendations: use of lead peroxide and nitrate, or minium and saltpetre.
1845.	V. Schrötter's discovery of red phosphorus.
1849.	Palmer's invention of vesuvians, and introduction of frame-dipping in place of bundle-dipping.
1850.	Manufacture in Germany of matches with igniting compositions containing red phosphorus.
„	Hynam's introduction of machinery for filling dipping frames.
1851.	Production in England and Austria of matches with igniting compositions containing red phosphorus.
1854.	Bell and Grimes's improvements in machinery for filling dipping clamps.
1855.	Lundström's invention of safety matches: red phosphorus on rubbers only.
„	Wagner's proposals.
1857.	Canouil's and Hochstätter's inventions: non-phosphoric matches.
1859.	Tillett's invention of the 'toothing and flaking' machines for cutting splints.
1860.	Phosphorus disease. Poggiale, Chevallier, and Duvergie's Report to the French Imperial Academy of Medicine.
1861.	Wiederhold's experiments and suggestions.
1862.	Phosphorus disease. Report of Children's Employment Commission, Great Britain.
1865.	Simlick's invention of automatic frame-filling machines.
1868.	Clanchy's combined match and fusee.
1872.	Pace and Howard's improvements in splint-cutting machinery.
„	French monopoly established.
1875.	Use of all matches but Swedish safety matches prohibited in Denmark.
„	Use of matches containing ordinary phosphorus forbidden in Switzerland.
1876.	Beecher's introduction of coil- or tape-dipping.
1880.	Sebold's (Durlach) invention of machinery for laying out from the dipping frames.
1882.	All matches but safety matches prohibited in Switzerland.
1884.	Introduction of machinery for automatic continuous manufacture (Mitchell, Fitch).
„	German legislation relative to arrangements and ventilation of match factories.
1885.	Bell's 'fusee-vesta'—a combined fusee-head and vesta-stem.
1890.	French monopoly taken over by the Government.

TABLE II.—MATCHES WITH

	Oxidisable ingredients					Oxidising agents								
—	Vitreous phosphorus	Sulphur	Grey antimony sulphide	Lampblack	Spent tan	Potassium chlorate	Potassium nitrate	Minium	'Oxidised minium'		Lead binoxide	Lead nitrate	Manganese binoxide	Ferric oxide
									Minium	Nitric acid				
Beyer, 1838 . . .	1	—	—	—	—	—	—	—	12	3	—	—	—	—
Siegel, 1838 . . .	2	—	—	—	—	—	—	—	—	—	—	—	—	—
Preschel and Kreutz, 1838 .	5	—	—	—	—	—	16	—	—	—	—	—	16	—
Moldenhauer, about 1838 .	1	—	0·5	—	—	—	2	—	—	—	—	—	—	?
Recipes of R. Böttger: 1841	10	—	15½	—	—	—	18	—	—	—	—	—	—	—
" " 1842 a	10	—	25	—	—	—	—	—	—	—	—	—	12½	—
" " 1842 b	4	—	—	—	—	—	10	5	—	—	—	—	—	—
" " 1842 c	17	—	—	—	—	—	38	24	—	—	—	—	—	—
" " 1843 a	9	—	—	—	—	—	14	—	—	—	—	—	14	—
" " 1843 b	4	—	—	—	—	—	16	3	—	—	—	—	—	—
Recipes of Winterfeld, 1845 a	10	—	11½	—	—	—	11½	—	—	—	—	—	—	—
Recipes of Winterfeld, 1845 b	⅞	—	—	—	—	—	1	1	—	—	—	—	—	—
Compositions used in Paris in 1845–6 a	2	—	—	—	2·5	3	—	—	—	—	—	—	—	—
Compositions used in Paris in 1845–6 b	2	—	—	—	2·5	5	—	—	—	—	—	—	—	—
A German composition, 1846	3	—	—	—	—	—	14	—	—	—	—	—	—	—
From the Journ. d. Chem. Méd. 1849	30	—	—	—	—	—	—	—	—	—	—	—	—	—
Compositions given by Payen, 1851 a	10	—	—	—	—	—	—	—	—	—	6¾	—	—	—
Compositions given by Payen, 1851 b	10	—	—	—	—	—	—	—	—	—	—	—	—	2
J. R. Wagner: 1855. . a	10	—	30	—	—	—	—	—	—	—	30	—	—	—
" " . b	8	—	—	—	—	—	24	—	—	—	24	—	—	—
Recipes given by H. Dussauce, 1864 a	4	—	—	—	—	2	—	—	—	—	—	—	—	—
Recipes given by H. Dussauce, 1864 b	4	1	—	—	—	2	—	—	—	—	—	—	—	—
Composition given in Knapp's Lehrb. d. Chem. Techn. 1865	10	—	—	—	—	—	—	—	—	—	—	—	—	—
Compositions given in Richardson & Watts' Chem. Tech. 1865 a	3	—	—	—	—	3	—	—	—	—	—	—	—	—
Compositions given in Richardson & Watts' Chem. Tech. 1865 b	3	—	—	—	—	—	—	—	—	—	2	—	—	—
Compositions given in Richardson & Watts' Chem. Tech. 1865 c	3	—	—	—	—	—	—	—	2	0·5	—	—	—	—
W. Jettel (analysis), 1869 .	3·1	—	—	—	—	—	—	—	36·36	15·27	—	—	—	—
Compositions given in Wagner's Handbk. of Chem. Tech., ed. by Crookes, 1872 a	1·5	—	—	0·5	—	—	—	—	5	2	—	—	—	—
Compositions given in Wagner's Handbk. of Chem. Tech., ed. by Crookes, 1872 b	3	—	—	—	—	—	—	—	—	—	2	—	—	—
Escach, 1871 . . .	7	—	—	—	—	—	—	—	—	—	—	40	—	—

Vitreous Phosphorus.

Binding ingredients							Indifferent bodies					Colouring matters							Remarks.
Glue	Gelatine	Dextrine	Gum arabic	Gum Senegal	Gum tragacanth	Water	Powdered glass	Sand	Magnesia	Whiting	Chalk	Cinnabar	Prussian blue	Vermilion	Smalt	Madder black	Ultramarine	Chrome yellow	[The mark ? signifies that the ingredient is present, but that the quantity is not stated.]
—	—	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	5	—	—	7–8	8–12	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	—	—	—	?	—	—	—	—	—	—	—	—	—	—
—	—	—	18	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
15	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2	—	—	—	Ferric oxide could be substituted for the minium.
21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	16	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
6	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	23	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	Winterfeld recommended varnishing the match-heads with an alcoholic solution of colophony resin.
—	—	—	2	—	—	2	—	—	—	—	—	—	—	—	—	—	—	—	Gum Senegal could be used instead of gum arabic.
—	—	—	2·5	—	—	—	—	—	—	—	—	—	·05	—	—	—	—	—	—
—	—	—	2	—	1	—	—	—	—	—	—	—	·04	—	—	—	—	—	—
—	—	—	16	—	—	—	—	—	16	—	—	—	—	—	—	—	—	—	—
60	—	—	—	—	—	100	—	10	—	—	—	—	—	—	—	—	—	—	—
—	—	—	1¾	—	—	—	—	6¾	—	—	—	—	—	—	—	—	—	—	'Sulphur-free' matches. Splints dipped in melted wax or stearic acid.
8	—	—	—	—	—	—	—	8	—	—	—	⅖	—	—	—	—	—	—	'Sulphur-free' matches. Splints dipped in melted stearic acid or wax.
26	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
21	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	The phosphorus was dissolved in carbon bi-sulphide. Gelatine could replace the glue.
—	2	—	7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	3	—	—	—	—	—	—	—	—	—	—	1*	—	—	—	—	* With lampblack, soot, &c.
20	—	—	—	—	—	—	—	3⅓	—	—	—	—	—	—	—	—	—	—	—
3·5	—	—	—	—	—	3	—	2	—	—	—	—	·1–·5*	—	—	—	—	—	* Or vermilion. Splints dipped in melted wax or stearic acid.
—	—	—	—	—	0·5	3	—	2	—	—	—	—	—	—	—	—	—	—	Splints dipped in stearic acid or wax.
—	—	—	—	—	0·5	3	—	2	—	—	—	—	—	—	—	—	—	—	Splints dipped in stearic acid or wax.
—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	3	—	—	—	2*	—	—	—	—	—	—	—	—	—	—	* Including smalt.
—	—	—	7	—	—	10	5	—	—	—	—	—	—	—	—	—	—	—	This composition said to be non-hygroscopic. Splints impregnated with a hot solution of a fatty body.

TABLE II.—

—		Oxidisable ingredients					Oxidising agents								
		Vitreous phosphorus	Sulphur	Grey antimony sulphide	Lampblack	Spent tan	Potassium chlorate	Potassium nitrate	Minium	'Oxidised minium' Minium	'Oxidised minium' Nitric acid	Lead binoxide	Lead nitrate	Manganese binoxide	Ferric oxide
Compositions of pastes given in Joseph Freitag's 'Die Zündwaaren Fabrikation,' 1876	*a*	6·4	—	—	—	—	—	—	—	—	—	50	—	—	—
	b	7	—	—	—	—	—	—	—	—	—	54	—	—	—
	c	6	—	—	—	—	—	—	—	40	20	—	—	—	—
	d	6·5	—	—	—	—	—	—	46·5	—	—	—	—	—	—
	e	7	—	—	—	—	—	—	45	—	—	—	—	—	—
	f	6·5	—	—	—	—	—	—	50	—	—	—	—	—	—
	g	6·5	—	—	—	—	—	—	50	—	—	—	—	—	—
	h	6·5	—	—	—	—	—	—	15	—	—	—	15	—	—
	i	6	—	—	—	—	—	—	—	—	—	50	—	—	—
	j	6	—	—	—	—	—	—	—	—	—	50	—	—	—
From Payen's Industrial Chem., ed. by Paul, 1878	*a*	2·5	—	—	—	—	—	—	—	—	—	—	—	—	0·5
	b	2·5	—	—	—	—	—	—	—	—	—	—	—	—	0·5
	c	3	—	—	—	—	3	—	—	—	—	—	—	—	3
	d	4·7	—	—	—	—	—	—	—	40	25	—	—	—	—
	e	2	—	—	0·12	—	—	—	—	—	—	—	—	1	—
	f	3	—	—	—	—	—	—	—	—	—	2	—	—	—
	g	25	—	—	—	—	—	—	5	—	—	—	—	—	—
Cooley's Encyclopædia, 1880		1·5–2	—	—	—	—	4–5	—	?	—	—	—	—	—	—
Spon's Encyclopædia, 1881	*a*	2	—	—	—	—	5	—	1·5	—	—	—	—	—	—
	b	0·5	—	—	—	—	4	—	—	—	—	—	—	—	—

TABLE III.—MATCHES WITH

—	Oxidisable bodies								Oxidising				
	Amorphous phosphorus	Antimony sulphide	Iron pyrites	Lead thiosulphate	Sulphur	Powdered charcoal	Lampblack	Graphite	Potassium chlorate	Potassium bichromate	Minium	Oxidised minium	Lead binoxide
Red Phosphorus in the Igniting Compositions.													
Camaille. *a.* 1852	25	—	—	—	—	—	—	—	50	—	—	—	—
" *b.* "	4	—	—	—	—	—	—	—	4	—	—	—	—
" *c.* "	40	—	—	—	—	—	—	—	40	—	—	—	—
" *d.* 1852–3	6	—	—	—	—	—	—	—	1·5	—	—	—	—
Payen. *a.* 1859	3	—	—	—	—	—	—	—	4	—	—	—	—
" *b.* "	3	—	—	—	—	—	—	—	4	—	—	—	—
Dussauce. *a.* 1864	1⅓ oz.	—	—	—	—	—	—	—	1⅓ oz.	—	—	—	—
" *b.* "	40	—	—	—	—	—	—	—	40	—	—	—	—
R. Hermann, patented by J. & J. B. Palmer 1868 . .	4	—	—	78	—	—	—	—	64	—	—	—	—
R. Hermann, patented by J. B. Palmer 1869 . .	1	—	—	—	—	—	—	—	16	—	—	—	—

continued.

Binding ingredients							Indifferent bodies					Colouring matters							Remarks.
Glue	Gelatine	Dextrine	Gum arabic	Gum Senegal	Gum tragacanth	Water	Powdered glass	Sand	Magnesia	Whiting	Chalk	Cinnabar	Prussian blue	Vermilion	Smalt	Madder black	Ultramarine	Chrome yellow	[The mark ? signifies that the ingredient is present, but that the quantity is not stated.]
—	—	30·6	—	—	—	13	—	—	—	—	—	—	—	—	—	—	—	—	Brown pastes.
—	—	35	—	—	—	14	—	—	—	—	—	—	—	—	—	—	—	—	Ditto.
—	—	35	—	—	—	14	—	—	—	—	—	—	—	—	—	—	—	—	Ditto.
—	—	32	—	—	—	15	—	—	—	—	—	—	—	—	—	—	—	—	Red pastes.
—	—	34	—	—	—	14	—	—	—	—	—	—	—	—	—	—	—	—	Ditto.
—	—	30	—	—	—	13	—	—	—	—	—	—	—	—	—	1·5	—	—	Ditto.
—	—	30	—	—	—	13	—	—	—	1·5	—	—	—	—	—	1·5	—	—	Ditto.
—	—	30	—	—	—	13	—	—	—	—	—	—	—	—	—	1	—	—	Ditto.
—	—	30	—	—	—	14	—	—	—	—	—	—	—	—	—	—	1·5–2	—	Blue pastes.
—	—	30	—	—	—	15	—	—	—	—	—	—	—	—	—	—	—	1–1·5	Yellow pastes.
2	—	—	—	—	—	4·5	—	2	—	—	—	0·1*	—	—	—	—	—	—	* Or Prussian blue.
—	—	—	2·5	—	—	3	—	2	—	—	—	0·1*	—	—	—	—	—	—	* Or Prussian blue.
—	—	—	2·5	—	—	3	—	2	—	—	—	·1–·5*	—	—	—	—	—	—	* Or Prussian blue. Splints partly carbonised at the ends by heating, and dipped into melted stearic acid.
—	—	—	14	—	—	12	—	—	—	—	—	—	—	—	—	—	—	—	—
5	—	—	—	—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	Phosphorus dissolved in carbon bi-sulphide.
—	—	—	·5	—	—	3	—	2	—	—	—	—	—	—	—	—	—	—	—
5	—	—	—	—	—	—	—	20	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	4	3–4	—	—	—	—	—	—	—	?	—	—	—	—
3	—	—	—	—	—	12	—	—	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	11	4	—	—	1	—	—	—	—	—	—	—	—	—

Red Phosphorus.

agents				Binding ingredients							Indifferent bodies				Colouring matters	Remarks.
Lead nitrate	'Plumbio plumbate' (Minium ?)	Manganese binoxide	Ferric oxide	Glue	Gum arabic	Gum Senegal	Gum tragacanth	Gelatine	Sodium silicate	Water	Powdered glass	Rottenstone	Clay	Infusorial earth	Chrome yellow	[The mark ? signifies that the quantity of the ingredient is not stated.]
—	—	—	—	100	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	7½	—	—	—	—	—	—	—	—	—	—	—	The glue in this case is 'liquid glue.'
—	—	—	—	—	60	—	—	—	—	—	25	—	—	—	—	Gum arabic 'in solution.'
—	—	—	—	—	—	—	20	—	—	—	10	—	—	—	—	Gum tragacanth 'in solution.'
—	—	—	—	—	3	—	—	—	—	3	4	—	—	—	—	—
—	—	—	—	2·5	—	—	—	—	—	5	1·5–2	—	—	—	—	—
—	—	—	—	—	1 oz.	—	—	—	—	1 oz.	6½ drms.	—	—	—	—	—
—	—	—	—	—	—	—	—	75	—	—	20	—	—	—	—	The above proportion of gelatine is of that substance dissolved in twice its weight of water.
—	—	4	20	8	—	—	—	—	—	—	—	—	—	—	4	Vitreous phosphorus could be substituted for the red phosphorus.
20	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	Instead of lead nitrate, the sulphite, sulphate, or oxide of lead may be used, or iron thiosulphate, &c.

TABLE III.—

		Oxidisable bodies								Oxidising				
		Amorphous phosphorus	Antimony sulphide	Iron pyrites	Lead thiosulphate	Sulphur	Powdered charcoal	Lampblack	Graphite	Potassium chlorate	Potassium bichromate	Minium	Oxidised minium	Lead binoxide
Red Phosphorus, &c.—continued.														
W. Jettel. 1870		0·5	—	—	—	1	—	—	—	4	—	—	—	—
Sudheim and Koppen. 1878-9 . .		1	—	—	—	—	—	—	—	6	—	2	—	—
R. Dimock, patented by von Nawrocki. 1880 . .		2	—	—	—	—	—	—	—	2	—	—	—	—
L. Horst. 1880		6	—	—	—	8	—	—	—	15	—	—	—	36
Safety Matches.—Red Phosphorus on the Rubbing Surfaces only.														
Lundström, patented in England by F. May. 1855	Igniting composition	—	2-3	—	—	—	—	—	—	6	—	—	—	—
	Rubbing surface .	10	8	—	—	—	—	—	—	—	—	—	—	—
Mennons. 1857.	Igniting compositions . . a.	—	—	—	—	—	1	—	—	2	—	—	—	—
	b.	—	—	—	—	1	—	—	—	1	—	—	—	—
Devilliers and Dalemagne. 1859	Igniting composition	—	—	—	—	—	1	—	—	2	—	—	—	—
	Rubbing composition	?	—	—	—	—	—	—	—	—	—	—	—	—
Mearing. 1861	Igniting composition	—	—	—	—	1	1	1	—	8	—	—	—	—
	Rubbing surface .	4	—	—	—	—	—	—	1	—	—	—	—	—
H. Wagner. 1867 . .	Igniting composition a.	—	—	1·5	—	—	—	—	—	11	2	—	—	—
	Igniting composition b.	—	—	2	—	—	—	—	—	10	1	—	—	—
	Rubbing surface . .	9	—	7	—	—	—	—	—	—	—	—	—	—
R. Hermann, patented in England by J. & J. B. Palmer. 1868 .	Igniting composition	—	—	—	8	—	—	—	—	96	—	—	—	—
	Rubbing surface .	24	—	—	260	—	—	—	—	14	—	—	—	—
Swedish, according to W. Jettel . . 1869	Igniting composition	—	—	—	—	1	—	—	—	4	0·4	—	—	—
	Rubbing surface .	1	1	1	—	—	—	—	—	—	—	—	—	—
1871	Igniting composition	—	—	—	—	1	—	—	—	$6\frac{3}{4}$	$\frac{4}{5}$	—	—	—
	Rubbing surface .	9·25	15·5	—	—	—	—	—	—	—	—	—	—	—
Swedish. J. G. Gentele. 1873 .	Igniting composition	—	24	—	—	—	—	—	—	32	12	32	—	—
	Rubbing surface .	8	9	—	—	—	—	—	—	—	—	—	—	—
Swedish, according to J. Freitag. 1876	Igniting composition a.	—	7	—	—	—	—	—	—	70	—	—	—	—
	Igniting composition b.	—	—	—	—	8	4	—	—	60	—	—	—	—
	Rubber . . . a.	5	5	—	—	—	—	—	—	50	—	—	—	—
	Rubber . . . b.	10	1·5	—	—	—	—	—	—	—	—	—	—	—
Swedish, according to H. Mastbaum. 1880 .	Igniting composition	—	8	—	—	—	—	—	—	8	—	—	8	—
	Rubber	1	—	7	—	—	—	—	—	—	—	—	—	—
Spon's Encyclopædia. 1881 .	Igniting composition	—	1	—	—	—	—	—	—	1	—	—	—	—
	Rubber	2	—	—	—	—	—	—	—	—	—	—	—	—
A. Rossel. 1881	Igniting composition	—	—	—	—	3	—	—	—	53·8	5	—	—	—
	Rubber	3	5	—	—	—	—	—	—	—	—	—	—	—

continued.

agents				Binding ingredients							Indifferent bodies				Colouring matters	Remarks.
Lead nitrate	'Plumbic plumbate' (Minium?)	Manganese binoxide	Ferric oxide	Glue	Gum arabic	Gum Senegal	Gum tragacanth	Gelatine	Sodium silicate	Water	Powdered glass	Rottenstone	Clay	Infusorial earth	Chrome yellow	[The mark ? signifies that the quantity of the ingredient is not stated.]
—	—	—	1·5	—	1	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	1	—	—	—	—	—	—	3	—	3	—	—	Heads protected from damp by dipping in a solution of nitrocellulose in alcohol and ether, with copal or Canada balsam.
—	8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	Naphthaline, stearine, sandarach, &c., also used.
—	—	9	—	8	—	—	—	—	—	—	6	—	—	6	—	Fine sand (6 parts) may be substituted for the glass.
—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	Splints, by preference, dipped in melted sulphur or stearine, before being dipped in the igniting composition.
—	—	—	—	3–6	—	—	—	—	—	—	—	—	—	—	—	Glue for igniting composition, and for rubbers, weighed dry. Manganese binoxide may be substituted, in the rubber, for the antimony sulphide.
—	—	—	1	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	1	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	1	?	—	—	—	—	—	—	—	—	—	—	—	End of splint carrying the igniting composition was sulphured.
—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	Rubbing for Mennons' matches a mixture of red phosphorus and glue.
—	—	—	—	—	2	—	—	—	—	—	—	4	—	—	—	Wood dipped in melted sulphur.
—	—	—	—	—	—	—	—	—	1	4	—	—	—	—	—	—
—	—	1	—	—	1	—	—	—	—	2	1·5	—	—	—	—	—
—	—	1	—	—	—	—	—	—	—	—	2	—	—	—	—	—
—	—	—	—	1	—	—	—	—	—	—	3	—	—	—	—	—
—	—	24	2	16	—	—	—	—	—	—	—	—	—	—	2	—
—	—	—	7	4	—	—	—	—	—	—	8	—	—	—	—	—
—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	2	½	1	—	—	—	—	—	—	1¼	—	—	—	—	—
—	—	4	1	1	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	11	—	12	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	18	—	—	—	—	—	10	—	—	—	—	—
—	—	—	10	30	—	—	—	—	—	—	—	—	—	—	—	—
—	—	15	—	60	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—
—	—	—	—	1	—	—	—	—	—	—	3	—	—	—	—	—
—	—	—	—	2	—	—	—	—	—	12	—	—	—	—	—	—
—	—	—	—	?	—	—	—	—	—	—	1	—	—	—	—	—
—	—	6	6	—	10	—	3	—	—	—	12	—	—	—	—	Splints dipped in paraffin.
—	—	1·5	—	4	—	—	—	—	—	—	—	—	—	—	—	—

TABLE IV.—MATCHES

		Oxidisable ingredients																	Oxidising				
—		Grey sulphide of antimony	Golden sulphide of antimony	Antimony oxy-sulphide	Iron pyrites	Sulphur	Lead thiosulphate	Lead thiocyanate (?)	Lead sulphide	Lead cyanide	Lead ferrocyanide (?)	Potassium ferrocyanide	Ferrous sulphate	Powdered charcoal	Iron thiosulphate	Powdered sugar	Gunpowder	Nitromannite	Potassium chlorate	Potassium nitrate	Potassium bichromate	Minium	Oxidised minium
Various compositions of G. Canouil, 1857.	1	—	—	—	35	—	—	—	—	—	—	—	—	—	—	—	—	—	75	—	—	—	—
	2	—	—	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	10	—	2	—	—
	3	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	7	—	2	—	—
	3a (Rubber)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	6	—	—	1	—
	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3	—	2	—	—
	5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	—	2	—	—
	6	—	—	0·5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	—	—	—
	7	—	—	—	—	0·5	—	—	—	2	—	—	—	—	—	—	—	—	6	—	—	—	—
	8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	2	—	—
	9	—	—	—	—	85	—	—	—	—	—	—	—	—	—	—	—	—	28·5	—	2·9	—	—
	10	—	—	—	—	1·3	—	—	—	—	—	—	—	—	—	—	—	—	7·3	—	2·3	—	—
	11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	2	—	—
	11a (Rubber)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	2	—	—
	12	—	0·8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	2	—	—
	13	—	—	—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	10	—	?	—	—
	13a (Rubber)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	5	—	?	—	—
Vaudaux and Paignon, 1857		15	—	20	—	—	—	—	—	—	—	5	—	—	—	—	—	—	90	—	45	20	—
Vaudaux, Paignon, and Mayer, 1857		20	—	—	—	—	—	—	—	20	—	—	—	—	—	—	—	—	26	—	20	—	—
Hochstätter, 1857	a	—	—	35	—	—	—	—	—	—	—	—	—	—	—	—	—	—	14	—	4	—	—
	b	—	—	18	—	2	—	—	—	—	—	—	—	—	—	—	—	—	18	—	4	—	—
	c	—	—	18	—	2	—	—	—	—	—	—	—	—	—	—	—	—	18	—	—	—	—
F. L. Lutz, 1858	a	280	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	235	—	5	—	—
	b	80	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	80	—	5	—	—
Kummer and Günther, 1861		8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8	—	—	—	8
Compositions suggested by Wiederhold, 1861	a	—	—	—	—	—	26	—	—	—	—	—	—	—	—	—	—	—	26	—	—	—	—
	b	—	—	—	—	—	26	—	—	—	—	—	—	—	—	—	—	—	52	—	—	—	—
	c	—	—	—	—	—	26	—	—	—	—	—	—	—	—	—	—	—	78	—	—	—	—
	d	3	—	—	—	—	7	—	—	—	—	—	—	—	—	—	—	—	10	—	—	—	—
	e	3	—	—	—	—	7	—	—	—	—	—	—	—	—	—	—	—	7	—	—	—	—
	f	7	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	10	—	—	—	—
	g	5	—	—	—	—	5	—	—	—	—	—	—	—	—	—	—	—	10	—	—	—	—
	h	3	—	—	—	—	7	—	—	—	—	—	—	—	—	—	—	—	10	—	—	—	—
	i	3	—	—	—	—	7	—	—	—	—	—	—	2	—	—	—	—	10	—	—	—	—
	j	8	—	—	—	—	5	—	—	—	—	—	—	—	—	—	2	—	10	—	—	—	—
	k	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	2	—	—
W. Schnell, 1861		1	—	—	1	—	3	—	—	—	—	—	—	—	—	—	—	—	2	—	—	—	—
Hjerpe, Holmgren, and Sundstedt, 1862	a	—	—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	4–6	—	2	—	—
	b	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4–6	—	2	—	—
	Rubber	20–30	—	—	—	—	—	—	—	—	—	—	3–6	—	—	—	—	—	—	—	2–4	—	—
C. Liebig, 1865		3	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	8	16	—	1	10	—
R. Hermann, patented in England by J. & J. B. Palmer, 1868.	Igniting compounds a	—	—	—	—	—	66	—	—	—	—	—	—	—	—	—	—	—	66	—	—	—	—
	b	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	—	—	10	—	—	—	—
	c	—	—	—	—	—	8	—	—	—	—	—	—	—	—	—	—	—	96	—	—	—	—
	Rubber	—	—	—	—	—	260	—	—	—	—	—	—	—	—	—	—	—	14	—	—	—	—
J. B. Palmer, 1869		—	—	—	—	—	—	—	—	—	—	—	—	—	30	—	—	—	30	—	—	—	—
W. Jettel, analyses by, 1869		—	0·25	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3	—	—	—	—
L. Wagner, patented in England by H. Wildt, 1879		6	—	—	—	1	34	—	—	—	—	—	—	5	—	—	—	—	16	4	—	—	—
H. Schwarz, 1881–84	a	—	1	—	—	—	—	3	2	—	—	—	—	—	—	—	—	—	9	—	—	—	—
	b	—	—	—	—	—	—	3	3	—	—	—	—	—	—	—	—	—	6	—	—	—	—
P. Garber, 1888	lbs.	—	—	—	—	1	—	—	—	—	—	—	—	—	—	½	—	—	14½	—	½	—	—

WITHOUT PHOSPHORUS.

agents							Binding ingredients								Indifferent bodies					Colouring matters	
Lead binoxide	Lead nitrate	Lead chlorite (Chlorate?)	Manganese binoxide	Ferric oxide	Barium chromate	Potassium picrate	Glue	Gelatine	Dextrine	Gum arabic	Gum Senegal	Wheat starch	Acetic acid (50 p.c.)	Water	Powdered glass	Powdered clinker	Emery	Sand	Pumice	Chrome yellow	Remarks. [? signifies that the ingredient is present, but that its quantity is not stated.]
35	—	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	—	—	Gum or glue may replace the dextrine.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	Glue or dextrine may be substituted for the gum.
—	2	—	—	—	—	—	—	—	—	6	—	—	—	18	—	—	—	—	—	—	Will inflame only on a surface coated with the composition 3a.
—	—	—	—	—	—	—	?	—	—	—	—	—	—	—	—	1	1	—	—	—	Sand, glass, or pumice may be substituted for the emery.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	3	—	—	—	—	—	Glue or dextrine may replace the gum.
—	1	—	—	—	—	—	—	—	—	6	—	—	—	—	4	—	—	—	—	—	Will ignite on a *similarly* coated surface; or, better, on No. 3a rubbing surface.
3	—	—	—	—	—	—	—	—	—	2	—	—	—	8	—	—	—	—	—	—	To ignite on ordinary rubbing surfaces: pounded glass, or fine sand, and stiff glue.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	8	—	—	—	—	—	—	Ditto.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	8	3	—	—	—	—	—	Ditto.
—	2·7	—	—	—	—	—	5·4	—	—	—	—	—	—	—	10·8	—	—	—	—	—	Ditto.
—	2·3	—	—	—	—	—	—	—	—	6·3	—	—	—	18	—	—	—	—	—	—	To ignite only on a surface coated with the composition 3a.
—	—	—	—	—	—	—	—	—	—	15	—	—	—	6	5	—	—	—	—	—	To inflame only on a surface coated with 11a.
—	—	—	—	—	—	—	?	—	—	15	—	—	—	6	5	—	6½	—	—	—	Rubber for No. 11.
—	—	—	—	—	—	—	?	—	—	15	—	—	—	—	—	—	—	—	—	—	Said to inflame on *any* surface.
—	—	—	—	—	—	—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	To inflame only on a surface coated with 13a.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	8	3	—	—	—	—	—	Rubber for No. 13.
25	—	—	—	—	—	—	—	—	—	15	—	—	—	55	15	—	—	—	—	—	An improvement upon Canouil's compositions.
25	—	—	—	—	—	—	—	—	—	5	—	—	—	20	4	—	—	—	—	—	—
9	—	—	—	—	—	—	—	—	—	—	—	—	—	—	4	—	—	—	6	—	—
9	—	—	2	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—	—	—
9	—	3	—	—	—	—	—	—	—	—	—	6	—	—	—	—	—	—	2	—	—
—	75	—	—	—	—	—	—	—	—	30	—	—	—	—	—	—	—	90	—	—	—
—	30	—	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	50	—	—	—
—	—	—	—	—	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	5	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	8	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	10	—	—	—	—	—	—	—	—	—	—	Used by Kalliwoda & Co., Ortenburg.
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	1·5	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
2	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	2	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	10	—	—	—	2	—	—	—	—	3	—	—	—	—	—	Sand or reddle can replace the glass-powder.
2	—	—	—	—	—	—	—	—	—	?	—	—	—	—	1	—	—	—	—	—	—
—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	?	—	—	—	—	—	Other binding ingredients may replace the glue.
—	—	—	2	—	—	—	3	—	—	—	—	—	—	—	?	—	—	—	—	—	Minium can be used instead of the manganese binoxide.
—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	Minium or ferric oxide named in specification as alternatives in place of the ferrous sulphate. Rubber for 1 and 2.
—	—	—	—	—	—	—	—	—	—	5	—	—	—	—	4	—	—	—	—	—	—
—	—	—	3	7	—	—	6	—	—	—	—	—	—	—	—	—	—	—	—	3	To ignite with ordinary friction.
—	—	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	2¼	2	—	—	16	—	—	—	—	—	—	—	—	—	—	—	—	2	—
—	—	—	—	7	—	—	4	—	—	—	—	—	—	—	8	—	—	—	—	—	—
—	—	—	—	—	—	—	3	—	—	—	—	—	—	—	—	—	—	—	—	—	To ignite with ordinary friction. Sulphite of iron or other sulphite usable in place of the thiosulphate.
—	—	—	—	—	—	—	?	—	—	—	—	—	—	—	—	—	—	—	—	—	—
5	—	—	—	—	—	—	1⅓	1⅓	1⅓	—	—	—	—	30	10	—	—	—	—	—	—
—	—	—	—	—	—	—	1	—	—	—	—	—	2	8-10	6	—	—	—	—	—	—
—	—	—	—	—	—	—	1	—	—	—	—	—	2	8-10	6	—	—	—	—	—	—
—	—	—	⅓	1½	¼	—	—	—	4	—	4	—	—	4¼	5	—	—	—	—	—	—

Table V.—Vestas, Vesuvians, &c.

—	Oxidisable ingredients						Oxygen compounds							Binding ingredients, &c.								Indifferent bodies, scenting agents &c.		Colouring matters					Remarks.
										'Oxidised minium'																			
	Vitreous phosphorus	Amorphous phosphorus	Grey antimony sulphide	Charcoal	Flour	Lampblack	Potassium chlorate	Potassium nitrate	Minium	Minium	Nitric acid	Lead binoxide	Manganese binoxide	Glue	Gum arabic	Venice turpentine	Shellac	Colophony	Stearine	Alcohol	Water	Powdered glass	Cascarilla bark, Lignum vitæ dust, Gumbenzoin, &c.	Vermilion	Ultramarine, Venetian red, &c.	White lead	Zinc white	Aniline dye	[The mark ? signifies that an ingredient is present, but that its quantity is not stated.]
Wax Vestas. Merckel, 1840 . .	12	—	3	—	—	—	—	—	—	35	21	—	—	—	14	—	—	—	—	—	—	—	—	0·1	—	—	—	—	Stems of wax, stearine, &c.
Wax Vestas. Merckel, 1840 . .	12	—	3	—	—	—	—	—	—	—	—	36	—	—	14	—	—	—	—	—	—	—	—	0·1	—	—	—	—	Stems of wax, stearine, &c.
'*Salon Matches.*' H. Wagner, 1867 .	lbs. 2·75	—	—	—	—	lbs. 0·25	—	lbs. 2–3	—	lbs. 21	lbs. 13	—	lb. 1	—	lbs. 5·5	lbs. 0·5	—	—	—	—	—	—	—	—	—	oz. 1	—	—	Varnished with an alcoholic solution of shellac, colophony, Venice turpentine, camphor, gum benzoin, &c.
Continuous Fusees. W. A. Leonard, 1876 .	13	14	—	—	—	—	32	—	12	—	—	—	—	—	—	—	40	—	—	4	—	—	—	—	—	—	—	—	—
Vesuvians. From Spon's Encycl., 1881 Heads	—	—	—	19	—	—	—	18	—	—	—	—	—	—	5–6	—	—	—	—	—	—	7	?	—	—	—	—	—	Stems of wood, &c.
Tips	2	—	—	—	—	—	5	—	1½	—	—	—	—	3	—	—	—	—	—	—	12	—	—	—	—	—	—	—	
'*Fusee Vestas.*' R. Bell, 1883 . Heads	—	½	—	—	3½	—	4	—	—	—	—	—	—	—	1	—	—	—	—	—	—	—	—	—	?	—	—	—	Igniting composition for the tips, as usual. Stems of jute, hemp, cotton coated with paraffin wax, or stearine, &c.
Continuous Lights. Gomez and Franco, 1889	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	kilos. 4	kilo. 1	—	—	—	—	—	—	—	grms. 200	grms. 50	Strips of Bristol board immersed in this composition, dried, and dipped in an ordinary igniting paste.

TABLE VI.—*Statistics of the British Match Trade*, 1870-1889.

Total value of lucifers and vesta matches of home manufacture exported to	1870	1871	1872	1873	1874	1875	1876	1877	1878	1879	1880	1881	1882	1883	1884	1885	1886	1887	1888	1889
	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£	£
Russia	—	2,274	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Holland	3,918	2,430	2,073	1,474	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Spain	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	9,164	8,428
France	—	21,570	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Germany	—	—	—	3,072	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Turkey Proper	—	—	3,489	6,102	6,464	6,738	2,437	—	3,311	2,032	1,910	2,906	—	—	—	—	—	—	—	—
United States : Atlantic	—	—	—	—	—	—	—	—	—	—	—	—	—	16,724	12,851	—	—	—	—	1,982
Java	7,241	3,958	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
China	4,865	6,948	5,477	10,583	5,029	5,385	6,202	4,592	5,505	7,286	16,131	8,738	22,472	3,528	—	—	—	—	—	—
Japan	2,712	—	2,289	3,031	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Peru	2,294	2,328	3,034	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chili	9,183	6,647	6,070	10,330	4,271	—	4,967	4,275	721	1,377	1,334	2,240	—	—	—	—	—	—	—	—
Brazil	14,463	10,125	5,159	4,436	2,948	7,059	4,860	7,304	2,185	—	2,903	2,098	—	—	—	—	—	—	—	—
Other countries	17,076	15,801	19,781	14,090	12,048	25,000	16,348	11,087	12,378	9,440	9,882	16,433	16,402	17,255	17,549	16,139	9,068	13,590	7,967	5,901
Total to Foreign Countries	61,747	72,061	47,372	53,118	30,760	44,182	34,814	27,258	24,095	20,135	32,160	32,424	38,874	37,507	30,400	16,139	9,068	13,590	17,131	16,311
British India :—																				
Bombay and Scinde	14,581	17,157	19,048	11,071	7,788	7,652	6,088	4,083	4,117	2,458	—	—	—	—	—	—	—	—	—	—
Madras	5,616	1,240	4,009	2,915	3,835	1,902	1,618	1,208	1,337	1,679	—	—	—	—	—	Brit. E. Indies 16,402	5,228	—	—	—
Bengal and Burmah	9,839 [Bengal and Pegu]	13,995	7,492	5,398	6,697	13,022	17,216	11,876	8,698	9,760	8,056	5,938	11,724	4,819	6,909	—	—	—	—	—
Straits Settlements	17,256	8,444	11,017	—	3,702	—	—	2,226	2,741	3,928	7,284	13,292	9,600	12,251	7,619	—	—	—	—	—
Ceylon	—	2,528	2,184	—	3,608	—	—	4,069	—	1,328	—	—	—	—	—	—	—	—	—	—
Hong Kong	5,872	6,778	2,541	3,487	3,442	7,096	3,275	6,305	—	4,027	3,695	4,907	4,611	3,898	3,499	3,819	4,009	—	—	—
British West India Islands and British Guiana	3,028	2,724	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Channel Islands	—	6,065	2,070	2,318	2,426	—	2,302	2,755	2,728	3,406	3,507	3,642	3,207	2,547	2,996	2,484	2,000	—	—	—
British Western Africa	—	—	—	—	—	—	—	—	—	1,510	—	—	—	—	—	—	—	—	—	—
British Poss. in S. Africa	—	—	2,520	2,579	2,922	—	—	—	—	—	1,212	—	—	—	—	—	—	—	—	—
Australasia :—	51,472	61,053	100,575	106,628	61,058	94,052	124,639	111,527	98,132	64,648	88,972	116,744	126,567	90,115	86,498	—	—	—	—	—
Victoria	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	29,086	39,268	39,406	29,080	29,869
New South Wales	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	38,802	50,307	26,768	38,088	27,828
Queensland	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	18,924	18,453	15,111	19,273
New Zealand	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	22,972	20,749	24,652	21,898	16,451
Other Colonies	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	22,104	4,638	4,884	3,903	4,969
Other British Possessions	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	3,528	6,030	8,951	8,776	7,072
Total to British Possessions	107,609	119,984	151,456	134,396	94,978	123,724	155,138	144,049	117,758	92,739	112,726	144,523	155,699	113,630	107,521	144,197	151,153	122,614	116,856	105,462
TOTAL	169,356	192,065	198,828	187,514	125,738	167,906	189,952	171,307	141,848	112,874	144,886	176,947	194,573	151,137	137,921	160,336	160,221	136,204	133,987	121,773

[*Continued on p.* 546.]

TABLE VI.—*continued.*

Total value of lucifers and vesta matches of foreign and colonial production exported from Great Britain to	1886	1887	1888	1889
	£	£	£	£
United States of America	—	—	9,351	7,758
China	—	10,355	—	—
Brazil	28,855	21,895	8,977	17,387
Other foreign countries	16,969	11,685	11,851	6,662
Total to Foreign Countries	45,824	43,935	30,179	31,802
British Poss. in S. Africa	—	—	5,515	6,562
British East Indies	159,101	156,444	187,366	116,723
Hong Kong	13,678	10,969	5,082	—
Australasia	16,980	12,080	11,606	7,814
British West Indies	—	—	7,480	5,127
Other British Possessions	15,495	14,610	5,100	5,830
Total to British Possessions	205,254	194,103	172,099	141,556
TOTAL	251,078	238,038	202,278	173,358

Total value of lucifers and vesta matches imported into the United Kingdom from	1886	1887	1888	1889
	£	£	£	£
Russia	—	1,420	—	—
Sweden	236,816	219,346	229,749	208,424
Norway	110,801	110,935	104,618	74,559
Denmark	6,693	10,888	18,933	5,323
Germany	4,341	9,903	7,942	5,099
Holland	17,196	10,472	6,274	5,711
Belgium	27,607	38,781	45,787	65,333
France	—	48	—	—
Italy	13,352	10,783	8,930	3,958
Untd. States of America	—	—	6,772	—
Other Foreign Countries	838	—	205	140
Total from Foreign Countries	417,644	412,576	419,205	368,547
Australasia	—	100	88	105
TOTAL	417,644	412,676	419,293	368,652

TABLE VII.—COMPLETE LIST OF APPLICATIONS FOR ENGLISH PATENTS, 1800–90, REFERRING WHOLLY OR IN PART TO IMPROVEMENTS AND NOVELTIES IN MATCH-MAKING MACHINERY.

[For Improvements in Compositions, Stems, &c., see Table VIII.]

Year	Number	Applicant	Nature of Invention
1832	6295	W. Newton	Manufacture of vesta-stems from waxed thread.
1839	8297	A. J. Mayer	Splint-cutting.
1842	9295	R. Partridge	„ (wood forced through perforations in a metal plate).
1843	9929	B. Parsons and E. Esdaile	Machine for cutting leaves or flakes of wood.
1845	10,631	C. M. Barker	Splint-cutting (see also Table VIII.).
1848	12,192	H. Archer	Production of taper matches.
1849	12,469	J. Palmer	Splint-cutting; and a dipping-frame (see also Table VIII.).
1850	13,206	J. Hynam	Machinery for filling dipping-frames.
1852	1098	G. Thomson	Splint-cutting (cutters between two endless bands).
1854	418	J. H. Johnson (from E. Zulzer, New York).	Preparing and cutting wax stems, and filling a perforated dipping-board.
	2691	G. Bell and G. C. Grimes	Machinery for filling dipping-frames or clamps.
1855	141*	S. A. Bell and J. Black.	Tapering splints for bundle-dipping.
1856	1120	W. E. Newton ('a foreign communication').	Splint-cutting (descending and intersecting knives).
	1275*	G. Bell and G. C. Grimes	Bevelling splints for bundle-dipping.
	2594	L. Urion	Machinery for splint-cutting, arranging for dipping, dipping, drying, and shaping boxes: continuous manufacture.
1857	2461	W. S. Clark and B. Moore ('a communication').	Splint-cutting (tubular cutters).
	2748	T. Cook	„ ; filling dipping-frames; and packing.
	2812	H. Hochstätter	A dipping-frame.
1858	1428	W. E. Newton ('a foreign communication').	Machinery for splint-cutting, sulphuring, and dipping (by roller half immersed in the igniting composition): continuous manufacture.
1859	746	F. Tillett	Splint-cutting (reciprocating lances or cutters, and a guillotine knife, at or about at right angles: 'toothing and flaking').
	1310*	L. D. Jackson	Splint-cutting.
	1987	H. Higgin	Pointing splints for bundle-dipping.
1860	44	L. F. Perrier	Splint-cutting, and delivering wax stems, as well as wooden splints, into frames.
1861	344*	H. Baker	Splint-cutting, *en bloc.*
	609	E. Frementin and M. Aubonnet.	„ (lancets and flaking-knife).
	655*	W. Schnell	„ ; and a composition (see also Tables IV. and VIII.).
	1307	J. Hynam	Filling dipping-clamps.
	1391	O. Muck	„ „
	1638*	S. A. Bell	„ „
	3096	T. Higgins	„ „
	3196	W. Clark (from J. and F. G. Lavallée, Paris).	Splint-cutting (two movable cylinders with circular grooves, and a reciprocating knife for cutting up the wood as it leaves the cylinders).
1862	1382	G. C. Grimes	Splint-cutting (dies or cutters applied separately or in sets, the wood receding after each stroke). See also Table VIII.
	2311	S. A. Bell and T. Higgins	Dipping-clamps, and machinery for dipping.
	2537	J. Whines	Filling dipping-clamps.
	3382	E. Precht and V. Toepken	Machinery for making and packing.

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TABLE VII.—*continued.*

Year	Number	Applicant	Nature of Invention
1863	59	G. C. Grimes	Machine for filling dipping-clamps.
	1926*	E. Pace	Splint-cutting.
1864	766	„	Machine for filling clamps.
1865	74	J. C. Brown	Splint-cutting (cutters in surface of a cylinder pressed against revolving block of wood; together with a broad knife to shave splints from surface of block).
	1003*	H. J. Simlick	Self-acting machinery, driven by steam or hand-power, producing the various motions of the frame-filling machine.
	2690*	J. W. Truman and H. Lovi	Splint-cutting (splints pointed or bevelled).
	2923	J. J. Long	Splint-cutting (two blocks of wood alternately travelling before horizontal cutters, and a vertical knife falling first on one and then on the other).
	3002*	S. A. Bell	Drying the dipped splints. Air, impelled by fans, admitted to drying room through pierced horizontal pipes, around the walls on a level with the coated ends of the matches, the clamps containing which are placed in racks.
1866	2166	T. Allen	Splint-cutting (lances and cutting-knife on rotating plate).
1867	126	A. Berens (from L. Anton, Darmstadt).	Machine for filling dipping-frames: frames in a horizontal position while filled.
	414	J. V. Toepken	Machine for packing or rolling into bundles the match splints, the free ends of which are packed alternately with bands of paper, so that the matches are ignited on withdrawal by contact with the prepared surface of the paper.
	2231	J. Birch	Cutting wax stems, and delivering them into laths or supports, for dipping.
1868	213*	J. J. Long	Machine for filling dipping-frames.
	1401*	„	Appliances for (1) cross-cutting, (2) filling, (3) drying, and (4) sulphuring or paraffining.
	2642	„	Splint-cutting (combined lances and flaking-knife).
	3727	C. Farrar	„ „ „
1869	887	F. de Bowens	Splint-cutting (blocks of wood arranged on circumference of a large wheel; cutters on a slide-rest moving across face of wheel).
	3412	L. Mount	Application of gearing to the ordinary filling machine, to dispense with hand-labour almost entirely.
1870	138	G. Baker	Splint-cutting (blocks of wood advanced diagonally against a series of cutters or lances).
	1828	W. Riddell	Splint-cutting (rotating circular cutters on a spindle or shaft; behind them planing-knives with edges at right angles to the cutters).
	2089*	O. Walch	Mechanism for filling dipping-frames.
1871	2288	G. Haseltine (from McC. Young, Maryland, U.S.A.).	Splint-cutting (the cut splints fed by the same machine into holes bored in a dipping-board).
	134	J. J. Long	Splint-cutting (flaking-knife on face of revolving vertical disc; lancets horizontal; splints received on an endless travelling web).
1872	369*	E. Pace	Splint-cutting (principle similar to that of Tillett's machine, 746, 1859, in which lancets or scoring-knives first cut or score wood to depth of splint, and then slicing-knife cuts the splints off from the wood).
	471	O. Walch	Machine for filling frames.
	1285	E. Pace and J. H. Howard	Splint-cutting (an improvement on Tillett's machine).
	2896	W. Bryant	Drying the cut splints by super-heated steam.
1873	3272	E. Pace	Splint-cutting (improvement on 1285, 1872).
1874	1362*	E. Pace and J. H. Howard	Splints received in trough, where made into bundles.
	3355	B. Mills (from V. B. Nielsen, Malmö, Sweden).	Splint-cutting (a veneer-cutting machine).
1875	1317*	G. Haseltine (from McC. Young).	Splint-cutting.
	2900	F. de Bowens	„
1876	1407	A. M. Clark (from H. T. Bartlett and G. W. Read, New York).	„ (a veneer-cutting machine).
	3122	E. Pace	Scoring and cutting 'squelettes' for match-boxes.
	4293	W. R. Lake (from E. B. Beecher, Westville, Conn. U.S.A.).	Arranging splints in coils, preparatory to dipping (prior to this, either bundle-dipping, block-dipping, or frame-dipping).
1877	1258	E. Pace	Splint-sorting and pointing, for bundle-dipping.
	2506	G. Evans (from E. B. Beecher)	Improvement upon 4293, 1876.
	2517	F. G. Bryant (from J. E. Lundström, Jönköping, Sweden).	Applying igniting composition to match-boxes.
	3649	G. Evans (from E. B. Beecher)	Unwinding and cross-cutting.
	3653	F. Holms and R. J. H. Saunders.	Splint-cutting.
1878	1992	J. J. Long	Splint-cutting (improvement on 134, 1871).
	3538	T. H. Bryant	Removing splints from dipping-frames (refers to 1317, 1875; punches used corresponding to holes in dipping-board).
	4272	T. J. Ditchburn	Splint-cutting (vertical V or W-shaped cutters, worked by cranks, cams, &c.).
1879	3169	A. M. Clark (from H. T. Bartlett and G. W. Read, New York).	Splint-cutting (a veneer-cutting machine, in which the steamed wood is first cut into a veneer or thin sheet, and then divided into strips or splints).
	4861	W. P. Thompson (from O. Walch, Paris).	Filling the boxes.
	5296*	J. H. Howard	Improved machine for filling frames.
1880	237*	A. M. Clark (from J. T. Connolly, Marseilles).	Manufacture of match-boxes.

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TABLE VII.—*continued.*

Year	Number	Applicant	Nature of Invention
1880	2476*	W. R. Lake (from La Société des Allumettes, Caussemille, Jeune & Cie., et Roche & Cie., Paris).	Splint-cutting (blocks of wood so cut with circular saws that splints remain attached, and can be dipped in block form).
	2911	M. Wiberg	Manufacture of match-boxes.
	4058	F. Wirth (from G. Sebold, Durlach, Germany).	Machine for laying out from dipping-frames.
1881	278	C. R. E. Bell . . .	Cutting wax tapers, and filling dipping-frames.
	802†	E. Pace and J. H. Howard .	Cutting, feeding, and bundling splints.
	3476	C. F. Parsons . . .	Splint-cutting (wood first flaked by vertical chopping-knife, then passed between rotating cylinders provided with cutters and grooves).
1882	1617	F. Wirth (from G. Sebold, Durlach).	Splint-cutting (a veneer-cutting machine: wood block mounted on a lathe-chuck and rotated while knife cuts a continuous spiral from the same. Small cutters at intervals are brought beneath the lower surface of the block, and cut parallel slits in its surface, corresponding to the length of the matches to be produced. At right angles to these are other cutters which slit the strips into splints).
1883	3196	F. H. F. Engel (from W. Holmström, Westervik, Sweden).	Dipping by machinery (splint-frames carried by endless straps past transversely placed feeding rollers).
	3524	W. R. Lake (from W. H. H. Sisum, Brooklyn, U.S.A.).	Arranging splints in coils preparatory to dipping.
1884	5507	T. Allen	Machine for filling dipping-frames automatically.
	11,686	S. Pitt (from J. H. Mitchell, Philadelphia).	Continuous manufacture.
	12,551	G. A. Sweetser . . .	Production of fusee stems from plastic materials.
	14,992	J. A. Elliott (from Edson Fitch, Quebec).	Continuous manufacture.
1885	6343	G. E. Norris and W. E. Hagan.	Splint-cutting (veneer split up by passage between rollers with cutting grooves); splints pointed for dipping; their surfaces polished; and they are put into boxes for dipping.
1886	3343	G. E. Norris and W. E. Hagan.	Addition to above machine, by which it will also effect the operation of dipping.
	4525	G. A. Sweetser . . .	Manufacture from plastic materials.
	17,062	H. H. Lake (from the Citizens' Match Company, Troy, U.S.A.).	Filling boxes.
1887	2900	F. Lundgren . . .	Machinery for making boxes.
	3554	J. Fraser	Arranging splints in coils for dipping.
	5390	C. J. Donelly . . .	„ „ „
	14,813	H. C. Zappert . . .	Machine for cutting splints from a veneer and arranging them in coils for dipping.
	16,353	„ . . .	Dipping and packing (the coils brought by endless chains past, rollers rotating partly in the dipping composition).
1888	8031	W. Ellis	Splint-cutting (a veneer-cutting machine).
1889	1595	R. Jex-Long . . .	Coil dipping; automatic mechanical stop motion for coiling machine.
	5208	C. R. E. Bell . . .	Continuous manufacture (automatic machine by which splints cut from veneers, heated, paraffined, dipped, dried, and packed).
	6595	L. Cobbaert	Ditto.
	10,714	H. Higgin	Cutting or 'halving' double-dipped splints.
	14,111	E. Paul	Machinery for cutting splints from veneer, and coiling between tapes for dipping.
1890	1074	W. E. Ellis	Splint-cutting (a veneer-cutting machine).
	4768	F. Lundgren . . .	Machinery for filling boxes.
	10,321	A. J. Boult (from H. H. Rosenfeld).	Improvements in manufacture.
	10,935	A. Hislop (from J. Storer) .	Making vestas.
	11,202	G. Bruck	Improvements in manufacture of headless matches.
	13,801	G. W. Thomas . . .	Improvements in matches, fusees, and the like.
	14,976	H. J. Allison (from A. P. Adams).	Splint-cutting.
	16,342	A. Lucien	Improvements in fusees and slow-matches.
	19,026	E. Paul	Match-making machinery.
	19,125	W. M. Nix	Improvements in the manufacture of friction matches.
	21,228	A. E. Ellinwood . .	Match-making machinery.
	21,229	„ . . .	Match-making machines.

* Provisional protection only. † Void.

TABLE VIII.—COMPLETE LIST OF APPLICATIONS FOR ENGLISH PATENTS, 1800–90, RELATING TO MATCH COMPOSITIONS, MATERIALS FOR THE STEMS, ETC.

[For Machinery, see Table VII.]

N.B.—John Walker's 'Lucifers,' 1827, not included in this table, the invention not having been patented.

Year	Number	Applicant	Nature of Invention
1824	4927	H. Berry	A light-producer, on Chanoel's principle: ignited by contact with asbestos, moistened with sulphuric acid.
1828	3732	S. Jones (from 'a foreigner')	'Prometheans.' Of the 'oxymuriate' class (see p. 520).
1832	6295	W. Newton	Waxen stems, made by passing cotton yarn from a reel into melted wax, and then through holes in a metal draw-plate. Tipped with an 'oxymuriate' mixture, perfumed if necessary, and ignited by sulphuric acid. Resin or tallow could replace the wax.
	6335	S. Jones	Friction matches of cloth, tape, &c., saturated or coated with wax or spermaceti, and 'charged or primed' with a composition containing potassium chlorate and antimony sulphide. Also matches soaked in a solution of potassium nitrate or chlorate ('fusees').
1834	6543	J. Boynton	Arrangement of dipping-phial for oxymuriate matches.
1836	7169	W. Newton	A box or case for friction matches, with receptacles, above which strips of sandpaper were so placed as to ignite the matches as withdrawn.
1842	9579	H. S. Rush	Very similar to the last.
1845	10,631	C. M. Barker . . .	Coating the tips of friction matches with sulphur. Also splint-cutting (see Table VII.).
1848	12,192	H. Archer	Taper matches, to hold vertically.
1849	12,469	J. Palmer	Fusees or cigar-lights. Also a dipping-frame (see Table VII.).
	12,573	W. H. Knapp . . .	Wood for splints dipped in resin oil.
1851	13,872	R. Heilbronner . . .	Stems coated with gelatine mixed with potassium nitrate, &c.
1854	1464	J. M. Bardet and F. Collette	Fusees. Sheets of paper, cardboard, wood, &c., saturated with scented saltpetre solution. Between two such sheets a thin layer of igniting composition mixed with glass, sand, or burnt alum. Sheets cut into strips and varnished.
1855	1854	F. May (from J. E. Lundström, Jönköping, Sweden).	Safety matches (see Table III.). Red phosphorus on rubber.
1856	1073	S. A. Bell and J. Black .	Similar.
	1275*	G. Bell and G. C. Grimes .	Splints dipped in resin or pitch instead of sulphur. Also ends bevelled (see Table VII.).
	2249	A. Albright	Matches with red phosphorus. Applying, after dipping in the oxidising mixture, a thin coating of amorphous phosphorus in a suitable cement.
	2512	H. Hochstätter . . .	Matches dipped in sulphur or wax: potassium nitrate, minium, &c., used as oxidising agents.
1857	1190	„ . . .	Non-phosphoric friction matches (see Table IV.).
	2817	G. Canouil	„ „ „ „
	3017	M. A. F. Mennons . .	Oxidising agent at one end of splint; red phosphorus and size at the other (see Table III.).
1858	2085	G. C. Grimes . . .	Fusees: wire stems.
	2877	G. Bell	Fusees: metal shafts.
1859	1173	„	Fusees: glass, earthenware, or pipeclay stems; or cotton or linen, stiffened with gum, chalk, &c.; also bass.
	1512	G. C. Grimes . . .	Fusees: introduction of wires, hooked or otherwise, into the composition-ends of splints, to give stiffness and prevent ash from falling off. Also, ends dipped in gum-water to prevent wires from coming out.
	1720	S. A. Bell and J. Black .	Fusees: stems of wire, coated with non-conducting composition, as glue and whiting, &c.
1860	2236*	W. Schnell	Composition for non-phosphoric friction matches: gum arabic, 2; lead peroxide, 6; antimony, 3; iron sulphide, 8; lead thiosulphate, 8; potassium chlorate, 6; and glass, 3.
	2565*	A. C. A. Bertrand . .	Safety matches: red phosphorus and gum on a flap attached to box.
	2661	T. G. Ghislin . . .	Various South African plants, *Juncus trista* &c., for Congreves and other matches.
1861	655*	W. Schnell	Composition. Also a machine (see Tables IV. and VII.).
	853	T. G. Ghislin . . .	*Juncus trista*, &c.
	1338	R. M. Letchford . . .	Dipping ends in solid paraffin or oil, with or without stearine and japan wax.
	1910	H. Mearing	Safety matches: red phosphorus on rubber (see Table III.).
	2718*	M. A. F. Mennons . .	„ „ „ „
	2988	H. Mearing	Safety matches: on rubber, glue or flour, 2 pts.; red phosphorus, 6 pts.; graphite, 1 pt.; sodium silicate, 1 pt. Dipping composition—potassium chlorate, 10 pts.; antimony oxide, 4 pts.; smalt, 5 pts.; and gum, 2 pts.
1862	973*	H. J. Simlick . . .	Vesuvians: composition put on a tube fitted on to the end of the splint.
	1072*	J. Childs	Vestas: use of a mixture of 1 part of Carnaüba wax with 9 parts of paraffin. High melting-point.
	1137	E. Dove	Continuous match: a band or strip in a case, with composition at intervals.
	1382	G. C. Grimes . . .	Vesuvians: dipping or coating splints in potassium nitrate or chlorate; ends dipped in resin or wax, so that splint would slip out when pastille composition ignited. Also splint-cutting (see Table VII.).
	1575*	R. M. Letchford . . .	Splints saturated with petroleum or rock oil.
	3123	J. W. Hjerpe, W. Holmgren and A. V. Sundstedt.	Non-phosphoric and other friction matches (see Table IV.).

* Provisional protection only.

TABLE VIII.—*continued.*

Year	Number	Applicant	Nature of Invention
	3238*	H. J. Simlick	Vesuvians : stems of spirally twisted wire.
1863	56*	W. C. Bruce	Stems immersed in boiling solution of nitre.
	1353	R. Barker	Vesuvians : pipeclay stems tipped at each end.
	1683	W. C. Bruce	Half of the length of the stems treated with boiling solution of nitre.
	2089†	H. J. Simlick	Vesuvians : stems of slag and powdered oyster shell, mixed to paste and kilned.
	2260	C. Battcock	Vesuvians : stems of slate or stone; also metal tubes filled with sawdust and gum-water, or black-lead dust. Perfume, benzoin or storax.
	2811*	H. J. Simlick	Vesuvians : stems of wire covered with a non-conductor.
	3080	G. C. Grimes	Vesuvians : stems terminating in metal plate or wire coil, to receive pastille and igniting compositions. Also pipe-lights of strands of cotton drawn through composition, dried and cut into lengths.
1864	2943	R. A. Brooman (from C. de Changy, Belgium).	Vesuvians : stems of a mixture of 5% quicklime, or 15% calcium sulphate or calcium carbonate, with coal, calcined at dull red heat.
1865	2153	G. G. Dennis	Vesuvians : splints of wood, paper, twine, straw, rushes, &c., dipped in sulphur and tipped at both ends with a mixture of phosphorus, chalk, and glue.
	3383	W. E. Newton (from P. B. Tylor, Mass.).	Continuous or repeating match : coiled tape, with composition at intervals.
1866	1324*	S. A. Bell	Vestas : tapers thoroughly air-dried, and then rendered waterproof by dipping into a solution of indiarubber or collodion.
	2381	R. M. Letchford	Vestas : jute as a substitute for cotton.
1867	414	J. V. Toepken	Matches ignited as withdrawn from a bundle (see Table VII.).
	3016	R. M. Letchford	Match-splints saturated with solution of resin before dipping.
	3336	"	Vesuvians : stems of bone.
1868	401	A. E. Borgen (from O. C. Green).	Composition for non-phosphoric matches : 15–20 lead thiosulphate; 8–10 potassium chlorate; 1-2 manganese peroxide; 1–1½ 'rolling stone' from Bornholm, Denmark; $\frac{1}{10}$–$\frac{1}{8}$ bloodstone; and 1–2 glue, dextrine, &c. Special rubber not required.
	455*	T. J. Clanchy	Combined match and fusee. One shaft or stem, with fusee-head at one end, and match-head at the other.
	1309	H. Howse	Match-splints, before dipping, saturated with a solution of any chemical salt which would prevent the wood from remaining red-hot after ignition.
	1483*	J. Palmer and J. B. Palmer (from R. Hermann).	Compositions : lead thiosulphate, &c.
	1762	J. Palmer and J. B. Palmer (from R. Hermann).	" " " (see Table IV.).
1869	775*	J. B. Palmer	Compositions (see Table IV.).
	1199	W. E. Newton (from W. H. Rogers, New York).	Flexible matches : any ordinary match composition mixed with caoutchouc or guttapercha; or the following mixture—1 oz. potassium nitrate, ½ oz. orris-root, ½ oz. minium, 1 oz. phosphorus, and 1 oz. dissolved caoutchouc or guttapercha.
	2675	J. B. Palmer	Similar to No. 775, but completed.
	3424	W. Perkins	Continuous match : igniting composition mixed with collodion and inclosed in a case like a pencil-case, so that the match could be withdrawn as desired.
1870	1865	J. Hynam and J. Dixon	From 1–15% of a 'cooling ingredient,' such as alum, zinc sulphate, ammonium sulphate, Epsom salt, fuller's earth, &c., added to the usual constituents of the igniting composition.
1871	314	W. H. Samuel	Continuous match : ordinary match composition combined with caoutchouc, guttapercha, or other gums, resins, &c., glue, gelatin, treacle, bitumen, oil solidified by chloride of sulphur, collodion, &c., and a scenting ingredient, such as cascarilla bark, or some essential oil. Material formed could be moulded into matches of any desired form, ignitable at any part of their length, with an agreeable odour, and flame of any desired colour.
	769	E. A. Crosnier	Safety matches : prepared rubbing-surface on exterior of a tube or cap, into which the end of splint opposite to that carrying the friction composition was inserted. To bring the two compositions together, splint was withdrawn, or match itself broken.
	1059	W. A. Brown and R. L. Jones	Preparing and dipping both ends instead of one.
1872	486	E. Ward	Vesuvians : ends of splints coated with non-combustible material, to prevent the heads from burning the stems, and so falling off.
	2392	R. M. Letchford	Splints heated in bundles, and both ends dipped in rock oil and then in melted paraffin, wax, &c.
	3894	W. Pidding	Vesuvians : stems incombustible, and both ends dipped in inflammable composition.
1873	703	A. M. Clark (from S. Grawitz).	Naphthalene, instead of sulphur, wax, resin, &c., as an addition to the phosphorus composition.
1874	615	J. Hynam	Vesuvians : asbestos stems.
	770	W. Cribb and J. Rackham	Vesuvians : stems of cardboard, stiffened calico, &c.
1875	4529	C. R. R. Grubb	Vesuvians : stems of wood, with internal wire.
1876	715*	G. Gilardi	Vesuvians : pastille composition for heads—100 pts. charcoal from vine stems, 1½ pts. potassium nitrate, 16 pts. flour, and 2 pts. gum.
1877	3740	R. Healy	Wax and other matches : waterproofing the heads with a liquid prepared by boiling together 8 lbs. African copal and 2 gallons clarified oil, adding 3½ gallons turpentine, straining, boiling, and cooling.
	4861*	A. Gutensohn	Solid striking tablets for safety matches : paper pulp, mixed with oxide of zinc treated with tartaric and nitric acids, zinc chloride, amorphous phosphorus, potassium bichromate, and gelatine or gum in water.

* Provisional protection only. † Provisional protection refused.

TABLE VIII.—*continued.*

Year	Number	Applicant	Nature of Invention
1878	148	A. Pollet (from T. Jonas, Paris).	Continuous match : strip of collodion with phosphorus composition at intervals.
	169	H. Klein	Continuous wax match : groove in a wax taper filled with composition.
	725	E. H. Cameron . . .	Waterproofing, by immersion in melted paraffin wax.
	1437	W. R. Lake (from W. W. Batchelder, New York).	Repeating safety match : separate 'sticks'—(1) Potassium chlorate 3 pts., clay 1 pt., and water ; (2) Red phosphorus 3 pts., clay 1 pt., and water.
	2009	A. Ford	Preparing wood for fusees, &c. : wood treated first with potash or soda solution, and then with a mixture of potassium nitrate (10 pts.), potassium chlorate (1 pt.), sugar (1 pt.), and water (12 pts.). Phosphorus (1 pt.) and potassium bichromate (2 pts.) occasionally added to 100 pts. of the solution, more or less.
	5008	R. W. Carter and A. Domeier.	Compositions for attachment to cigars and cigarettes, by which separate fusees or matches dispensed with.
1879	2061	J. L. Field	Stems rendered uninflammable by soaking in solutions of phosphoric acid, ammonium phosphate, borax or boracic acid and ammonium phosphate, &c.
	4373	H. Wildt (from L. Wagner, Mulheim).	Non-phosphoric match composition (see Table IV.).
1880	2289	G. W. v. Nawrocki (from R. Dimock, New Haven, Conn. U.S.A.).	Composition containing red phosphorus (see Table III.).
	3135*	H. Constable . . .	Delivering and igniting automatically.
1881	5235	J. L. Mapple . . .	Splints boiled in oil or tallow, to increase inflammability.
1882	1986	J. L. Field	Safety matches : composition on end of splint, and rubber on staff of another match.
	2446	F. H. V. Byrt . . .	Vesuvians : stems of jute, wire, and glue ; wire in double spiral screw.
	2777	W. T. Evans . . .	Vesuvians : stems rendered incombustible by coating of asbestos paint, or treatment with solution of sodium tungstate.
1883	143	L. A. Groth (from H. R. R. Hosemann).	Vesuvians : fire-proof coating for part of stem.
	834	G. W. v. Nawrocki (from F. Gerken and G. Gollasch & Co., Berlin).	Each match ignited as withdrawn from a case, by contact of its head with a rubbing surface on the stem of an adjacent match.
1884	13,109	G. A. Sweetser . . .	Vesuvians : pastille composition for—charcoal, 2 ; potassium chlorate, 1 ; whiting, and gum-water Tipped with any ordinary composition.
	13,110	" . .	Vesuvians : stems for, of plastic material, such as glue and whiting.
1885	1965	R. Bell	'Fusee-vesta,' or 'vesta-fusee' : a combined fusee and wax match (see Table V.).
	13,938	"	Fusee-vestas : wire cores introduced into the stems.
1886	4525	G. A. Sweetser . . .	Fusees : moulded, pressed, or stamped from suitable material.
	5494	B. v. Schenk . . .	Igniting surface of porcelain.
	11,135	A. F. Hawksley . . .	Continuous lighter, for cigars.
	16,079	C. R. E. Bell . . .	Hollow cylinders or beads of combustible material, for application to matches or vestas.
	16,888†	J. T. Coles	Fusee-vestas.
1887	16,083	W. H. Percival . . .	Self-extinguishing matches : end held in hand dipped in cyanite, &c. Rest of stem impregnated with weak gummy varnish, to prevent embers from falling.
	17,112	H. H. Lake (from P. Fournier, Vienne).	Igniting tinder : a mixture of sodium, potassium, and sand, for application to a cotton or similar wick.
1888	4557	A. Buisson	Igniting tinder : alloy of potassium and sodium, for application to carbonised wick.
1889	5771	W. D. Borland . . .	Nitrocellulose attachment to cigarettes and cigars.
	11,320	A. F. Hawksley . . .	Continuous match or lighter.
	12,763	G. Lutz and L. Oltósy .	Safety matches : ends of splints impregnated with the following composition :—water, 30 pts. ; sodium chlorate, 20 pts. ; ammonium sulphate, 4 pts. ; and gum or the like, 2 pts. No dipping-frame necessary, the splint-bundles being just dipped in the solution and allowed to dry. Rubber : equal parts of red phosphorus and black antimony sulphide, together with gum arabic.
	14,862	J. G. Gomez and P. Franco	Vestas : to burn throughout their whole length with flame (see Table V.).
	16,028	P. Molyneux . . .	Vestas : paper or wood pulp, impregnated with paraffin and stearine, in place of cotton yarn or wick.
	19,309	G. Tattersall and F. W. Streatfield.	Vestas : production of free haloids during combustion for disinfecting purposes. Iodoform, bromonaphthalene, &c., mixed with the compositions.
1890	418	H. R. Troup . . .	Holding and igniting matches.
	1995	W. P. Thompson (from J. Hess).	Safety matches : special rubbing-surface on part of stem, or at one end of each match. Stems broken, to bring igniting and rubbing-surfaces in contact.
	3176	C. F. Martin . . .	Matches.
	3865	M. E. Steedman . . .	Lucifer match.
	6014	W. Hurst	Making wax matches, vestas, and tapers.
	7839	W. Cross	Matches and boxes therefor.

* Provisional protection only.

† Void or abandoned.

TABLE IX.—SOME OF THE MORE IMPORTANT FOREIGN PATENTS, 1800–90, CONNECTED WITH THE PRODUCTION OF MATCHES.

Year	Country	Number or Date	Patentee	Nature of Invention
1809	French Patent	June 30	Derepas	Phosphoric matches.
1820	” ”	—	Pelletier (Paris)	Splint-cutting.
1825	Austrian Patent	June 29	H. Peters	‘Chemical’ matches: potassium chlorate, 4; sulphur, 2; sugar, 1; and coal dust, 1. Inflamed by dipping in phial containing asbestos moistened with sulphuric acid.
1828	French Patent	Mar. 26	Anger et Cie.	Machine for match-making.
1830	” ”	—	Cochot	Splint-cutting.
	German Patent	—	Märklin	‘Chemical’ matches.
	” ”	Mar. 5	A. Wagner	” ”
1832	French Patent	Feb. 11	G. E. Merckel	” ” (‘Allumettes pyrogenes’).
	Austrian Patent	Sept. 10	J. Siegel	” ” and non-phosphoric friction matches.
1833	French Patent	Mar. 30	Joseph et Cie.	Friction matches.
1834	Austrian Patent	Jan. 4	S. v. Römer	Phosphoric friction matches.
	French Patent	June 26	Allien	Matches.
	” ”	June 27	Perpigna	”
1835	Austrian Patent	Feb. 20	J. Siegel	‘Chemical’ matches, friction matches (non-phosphoric), and phosphoric igniting tinder (Zundschwämmen).
1836	” ”	Jan. 27	S. v. Römer	Improvements in the manufacture of matches.
	American Patent	Oct. 24	A. D. Phillips (Springfield, Mass.)	Friction match.
	Austrian Patent	June 18	R. Ehrlich (Prague)	‘Chemical’ matches.
	French Patent	Nov. 26	S. G. Merckel	” ”
1837	Austrian Patent	Jan. 23	J. Eggert	Phosphoric friction matches.
	” ”	Feb. 3	S. v. Römer	Use of lead peroxide, instead of potassium chlorate, in phosphoric friction matches.
	French Patent	April 5	Klug	Waterproofing, by varnishing with a solution containing sandarach, mastic, turpentine, &c.
1838	Austrian Patent	June 20	Preschel & Kreutz (Vienna)	Phosphoric friction matches (see Table II.).
	” ”	Aug. 3	A. Beyer (Vienna)	” ” ” ”
	” ”	Sept. 5	J Siegel	” ” ” ”
1840	French Patent	July 15	Jeunet	Manufacture of matches.
1842	” ”	Sept. 28	Dasseville	Chemical matches.
	” ”	Dec. 21	Fosse	Splint-cutting.
1843	Austrian Patent	June 14	L. Riess (Vienna)	Phosphoric friction matches.
1845	French Patent	May 30	Crépu	Splint-cutting.
	” ”	June 20	Jeunet	Machinery.
	German Patent	—	Neukrantz (Berlin)	Splint-cutting.
1848	” ”	—	Krutzsch (Wünschendorff)	” ”
1851	” ”	June 20	Rudolph & Leitherer (Bamberg)	” ”
1854	French Patent	20,814	Camaille	Compositions containing red phosphorus.
1856	” ”	27,179	Dianoux (Paris)	Composition containing vitreous phosphorus.
	” ”	28,789	Coignet	Compositions ” red phosphorus.
	” ”	28,976	Camaille	Match compositions containing red phosphorus.
1857	” ”	31,450	G. Canouil (Paris)	Non-phosphoric compositions (see Table IV.).
	” ”	31,952	H. Hochstätter (Langen)	” ” ”
	” ”	33,904	G. Canouil	” ” ”
1858	” ”	37,832	G. Canouil	Waterproof matches.
1860	German Patent	—	C. Puscher (Nuremberg)	Compositions. Use of phosphorus sulphide.
1864	French Patent	63,277	O. Walch	Dipping machinery.
1865	French Patent	—	C. Liebig	Non-phosphoric composition (see Table IV.).
1866	German Patent	—	H. Wagner (Pfungstadt)	Compositions and varnish (see Table III.).
1868	French Patent	81,866	Charles & Co. (Bordeaux)	Splint-cutting.
1871	” ”	92,723	Escach	Composition for non-sulphurous, non-hygroscopic matches (see Table II.).
1876	American Patent	184,043	W. A. Leonard	Composition for a continuous match (vitreous and red phosphorus) (see Table V.).
1877	German Patent	314	G. Pernet-Jouffroy	Splint-cutting, &c.
	” ”	696	C. Beck (Cassel)	Machinery for tipping and steam-drying.
	French Patent	Dec. 31	L. F. Perrier	Machine for filling wax matches into dipping frames. An addition to an earlier patent, 91,677, 1871.
1878	German Patent	2773	E. H. Cameron	Waterproofing by dipping in wax or paraffin.
	” ”	3386	Streiber Bros.	Splint-cutting.
	” ”	6051	Sudheim & Koppen	Non-poisonous matches, inflammable on any surface (see Table III.).
1879	” ”	7350	G. Sebold	Machine for laying out from the dipping frames.
	” ”	7595	W. Holmström (Westervik, Sweden)	Apparatus for paraffining matches.
	” ”	7784	Sudheim & Koppen	Addition to previous patent (see Table III.).
	” ”	9126	C. Beck	Machinery for filling, drying, &c. (addition to last patent).
1880	” ”	10,458	P. Popovic (Vienna)	Dipping frames.
	” ”	11,474	L. Wagner (Mülheim)	Non-phosphoric composition (see Table IV.).
	” ”	12,113	G. Sebold	Laying out.
1881	” ”	17,551	”	Splint-cutting.
	” ”	17,857	”	Laying out.
	” ”	18,656	H. Schwarz, and Pojatzki & Co.	Non-phosphoric composition (see Table IV.).
	” ”	18,802	O. Jordan	Filling machine.
1882	” ”	22,308	H. Arlow	Machinery for production (see p. 532).
	” ”	22,735	P. Hosemann	Non-flaming matches.

TABLE IX.—*continued.*

Year	Country	Number or Date	Patentee	Nature of Invention
1883	German Patent .	25,149	A. Roller	Machinery for dipping.
	" " .	25,788	W. Holmström . . .	" "
	" " .	26,650	A. Roller	" "
	" " .	26,937	G. Sebold	Filling machine.
1884	" " .	30,413	H. Kappler	Filling.
	" " .	33,192	H. Schwarz	Non-phosphoric composition (see Table IV.).
1885	" " .	33,234	B. v. Schenk . . .	Rubber.
	" " .	33,791	G. Arehn (Stockholm) .	Manufacture of boxes.
	" " .	33,794	M. Wiberg (Stockholm) .	Manufacture of match-boxes.
	" " .	34,796	Norris & Hagan (Troy, U.S.A.)	Splint-cutting, &c.
	" " .	34,863	J. B. Mitchell . . .	Wax matches.
	" " .	35,796	Aktiebolaget Göranssons, Mekaniska Werkstad (Stockholm)	Manufacture of boxes.
1886	American Patent	341,809	L. Kittinger. . . .	Match-making machine.
	" " .	349,113	C. Martin	Match-making and dipping machine.
	German Patent .	36,905	O. Walch	Laying out, counting, and boxing.
	" " .	37,417	Norris & Hagan . . .	Machinery for match-making.
	" " .	38,335	W. Holmström . . .	Machinery for dipping.
	" " .	38,569	J. Schnetzer . . .	Machine for laying out.
1887	" " .	39,429	G. Sebold	Filling, &c.
	" " .	40,362	C. R. E. Bell . . .	Fusees.
	" " .	40,841	F. Lundgren . . .	Machinery for boxing, &c.
	" " .	41,798	L. Cobbaert . . .	Drying.
	American Patent	356,485	C. Martin	Match-making machine.
	" " .	356,719	L. Kittinger . . .	Match-machine.
	Belgian Patent .	75,891	L. Cobbaert . . .	Machinery for production.
	" " .	76,327	" . . .	" "
	German Patent .	41,994	G. Sebold	Laying out.
	" " .	42,595	P. Gunder (Darmstadt) .	Splint-cutting.
1888	" " .	43,331	K. Pruner	Filling.
	" " .	45,622	N. M. Ström (Nörrkoping).	Boxing.
	" " .	46,571	F. Barckhausen . . .	Machinery for dipping.
	" " .	48,620	Sun Match Company (Ltd.), London	Cutting and arranging splints.
	" " .	48,678	F. Lundgren . . .	Boxes.
	American Patent	386,264	K. Peukert	Match-making machine.
	" " .	389,435	E. B. Beecher . . .	" " "
	" " .	389,950	J. A. Baughman . . .	" " "
1889	" " .	398,322	W. Getz	Match-making.
	" " .	407,717	F. Bommarius . . .	Flexible matches.
	" " .	415,933	M. Young	Machine for unfilling.
	" " .	415,934	" "	Machine for cutting and filling.
	German Patent .	52,842	Oltósy & Son . . .	Headless safety matches.
1890	American Patent	418,887	D. Casey, J. Mantion, and G. H. Millen	Match-boxing machine.

E. G. C.

MATECERIC ACID. An acid obtained from the wax of the yerba maté (*Ilex paraguayensis*). When the solution obtained by exhausting the leaves of this plant with ether, or better with ether-alcohol, is treated with lime, then filtered and evaporated, a waxy residue is left, which may be freed from chlorophyll by treating its ethereal solution with animal charcoal. This solution, agitated with water to remove caffeïne and other substances, and evaporated, leaves the pure waxy matter, which, when boiled with aqueous potash, partly dissolves, leaving a residue soluble in ether, much more butyraceous than the original substance and separable by treatment with alcohol into an insoluble yellow transparent substance, and a soluble portion which is white and melts at 55°. On neutralising with hydrochloric acid, the alkaline solution obtained by saponification of the wax, mateceric acid, is obtained as a white precipitate which has acid properties, and is soluble in ether and in boiling alcohol. It melts at 105°–110°, and has a density of 0·8151 at 26°. From the results of its analysis, it does not appear to belong to the acetic series, but its molecular weight is very high (Arata, Gazz. Chim. Ital. 1877, 366).

MATEZITE. A saccharine substance obtained by Girard from Madagascar caoutchouc; when treated with hydriodic acid, yields methyl-iodide and *matezo-dambose*, an isomeride of glucose. Crystallises in radiating nodules. Rotatory power $[\alpha]_D + 65$; m.p. 187° (Girard, C. R. 77, 995, and 100, 84-86; Combes, C. R. 110, 46).

MATICO CAMPHOR *v.* CAMPHOR.

MATLOCKITE. An oxychloride of lead, $PbCl_2.PbO$, of a yellowish colour, found near Cromford, Derbyshire; sp.gr. 7·21.

MATRASS. An egg-shaped glass vessel with a narrow neck, used by the older chemists, mainly for sublimations.

MAURITIUS ELEMI *v.* OLEO-RESINS.

MAUVANILINE, $C_{19}H_{17}N_3$. A base isolated by Girard, De Laire, and Chappolot, from the insoluble residues obtained in the manufacture of rosaniline (Z. 1867, 236).

MAUVE or **MAUVEÏNE** *v.* AZINES AND COLOURING MATTERS DERIVED FROM THEM. Is known also as *chrom-violet* and *Rosolane.* Formerly also as *Indisin, Anileïn, Violeïn, Aniline-violet, Perkin's violet, Phenamin, Phenameïn, Purpurin, Roseïn, Tyraline, Lydin.*

MAYNAS RESIN or **CALABA** *v.* RESINS.

MEADOW ORE. A synonym for bog-iron ore *v.* IRON.

MEADOW SAFFRON *v.* COLCHICUM.

MECCA BALSAM. *Opobalsam*; *Balm of Gilead* v. Oleo-resins.

MECONIC ACID, $C_7H_4O_7$. An acid obtained from opium v. Vegeto-alkaloids.

MECONIDINE v. Vegeto-alkaloids.

MEDULLIC ACID, $C_{20}H_{41}.CO_2H$. An acid found as a glyceride in beef suet and in beef marrow, associated with oleic and palmitic acids; m.p. 72·5.

MEERSCHAUM. A hydrated magnesium silicate, occurring in nodules and compact masses, of white, grey, or creamy colour. From its appearance and its extreme lightness (sp.gr. 0·988 to 1·279) it has acquired the name of *meerschaum* or 'sea-froth' (*écume de mer*), though it is sometimes described by mineralogists under the name of *sepiolite*, a word introduced by Glocker to indicate its resemblance to the light white porous material known as the bone of the cuttle-fish or sepia. Meerschaum is a soft mineral (hardness 2 to 2·5), easily carved; has a greasy feel, and readily adheres to the tongue. In consequence of this porosity, a meerschaum pipe absorbs the oily matter of the tobacco; and, for a like reason it is difficult to determine the proportion of water in the mineral. The following analyses illustrate the composition of meerschaum:—

—	I	II	III
Silica . . .	60·87	61·30	53·8
Magnesia . .	27·80	28·39	23·8
Alumina . .	—	—	1·2
Water . . .	11·29	9·74	20·0
Total .	99·96	99·43	98·8

I. From Asia Minor, by Lychnell. II. From Greece, by Scheerer. III. From near Madrid, by Berthier.

Meerschaum is found in alluvial deposits in the plains of Eski-shehr, in Asia Minor, where it is associated with magnesite, or magnesium carbonate. It also occurs at Kiltschik, near Konieh, in Natolia; in Greece, Negroponte and Samos; in Moravia and in California. At Vallecas, near Madrid, it is said to be used as a light material for constructive purposes. Meerschaum has been employed as an ingredient in porcelain, while in Turkey it is used, when fresh, in the place of soap, and as a kind of fuller's earth. From the East large quantities are sent to Vienna to be carved as pipes. The pipes are prepared for use by being soaked in melted tallow and wax, and are polished with shave grass. Imitations are fabricated in plaster of Paris hardened with paraffin, and in a preparation of potatoes treated with dilute sulphuric acid. F. W. R.

MEILER. The German name for the stack of timber piled up for burning into charcoal v. Carbon.

MELACONITE. Native copper oxide CuO v. Copper.

MELANCHROÏTE. Native lead chromate v. Chromium.

MELANTERITE. Native ferrous sulphate v. Iron.

MELDOLA'S BLUE v. Oxazine colouring matters.

MELDOMETER. An instrument designed for the purpose of ascertaining the melting and boiling points of small quantities of substances. It consists essentially of two pairs of forceps mounted on a stage and carrying between them a thin platinum ribbon. Through this ribbon an electric current may be passed, the strength of the current being regulated by a carbon-mercury rheostat. The apparatus is mounted on the stage of a compound microscope, provided with a one-inch objective. The substance to be examined is placed in focus on the platinum ribbon, and then the current is gradually increased until the substance is melted or volatilised. Experiments made in this way show interesting phenomena, sufficiently characteristic in many cases to identify a substance at once. By arranging side by side different fragments it is easy to find their order of melting-points with greater exactness than can be the case when the blow-pipe is employed.

The meldometer is also of value in studying sublimates. A piece of glass is held over the heated strip and upon this the sublimate deposits. A long series of trials have led to the conclusion that the appearances so obtained are excellent as tests to the mineralogist and chemist (J. Joly, Industries, 1889, 20, and S. C. I. 8, 306).

MELEZITOSE $C_{18}H_{32}O_{16}2H_2O$ (Alĕkhine). A sugar found in 1833 by Bonastre (J. Ph. 2, 19, 443) in the Manna of Briançon, which is obtained as an exudation from the young twigs of the larch (*Abies Larix*; Fr. *Mélèse*). More completely investigated by Berthelot (A. Ch. [3] 55, 282) and by Alĕkhine (A. Ch. [6] 18, 532). Found also in *turanibin* or *terenjabine*, an exudation from *Alhagi Maurorum* growing in Afghanistan, Persia, and in the deserts of the East, and used in Northern India as a laxative (Villiers, A. Ch. [5] 12, 43). This substance is a brown semi-solid mass, of a slightly sweet taste, due mainly to the presence of dextrose. To obtain melezitose from this product it is treated with four times its weight of lukewarm water and the liquid passed through a sieve to separate husks, leaves, &c., and after standing to allow of the deposition of earthy matter, it is evaporated to half its bulk. On standing for a few days the greater part of the melezitose crystallises out. The crystals are redissolved in twice their weight of hot water, the solution heated on the water-bath, diluted with its own volume of alcohol, heated to boiling to separate earthy and coagulable matter, and filtered whilst hot. On cooling melezitose separates out and may be obtained pure by two or three recrystallisations. It forms large rhombohedral prisms $C_{18}H_{32}O_{16}.2H_2O$, which effloresce in air and become opaque; they lose the whole of their water at 110°. Dehydrated melezitose fuses at 146°–148°, sp.gr. $\frac{17\cdot5}{\;} = 1\cdot540$; 100 pts. of water dissolve of anhydrous melezitose 26·8 pts. at 17·5°; 34·4 pts. at 25°; 75·6 pts. at 100°; sparingly soluble in alcohol, insoluble in ether. Sp. rotatory power $= (\alpha)_D = +83 + \cdot07014\,p$, where p is the weight in grams of the substance in 100 grams of the solution. Melezitose yields no crystalline compounds with alkaline chlorides; with phenylhydrazine it forms small yellow acicular crystals; with anhydrous acetic acid it forms *endecacetylmelezitose* $C_{18}H_{21}O_{16}(C_2H_3O)_{11}$, crystallising in shining monoclinic prisms, m.p. 117°, sp.gr. $\frac{0}{4}=1\cdot32$, insoluble in water but readily soluble in alcohol, ether, benzene, and acetic ether. Melezitose decomposes at about 200°. On boiling with dilute sulphuric acid it yields *turanose* (Alĕkhine) and dextrose. It has no action on an alkaline solution of copper and is unchanged by diastase or yeast. Nitric acid transforms it into oxalic acid without intermediate formation of mucic acid.

MELISSA. The leaves and tops of *Melissa officinalis* contain a small quantity of a volatile oil. They are used occasionally in the form of a warm infusion as a diaphoretic in slight febrile conditions.

MELISSIC ACID *v.* Fatty Acids.

MELITOSE $C_{12}H_{22}O_{11}.3H_2O$. The name given by Berthelot to a sugar discovered by Johnston in 1843 and contained in the manna from *Eucalyptus mannifera* found in Tasmania. To obtain melitose the manna is dissolved in hot water, the solution decolourised by animal charcoal, and evaporated to the crystallising point. Melitose has a slight sweet taste, is sparingly soluble in cold water, but more readily in hot water and in alcohol. It loses two mols. of water at 100° and the remainder at 130°. When boiled with dilute acids or when its aqueous solution is fermented with yeast (invertin) it is converted into lævulose and so-called *eucalyn* $C_{12}H_{22}O_{11}$ (the melitose of Scheibler and Mittelmeier) $(\alpha)_D=104\cdot3$.

Melitose is identical with the *raffinose* of Loiseau obtained from molasses and the *gossypose* of Böhm which Ritthausen obtained from cotton-seed (Tollens and Rischbiet, A. 232, 169; Scheibler and Mittelmeier, B. 22, 3118).

MENACCANITE. A variety of titaniferous magnetic oxide of iron found in grains and small angular fragments at Menaccan near Helstone, and other places in Cornwall, *v.* Titanium.

MENDIPITE. An oxychloride of lead $PbCl_2.2PbO$ found near Churchill on the Mendip Hills in Somersetshire. Crystallises in yellowish white rhombic prisms; fracture conchoidal, uneven; adamantine lustre, sp.gr. 7·1. Known also as *kerasin.*

MENHADEN OIL. An oil obtained from *Alosa menhaden*, a species of herring. It forms a lime-soap which when distilled with excess of lime yields a mixture of hydrocarbons belonging to the C_nH_{2+2n} and C_nH_{2n} series. Warren and Storer, Mem. Amer. Acad. (new series), 9, 177).

MENISPERMIN *v.* Vegeto-alkaloids.

MENTHOL *v.* Camphors.

MENTHONE *v.* Camphors.

MERCURY. *Quicksilver.* *Mercure* (Fr.); *Quecksilber* (Ger.). Hg. At. w. 199·8 (Turner Erdmann and Marchand, Millon).

Occurrence.—Mercury occurs in small quantities in the metallic state, principally disseminated through the natural sulphide. It has been found to the extent of 0·0029 p.c., in minute globules, in a patch of soil at Cedar Grove, Louisiana (Wilkinson, Am. S. 29, 280).

Alloyed with silver it is found in crystals belonging to the cubic system at Arqueros, near Coquimbo, and in other silver mines. It occurs alloyed with gold in Columbia, &c., and with gold and silver, with native platinum, in Choco, New Granada. A lead amalgam is also known.

The most important ore is the *sulphide* HgS. This ore, known as *cinnabar*, occurs in large deposits at Almaden in Spain, Idria in Carniola, New Almaden, in Santa Clara County, California, and in many other localities near San Francisco; in the Bavarian Palatinate, and in Southern Peru, Chili, China, and Japan. It is said to occur in quantity in Borneo. The zinc blende roasted at Oberhausen contains about 0·02 p.c. of mercury, which is extracted from the condensation products (F. Bellingrodt, C. Z. 10, 1039).

Mercury occurs in small quantities as selenide and sulphoselenide (*onofrite*), as chloride Hg_2Cl_2 in *horn mercury*, and as iodide and bromide.

Extraction.—The extraction from the sulphide depends simply on the removal of the sulphur and volatilisation and condensation of the liberated mercury. The sulphur may be oxidised to sulphurous oxide by ignition of the ore in a current of air, or it may be removed as sulphide of lime or of iron by ignition with lime or smithy scales. The first method is almost invariably adopted.

At Idria the sulphide occurs as a dark-red slaty deposit, disseminated through shales and limestones of the triassic period. It appears to have been deposited by infiltration from below, as the deeper portions are richer. The north-western deposits are bituminous (*v.* Phillips, Ore Deposits, 329).

The deposits were discovered about four centuries ago, and in 1504 were worked by a mining corporation. In 1510 the mines were leased by the Emperor Maximilian to the St. Achazi Company; but in 1580 they reverted to the Crown, and the mining reservation for the Montanwerk was founded by the Caroline mining law for Idria. The principal entrance to the mines (the 'Anthoni-Stollen') is in the centre of Istria, and the necessary water is supplied by the Idrizza river. The mines cover an area of about 111 acres, are worked by over 1,000 hands, and are provided with six shafts.

The quality of the ore varies between wide limits—from the *stahlerz* containing 75 p.c. of mercury to the *smalls* containing about 0·5 p.c. The ore roasted averages about 1·3 p.c. About 475,000 cubic feet are worked annually.

The finest 'ores' are powdered, mixed with a proportion of quicklime (15 p.c. of lime for a 10 p.c. ore), pressed into bricks, and roasted for about four hours in a set of twelve muffles, each having a capacity of about 150 lbs., contained in six furnaces.

The 'sands' and coarser 'ores' are roasted in six double reverberatory furnaces known as *Alberti* furnaces, having iron condenser pipes cooled with water. These furnaces roast about 6·5 tons daily, with a consumption of about 100 cubic feet of fuel.

The 'smalls' are mixed with charcoal and worked in seven ironclad shaft furnaces slightly lined with masonry (*v.* extraction at New Almaden).

The ores are divided, according to their richness and size, into three qualities, of which the general composition is as follows:—

——	'Smalls'	'Sands'	'Ores'
Mercury sulphide	0·62	1·25	8·58
„ chloride	tr.	tr.	0·22
„ sulphate (basic)	—	—	tr.
Iron carbonate	0·76	3·17	4·27
Calcium carbonate	35·75	27·21	14·71
„ sulphate	0·53	1·46	2·42
Magnesium carbonate	27·17	20·33	4·20
„ sulphate	0·21	0·55	1·11
Iron pyrites	4·24	4·31	5·09
Alumina	1·64	1·61	1·30
Phosphoric acid	—	—	tr.
Aluminium silicate	16·48	22·75	15·82
Iron silicate	—	tr.	20·18
Silica	11·52	16·48	17·64
Bitumen	1·08	1·63	3·97
Water and loss	—	—	0·49
	100·00	100·00	100·00

The mercury vapours liberated pass with the products of combustion into a series of main and branch flues and of four chambers of masonry on each side of the furnace, the flues and chambers having a capacity respectively of 30,000 and 62,000 cubic feet. In the last chamber are a number of coarse screens covered with sawdust which assist in condensing the remaining mercury.

From the shaft furnaces the gases pass through a series of U-shaped iron tubes cooled by water into condensers of wood lined with masonry, thence through underground flues to a distant chimney about 400 feet above the works.

The mercury runs from the inclined floors of the condensers through tubes into underground reservoirs. It is strained through coarse linen cloths, and exported in iron screw-stoppered bottles weighing about 25 lbs., and containing about 76 lbs. of mercury. It is sometimes stored in leather bags.

In the chambers and flues a considerable quantity of a black deposit, known as 'stupp,' is found. It consists of soot from the fires, but contains about 6·5 p.c. of free mercury and about 13·5 p.c. of mercury as sulphate, sulphide, and chloride, together with ore dust, water, &c. It is made into bricks with the required amount of lime, and roasted in muffles as for 'ores.'

The losses of mercury are: (1) Traces remaining in the roasted residues, amounting to about 0·001 p.c. (2) Mercury absorbed by the masonry; this loss, however, is only temporary, as the metal is always re-obtained by roasting when the old condensers are destroyed. (3) Vapour of mercury passing out with the combustion products. (4) Fine particles of mercury carried away mechanically as 'mist.'

The two last only are of consequence. The loss as vapour may be calculated from the vapour pressure of mercury at the temperature of the issuing gases; it is estimated at 2·32 p.c. of the total mercury. The mist loss cannot be calculated; it depends on the method of condensation and on the velocity with which the gases traverse the condensers. It is estimated at Idria at about 2½ times the vapour loss.

As the loss depends on the perfection of the condensation, and not on the ore richness, the percentage loss on a poor ore is far greater than that on a richer mineral. Thus, the loss on 'smalls' is estimated at 16 p.c. of the ore content, that on 'sands' at about 6·8 p.c., and that on ores roasted in muffles at a lower figure. A total loss of about 8 p.c. on the poor Idrian ores may therefore be considered satisfactory. It must be noted that these figures are only rough approximations (comp. Exeli, Chem. Zeit. 56, 8, 1008).

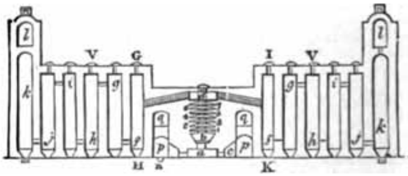


FIG. 1.

Figs. 1 to 4 show the great distillation apparatus employed at Idria, the following parts being indicated: *a*, fire-place door; *b*, furnace; *c*, ash-pit door; *d*, a space in which the ores are deposited on seven arches, 1 to 7; *e*, brick tunnels for carrying the combustion products and mercury vapour into chambers *f*, from which they pass successively through chambers *g*, *h*, *i*, *j*, *k*, *l*; *m m*, receivers for the condensed mercury: *n n*, a trench into which the mercury runs from the receivers; *o*, a chamber receiving the mercury; *p p*, vaulted arches insuring circulation round the furnace; *q q*, vaults of the upper stories; *r r*, vaults permitting access to the tunnels *e e*; *s s* and *t t*, doors to the

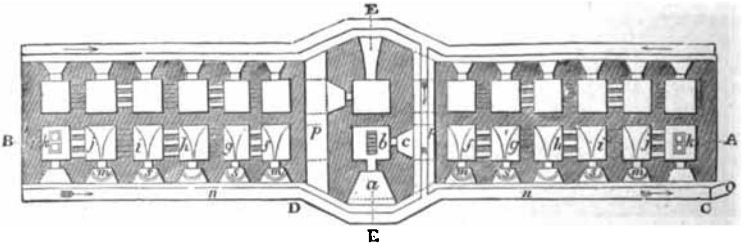


FIG. 2.

chambers *fk* and *fk*; *uu*, doors of the vaults 1-7; *vv*, openings to the chambers, closed by luted plugs; *x*, *y*, *z*, floors corresponding to the doors *uu*. A complete charge for the double apparatus requires from 1,000 to 1,300 quintals of ore. The furnace takes from five to six days to cool, so that only one distillation can be performed weekly.

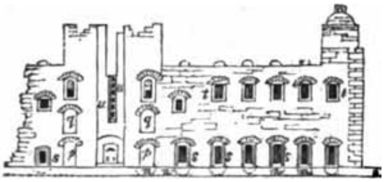


FIG. 3.

At Almaden (Spain) the ore occurs in quartz, frequently impregnated with clay and bitumen, and often containing iron pyrites, barium sulphate, calcium carbonate, and sometimes selenium. The ores worked vary considerably in richness, but appear to average about 8 p.c. of mercury. The following table shows their general composition (Escosma):

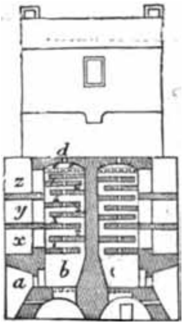


FIG. 4.

—	Metal		Requiebro		Vaciscos		China	
	1	2	3	4	5	6	7	8
Mercury sulphide .	29·1	21·2	13·3	10·2	5·1	2·8	1·2	0·86
Iron pyrites . .	2·2	2·0	2·0	1·9	12·3	1·5	2·1	2·80
Bituminous matter .	0·6	1·0	1·0	1·2	4·6	0·7	3·4	0·90
Gangue . . .	67·5	74·8	82·1	76·5	77·5	93·3	90·2	93·50
Total . . .	99·4	94·0	98·8	98·9	99·5	98·3	98·7	98·06
P.c. of mercury .	25·05	18·28	11·47	8·64	4·40	2·41	1·03	0·75

The ores having been crushed, are divided, according to their size and quality, into four lots: (1) *Metal*, containing not less than 15 p.c. of mercury, and measuring over 20 c.c. (2) *Requiebro*, containing 7 to 15 p.c. of mercury, and of the same size as *metal*. (3) *China*, the poor ore, measuring 10–20 c.c. (4) *Vaciscos*, containing the *débris* from the former ores. All those ores which appear inferior to metal or requiebro, are broken sufficiently to belong to the two latter classes.

The furnaces are 2 metres wide internally, and 3·7 metres high above the brick grate. Two furnaces are always built side by side, and are worked together. They are known as *Bustamente* or *aludel furnaces*, and are peculiar to Almaden.

On the furnace-grate is placed 2 tonnes (2,000 kilos.) of very poor or spent ore, or preferably of quartz. This is covered by about 10 tonnes of the mineral, poor ore being added first, followed, in order, by china, metal, requiebro, more china, and finally, vaciscos made into balls. The charge is generally constituted as follows:

2,200 kilos. quartz or poor ore, constituting 19 p.c. of the charge.

3,500 kilos. china, constituting 30·5 p.c. of the charge.

1,800 kilos. metal, constituting 15·5 p.c. of the charge.

1,700 kilos. requiebros, constituting 15·0 p.c. of the charge.

2,300 kilos. vaciscos, constituting 20·0 p.c. of the charge.

Total, 11,500 kilos. (nearly 11·5 tons).

The furnace is next closed, and the *aludels* are luted together in position. These are earthenware, pear-shaped condensers 40 cm. long, 11 cm. wide at the narrow end, 18 cm. at the wide end, and 27 cm. in the middle. The narrow end of each passes into the wide opening of the one in front. They pass in 6 rows, each containing 47 aludels, from 6 openings in a chamber known as *camareta*, above the furnace. They are supported on a roof of masonry sloping from both ends at about 10° towards a trough in the middle. The further end of each row passes into another chamber over a cistern of water, which condenses most of the remaining mercury. This chamber opens into the chimney. Those aludels which rest on the trough are pierced below to permit the escape of the condensed mercury.

Wood fires are lighted beneath the grate, and maintained for twelve hours. The whole of the ore and furnace having thus become strongly heated, the fire is withdrawn and air is admitted. In passing through the grate the air becomes heated to 200 or 300°C., and ignites and reduces the cinnabar.

The sulphurous oxide and mercury produced pass into the *camareta*, and thence into the aludels, which gradually become heated until, after about twelve hours, the first aludel has a temperature of over 200°C.

After eighteen hours the mass begins to cool, the terminal aludels having then a temperature from 3° to 27° above that of the surrounding air. After twenty-four hours the furnace is fully opened and allowed to cool. The mercury condensing in the aludels runs into the lowest and passes through its opening into the gutter, which conveys it into a vessel where it remains beneath the surface of water.

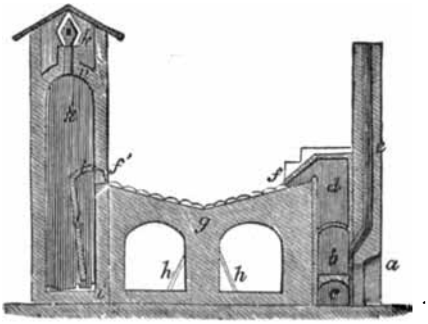


FIG. 5.

Two furnaces similar to those used at Idria are also used, but the aludels are preferred. The finer vaciscos are still made into bricks (*adobes*)

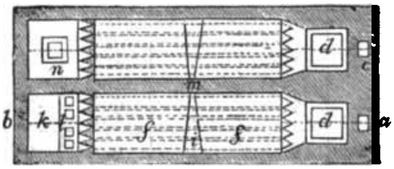


FIG. 6.

with lime, and are roasted. The total loss of mercury with the aludel furnaces is roughly estimated at 5 p.c. As the ores are comparatively rich, this result does not compare favourably with those obtained at Idria or New Almaden.

Fig. 5 to 8 show two aludel furnaces, in elevation and plan, the following parts being indicated: *a*, door; *b*, fireplace; *c*, ashpit; *d*, chamber in which the ores are distributed on open arches; *f* and *o*, aludels on sloping terraces having two gutters inclined towards an intermediate wall *m*. In one arrangement, mercury running from the aludels passes through wooden pipes *h h*, into cisterns filled with water. The uncondensed mercury passes into a chamber *k*,

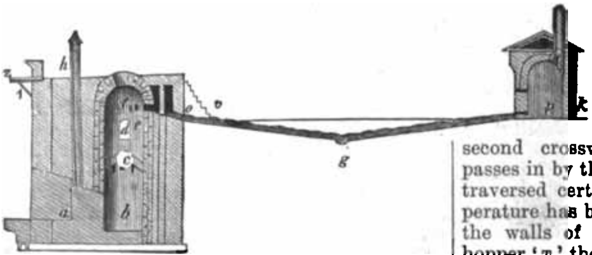


FIG. 8.

a portion being condensed in a water cistern *i* while passing under a partition *l*. Any remaining vapour passes through a chamber by a small chimney *n*. In the other arrangement the mercury collects in basins at *q*.

See further, Moreau (Le Génie Civil, 1884, 380); Kuss (Ann. des Mines, 13, 39–151, and 15, 524); Engineering and Min. Journ. 32, 335.

Channel (fig. 9) furnaces are employed for the treatment of fines rich in mercury at Almaden. The size of the fines for these furnaces must not exceed 10 c.c. The furnaces mentioned have the great advantage of being continuous in their operation, to such an extent that in seven months not the slightest interruption occurred.

The hearth is an inclined plane constructed of fire-brick 2·50 metres in width by about 8 metres in length, the grade of which is equal to or a little steeper than the natural slope of the fines. Every 40 centimetres this floor has a rise of 2 centimetres, as can be seen in the illustration. It is divided by partitions formed of fire-brick 30 centimetres high, into 12 channels, 12 centimetres wide, in which the ore runs. Transversely in the channels, and supported on their partitions, there are placed bricks, called 'taws' ('stoppers'), which are above the floor of the hearth 4 centimetres, this being the thickness of ore in each channel. Arranged in the same way there are others called 'petacas' ('trunks'), situated immediately at the bottom of the rises and at the same distance from the hearth as the 'stoppers,' which serve to break up the fine ore on them so as not to present invariably the same surface to the action of the heat. On the lower part of the hearth there is another inclined plane M, perpendicular to it. This is also divided into 13 channels, but there are no 'stoppers' or 'trunks' on it. The ore, already calcined on the first plane, travels to the second, at the end of which, M, a boy is placed, whose duty it is to make it run over the hearth. A little above the second plane and facing the first, but separated from it by the bridge *x*, is placed the fire-place, the grate of which is divided into two equal parts by a partition which rises to the arched roof of the fire-place. The fire-grate is formed of two systems of bars, *p*, *q*, and *r*, *s*, the first placed lengthwise and irregular in height, and the second crosswise. The air for combustion passes in by the ash-pit to the fireplace, having traversed certain passages *e*, *g*, where its temperature has been raised by the heat taken from the walls of the furnace. By means of the hopper 'T' the channels are filled with ore, and when it has been sufficiently exposed to the heating and reducing action of the gases, the boy placed at M withdraws a portion of the ore placed on the lower edge of the second inclined

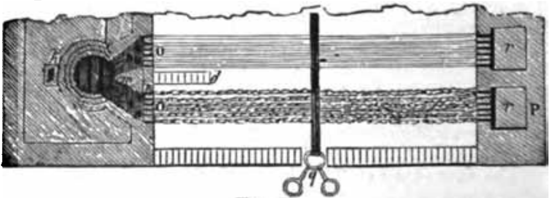


FIG. 7.

plane. The ore remains subjected to the action of the heat for about four hours. The calcined fines are ejected by a hopper to the passage G, whence they are taken out in cars. They do not now contain more than two to four hundredths p.c. of mercury. The condenser is formed by two series of chambers, the first of which communicates with the furnace by a throat in the shape of a truncated pyramid of iron plate protected with brick. The six chambers which constitute this first series are of brick, with thin walls, and are divided into partitions, which have openings arranged for the passage of the fumes, so as to run in double zigzag. The bottom of each division is formed of two inclined planes, whose intersection has a small inclination towards a channel common to all the chambers in which is collected the mercury condensed in them. The bottoms are of iron plate in the three chambers nearest to the furnace, and of slate in those furthest away, this arrangement being in consequence of the iron being attacked by the mercury in the latter. The last part of the condenser is formed of wooden chambers with glass, divided into four parts by vertical partitions. These chambers are arranged so that the air can circulate below and around the sides, and allow of observation in case of any filtration of mercury through the bottom.

Coal was first employed as fuel, but coke is now found to give better results in regard to the smaller quantity of soot which is produced (Eng. and Min. J. 47, 544–545; S. C. I. 8, 708).

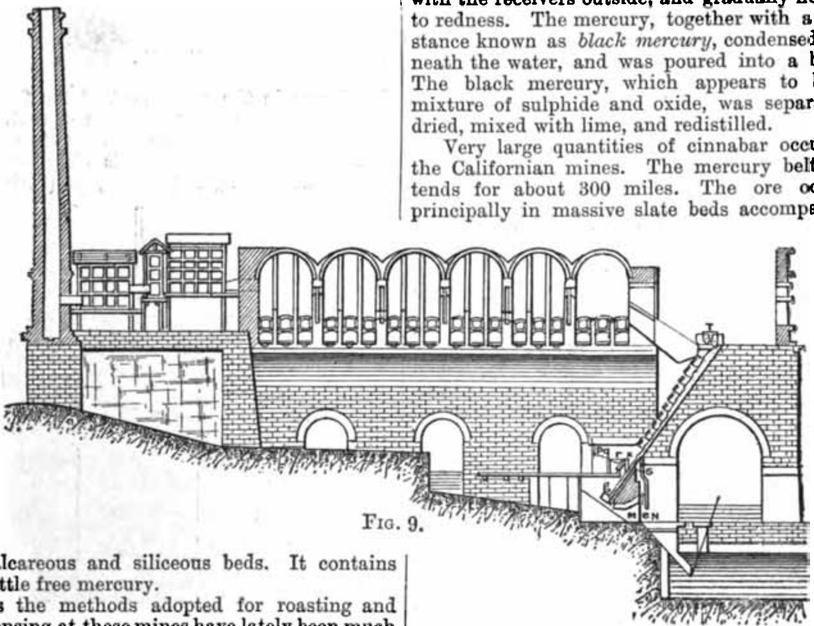


FIG. 9.

At Zweibrucken, in the Bavarian Palatinate, considerable quantities of mercury were formerly prepared by the following process. About 60 lbs. of the ore was mixed with 16 lbs. of lime and placed in cast-iron flask-shaped retorts, to the mouths of which stoneware receivers, half-filled with water, were luted. These were arranged in rows, one above another, in a furnace, with the receivers outside, and gradually heated to redness. The mercury, together with a substance known as *black mercury*, condensed beneath the water, and was poured into a bowl. The black mercury, which appears to be a mixture of sulphide and oxide, was separated, dried, mixed with lime, and redistilled.

Very large quantities of cinnabar occur at the Californian mines. The mercury belt extends for about 300 miles. The ore occurs principally in massive slate beds accompanied by calcareous and siliceous beds. It contains but little free mercury.

As the methods adopted for roasting and condensing at these mines have lately been much modified, we select that employed at New Almaden, for a more detailed description. We are indebted for the account principally to a paper by S. B. Christy (Trans. Amer. Inst. Min. Engrs. 13, 547–584, and 14, 206–264).

The ore, which usually contains bitumen, and is mixed with serpentine, dolomite, and other gangue, is conveyed to the dressing floors and thrown upon screens of 1 to 1¼ inch mesh. The portions passing through are known as *tierras* and contain 1 to 3 p.c. of mercury. The larger ore is picked over, the apparently worthless ore, amounting to about five-sixths, is rejected, and the remainder is put aside as *granza* and contains about 6 to 8 p.c. mercury. It is again screened, and the pieces varying between 1¼ and 3½ inches are separated as *gransita* containing 1 to 3 p.c. of mercury. A considerable quantity of the old ore, which was formerly rejected, is now worked. It is washed, and if showing a trace of cinnabar is put aside as *terrero*, and contains about 1 to 2 p.c. mercury.

The ores worked in 1850 averaged 36 p.c., those now worked average only about 2 p.c. of mercury. The furnace formerly used resembled those of Idria, but was soon replaced by an intermittent furnace which is still used, in which the ore is supported on a solid bed instead of on arches. The finer ores, amounting to about two-thirds of the whole, were then mixed with clay and made into *adobes* weighing about 12 lbs., and sun-dried before they could be roasted. Two continuous ore furnaces similar to Count Rumford's lime furnace and resembling those used at Idria were next introduced. The latest furnace is that of Hüttner and Scott, in which fine ores can be continuously treated without the manufacture of *adobes*.

The ore chamber in the old intermittent furnace is 12 × 9 × 17 feet, and has a capacity of 80 to 100 tons. It is separated from the furnace and condensers by two convex walls perforated by a large number of pigeon-holes whose convexity is towards the ore chamber. The coarser portions of the charge (granza and terrero) are first arranged in channels followed by coarse ore, added indiscriminately, next more ore, arranged in channels, and finally a layer of tierras and mercurial soot, until the chamber is filled. The average charge consists of 73 tons granza, 9·6 tons terrero, and 6 tons tierra. The whole is covered by sheets of old iron, then by a 3-inch layer of straw manure, and finally by a 3-inch coating of moist clay. The fire being lighted, the heated gases pass through the pigeon-holes, penetrating and oxidising the ore, and the sulphurous and mercurial vapours pass through the opposite walls into the condensers. The roasting occupies five days, and the subsequent cooling, during which the furnace is opened, takes about three days. Three charges are thus worked monthly.

In this furnace, the cost for roasting 1 ton of ore is, for fuel 0·885 dollars, and for labour 0·483 dollars. The continuous coarse ore furnaces known as *ironclads* or *monitors* (figs. 10 and 11) are hexagonal in plan at the base, with three abutments on alternate sides, each having a fireplace and an ashpit. Above the abutments the furnace is cylindrical. The vapour chamber is at the shaft top, above the ore, and conveys the fumes to the condensers through 12-inch iron pipes, each provided with movable discs to keep them free from soot. The furnace shaft is lined with firebrick, and is provided with four equidistant peep-holes. It is 6 feet wide and 11 feet high, terminating below in a cone frustum 8 feet deep, which contracts to four feet in width at the bottom. At the shaft top, is an airtight chamber closed above by a cover which is penetrated airtight by a rod connected to a cone upon which the ore is placed, and which closes the chamber below. When first charged, the shaft is filled to about the depth of the fireplace with spent ore, and above, to about 3 feet from the top, with granza (averaging about 6–8 p.c.) mixed with coke, charcoal, or coal, 1,600 lbs. of ore to about 24 lbs. of coke. A good wood fire is maintained in each fireplace. When the peep-holes show that the ore is at a cherry-red heat, some spent ore is removed from below into the ash-pit. The cone above is then lowered and its charge of ore is introduced. It is then replaced, and is again charged with ore through the upper door of the chamber. As the chamber is always closed above when the cone is lowered, and is closed below by the cone when being recharged, no fumes can escape though the ore is at a red heat below. A fresh charge is thus introduced about every two hours. The spent ore is not removed from the ash-pit until quite cool and free from mercurial vapours. These furnaces have a capacity of about 21 tons, and pass 10 tons in 24 hours. The cost of working per ton is, for fuel 0·555 dollars, and for labour 0·404 dollars. The continuous furnace of Hüttner and Scott is especially constructed for the roasting of fine ores. The fuel is wood. The air supplied for combustion is heated by passing through a long earthenware pipe traversing the condensers; branch pipes therefrom also supply hot air to the flames in the upper part of the fireplace, and thus reduce the production of soot. The peculiarity of this furnace is in the ore chamber (fig. 12). The height of this chamber is 27 feet, its width only 25½ inches, its (horizontal) length 11½ feet. Two are built side by side. The ore is fed from above in a manner similar to that described above, so that it falls equally into each chamber. On opposite sides of each

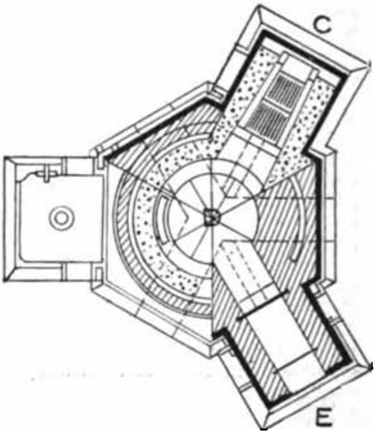


Fig. 10.

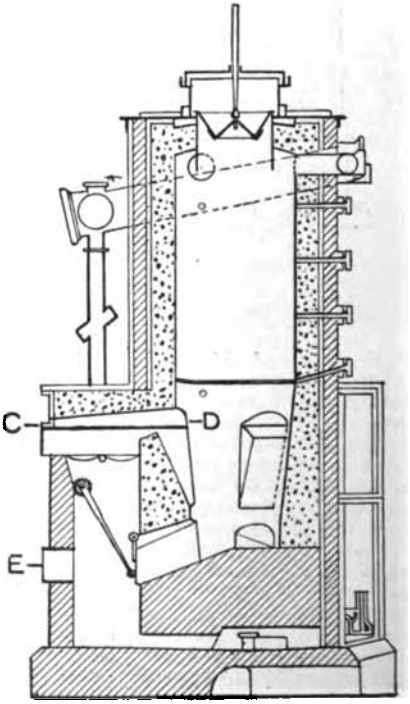


Fig. 11.

chamber are fixed, at distances of 30 inches, fireclay tiles 36 × 16 × 3 inches, four of which fill the chamber lengthwise. They are inclined at an angle of 45° to the sides, so that they face one another at an angle of 90°, the front of each facing the middle of the opposite tile, and leaving a space of 3″ between. The ore, as it is fed from above, falls from side to side, from one tile to another, until it reaches the bottom. It then forms a continuous sinuous layer about 3″ thick, extending over the whole of the tiles, and exposing a large surface to the action of the blast. The hot air from the furnace passes through pigeon-holes on one side of the chambers, over the ore, and through similar holes on opposite sides carrying the mercurial vapours &c. into the condensers. As the ore becomes spent, it is removed from below, and its place is supplied by fresh ore above. The process is therefore continuous and very effective, as the ore is completely turned in its passage from one ledge to another, *i.e.* about 20 or 30 times during its descent. At the upper ledges, rakes are supplied, worked by external handles for breaking up the ore, which occasionally cakes when damp. Four of these furnaces are worked in pairs. In 1883 they roasted 38,581 metric tons of ore. The largest has a capacity of 45 tons, and roasts 1 ton in 40 minutes at a cost for fuel of 0·352 dollars, and for labour 0·288 dollars. The average cost for the four furnaces is 0·445 dollars and 0·356 dollars respectively.

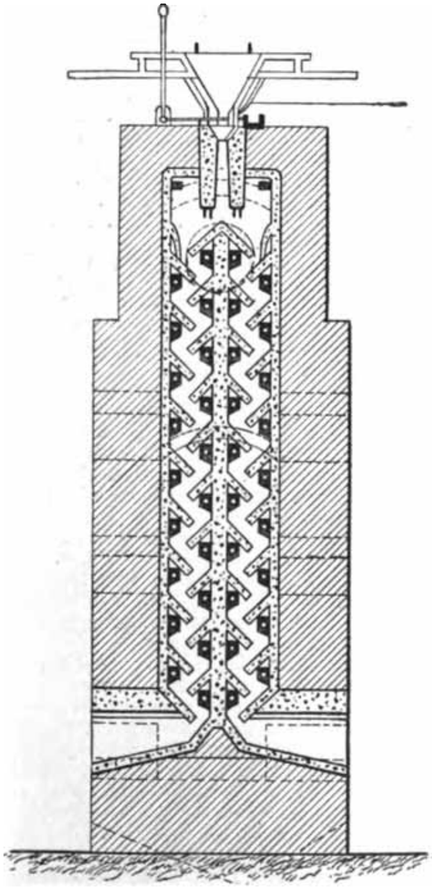


FIG. 12.

These furnaces are also used at the Sulphur Bank Mines (Cal.), where the ore is liable to form a paste from the presence of alkaline borates. The reduction of the ore by any of these furnaces is very complete, only a trace of mercury being found in the residues.

Condensation.—The volatility of mercury, even at low temperatures, and the large volume of gases with which it is mixed render the condensation very difficult. Although only about double the amount of air theoretically required is used at New Almaden, the amount of mercury vapour present in the gases entering the condensers is frequently under 1 p.c. by volume. The velocity with which the oxidising vapours traverse the ore influences the amount of loss by mist.

The temperature of the furnace should be so regulated that the vapours enter the condensers as nearly as possible at the boiling-point of mercury. According to Smedberg, the temperature of the fumes at the upper peep-hole of the monitor furnace is only about 12°C. above this point.

Iron condensers are only applicable for cooling the gases while above the boiling-point of water. At a lower temperature sulphurous and sulphuric acid liquors commence to condense and rapidly corrode the pipes. The use of lead is precluded by the action of the mercury. Even masonry is gradually acted on by the acid liquors with formation of crystalline sulphates which crack the walls and cause considerable loss of mercury. Chambers of thin glass in wooden frames have been largely adopted as condensers where the gases have become comparatively cool. They are 4½ feet square and 25 feet high, connected alternately at top and bottom to give a circuitous route to the vapours.

The large heavy brick condensers such as are used at Idria work satisfactorily with the intermittent furnaces, where they have a few days to cool between the operations, but are quite inadequate with continuous furnaces. They are now replaced by condensers having a much larger surface, connected by earthenware or iron pipes. These are usually 27 feet high; the floors are of brick, well laid and coated with cement. Those which receive the cooler vapours are coated with asphalt to prevent penetration by mercury. The floors have an inclination of about 10° towards either side, and the metal runs into inclined gutters lined with asphalt, which conduct it through boxes and pipes into a weighing and bottling room attached to each furnace.

The hotter condensers are sometimes covered by iron plates on which the damp ores may be dried, serving at the same time to cool the gases.

In the case of the intermittent furnace the vapours pass through a chamber containing the damp ore to be used for the following charge before entering the condenser proper. In another form the ores to be dried are spread on ledges resembling those used for roasting in the Hüttner and Scott furnace.

The following iron condenser has been satisfactorily applied to two furnaces. The fumes from each ore chamber, having passed through a brick condenser to deposit ore dust, pass through three sheet-iron pipes 20 feet long and 22 inches internal diameter, inclined at 20°, into three cast-iron condensers, which consist of three tubes (22 inches diameter) fitted together into a ⊔ shape and surrounded by a tank of water. They are coated thickly with coal tar and asphalt and are provided with discs to prevent the accumulation of soot. The lower limbs are inclined at 20° and convey the mercury into a reservoir. These condensers are also used at Idria.

A system of 'water backs' is also used. Two cast-iron boxes, 3½ × 16½ × 14½ feet internally, are set opposite one another and connected by iron tubes in the end of a brick condenser. One of them consists of two compartments. Water is introduced into the lower division; it passes thence through five tubes into the opposite box, and back through a second set of tubes to the upper compartment, maintaining a constant current of cold water and offering an effective condensing surface. Two pairs of water backs set in a hot condenser are said to be equal to two additional condensers. The second and third condensers are then found to contain the greater part of the mercury, whereas formerly the fourth and fifth showed the largest yield.

Friction condensers are also used under the name of *revolving screens*, though they remain at rest while working. They consist of a heavy wooden axle carrying a damper blade and a number of wooden arms set helically, which continually alter the direction of the vapours and thus assist the deposition of mercury. Three of these screens are superposed in a condenser.

In the case of one furnace, the vapours pass through a condenser containing two water backs, through two condensers containing revolving screens, thence by wooden flues to a number of glass condensers, through wooden flues over 100 feet long into brick towers, and thence through brick flues 650 feet long, built on and in the hill-side, to a chimney 80 feet in height.

Three furnaces deliver their fumes into one tower, which has, at its base, an auxiliary fire or fan to increase the draught when necessary.

It is estimated that the fumes, from the furnace to the chimney top, traverse a distance of nearly 1,000 feet, and pass over a cooling surface of 18,650 square feet.

According to Smedberg, the fumes from the monitor furnaces enter the downtake to the first condenser at 372°C., which they enter at 191°C.; they enter the third brick condenser at 37·8°C., leave the sixth glass condenser at 13·9° and enter the chimney at 13·3°C., only about 0·5° above the external temperature.

In the first brick condenser a small quantity of ore dust, carried over mechanically, is found. It has been occasionally found to contain mercury sulphate.

The interior of the walls &c. of the condensers and flues is covered with a black soot containing carbon and tarry matters and considerable quantities of mercury, principally in the free state. The amount of soot is only one-third that obtained at Idria. The soot obtained from the hot condensers and the flues is dry; that from the glass chambers forms a black mud containing acid waters holding sulphates in solution, and a little free mercury.

It is removed periodically through the man-holes with wooden or indiarubber hoes, and the walls are occasionally washed down with a hose and the whole of the soot removed by men, well masked, who enter the condensers.

From the acid waters the mercury is separated by simple washing. The dry soot is spread on an inclined floor and rubbed with dry wood ashes to brighten the metal. About 4 or 5 p.c. of the total mercury in the ore is thus recovered. The residues are roasted with a fresh portion of furnace charge.

The loss, omitting the temporary loss from absorption by the masonry, &c., is estimated by Christy at 4 or 5 p.c. of the total mercury, the *vapour* loss being about 0·8 p.c. and the *mist* loss about three times that amount. This loss, considering the poverty of the ore, compares most favourably with that at Almaden, and is also lower than that at Idria. *V.* further Rolland (Bull. Soc. d'Encourag. Ind. 1878, 487–514) and Egleston (Trans. Amer. Inst. Min. Engrs. 3, 273–307).

The following description of two continuous furnaces erected by 'El Porvenir' Company in Asturias, for the treatment of quicksilver and arsenical ore, is taken from the *Revista Minera* of Madrid (*v.* S. C. I. 1890, 93, and Eng. and Min. J. 1889, 430). Fig. 13 shows a double retort furnace so constructed that the discharge mouth is partially opened for the entrance of air, the escape of fumes being prevented by a constant draught caused by an hydraulic ventilator. The retorts are of cast iron and have a common hearth on which small coal is burned.

This furnace will treat 1,600 kilos. of rich ore every twenty-four hours, 50 kilos. being introduced in a finely crushed state every hour and a half. Rich ore is supplied in small pieces, and, when containing 15 p.c. or upwards of mercury, is mixed with lime.

The condensing apparatus comprises two large and two smaller chambers, a wooden compartment with a layer of water on the bottom, and the ventilator and tubing which carry the fumes to the chimney. The first condensers collect 90 p.c. of the mercury, and the second condensers retain nearly all the remainder, scarcely 1 kilo. of mercury being collected per annum in the wooden compartment. Rodriguez estimates the loss by this furnace as under 1 p.c., the cost of treatment amounting to one dollar per ton of ore. The cost may be materially reduced by employing six retorts instead of two, to each furnace. The consumption of coal per twenty-four hours is 3½ metric cwts., valued at 57 cents.

Fig. 14 shows a construction of *stack furnace*. The furnace, which is slightly conical, is 2 metres in diameter above the grate, and 1·85 metre at the height of the throat, and terminates in a round arch containing the charging hopper. The lower, or hearth chamber is 2·85 metres in height, the portion above being of the same height. The hearth forms a chamber less in diameter than the rest of the furnace. The grate, whose diameter is 1·1 metre, is at a height of 85 cm. from the floor. The walls continue vertically above the grate for 80 cm. and then form a cone 50 cm. in height and 60 cm. in diameter at the top. The cone is surmounted by a cylinder 60 cm. high and covered by a round arch, through which the combustion products pass from the hearth. This part of the furnace is strengthened by constructing over the grate two low arches sustaining five courses of bricks which uphold the upper portions of the furnace.

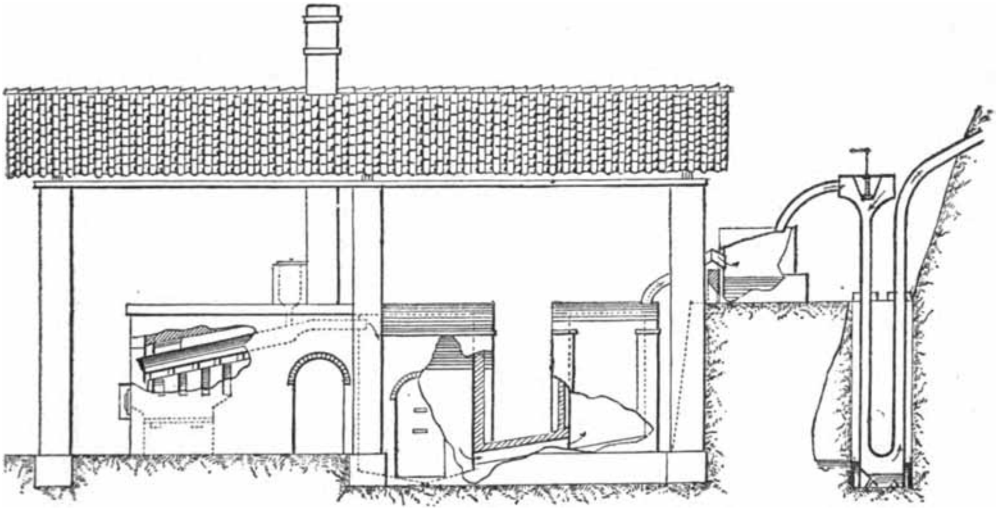


Fig. 13.

The central opening is protected by a cast-iron cap, and the openings beneath it are of angular section, in order that escape of the fumes may proceed during admission of ore to the hearth. The furnace chamber is conical externally and has an iron cover permitting removal of the calcined ore through doors P.

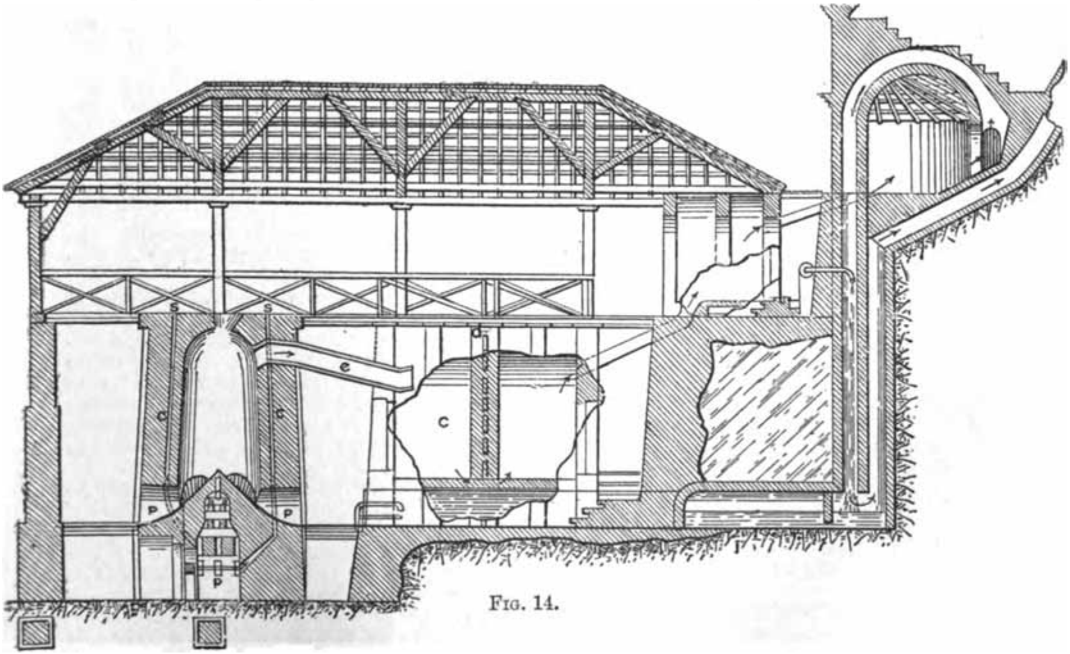


Fig. 14.

The furnace has a lining of firebrick 30 cm. thick and surrounded by four roomy spaces, 10 cm. wide and 80 cm. long, which rise to the top of the body of the furnace and communicate below with the hearth at the level of the grate. A tower of ordinary material 60 cm. in thickness incloses the whole of the furnace. The throat is a cast-iron pipe 50 cm. in diameter and

4 metres long, placed with a slope towards the condensing chambers, on meeting which it branches off to communicate with the two series of condensers.

The condensing apparatus comprises four chambers, each of about 10 metres capacity arranged in pairs to the right and left of the above pipe, whose branches communicate with the upper part of the first chamber of each pair. The chambers communicate through two little openings of rectangular section near the floor, sloping towards the chamber sides and formed by a conduit, below which runs a stream of water.

The chimney is placed on steep ground at a distance of 100 metres, and, in order to minimise smoke, is partially closed at its mouth by loose bricks, over which is placed a layer of coke 30 cm. in thickness.

This furnace calcines 8½ tons of ore per twenty-four hours. Each charge, which consists of lumps of ore from 600–800 c.c. in size or even larger, weighs 443 kilos. and is mixed with a quantity of coke which amounts, for the ore calcined in twenty-four hours, to 42½ kilos. A fresh charge is inserted every seventy-five minutes. The calcined residue contains only from 0·01 to 0·02 p.c. of mercury.

The following shows the recent production in bottles of mercury from some of the largest mines:—

—	1889	1888	1887	1886	1885	1884
	Bottles	Bottles	Bottles	Bottles	Bottles	Bottles
Spanish †	49,778	53,243	51,011	48,537	45,813	48,098
Italian †	10,498	10,460	7,400	8,090	7,888	8,040
Austrian *	14,000	14,000	14,000	14,000	14,370	14,680
Californian	28,000	33,250	33,760	29,981	32,073	31,913
Borneo ‡	1,559	1,559	1,559	1,559	1,559	1,559
Total	103,835	112,512	107,720	102,167	101,703	104,290
Exports from United Kingdom † .	55,366	45,806	64,049	66,974	50,942	50,634
	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.	£ s. d.
Highest prices of Spanish . .	9 15 0	10 10 0	11 5 0	7 10 0	6 17 6	6 15 0
Lowest prices of Spanish . .	7 7 6	6 15 0	6 10 0	5 13 0	5 10 0	5 1 6

From W. T. Sargant & Son's Annual Circular (S. C. I. 9, 129).

* Estimated. † Calculated: November to November. ‡ Average production.

Purification.—Mercury may be freed from mechanical impurities, and from a portion of the metallic impurities, by forcing through chamois leather or by filtering through punctured blotting paper.

From lead, tin, and other metals, it may be separated by distillation under a layer of iron filings to prevent spitting, or, preferably, by distillation *in vacuo.* An effective apparatus for this purpose is described by F. W. Clarke (Proc. Phys. Soc. 5, 328).

It may also be purified by boiling, or digesting in the cold, with frequent shaking, with a solution of mercurous nitrate or with dilute nitric acid. In the latter case mercurous nitrate is first produced, and gradually oxidises and removes the other metals. L. Meyer (Fr. 2, 241) passes the mercury several times in a thin stream into a long column of dilute nitric acid. A solution of ferric chloride may replace the nitric acid or nitrate.

It may also be cleansed by digestion for some days with concentrated cold sulphuric acid. Deville covers the metal in a large separating funnel with the concentrated acid, saturated with mercury sulphate. The purified metal may be removed below, and replaced above after use.

Brühl (B. 12, 204) shakes the metal twice or thrice with an equal volume of a solution of 5 grams potassium bichromate with a few c.c. of sulphuric acid in 1 litre of water. Each shaking is continued until the red chromate at first produced has disappeared, and the solution has become a pure green. It is then washed until free from the fine green precipitate which forms on the surface. The loss of mercury amounts to less than 0·5 p.c.

Pure mercury should run in a spherical form on a rough surface, leaving no 'tail.' When dissolved in nitric acid, evaporated, and ignited, it should be perfectly volatile.

Detection.—Dry solid substances to be tested for mercury are best heated to redness in a narrow glass tube closed at one end, with a little anhydrous sodium carbonate or quicklime. The liberated mercury forms a ring of globules on the cooler parts of the tube.

If the ring be very ill-defined a crystal of iodine may be added and the tube closed. In a few hours the ring, if mercurial, will become converted into the yellow iodide, changing slowly to a scarlet. Merget recommends the use of paper moistened with an ammoniacal solution of silver nitrate as a test for mercurial vapours. It is blackened in presence of a minute trace of mercury.

Even minute traces of this metal may be separated from solution as follows. A piece of gold foil or wire, or bright copper foil, or, preferably (as in Smithson's pile), a tin or zinc wire wrapped round a gold wire, is inserted in the slightly acidulated liquid. In presence of mercury the gold acquires a white coating, sometimes only after two or three hours. The gold is then removed, washed, dried, and heated strongly in a tube, and the metallic ring treated with iodine when necessary. It must be remembered that arsenic will be similarly deposited and volatilised.

Mercurous salts in solution produce a white insoluble precipitate of calomel on addition of hydrochloric acid or a soluble chloride even in the most dilute solutions (distinction from lead). The precipitate is blackened on the addition of ammonia (distinction from silver).

Mercuric salts give, on gradual addition of sulphuretted hydrogen, a white precipitate, changing to yellow, brown, and finally, to black. Potassium iodide produces an intense red precipitate soluble in excess of the mercuric salt or of the precipitant. Stannous chloride produces a white pearly precipitate of mercurous chloride, or when added in excess, a grey precipitate of metallic mercury.

Estimation.—The dry mercurial ore or salt (excluding mercuric iodide) is finely powdered, and about 5 grams is weighed into a basin and mixed with powdered *quicklime*. A piece of combustion tube about 18 inches long is closed at one end and about 2 inches of sodium bicarbonate or of magnesite is added, followed by about 1 inch of quicklime, then by the whole of the mixture of ore and lime, measuring about 5 inches. The basin which contained the ore is rubbed with a small quantity of lime, which is added to the tube, followed by a further amount of quicklime, and finally by a loose plug of asbestos. The tube is then drawn out at the blowpipe, bent at right angles and cut off, leaving the bent portion about 6 inches long. It is then gently tapped to leave a passage for the vapours, and laid in a combustion furnace with its mouth dipping below the surface of water.

The portion of the tube in front of the mixture containing the mercury is first heated to redness, beginning at the asbestos. The ore mixture is then heated to redness. The greater portion of the compound is at once decomposed with liberation of mercury, but those portions which volatilise unchanged are reduced in passing through the heated length of lime.

In a short time the whole is decomposed; the end containing the bicarbonate is then heated, to liberate a current of carbonic dioxide, carrying forward all the mercurial vapours, which condense in the cooler portions of the tube and beneath the water.

The tube is then cut off just above the condensed mercury, which is washed into the water, agitated to produce one globule, washed with clean water, decanted into a crucible, freed from water with filter paper, placed upon a weighed watch glass, dried in a desiccator for one hour, and weighed.

In the case of mercuric iodide the same operations are performed, but the lime, which does not completely decompose this salt, is replaced by copper filings.

All ores of cinnabar, especially those containing less than 2 or 3 p.c. of mercury, may be analysed as follows. The finely-powdered ore, if bituminous, is first extracted with benzene and thoroughly dried. The residue is digested in a solution of barium sulphide, one litre of which contains 50 grams of barium. The filtered solution is treated with hydrochloric acid, and the precipitated mercury sulphide is filtered, dried, digested with carbon bisulphide to remove free sulphur, and dried. For rough estimations this precipitate may at once be weighed (W. J. 1866, 834).

Where greater accuracy is required this sulphide is dissolved in aqua regia, concentrated, mixed with a solution of phosphorous acid, digested in the cold for 12 hours, and the precipitated Hg_2Cl_2 is collected on a weighed filter, washed, dried at 100°C., and weighed.

The phosphorous acid is prepared by the addition of small pieces of phosphorus to a saturated solution of copper sulphate, with frequent agitation, in a closed flask. After a time the mixture of phosphorous and sulphuric acids is decanted from the precipitated copper phosphide, freed from sulphuric acid by the cautious addition of barium hydrate, clarified, and the clear solution of phosphorous acid decanted into a stoppered bottle.

Properties.—Mercury is a silver-white, liquid metal. In extremely thin films it transmits violet light. Its sp.gr. at 0°C. is 13·596 compared with water at 4°C. (Regnault, Balfour-Stewart, Volkmann). Its heat conductivity is low, but greater than that of water. It is constant between 40° and 160°C. (Herwig). Its electric conductivity is $\frac{1}{67}$th that of pure silver (Matthiessen).

Mercury contracts uniformly when cooled, even to the solidifying-point (Ayrton and Perry, P. M. [5] 22, 325). At −38·8°C. it solidifies (Balfour-Stewart), contracting considerably, and forming a tin-white, ductile, malleable, crystalline metal of sp.gr. 14·193 at its m.p. (water at 4° = 1) (Mallet, P. M. [5] 4, 145).

It boils at 357·25°C. under 760 mm. pressure (Regnault), forming a colourless vapour of density 100·93 corresponding to a molecular weight of 201·86. Its molecule, therefore, appears to contain only one atom at that temperature. Mercury evolves vapour even below 40°C. (Merget). Revised tables of vapour pressures from 40°–512°C. are given by Ramsay and Young (C. J. 1886, 46, 49, 50).

It is unaltered in air, oxygen, or ordinary inert gases, and in nitrous and nitric oxides and alcohol. When heated in air to near the boiling-point it becomes gradually converted into the red oxide, which is again reduced to metal at a temperature below redness.

When agitated with turpentine, oils, &c., or triturated with antimonious or other sulphide, or with a fine powder such as chalk, it forms a fine grey powder, consisting of minute globules from ·002 to ·004 mm. in diameter, containing a little oxide. This operation, known as the *deadening* of mercury, is used in the preparation of ointments and pills. Such mercury has poisonous properties, though, in the massive form the metal appears to be harmless.

This *deadening* under the influence of sulphides is the cause of considerable loss of mercury in the amalgamation of pyritic or sulphurous ores of gold and silver.

Hydrochloric acid has no action on mercury. Dilute sulphuric acid attacks it slowly; the strong acid has no action in the cold, but when warmed forms the sulphate, with evolution of sulphurous anhydride. Cold dilute nitric acid dissolves it slowly; the strong acid acts rapidly with evolution of nitric oxide fumes. Aqua regia converts it into the chloride. Mercury on warming is quickly converted into the dichloride by the action of chlorine gas.

Mercury is used on the large scale for the separation of gold and silver from their ores; for the manufacture of vermilion; in chemical and physical operations on account of its fluidity and non-solvent powers; for the preparation of its salts, and in medicine.

Alloys or amalgams.—Mercury alloys with most metals. The combination may be produced by direct action of mercury on the metal; by addition of mercury or the mercury-sodium amalgam to a solution of a metallic salt, or of a metal to a mercurial solution, or by the electrolysis of metallic solutions, using a negative pole of mercury.

The combination is accompanied in some cases by the evolution of heat, as in the case of the alkali metals, or with absorption of heat, as with tin. In the case of tin and lead, and especially of silver and gold, marked contraction takes place.

The alloys are liquid when containing an excess of mercury. The solid alloys are frequently crystalline. The liquids vary but little in conductivity from pure mercury, but the solids are very variable in this respect.

The alloys with lead, tin, cadmium, and bismuth evolve the whole of their mercury when heated to 440°C.; those of gold, silver, copper, and the alkalis retain a portion at that temperature, usually in atomic proportions. It has been shown by Joule (Mems. Manch. Lit. and Phil. Soc. [3] 2, 115), that even those in atomic proportions can be partially decomposed by prolonged or extreme pressure.

The presence of $\frac{1}{10,000}$ part of lead is said to reduce the distillation speed of mercury by 30 p.c., while gold, silver, arsenic, &c., have not this property, and the presence of platinum is said to have the opposite effect (Gmelin-Kraut).

Many of the amalgams are used in the arts. Tin amalgam is employed for silvering mirrors; that of tin and zinc for the rubbers of electrical machines; those of cadmium, copper, or gold, or of gold, silver, and tin, are used in dentistry.

Many of these amalgams have been described under their respective metals.

With *copper*, mercury may be united directly, or by addition of copper to a solution of mercurous nitrate or by electrolysis of a copper sulphate solution, using a negative pole of mercury. The amalgams containing 25–33 p.c. of copper are harder than tin. They possess the property of becoming soft and plastic when heated to 100°C. and worked in a mortar, but still possess the same density. In this condition they may be used for closing bottles, tubes, &c. In 24 hours or less, they regain their former hardness, but may at any time be softened by warming and working in a mortar. On this account the amalgam is sometimes used as a tooth-stopping; 1 part of mercuric sulphate is rubbed with 1 part of finely divided copper, moistened with warm water, well washed, and pressed in chamois leather to remove excess of mercury, and used while soft.

When heated to 440°C. an alloy remains corresponding to $Cu_{19}Hg$ (De Souza, B. 88, 166).

Silver and mercury combine slowly in the cold, rapidly when finely divided silver is added to heated mercury; considerable contraction takes place. Mercury precipitates silver from weak, slightly acid solutions of the nitrate, as a crystalline amalgam known as the *silver tree.* When heated to 440°C., the residue corresponds to $Ag_{12}Hg$ (De Souza).

Silver amalgam occurs in octahedra and other cubic forms at Moschellandsberg in the Bavarian Palatinate, having nearly the composition Ag_2Hg_2 and Ag_2Hg_3. An amalgam containing *silver* and *gold* occurs with native platinum in Choco, New Granada.

With *gold*, amalgamation is easy and rapid. Gold-leaf or foil absorbs minute traces of mercury vapours, and removes mercury from weak solutions. The whole of the mercury is liberated on strongly heating.

Mercury will remain liquid while still containing a large proportion of *gold*, but becomes stiff with excess. When the liquid amalgam is pressed in chamois leather, the excess of mercury is removed, leaving a white pasty mass containing 2 parts gold and 1 part mercury.

The amalgam left on heating to 440°C. corresponds to Au_8Hg. Henry has obtained the same alloy in lustrous four-sided prisms (P. M. [4] 9, 468).

For stopping teeth 1 part gold and 2 parts silver are melted together, cooled, and filed to a powder. The required amount of the filings is mixed with sufficient mercury to form a paste, pressed in chamois leather to remove excess of mercury, worked in the hand and forced into the opening while warm.

An amalgam of 1 part gold, 3 parts silver, and 2 parts tin, similarly treated, forms a very satisfactory stopping.

With *tin* combination is rapid; contraction always takes place. The silvering of mirrors consists of this amalgam. An alloy of 2 parts tin and 1 part cadmium in filings, treated as above, is nearly equal to that containing gold for dentistry.

The amalgam for the rubbers of electrical machines is prepared by fusing 1 part tin with 1 part zinc, and adding 2 parts mercury; the powdered alloy is mixed with pure fat before application. Sometimes the proportions used are 1 tin, 2 zinc, and 5 mercury.

With *zinc* combination is slow in the cold, more rapid near the boiling-point of mercury, or when that metal is added to molten zinc. In presence of an acid, or when the surface of the zinc is quite clean, amalgamation is rapid.

With 1 part zinc and 4 or 5 parts mercury, the amalgam is brittle, melting at 315°C. and burning brilliantly at a strong red heat.

Zinc amalgams are but slowly affected by dilute hydrochloric or sulphuric acids. Mercury is therefore used for amalgamating the zinc plates of galvanic batteries.

With *potassium* combination takes place in the cold with evolution of much heat. When containing 70-96 parts of mercury to 1 part of potassium, the amalgam is solid and crystalline. With 30 parts of mercury it is hard and brittle. The amalgams fuse at a gentle heat; that containing 36 parts of mercury melts at about 75°C. When heated to 440°C., they all leave a crystalline amalgam containing HgK_2; below a red heat the whole of the mercury is evolved.

In damp air or in water, hydrogen is evolved, with liberation of mercury and formation of potassium hydrate. On this account potassium amalgam is a powerful reducing agent.

With *sodium* the combination resembles that with potassium. Small pieces of sodium added to gently warmed mercury, combine with flashes of light and slight explosion. With 30 parts mercury to 1 part sodium, the alloy is hard, crystalline and laminar; with 32 parts mercury it melts at 150 to 160°C.; with 40 parts mercury it is softer, and with 60 parts it is pasty at 21°C. When heated to 440°C., a crystalline amalgam is left corresponding to Na_3Hg, which ignites on exposure to air. Sodium amalgams are largely used as reducing agents. When added to solutions of many metallic salts, the metals are precipitated and form amalgams, while the sodium enters into solution.

Ammonium amalgam is produced when an electric current is passed through a solution of ammonium chloride or ammonia, using a negative pole of mercury; or when sodium amalgam is placed in a concentrated solution of ammonium chloride.

In either case the mercury swells to a large bulk, frequently to 20 times its original volume, forming a shining pasty mass which may be lifted as a whole and worked in the hand. At the low temperature produced by the addition of ether to solid carbon dioxide, it forms a solid, dark-grey mass, crystallising in cubes, and having no tendency to decompose. At higher temperatures, however, even at 29°C., it evolves a mixture of ammonia and hydrogen, leaving a residue of pure mercury (*cf.* p. 84, vol. i.).

Iron does not unite directly with mercury. The amalgam may be produced by addition of sodium amalgam to a saturated solution of ferrous sulphate.

By electrolysis of ferrous sulphate solution, using a negative pole of mercury, Joule has prepared it in greyish white crystals and in other forms, quite magnetic, even when containing only a small amount of iron.

Under water, or when violently shaken, it is rapidly decomposed into mercury and a black powder containing the iron (*v.* AMALGAM, vol. i.).

COMPOUNDS OF MERCURY.

Mercury forms two oxides, *mercurous* and *mercuric* oxides, each of which forms a stable series of salts.

Mercurous oxide Hg_2O is obtained as a blackish-brown powder by the addition of alkalis to a solution of mercurous salt, or by triturating a solution of alkali with calomel. It is washed, dried spontaneously, and kept in the dark. By the action of light or of a gentle heat it is decomposed into the red oxide and mercury.

Mercuric oxide, *Red oxide of mercury, Red precipitate,* HgO. This oxide is slowly produced when the metal is heated in air to near the boiling-point. It is usually prepared by heating the nitrate until nitrous fumes cease to be evolved, but not sufficiently to decompose the oxide itself. When prepared slowly on the large scale the oxide is obtained in fine brick-red crystalline plates of sp.gr. 11·163 (Playfair and Joule).

By precipitating a mercuric salt with potash, the oxide is obtained as an orange-yellow powder of the same composition, but more easily acted on by reagents. With oxalic acid it produces the oxalate, while the crystalline oxide is not so affected. When heated with mercuric chloride solution it rapidly forms an oxychloride; the crystalline form is only slowly converted. The amorphous oxide is also more easily decomposed by heat.

Mercuric oxide is a powerful poison. It dissolves in about 20,000 parts of water after standing (Wallace). When heated it becomes of a bright red, and finally nearly black, but regains its colour on cooling. When further heated, it is decomposed into mercury and oxygen. By this reaction oxygen was first prepared by Priestley.

When heated with zinc, tin, or antimony filings, the oxide is reduced to metal with incandescence. When added to fused sodium the action is still more intense. The mixture with sulphur explodes violently when heated. Mixed with phosphorus it detonates when struck. At a red heat it is converted by chlorine into mercuric chloride, with liberation of oxygen. It dissolves in fused potash with formation of a double oxide, without evolution of gas.

Mercuric oxide is frequently used as an oxidising agent in chemical operations.

Mercuric sulphide, *Vermilion, Cinnabar,* HgS. The whole of the mercury of commerce is produced from the sulphide. Native cinnabar is not of sufficient purity to be used directly as a pigment.

The sulphide is produced as a black precipitate on passing sulphuretted hydrogen through a solution of a mercuric salt. It is converted into the red variety on sublimation.

A black powder, consisting of a mixture of mercuric sulphide and sulphur, is prepared by triturating mercury with sulphur. It was formerly used in medicine as *æthiops mineral.*

The red variety is prepared on the large scale, and used as a pigment. Two distinct methods are adopted, the *dry* and the *wet* processes.

Dry processes.—The following method was formerly largely used in secret in Holland. 1,080 lbs. of mercury and 150 lbs. of powdered sifted sulphur are moderately heated in an iron pan with constant stirring, and the black *æthiops* obtained is cooled and powdered. This is introduced in charges of about 25 lbs. four times an hour into long subliming pots of refractory clay, each holding about 410 lbs., heated from below to about two-thirds of their height. As each charge is added it ignites, and a long flame escapes from the pot; when this has subsided, the pot is covered with an iron plate. The operation occupies about thirty-six hours. The pots are cooled and broken, and the vermilion, which is principally in the upper portions, is ground with water between stones, sifted, elutriated, and dried.

It is said that if 1 part of antimonious sulphide be added to the mixture of sulphur and mercury before sublimation, and the vermilion be digested with potassium sulphide, an improved pigment is obtained which contains no antimony.

At *Idria*, a mixture of 8 lbs. sulphur and 42 lbs. mercury is placed in a well-bound cask, which is rotated for some hours until the contents consist of a uniform brownish powder.

A number of vertical, cast-iron cylindrical retorts heated to dull redness are charged with the mixture, and immediately covered. When crackling has ceased the covers are replaced by stoneware necks, each connected with a tube and receiver. The fire is then increased to drive the whole of the sulphide from the retort.

When cooled the necks are taken off, and the cake of vermilion removed. That nearest the retort is best, while that in the receiver contains free sulphur, and is resublimed with a fresh charge. The cakes are broken, ground with water, boiled with sodium hydrate solution, washed and dried.

The *Chinese* vermilion is celebrated for its fine colour, which inclines to carmine. It is said to be prepared as follows :—

About half a bottle (38 lbs.) of mercury and 17⅓ lbs. of sulphur are mixed in an iron pan, about 25 inches wide and 7 or eight inches deep, heated by charcoal. When melted, it is stirred with an iron spatula, and the remainder of the bottle of mercury is gradually added. When the metal has disappeared it is removed from the fire, cooled by the addition of a little water, rapidly stirred, and coarsely powdered. The reddish or black semicrystalline powder, which contains free mercury and sulphur, is placed in a fixed iron pan, and covered with porcelain tiles 8 inches diameter (many of which are broken), arranged in the shape of a dome. The whole is covered by a pan 4 inches less in diameter than the fixed one, to which it is luted by clay, leaving four holes in the luting for the escape of gases. The charcoal fire is then lighted and kept fiercely burning for eighteen hours; blue flames are seen burning round the holes, showing loss of sulphur and of mercury. The fires are then allowed to die out and the pans to cool. Most of the vermilion is found adherent to the porcelain, and is removed. That attached to the iron is inferior, and is made with the other waste into cakes with alum and glue water, dried, and resublimed. The sulphide on the porcelain is blood-red and crystalline. It is powdered and ground with water in a handmill between stones, and washed into a vessel. At the close of a day's work a solution of alum and glue (1 ounce of each to 1 gallon of solution) is stirred well with the powder, and the whole is allowed to stand until morning. The glue tends to lengthen the period of deposition, and to render the stratification into the various qualities more perfect. The alum is said to improve the colour. The liquid is decanted, and the upper portions of the deposit are set aside. The lower parts are reground and treated as before, the grinding being sometimes repeated several times. The fine vermilion is stirred in water and settled, and the water is decanted. The residue is dried in the open air, powdered, sifted through muslin, and packed in papers holding about 1⅓ ounce each (*v.* C. N. 50, 77, and S. C. I. 1, 195). It is used for making Chinese red-ink ; for painting on porcelain and wood and colouring candles and paper. Most of the numerous temples throughout China are painted red, and everything lucky and pleasant among the Chinese is of vermilion colour.

It is said that China imported in 1880 mercury to the value of 170,032 dollars, the whole of which was converted into vermilion.

Wet processes.—These processes all depend on the action of alkaline sulphides on the amorphous mercury sulphide. The temperature adopted largely influences the colour.

The action of these sulphides is attributed by Ditte (C. R. 98, 1380) to the alternate production and decomposition of a double sulphide of mercury and alkali. In the case of potassium sulphide the compound $K_2S, 5HgS$ is first produced, and is decomposed at about 45°C. (the temperature generally employed), with decomposition of the *red crystalline* mercuric sulphide, while the liberated alkaline sulphide dissolves a further amount of the more readily attacked amorphous sulphide, and reforms the double sulphide, which is again decomposed as before.

In order to prepare a polysulphide free from hyposulphite (which is said to exert an injurious action on the colour), potassium sulphate is converted into sulphide by ignition with carbon. The mass is extracted with water, and boiled with sulphur out of contact with air.

Of this strong solution 2¼ kilos. is digested and agitated with 1 kilo. sulphur and 5 kilos. mercury at a gentle heat. The mixture gradually becomes heated, and in about two hours acquires a greenish-brown colour. After a further period of two hours it becomes of a rich brown, and is allowed to cool to 50°C., and is maintained at that temperature for three or four days with frequent agitation. A fine-coloured vermilion gradually settles down; it is washed with potash, then with dilute nitric acid, and finally with water.

According to Liebig, a fine vermilion is produced by immersing recently precipitated *white precipitate* in a solution of ammonium polysulphide. The mixture at first produced is black, but when heated to about 45°C. gradually acquires a fine colour resembling that of Chinese vermilion. It may be digested with potash, and washed to improve the colour.

Hausmann (B. 7, 1746) adds excess of dilute ammonia to a solution of mercuric chloride, and dissolves the precipitated *mercuric ammonium chloride* in a slight excess of sodium hyposulphite. On warming to 70° or 80°C. the vermilion begins to precipitate. The heat is continued until the mass has become pasty, the sulphide is then separated as usual. The above temperature and the presence of the ammonia and ammonium chloride is said to be essential.

One of the best processes is that of Brunner. A mixture of 100 parts mercury with 38 parts sulphur (flowers) is triturated for some hours, mixed with a solution of 25 parts potash in 150 parts water, and digested at a temperature below 45°C., keeping the liquid at constant volume as it evaporates.

After two or three hours it becomes brownish, and then gradually brightens. The temperature must be carefully regulated and the volume kept constant, or the precipitate loses its pulverulent character and becomes inferior in colour. At the proper point, usually after about eight hours, the heating is stopped and the contents are washed as quickly as possible, as the further action of the potash would produce a brown colour. It is lixiviated to separate any black sulphide, and dried.

The method of Gauthier Bouchard is strongly recommended. Concentrated ammonia solution is saturated with sulphuretted hydrogen, and 400 c.c. of the solution is digested in a stone bottle with flowers of sulphur, with production of a solution of ammonium sulphide of sp.gr. 1·034. This is mixed with 200 grams of sulphur and 1,000 grams of mercury (as pure as possible) agitated well in a closed vessel for about seven hours, and finally heated for three or four hours to 50°C. The liquid is decanted and the residue is washed with water, followed by dilute nitric acid and finally by water.

Vermilion is adulterated with red lead, red ochre, chrome red, and frequently with gypsum. These all remain on volatilisation of the vermilion in a glass tube. Dragon's blood, if present, gives a characteristic odour on heating; it also dissolves in alcohol with a red colour. Chinese vermilion usually contains a little glue, which is not, however, an adulteration.

Mercuric sulphide when heated in the air is reduced to metal with formation of sulphurous oxide. With lime, alkaline carbonates, or metals such as iron, copper, and tin, it is reduced with formation of alkaline or metallic sulphide. When heated with litharge both lead and mercury are reduced, the oxygen and sulphur combining, and passing off as sulphurous oxide.

If boiled in water with powdered zinc, metallic mercury is liberated. A similar but slower action occurs with copper.

Concentrated nitric acid has no action except after prolonged heating. It is then converted—especially if freshly precipitated—into a white insoluble compound containing both sulphide and nitrate of mercury. It dissolves easily in aqua regia and in cold concentrated hydriodic acid. Barium sulphide readily dissolves it.

Mercurous chloride, *Calomel,* Hg_2Cl_2.

Calomel occurs in small quantities as *horn mercury* with other mercurial ores.

It may be prepared by addition of an alkaline chloride to a solution of mercurous nitrate or other mercurous salt. The precipitate is washed well to remove the alkaline chloride, which if allowed to remain would render the calomel slightly soluble. It may be prepared on the large scale by mixing 17 parts of corrosive sublimate with a little alcohol or water to prevent the escape of irritating fumes, and rubbing in 13 parts of mercury until *deadened.* The mixture is then sublimed in glass flasks in the upper portion of which the calomel condenses as a solid, translucent, fibrous cake. The flasks are broken and the cake is removed, ground to a powder, washed repeatedly with boiling water to remove mercuric chloride, and dried. The powder has usually a slight yellowish tinge.

It is also prepared from the sulphate; 1 kilo. of mercury is mixed with 1·5 kilos. of concentrated sulphuric acid in an iron boiler, gently heated until the fumes of sulphurous oxide cease to escape, and evaporated to dryness. It is then mixed with 1 kilo. of mercury and 1½ kilos. of common salt until *deadened,* and is sublimed as usual.

Instead of condensing the calomel in a cake, the vapours may be led into chambers containing air or steam, in which it falls as a very fine powder, which requires no grinding. Sometimes the distillation is conducted in an iron tube whose mouth enters the condenser.

At Apothecaries' Hall the proportions used are 62 parts of mercury sulphate, 40⅓ parts of mercury, and 34 parts of common salt.

In preparing calomel by the wet way, 9 parts of mercury are digested in 8 parts of nitric acid (sp.gr. 1·2) with the aid of heat towards the end, until no more dissolves. The decanted solution is mixed with a boiling solution containing 8 parts of common salt in 64 parts of water and a few drops of hydrochloric acid. The precipitate is *well* washed with water. This form is said to be more effective for medicinal purposes than that prepared in the dry way.

Calomel is a heavy, white, tasteless powder, insoluble in water, alcohol, or dilute nitric acid. It crystallises in four-sided prisms terminating in pyramids. At 400-500°C. it volatilises without fusion. The vapour appears to contain free mercury.

By treatment with alkalis and alkaline carbonates it is converted into mercurous oxide, ammonia converts it into black mercurous ammonium chloride. By digestion with ammonium chloride it is gradually converted into corrosive sublimate. Hydrochloric acid or sodium chloride acts less rapidly. The prolonged action of steam, hot water, or hot air has a similar effect.

Calomel is largely used in medicine. The usual adulterations or impurities are corrosive sublimate, ammonium and sodium chlorides, lead and calcium carbonates and barium sulphate. The last three may be distinguished by their non-volatility, the others by their solublity in water or alcohol. According to Bonnewyn, if the calomel be shaken with a little alcohol and a polished knife-blade be inserted, it will be blackened in presence of $\frac{1}{50000}$th part of corrosive sublimate.

Mercuric chloride, *Corrosive sublimate,* $HgCl_2$. Mercury is converted into this salt when acted on by chlorine or aqua regia.

On the large scale it is prepared by distilling mercuric sulphate with common salt. Mercury is gently heated with concentrated sulphuric acid in an iron boiler until sulphurous oxide ceases to be evolved. The whole of the metal having dissolved, a slight excess of sulphuric acid is added to ensure the absence of mercurous sulphate, and a portion is tested by the addition of sodium chloride. If a precipitate of calomel falls, more acid is added. The mixture is evaporated and thoroughly dried. 20 parts of the sulphate is mixed intimately with 8 parts of sodium chloride and 1 part of manganese dioxide (to minimise the production of calomel) and introduced into glass subliming pots which are placed on iron plates, surrounded by sand to the necks and gently heated to remove moisture, which passes through hoods placed over the necks, into a flue.

The moisture being removed, the hoods are replaced by small inverted conical condensers. Sufficient sand is then removed to uncover the upper half of the flasks, and the heat is increased until the whole has sublimed. The heat is finally raised sufficiently to render the sublimate coherent, but not to melt it. When cooled, the upper half of the flask is cracked away and the cake of sublimate is removed.

On the lower part of the cake is frequently found a small quantity of the less volatile *calomel*; this is removed and added to a subsequent sublimation. Wagner (D. P. J. 186, 135) recommends for the preparation on the large scale the decomposition of *turpeth mineral* (*v. Mercuric sulphate*) with hydrochloric acid. Mercuric chloride is thus obtained in a solution of sulphuric acid containing excess of mercuric oxide and is removed by crystallisation:

$$HgSO_4 2HgO + 2HCl = HgCl_2 + H_2SO_4 + 2HgO.$$

For the crude salt, he precipitates mercuric oxide by the addition of sodium hydrate to mercuric nitrate and digests the precipitate with crude magnesium chloride (the mother-liquor from *carnallite*). Where the presence of potassium chloride is not injurious the carnallite itself may be used, in which case the crystals obtained on evaporation contain $KCl, HgCl_2H_2O$.

Mercuric chloride occurs as a white, satiny, translucent mass, or, when crystallised from solutions, as needles or four-sided prisms. It fuses at 288°C. (Carnelley) and boils at 303°C. (Carnelley and Williams).

100 parts of water dissolve at 10°C. 6·57 parts, and at 100°C. 53·96 parts of the salt. The solution is acid to test-papers. In presence of other chlorides, especially those of the alkalis, its solubility is increased on account of the formation of double chlorides. It *gradually* deposits calomel on exposure to light. The solution is highly poisonous, the best antidote is the white of egg, as the salt forms an insoluble precipitate with albumen. Mercuric chloride dissolves in 3 parts of cold alcohol and in about 1½ parts of boiling alcohol. It is soluble in 4 parts of cold ether; ether will remove it from aqueous solution on agitation.

In warm hydrochloric acid it dissolves, and forms crystals on cooling, which contain hydrochloric acid. On exposure to air they effloresce, losing the acid and reproducing the normal chloride. In nitric acid it dissolves, and crystallises out on cooling. Sulphuric acid has no action.

When boiled with mercuric oxide it produces a number of oxychlorides.

The dry salt, heated with arsenic, zinc, tin, &c., is reduced to calomel or mercury. Stannous chloride solution precipitates calomel and mercury from solutions of the salt.

Corrosive sublimate is used in medicine. It is a powerful antiseptic and is largely used by naturalists &c. for the preservation of specimens. It was formerly employed for the preservation of wood, but is now entirely superseded by creosote in this country.

Mercuric ammonium chloride, *White precipitate*, NH_2HgCl, is prepared by the addition of ammonia to a solution of mercuric chloride. For medicinal purposes 1 ounce of mercuric chloride is dissolved in 3 quarts of water, and to the cool solution 8 fluid ounces of concentrated ammonia is added with frequent agitation, and the precipitate is washed and dried.

It is a white, inodorous, highly poisonous powder, totally volatile on heating, slightly soluble in boiling water, easily soluble in nitric, hydrochloric and sulphuric acids, insoluble in alcohol.

Mercurous iodide Hg_2I_2 is a green insoluble powder employed medicinally. It is prepared by triturating a mixture of 5 parts iodine and 8 parts mercury, moistened with alcohol, or by precipitation of a mercurous salt with potassium iodide. When heated gradually, it is decomposed into the red iodide and mercury. It dissolves slightly in various oils. The best solvent is castor oil, of which 100 parts dissolves 2 parts of the iodide.

Mercuric iodide HgI_2. A mixture of 5 parts iodine and 4 parts mercury is moistened with a little alcohol, triturated, and sublimed. Dublanc pours 1 kilo. of alcohol upon 100 grams of mercury and adds 124 grams of iodine in 10 successive portions, triturating each time until the alcohol becomes colourless. The last 4 grams usually produce a permanent colour. The precipitate is then washed with alcohol and dried.

In the wet way, which is the best, a solution of 10 parts potassium iodide is added to a solution of 8 parts mercuric chloride, and the precipitate, which is salmon-coloured at first but soon becomes red and crystalline, is washed. A slight excess of either the chloride or iodide will redissolve a portion of the precipitate.

It forms quadratic prisms and pyramids, which melt at 238° and boil at 339–359°C. (Carnelley and Williams). 1 litre of absolute alcohol at 18°C. dissolves 11·18 grams of the salt; 80 p.c. alcohol dissolves only 2·86 grams. It is almost insoluble in water; 1 litre at 17·5° dissolves 0·0403 grams (Bourgoin, Bl. 42, 620).

In potassium or other alkaline iodide, it dissolves freely with formation of a double iodide.

The solution in potassium iodide is a more powerful antiseptic than mercuric chloride. It has been employed in the preparation of an antiseptic soap (Thomson, S. C. I. 1888, 192). An alkaline solution of mercuric iodide in potassium iodide is employed as a delicate test for ammonia and its compounds, being known as *Nessler's solution*.

In mercuric chloride it dissolves readily, forming a double chloride and iodide.

When the red iodide is heated to about 150°C. it becomes converted into an allotropic form condensing in yellow crystals, which may retain their colour for a considerable time but ultimately (rapidly if rubbed) become again converted into the red variety with a crackling sound, and with evolution of heat (*v.* Rodwell and Elder, Pr. 28, 284).

When triturated with certain metals, mercury is liberated. This takes place with incandescence when potassium is used.

Mercuric bromide $HgBr_2$ may be prepared by the combination of mercury with bromine, or by dissolving mercuric oxide in hydrobromic acid. It forms glistening scales which melt at 244°C. and boil at 309°C. (Carnelley and Williams). They are soluble in water and alcohol.

Mercurous sulphate $Hg_2(SO_4)_2$ is prepared by dissolving 2 parts mercury in 3 parts sulphuric acid with the aid of a gentle heat, or by the addition of sulphuric acid to a solution of mercurous nitrate.

It is used in Marié-Davy's sulphate of mercury battery.

Mercuric sulphate $HgSO_4$ is prepared by dissolving mercury in strong sulphuric acid, with the aid of heat. Its preparation has been described under *Mercuric chloride*.

It is a white crystalline powder, soluble in sodium chloride solution. When heated with water it produces a yellow basic sulphate $HgSO_4 2HgO$ known as *turpeth* or *turbith mineral* which is soluble in 2,000 parts of cold and 600 parts of hot water.

From solution in sulphuric acid it crystallises in small, silvery, stellate plates. When strongly heated, it becomes reduced to mercurous sulphate with evolution of oxygen, mercury, and sulphurous oxide.

Nitrates. Several nitrates of mercury are known. When excess of mercury is dissolved in a cold mixture of 1 part nitric acid and 4 parts water, the *mercurous* salt is formed. If the acid be sufficiently strong to effervesce, or be used in excess, or if the mixture be heated, *mercuric* nitrate is produced.

Mercurous nitrate $Hg_2(NO_3)_2$ forms monoclinic tables containing 2 molecules of water. They effloresce and become anhydrous in dry air. In a small quantity of water they dissolve, but the solution is decomposed by excess of water with precipitation of an insoluble yellow basic salt.

Mercuric nitrate $Hg(NO_3)_2$ is produced by boiling mercury with nitric acid until the solution no longer gives a precipitate with sodium chloride. Large crystals containing

$$2Hg(NO_3)_2H_2O$$

separate on concentration, while the mother-liquor contains $Hg(NO_3)_2 2H_2O$ and, on evaporation, deposits a basic salt in prisms which when washed give other more basic salts, and finally mercuric oxide.

Mercuric cyanide $Hg(CN)_2$ is prepared by boiling a solution of 1 part potassium ferrocyanide and 2 parts mercuric sulphate in 7 parts water:

$$2K_4Fe(CN)_6 + 7HgSO_4$$
$$= 6Hg(CN)_2 + 4K_2SO_4 + Fe_2(SO_4)_3 + Hg.$$

It crystallises in white needles or quadratic prisms soluble in 8 parts of cold water, insoluble in absolute alcohol. When ignited, it decomposes with evolution of cyanogen. It is decomposed with formation of hydrocyanic acid by hydrochloric, hydrobromic, and hydriodic acids, or by sulphuretted hydrogen but not by dilute sulphuric or nitric acids.

Mercuric thiocyanate $Hg(CNS)_2$ is prepared by the addition of an excess of mercuric chloride to a solution of ammonium thiocyanate. It forms a white crystalline precipitate which burns freely when ignited and forms a most voluminous ash with evolution of mercurial vapours.

It is occasionally made into a thick paste with gum and worked into pilules which when dried are sold as *Pharaoh's serpents' eggs*.

MERCURIC FULMINATE *v.* FULMINIC ACID; also EXPLOSIVES.

MESITE *v.* WOOD, DISTILLATION OF.

MESITOL *v.* PHENOL AND ITS HOMOLOGUES.

MESITYLENE *v.* CUMENES.

MESORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

META-ARABIC ACID *v.* GUMS.

METACETONE. Fremy obtained by distilling sugar with lime, a substance to which he gave the name *metacetone* and the formula $C_6H_{10}O$. Fischer and Laycock find that this body is in reality a mixture of *propylaldehyde*, *dimethylfurfuran*, a third substance with the properties of a hydrocarbon, and a number of other lower and higher boiling homologues. Fischer and Laycock distilled 100 kilos. of sugar and 300 kilos. of burnt lime, and collected the distillate in fractions. Fraction *a*, distilling below 65°, combined partly with phenylhydrazine, and this consisted of the hydrazone of propylaldehyde. The distillate from this, and boiling at 25°-45°, consisted of furfuran, and that boiling at 45°-65° is probably methylfurfuran. Fraction *b*, distilling at 65°-115°, was treated like fraction *a*, phenylhydrazine being added, and the product distilled. The distillate consisted of a hydrocarbon and a substance which dissolved on heating with dilute hydrochloric acid to 170°, forming acetonylacetone, and which is probably dimethylfurfuran. The residue, which combined with phenylhydrazine is the hydrazone of propylaldehyde. The fraction boiling above 115° is a complex mixture, consisting of higher homologues of furfuran and aldehydes, which could be removed with sodium bisulphite.

Fischer and Laycock have investigated wood tar, and found that this likewise contains propylaldehyde and dimethylfurfuran (B. 22, 101-105).

METACETONIC ACID. *Propionic acid* *v.* FATTY ACIDS.

METALDEHYDE *v.* ALDEHYDE.

METANIL YELLOW *v.* AZO- COLOURING MATTERS.

METARABIN *v.* GUMS.

METAXYLORCINOL *v.* PHENOL AND ITS HOMOLOGUES.

METHANE. *Methyl hydride* *v.* METHYL COMPOUNDS.

METHYL CH_3 is a univalent, compound radicle, not known in the free state. The compound C_2H_6 discovered by Frankland and Kolbe (C. J. 1, 60), was called methyl, and believed to be the free base, and even when its molecule was recognised as dimethyl $(CH_3)_2$, it was at first thought to be distinct from ethane, the gas obtained by Frankland from ethyl iodide by heating with zinc and water. It was, however, proved to be identical with that body by Schorlemmer (C. J. 17, 262).

METHYL COMPOUNDS.

Methyl acetate *v.* *Alkyl acetates*, art. ACETIC ACID.

Methyl alcohol CH_3OH. *Methyl hydrate, wood spirit, pyroxylic spirit, wood naphtha, hydroxymethane.* B.p. 66·78° (Regnault); 64·8° (Vincent and Delachanal, Bl. 33, 469); 65·75°-66·25° (Grodzki and Krämer, B. 7, 1495); 65·8-66° cor. (Perkin, C. J. 45, 465); 64·96° at 760 mm.

(Dittmar and Fawsitt, Tr. E. 33, 509); 64·8° at 763 mm. (Schiff, A. 220, 100). Sp.gr. $\frac{0^\circ}{} = \cdot8142$ (Kopp); $\frac{15^\circ}{15^\circ} = \cdot79726$, $\frac{25^\circ}{25^\circ} = \cdot78941$ (P.); $64\cdot\frac{8^\circ}{4^\circ} = \cdot7476$ (Schiff); $\frac{0^\circ}{4^\circ} = \cdot81015$, $\frac{15\cdot56^\circ}{4^\circ} = \cdot79589$ (Dittmar and Fawsitt, Tr. E. 33, 509). Capillarity constant at b.p. $a^2 = 5\cdot107$ (Schiff, A. 223, 69), M.M. at 18·7° = 1·640° (P.). Vap. pressure at 15° = 72·4 mm.; at 29·3° = 153·4 mm., at 43·0° = 292·4 mm., at 53·9° = 470·3 mm., at 65·4° = 756·6 mm. (Konowalow, P. [2] 14, 40); H.C. = 170·6 (Stohmann, Kleber, and Langbein, J. pr. [2] 40, 341); H.F. = 61·4 (S., K., and L.)

Boyle found that the liquid obtained by distilling wood contained two constituents, an acid portion and a neutral spirit.

Various conjectures were made as to the nature of this 'spirit,' the first investigation of which was made by Dumas and Peligot in 1834 (A. Ch. 58, 5; 61, 193). They gave it the name 'methyl alcohol' (μέθυ, wine; ὕλη, wood).

Formation.—By the dry distillation of wood, of beet-sugar molasses (Vincent, Bl. 27, 148), or of calcium formate (Paterno and Lieben, A. 167, 293); Friedel and Silva, J. 1873, 526).

Preparation.—Methyl alcohol is prepared on the large scale from the distillate from wood, which contains various tarry matters, acetic acid, and the methyl alcohol. The distillates from the wood are allowed to stand for some time, when the tarry, resinous, and oily matters precipitate; the supernatant liquid is then filtered through gravel into another vessel, from which it is either distilled at once or with previous neutralisation with lime. The distillation is effected in the first case in copper stills, and heat is applied by coils of copper pipes conveying steam; in the second case boilers of sheet iron are employed, and the heat applied by the direct fire.

The distillate is then purified by repeated redistillations from caustic lime, and lastly, from a little sulphuric acid (in order to remove NH_3 and amines). In some cases chalk is used instead of lime, and sometimes chalk and sodium bicarbonate.

The distillation is carried on in copper stills heated by steam coils, or the retorts are guarded by iron jackets, and heated over the fire. The crude spirit thus obtained is colourless, and its specific gravity varies from ·87 to ·82.

The disagreeable-smelling constituents are sometimes got rid of by Wildsmith's process, which consists in the application of oxidising agents, *e.g.* potassium bichromate, aided by the action of light, to the crude spirit, by which means the hydrocarbons &c. are destroyed, and a colourless, almost odourless, liquid obtained.

The usual yield of pyroxylic spirit is from 1 to 3 gallons from each ton of wood distilled, but the quantity depends upon the kind of wood employed, and also upon the proper regulation of the temperature during distillation.

Large quantities of methyl alcohol are now made by the distillation of residues obtained by the evaporation of the spent wash in the preparation of ordinary alcohol from beet-sugar molasses. The distillate contains ammoniacal compounds, methylamine, methyl cyanide, and methyl alcohol. After neutralising with sulphuric acid the mixture is evaporated, the vapours being condensed; these contain methyl cyanide and methyl alcohol; the former is decomposed by rectification over lime, and the distillate, which contains dilute methyl alcohol, is dehydrated by means of lime.

Commercial wood spirit contains very variable proportions of the pure alcohol, from as low as 35 p.c. to as high as 95 p.c. It contains acetone, methyl acetate, and often, various empyreumatic bodies; these have considerable influence, not only upon its density, but also upon its solvent powers for shellac and other resins. The purest spirit is always preferred for use in lamps as a fuel, but for the use of the varnishmakers and polishers some of the impurer varieties, containing essential oils &c., are sometimes chosen.

Purification.—According to a method patented by Piper and Rotten of Berlin (Germ. pat. 36, 827, Jan. 22, 1886), the wood spirit is first distilled with lime and then by fractional distillation the acetone is reduced to 1 or 2 p.c. To remove the remaining acetone the spirit is heated to boiling (with reflux condenser), and dry chlorine is passed into it; portions are tested from time to time by distilling, and testing the distillate for acetone by the iodoform reaction. When this reaction is no longer given the passage of the chlorine is stopped, and the methyl alcohol separated by fractional distillation from the high boiling chlorinated acetone, and purified by distillation over lime from traces of chlorine. The methyl alcohol thus obtained is perfectly free from acetone; the chloracetone can be reconverted into acetone by reducing agents.

In order to obtain pure methyl alcohol, the oxalic or formic ester is prepared, and then decomposed by heating with water (Wöhler, A. 81, 376), or ammonia (Grodzki and Krämer, B. 7, 1494). Methyl benzoate when heated with a solution of 1 part sodium hydrate in 5 parts of water yields methyl alcohol (Carius, A. 110, 210). Pure methyl alcohol may be prepared by treating 10 parts of commercial wood spirit with 1 part of iodine, and then adding caustic soda until the colour of the iodine disappears, and distilling (Regnault and Villejean, Bl. 42, 255). 100 c.c. of the crude spirit are digested with 150 grams of solid caustic soda, and afterwards distilled, 500 grams of oxalic acid are mixed with 200 c.c. of sulphuric acid, and then 400 c.c. of the purified alcohol are added, and the mixture is heated on the water-bath; the crystals of methyl oxalate are dried by pressure and saponified by heating with water at 70°. The distillate is then dehydrated by means of baryta, lime, and anhydrous copper sulphate (Dittmar and Fawsitt, Tr. E. 33, 509).

Properties.—A colourless liquid with an odour like that of ethyl alcohol; miscible with water in all proportions, and with contraction and evolution of heat (*v.* table). It burns with a blue flame. It possesses, like ethyl alcohol, remarkable solvent powers, dissolving most substances which are soluble in ethyl alcohol, consequently it may be used in many cases instead of that liquid.

Its vapour pressure at various temperatures is given in the following table (Dittmar and Fawsitt):—

Temperature	Vapour pressure	Temperature	Vapour pressure
°C.	mm.	°C.	mm.
0°	29·7	40°	259·4
5°	40·2	45°	327·3
10°	53·8	50°	409·4
15°	71·4	55°	507·7
20°	94·0	60°	624·3
25°	122·7	65°	761·1
30°	158·9	64·96°	760·0
35°	203·9		

Anhydrous copper sulphate is slightly soluble in absolute methyl alcohol, yielding a bluish-green solution, hence it cannot be used as a test of the freedom of methyl alcohol from water (Klepl, J. pr. [2] 25, 526). This blue solution deposits crystals of $CuSO_4.2CH_3OH$ (Forcrand, C. R. 102, 551). Methyl alcohol combines with many salts in a manner similar to water of crystallisation, *e.g.* $LiCl,3CH_3OH$; $MgCl_2,6CH_3OH$; $CaCl_2,4CH_3OH$, six-sided tables, decomposed by water, may be heated to 100° without decomposition (Kane, P. M. [3] 10, 45). A compound with barium oxide, $BaO,2CH_3OH,2H_2O$, is obtained in brilliant prisms, when BaO is dissolved in aqueous methyl alcohol, and the liquid evaporated at the ordinary temperature (Forcrand, C. R. 102, 1557).

When passed over heated zinc, methyl alcohol yields carbon monoxide, hydrogen, and a small quantity of methane (Jahn, B. 13, 983). By the action of zinc chloride, hydrocarbons C_nH_{2n+2} are the chief products, also some hexamethyl benzene (Lebel and Greene, J. 1878, 388). By electrolysis in presence of sulphuric acid, *methylal* $CH_2(OCH_3)_2$ is produced (Renard, A. Ch. [5] 17, 290).

Potassium or sodium liberates hydrogen and forms methylates; sodium methylate $NaCH_3O$ combines at 160° with CO to form sodium acetate.

According to A. J. Brown (C. J. 49, 178), *Bacterium aceti* has no action on methyl alcohol. With caustic alkalis it forms compounds, *e.g.* $5NaOH, 6CH_3OH$; $3KOH, 5CH_3OH$, m.p. 110° (Göttig, B. 21, 561, and 1832).

Impurities.—The impurities of commercial wood spirit are small quantities of aldehyde, dimethylacetal, allyl alcohol, acetone, methylethyl ketone and higher ketones.

Acetone is the most objectionable, especially when the alcohol is to be used in the preparation of aniline colours. In order to estimate the amount of acetone 1 c.c. of the wood spirit is mixed with 10 c.c. of a double normal solution of soda, and 10 c.c. of a double normal solution of iodine are added with constant shaking, and then 10 c.c. of absolute ether. The ethereal layer is then measured, an aliquot portion taken and evaporated on a watch-glass and the residual iodoform weighed. The weight of the iodoform (calculated to the total volume of ethereal solution) multiplied by ·28 gives the amount of acetone in 1 c.c. of wood spirit (Krämer, B. 13, 1002).

Table giving the specific gravities of aqueous methyl alcohol at 0° and 15·56°C. Water at 4° = 1000.

P.c. by weight of CH_3OH	Sp.gr. at 0°	Sp.gr. at 15·56°	P.c. by weight of CH_3OH	Sp.gr. at 0°	Sp.gr. at 15·56°
0	999·87	999·07	51	926·91	916·61
1	998·06	997·29	52	925·07	914·65
2	996·31	995·54	53	923·20	912·67
3	994·62	993·82	54	921·30	910·66
4	992·99	992·14	55	919·38	908·63
5	991·42	990·48	56	917·42	906·57
6	989·90	988·93	57	915·44	904·50
7	988·43	987·26	58	913·43	902·39
8	987·01	985·69	59	911·39	900·26
9	985·63	984·14	60	909·17	897·98
10	984·29	982·62	61	907·06	895·80
11	982·99	981·11	62	904·92	893·58
12	981·71	979·62	63	902·76	891·33
13	980·48	978·14	64	900·56	889·05
14	979·26	976·68	65	898·35	886·76
15	978·06	975·23	66	896·11	884·43
16	976·89	973·79	67	893·84	882·02
17	975·73	972·35	68	891·54	879·70
18	974·59	970·93	69	889·22	877·14
19	973·46	969·50	70	886·87	874·87
20	972·33	968·08	71	884·70	872·62
21	971·20	966·66	72	882·37	870·21
22	970·07	965·24	73	880·03	867·79
23	968·94	963·81	74	877·67	865·35
24	967·80	962·38	75	875·30	862·90
25	966·65	960·93	76	872·90	860·42
26	965·49	959·49	77	870·49	857·98
27	964·30	958·02	78	868·06	855·42
28	963·10	956·55	79	865·61	852·90
29	961·87	955·06	80	863·14	850·35
30	960·57	953·55	81	860·66	847·79
31	959·21	952·11	82	858·16	845·21
32	957·83	950·53	83	855·64	842·62
33	956·43	948·94	84	853·10	840·01
34	955·00	947·32	85	850·55	837·38
35	953·54	945·67	86	847·98	834·73
36	952·04	943·99	87	845·39	832·07
37	950·51	942·28	88	842·78	829·38
38	948·95	940·55	89	840·15	826·68
39	947·34	938·77	90	837·51	823·96
40	945·71	936·97	91	834·85	821·23
41	944·00	935·10	92	832·18	818·49
42	942·39	933·35	93	829·48	815·72
43	940·76	931·55	94	826·77	812·93
44	939·11	929·75	95	824·04	810·13
45	937·44	927·93	96	821·29	807·31
46	935·75	926·10	97	818·53	804·48
47	934·03	924·24	98	815·76	801·64
48	932·29	922·37	99	812·95	798·76
49	930·52	920·47	100	810·15	795·89
50	928·73	918·55			

(Dittmar and Fawsitt, Tr. E. 33, 531–533.)

According to Messenger (B. 21, 3366), this method gives too high results if the quantity of acetone be small. He has devised a volumetric method. 20 c.c. of normal potash solution and 1 or 2 c.c. of the wood spirit are shaken in a stoppered flask and 20 c.c. to 30 c.c. of $\frac{N}{5}$ solution of iodine run in and again shaken. The mixture is then acidified with hydrochloric acid (sp.gr. 1·025) and an excess of $\frac{N}{10}$ sodium thiosulphate is added and titrated back with iodine solution; 3 molecules of iodine are required to convert 1 molecule of acetone into iodoform.

In order to estimate the amount of methyl alcohol in wood spirit 5 c.c. are mixed very slowly with 30 grams of phosphorus iodide, warmed on the water-bath with reflux condenser for five minutes and then distilled, the distillate is made up to 25 c.c. with water and the volume of the methyl iodide determined (Krell, B. 6, 1310). 15 grams of phosphorus iodide and 5 c.c. of a solution of iodine in hydriodic acid (sp.gr. 1·7) may be used instead of the above (Grodzki and Krämer, B. 9, 1928).

Dimethylacetal $C_2H_4(OCH_3)_2$ gives methyl iodide when treated as above, and so the results are often too high.

Methyl boride $B(CH_3)_3$, *bormethyl, trimethylborine.* V.D. 1·9108 (calc. = 1·9314), a gas obtained from methyl borate by the action of zinc methyl; (Frankland and Duppa, Tr. 153, 167); has an intensely disagreeable smell, ignites spontaneously in the air; can be liquefied by a pressure of three atmospheres at 10°. Caustic potash absorbs the gas and yields, on evaporation, a viscid residue of $B(CH_3)_3.KOH$. Ammonia forms a compound, $B(CH_3)_3.NH_3$, which can be crystallised from ether in large crystals; m.p. 56°; b.p. 110°.

Methyl bromide CH_3Br, *bromethane*; b.p. 4·5° (cor.) (Perkin, C. J. 45, 451); sp.gr. $\frac{\cdot 8^\circ}{\cdot 8^\circ}$ = 1·73306, sp.gr. $\frac{2\cdot 2^\circ}{2\cdot 2^\circ}$ = 1·72345; MM. = 4·644 at 15° (P.).

Preparation.—By heating the cacodyl compound, $As(CH_3)_2(OH)_2Br$ (Bunsen, A. 46, 44); from methyl alcohol, bromine, and phosphorus; (Pierre, A. Ch. [3] 15,325). 133 grams red phosphorus, 800 grams methyl alcohol, are mixed in a retort, and 800 grams of bromine are gradually added; after some hours the mixture is distilled (Merrill, J. pr. [2] 18, 293).

Methyl bromide is a colourless mobile liquid with a smell resembling that of chloroform, unites with water to form a crystalline hydrate $CH_3Br.20H_2O$ (?) which is decomposed at 4° (Merrill).

For brominated compounds of methyl bromide *v. Methylene bromide*, art. METHYLENE; BROMOFORM; and *Carbon tetrabromide*, art. CARBON.

Methyl chloride CH_3Cl, *chlormethane*; b.p. −23·73° (Regnault); −21° (Berthelot); −23° (Vincent and Delachanal); sp.gr. $\frac{-23^\circ}{}$ = ·99145 $\frac{0^\circ}{}$ = ·95231, $\frac{15^\circ}{}$ = ·9247, $\frac{39^\circ}{}$ = ·87886 (Vincent and Delachanal, Bl. 31, 11). Vap. press. at 0° = 2·48 atmospheres; at 15° = 4·11, at 30° = 6·50 (Vincent and Delachanal).

Preparation.—From methyl alcohol, common salt and sulphuric acid (Dumas and Peligot, A. 15, 17); from marsh gas and chlorine (Berthelot, A. Ch. [3] 52, 97); by heating the cacodyl compounds $As(CH_3)_2(OH)_2Cl$ or $As(CH_3)_2Cl$ (Bunsen, A. 46, 44).

On the large scale by the dry distillation of 'vinasses' from beetroot. The methylamine is saturated with hydrochloric acid and concentrated, then heated to 260°–300°, when methyl chloride together with mono- and trimethylamine is evolved; the bases are removed by means of hydrochloric acid and the methyl chloride dried over calcium chloride and condensed by pressure in wrought-iron cylinders (Vincent and Delachanal, Bl. 31, 11; J. 1878, 1135). One part of melted zinc chloride is dissolved in two parts methyl alcohol and hydrochloric acid led into the mixture (Groves, C. J. 1874, 641).

Properties.—Methyl chloride is a colourless gas with ethereal odour, burns in air when ignited with a greenish flame. One part of water dissolves 4 volumes of methyl chloride, 1 of absolute alcohol, 35 volumes and 1 of acetic acid, 40 volumes (Berthelot). The neutral solution is not precipitated by silver nitrate.

With water at temperatures below 7·3° at 760 mm. it forms a solid hydrate $CH_3Cl.9H_2O$ (De Forcrand and Villard, C. R. 106, 1402).

With chlorine in sunlight it yields methylene chloride (CH_2Cl_2, chloroform $CHCl_3$ and finally carbon tetrachloride CCl_4 *q.v.*); the chlorination can also be effected by leading a mixture of chlorine and methyl chloride over animal charcoal at 250°–350°.

Bromine forms methylene bromide, bromoform and carbon tetrabromide (Damoiseau, J. 1881, 376).

Methyl chloride is extensively used in the preparation of various coal-tar colours and also as a means of producing cold. By its evaporation a temperature of −23° is produced, or if the evaporation be accelerated by blowing in air −55° is easily reached, and since its vapour is non-poisonous, its superiority to liquid sulphur dioxide for this purpose is evident.

Methyl cyanate $CNOCH_3$. Formed by leading chloride of cyanogen into a solution of 1 part of sodium in 20 parts pure methyl alcohol (Hoffmann and Olshausen, B. 3, 271); a liquid which polymerises on standing.

Methyl isocyanate $CH_3.N.CO$, *methyl carbimide*; b.p. 43°–45° (Gautier). Formed by the distillation of a mixture of 1 part of potassium cyanate with 2 parts of potassium methyl sulphate (Wurtz, A. Ch. [3] 42, 43). A liquid with intensely suffocating smell, converted by dry ammonia into methyl-urea $NHCH_3.CO.NH_2$ which forms prisms soluble in water. Water converts it into dimethyl-urea $NHCH_3.CO.NHCH_3$.

Methyl cyanurates.

Methyl cyanurate $(CH_3O.CN)_3$; m.p. 135°; b.p. 265° (Hofmann, B. 19, 2061). By the action of sodium methylate upon tricyanogen chloride or bromide, or, in small quantity, from silver cyanurate and methyl iodide in the cold (Ponomareff, B. 18, 3264). Hofmann, however (B. 19, 2084), could not obtain this latter reaction. Forms needles soluble in water; decomposed by phosphorus pentachloride into tricyanogen chloride, methyl chloride, and phosphoryl chloride (Hofmann, B. 18, 2799).

Dimethyl isocyanurate $(CH_3)_2H(CNO)_3$, *dimethyl isocyanuric acid*; m.p. 222°. By the dry distillation of methyl acetyl urea (Hofmann, B. 14, 2728); also by the action of methyl iodide upon silver cyanurate (H., B. 19, 2061, and C. J. 50, 930). Forms unstable salts, of which the silver compound is crystalline and slightly soluble in water.

Trimethyl isocyanurate $(CH_3)_3(CNO)_3$; m.p. 175°–176°; b.p. 274° (Wurtz). By the distillation of potassium cyanate or cyanurate with potassium methyl sulphate; also, together with the cyanurate, by heating methyl iodide with silver cyanurate (Ponomareff, B. 18, 3271).

Methyl cyanide $CH_3.CN$, *acetonitrile*; b.p. 81·6°; sp.gr. 0° = ·8052, 15° = ·7891 (Vincent and Delachanal, Bl. 33, 405); b.p. 81·2°–81·4° at 757·3 mm.; sp. gr. $\frac{81{\cdot}2^\circ}{4^\circ}$ = ·7157 (Schiff, B. 19, 567). H.C. at 18° = 312·14 (Thomsen, Th. 4, 128) = 291·6 (Berthelot and Petit, C. R. 108, 1217). Mol. refraction 18·0 (Kanonnikoff, J. pr. [2] 31, 361).

From ammonium acetate and phosphorus pentoxide (Dumas, C. R. 25, 383), from acetamide and phosphorus pentoxide; also by the distillation of potassium methyl sulphate with potassium cyanide (Dumas, Malaguti, and Leblanc, A. 64, 333); cyanacetic acid decomposes on heating to 165° into acetonitrile and carbon dioxide (Hoff, B. 7, 1382).

Preparation.—A mixture of 5 molecules of acetamide and 1 molecule of phosphorus pentasulphide is distilled, the product washed with caustic soda and digested with lead oxide (Henry, A. 152, 149). By long heating of a mixture of acetamide and glacial acetic acid with a reflux condenser (Demarçay, Bl. 33, 456).

Acetonitrile is a colourless liquid with a pleasant ethereal smell, miscible with water, from which it separates on the addition of common salt. It burns in air with a violet-red flame; with acetic acid at 200° it produces diacetamide. It is miscible with methyl alcohol or with ethyl alcohol, and its b.p. is lowered by such admixture—a liquid containing 80 p.c. wood spirit and 20 p.c. acetonitrile has the lowest b.p. (63·7°), while, in the case of ethyl alcohol, a mixture of 56 p.c. spirits of wine and 44 p.c. acetonitrile boils at 72·6° (Vincent and Delachanal, Bl. 33, 405). It combines easily with hydrobromic and hydriodic acids, more difficultly with hydrochloric acid (Gautier, A. 142, 291). $CH_3CN.2HBr$ forms crystals melting at 47°–50° (Engler, A. 149, 306). Bromine combines with acetonitrile at 100° to form a compound—$CH_2Br.CN.HBr$—crystallising in prisms which melt at 65°, and are decomposed by moist air, forming ammonium bromide, acetic acid, and dibromdiacetamide (Engler, A. 133, 137; 142, 69).

By the action of sodium upon methyl cyanide we get marsh gas, an oily body soluble in ether and of the composition $C_4H_6N_2$ (Holtzwart, J. pr. [2] 38, 343), sodium cyanide, and *cyanmethine* $C_6H_9N_3$ (Bayer, B. 2, 319). This is best obtained by heating 6 parts methyl cyanide with 1 part of sodium under a pressure of 100 mm., distilling off the excess of methyl cyanide and crystallising the residue from alcohol (Meyer, J. pr. [2] 27, 153). It forms monoclinic crystals (m.p. 180°–181°, which dissolve in ·64 parts of water or 5·25 parts of alcohol at 18°. Cyanmethine unites with many acids, *e.g.* $C_6H_9N_3.HCl$, needles soluble in water; b.p. 200°–250° $(C_6H_9N_3)_2H_2SO_4$, crystallises with difficulty. It also forms chlorine and bromine derivatives (Baeyer, B. 4, 176).

Substitution products of acetonitrile.

Chloracetonitrile $CH_2Cl.CN$, from chloracetamide and phosphorus pentoxide (Bisschopinck, B. 6, 732). A liquid; b.p. 123°–124°, sp.gr. 11·2° = 1·204, 20° = 1·193 (Engler, B. 6, 1003).

Dichloracetonitrile $CHCl_2.CN$; b.p. 112°–113°; sp.gr. 11·4 = 1·374.

Trichloracetonitrile $CCl_3.CN$; b.p. 83°–84°, sp.gr. 12·2° = 1·439. From trichloracetamide and phosphorus pentoxide (Bisschopinck, B. 6, 732). By action of chlorine upon acetonitrile in presence of iodine (Beckurts, B. 9, 1594).

Bromacetonitrile $CH_2Br.CN$; and *Dibromacetonitrile* $CHBr_2.CN$, m.p. 142°, are also known (*v.* Engler, A. 142, 69, and Hoff, B. 6, 1571; also Henry, C. R. 103, 413).

Iodacetonitrile $CH_2I.CN$; b.p. 186°–187°; sp.gr. 12° = 2·3065; from chloracetonitrile and sodium iodide in alcoholic solution (Henry, C. R. 103, 413).

Nitroacetonitrile $CH_2(NO_2).CN$ *v.* FULMINIC ACID; also EXPLOSIVES.

Dinitroacetonitrile $CH(NO_2)_2.CN$, a syrupy liquid obtained by the action of sulphuric acid upon the ammonia compound $CH(NO_2)_2CN.NH_3$. This compound is obtained by the reduction of an ethereal solution of trinitroacetonitrile by means of dry sulphuretted hydrogen:

$$\begin{gathered} C(NO_2)_3CN + 4H_2S \\ = CH(NO_2)_2CN.NH_3 + 2H_2O + 4S \end{gathered}$$

(Schischkoff, A. 101, 215).

Trinitroacetonitrile $C(NO_2)_3.CN$, a solid, m.p. 41·5°; explodes when heated to 220°. Formed by the action of a mixture of fuming nitric and sulphuric acids upon sodium fulminate (Schischkoff, A. Ch. [3] 49, 310). Soluble in ether, but decomposed by alcohol, water, or alkalis.

Methyl isocyanide $CH_3.NC$, *iso-acetonitrile*, *methyl carbylamine*; b.p. 59·6°; sp.gr. $\frac{14^\circ}{}$ = ·7557 (Gautier, A. 152, 222). From methyl iodide and 2 molecules of silver cyanide at 130° (Gautier, C. R. 65, 468); also from chloroform, methylamine, and alcoholic potash (Hofmann). It is also formed in small quantity when potassium methyl sulphate is distilled with potassium cyanide.

Methyl isocyanide is a liquid with a very unpleasant smell; soluble in 10 parts of water at 15°; forms crystalline salts with acids.

Methyl fluoride CH_3F. A gas, sp.gr. (H = 1) 17·38, calc. = 17·05 (Collie, C. J. 55, 110). Obtained from potassium methyl sulphate and potassium fluoride (Dumas and Péligot, A. 15, 59); by the action of heat upon tetramethyl ammonium fluoride (Collie); from a mixture of methyl iodide and silver fluoride (Moissan and Meslans, C. R. 107, 1153; C. J. 56, 364). Liquefied by a pressure of 30 atmospheres at ordinary temperatures; slightly soluble in water, more in methyl alcohol. It is very stable; critical temp. 44·9°; pressure 47123 mm. (Collie). Chlorine in sunlight displaces hydrogen and forms CH_2ClF, a gas soluble in water and of sp.gr. 34·18 (calc. = 34·25).

Methyl formamide $N.(COH)(CH_3)H.$; b.p. 180–185° (Gautier, J. 1869, 618); 190° (Linnemann, J. 1869, 601); sp.gr. $\frac{19^\circ}{}$ = 1·011. A thick, oily liquid soluble in water and alcohol, insoluble in ether, formed by the distillation of methyl ammonium formate.

Methyl formate CH_3OCHO; b.p. 32–32·5° cor. (Perkin, C. J. 45, 491); 30·4° at 712 mm. (Volhard, A. 176, 133). Sp.gr. $\frac{15^\circ}{15^\circ}$ = ·98239, $\frac{25^\circ}{25^\circ}$ = ·96948 (P.); $\frac{0^\circ}{4}$ = ·99839 (Elsässer, A. 218, 312), $\frac{32{\cdot}3^\circ}{4^\circ}$ = ·9566 (Schiff, A. 220, 106). H.C.p. = 238·7 (Berthelot and Ogier, A. Ch. [5] 23, 204). M.M. at 16·5° = 2·495 (Perkin).

Preparation.—130 parts of methyl alcohol saturated with hydrochloric acid are gradually poured upon 100 parts of calcium formate; the mixture is then digested for some time, and finally distilled (Volhard, A. 176, 133). A mixture of equivalent proportions of sodium formate, hydrochloric acid, and wood spirit may be used (Bardy and Bordet, A. Ch. [5] 16, 561). Wood spirit is digested with glacial formic acid and distilled; the distillate is then dehydrated by means of phosphorus pentoxide.

Methyl formate is a colourless liquid with a characteristic smell; its vapour is decomposed at a red heat, forming carbon monoxide and methyl alcohol. Chlorine in presence of sunlight yields *trichloro-methyl chloroformate* $CClOOCCl_3$, b.p. 127·5–128°, sp.gr. $\frac{14^\circ}{\ }$ = 1·6525, which, when heated to 340–350°, yields the isomeric carbonyl chloride $COCl_2$ (Hentschel, J. pr. [2] 36, 99). If the action be stopped at an earlier stage, a compound $C_4H_3Cl_5O_4$, b.p. 108–109°, sp.gr. $\frac{27^\circ}{27^\circ}$ = 1·4741, is formed.

Methyl hydrate *v. Methyl alcohol.*

Methyl hydride $CH_3.H$, *marsh gas, methane*; sp.gr. ·559 (air = 1); b.p. = −164·0° at 736·6 mm. (Olszewski, A. Ch. [2] 31, 58); sp.gr. of liquid = ·415 (O.). H.F.p. = 21,750 cals.; H.F.v. = 21,170 cals.; H.C.p. = 211,930 cals. (Thomsen, Th. 4, 50); H.C.p. = 213,500 cals. (Berthelot, A. Ch. [5] 23, 179). 1 vol. of water at t° absorbs $\cdot05449 - \cdot001807t + \cdot0001028t^2$ vols. of marsh gas, 1 vol. of alcohol at t°, $\cdot522586 - \cdot0028655t + 0000142t^2$ vols. (Bunsen).

Marsh gas is emitted from the surface of the ground in many parts of the world, notably in Italy, N. America, and in the vicinity of the Caspian Sea. It is formed by the putrefaction of vegetable matter under water, and hence occurs in marshy places. It is evolved in large quantities from the mud volcanoes of Sicily, Italy, and the Crimea. It also occurs in the coal measures, and, in small quantities, in the gases of the human intestines (Ruge, J. 1862, 528), and in the breath of calves and sheep (Reiset, J. 1863, 638).

It is formed by the putrefaction of cellulose. According to Hoppe-Seyler (H. 10, 401), this is due to the action of a fungus (*Amylobacterium*, Van Tieghem, C. R. 88, 205), and cellulose (sterilised filter-paper was used) is converted into a non-reducing sugar $C_6H_{12}O_6$, which splits up into $3CO_2$ and $3CH_4$; this action is stopped by a temperature above 60°.

Marsh gas is also produced by the destructive distillation of carbonaceous matter—*e.g.* wood or coal—and hence occurs, to the extent of about 40 p.c. by volume, in coal gas.

It can be obtained from chloroform or carbon tetrachloride by passing the vapour, mixed with hydrogen, through a hot tube, or by heating with copper, potassium iodide, and water (Berthelot, J. 1857, 267). Also by passing a mixture of the vapour of carbon bisulphide and sulphuretted hydrogen over heated copper or iron (Berthelot, A. Ch. [3] 53, 69). Also by the action of the silent electrical discharge upon a mixture of hydrogen and carbon monoxide (Brodie, Pr. 21, 245).

Preparation.—By heating potassium acetate with caustic potash

$$KC_2H_3O_2 + KOH = K_2CO_3 + CH_4.$$

Sodium acetate and a mixture of equal volumes of calcined soda and powdered lime are heated in an iron or copper vessel (Schorlemmer, C. N. 29, 7). Hydrogen and ethylene are also produced in this reaction (Kolbe); the latter may be removed by means of sulphuric acid.

It can also be obtained by the action of the copper-zinc couple upon a mixture of equal volumes of alcohol and methyl iodide (Gladstone and Tribe, C. J. 45, 154).

Properties.—Marsh gas is colourless and odourless, and forms an explosive mixture with air ('firedamp'). It is very stable, and is not affected by phosphorus pentoxide or antimony pentachloride, or even by strong nitric acid. Dry chlorine has no action in the dark, but in sunlight the mixture explodes; in diffuse daylight chlorine substitution derivatives are formed. When passed through a hot tube, a very small portion is converted into naphthalene, but the greater portion remains unaltered.

It forms a hydrate with water at −2° or −3° under a pressure of 30 atmospheres. Tension of dissociation at 0° = 27·5 atmospheres; crit. temp. = 21·5° (Villard, C. R. 107, 895).

Methyl iodide CH_3I; b.p. 42·3° cor. (Perkin. C. J. 45, 459); 44·3° (Pierre, A. 56, 147), Sp.gr. $\frac{15^\circ}{15^\circ}$ = 2·28517, $\frac{25^\circ}{25^\circ}$ = 2·25288 (P.); $\frac{15^\circ}{\ }$ = 2·2677 (Bardy and Bordet, A. Ch. [5] 16, 569). Formed by the action of phosphorus and iodine upon methyl alcohol (Dumas and Péligot, A. 15, 30).

Preparation.—In a similar manner to that of ethyl iodide (*q. v.*). 35 parts methyl alcohol, 100 parts iodine, and 10 parts of phosphorus are the proportions usually employed. These substances are allowed to remain in contact for some hours; the methyl iodide is then distilled off, washed with dilute caustic soda solution, and dried by means of calcium chloride.

It forms a colourless liquid which turns brown on exposure to light owing to the liberation of iodine. It is extensively used in the preparation of various aniline colours owing to the ease with which it undergoes decomposition; it thus affords a ready means of introducing methyl into other compounds.

Methyl nitrate CH_3NO_3; b.p. 65°; sp.gr. $\frac{5^\circ}{5^\circ}$ = 1·2322, $\frac{10^\circ}{10^\circ}$ = 1·2241, $\frac{15^\circ}{15^\circ}$ = 1·2167, $\frac{25^\circ}{25^\circ}$ = 1·2032; M.M. at 9·5° = 2·057 (Perkin, C. J. 55, 682).

Preparation.—200 c.c. pure wood spirit are distilled with 40 grs. urea nitrate and 150 c.c. pure nitric acid (sp.gr. 1·31) until two-thirds have distilled off; to the residue 170 c.c. of methyl alcohol and 130 c.c. nitric acid are added, again distilled, and then 150 c.c. methyl alcohol, 110 c.c. nitric acid, and 10 grams urea nitrate are added to the residue, and distillation again continued (C. Lea, Am. J. [2] 33, 227).

Can also be prepared by mixing methyl alcohol and sulphuric acid, and adding 2 parts of this liquid to a mixture of 1 part nitric acid and 2 parts sulphuric acid. The distillate is washed with potassium carbonate solution.

Methyl nitrate is a colourless liquid with a pleasant smell; explodes when heated to 150°, or by percussion.

Methyl nitrite CH_3NO_2; b.p. $-12°$; sp.gr. of liquid $\frac{15°}{-}$ = ·991. A gas, prepared by treating 1 molecule methyl alcohol with 1 molecule isoamyl nitrite (Bertoni, G. 12, 438). Also by the action of nitric acid upon copper (or arsenious acid) and methyl alcohol, or by the action of nitric acid upon brucine (Strecker, A. 91, 76).

Methyl nitride *v. Methylamine.*

Methyl oxalate $(CH_3)_2C_2O_4$; m.p. 54°; b.p. 163·3° cor.; sp.gr. $\frac{54°}{-}$ = 1·1470 (Weger, A. 221, 86); m.p. 50–51°; b.p. 174·2° (Regnault); sp.gr. $\frac{50°}{-}$ = 1·1702 (Kopp). Oxalic acid (dried at 100°) is mixed with boiling methyl alcohol, and on cooling the crystals separate out (Erlenmeyer, J. 1874, 572).

Forms monoclinic plates, which, by action of chlorine yield, first, an oily liquid of the composition $C_2O_4(CHCl_2)_2$ (Malaguti, A. 32, 49), and by prolonged action in sunlight, a body $C_2O_4(CCl_3)_2$, which crystallises in leaflets (Cahours, A. 64, 318).

Methyl hydrogen oxalate $HCH_3.C_2O_4$, crystallises in leaflets, and is obtained by the action of a solution of potassium methylate in methyl alcohol upon dimethyl oxalate (Salomon, B. 8, 1509).

Methyl oxide $(CH_3)_2O$, *dimethyl ether*; b.p. $-23·65°$ (Regnault, J. 1863, 70); $-21°$ (Berthelot); absolute boiling-point, 129·6° (Nadeschdin, J. R. 15 [2] 27); sp.gr. (air = 1) 1·617; H.C.p. = 344·2 cals.; H.F. = 56·8 cals. (Berthelot, A. C. [5] 23, 185); H.C. = 349·36; H.F.p. = 49·64; H.F.v. = 48·19 cals. (Thomsen, Th. 4, 147).

Formed by heating methyl alcohol with sulphuric acid (Dumas and Péligot, A. Ch. [2] 58, 19), or with boron trioxide (Ebelmen, A. Ch. [3] 16, 138; A. 57, 328).

1·3 parts of wood alcohol are mixed with 2 parts of sulphuric acid, and heated to 140°. The gas evolved is passed into strong sulphuric acid, which absorbs 600 times its volume; the gas is then set free by diluting the acid with water (Erlenmeyer and Kriechbaumer, B. 7, 699).

Methyl ether is a colourless gas with a pleasant odour; 1 vol. of water at 18° absorbs 37 volumes of the gas (Dumas and Péligot). It unites with hydrochloric acid to form a compound $(CH_3)_2O.HCl$, which boils at 2° (Friedel, Bl. 24, 160, 241).

Chlorine substitution products.

Chlormethyl ether $CH_2Cl.O.CH_3$; b.p. 59·5° at 759 mm.; formed by bringing together, in daylight, chlorine and excess of methyl oxide (Friedel, Bl. 28, 171).

Dichlormethyl ether $(CH_2Cl)_2O$; b.p. 105°; sp.gr. $\frac{20°}{-}$ = 1·315; formed by the action of chlorine upon methyl oxide (Regnault, A. 34, 31).

Tetrachlormethyl ether $(CHCl_2)_2O$; b.p. 130°; sp.gr. $\frac{20°}{-}$ = 1·606 (Regnault).

Perchlormethyl ether $(CCl_3)_2O$; b.p. 100° (with decomposition); sp.gr. = 1·597; by the action of chlorine upon methyl oxide in sunlight (Regnault). Decomposed by heat, yielding carbon tetrachloride and carbonyl chloride.

Methyl Phosphates and Phosphite.

1. *Normal methyl phosphate* $(CH_3)_3PO_4$; b.p. 197·2° (cor.); sp.gr. $\frac{0°}{-}$ = 1·2378 (Weger, A. 221, 89). From methyl iodide and silver phosphate (Hall, C. J. 51, 754).

2. *Dimethyl phosphoric acid* $(CH_3)_2HPO_4$; a syrupy liquid, produced when phosphoryl chloride $POCl_3$ is dropped into methyl alcohol (Schiff, A. 102, 334). The salts are very soluble in water.

3. *Monomethyl phosphoric acid* $CH_3H_2PO_4$ is produced when methyl alcohol is dropped into phosphoryl chloride (Schiff, A. 102, 337).

Methyl phosphorous acid $CH_3H_2PO_3$, a syrupy liquid formed by the action of phosphorus trichloride upon methyl alcohol (Schiff, A. 103, 164). It is miscible with ether, and forms salts which are amorphous, and decomposed by water into methyl alcohol and phosphites.

Methyl Sulphates.

1. *Hydrogen methyl sulphate* CH_3HSO_4, *methyl sulphuric acid.* The free acid is an oily body, which remains liquid at $-30°$. Obtained from methyl alcohol and sulphuric acid (Dumas and Péligot, A. 15, 40), or from methyl alcohol and chlorsulphonic acid in the cold (Claesson, J. pr. [2] 19, 240).

Preparation.—One part of methyl alcohol is mixed with two parts of concentrated sulphuric acid, allowed to stand in a warm place for some hours, diluted with water and neutralised with barium carbonate, filtered and the barium precipitated by the proper quantity of sulphuric acid. Methyl sulphuric acid forms salts with the metals, which are soluble and readily crystallise.

Chloride of methyl sulphuric acid CH_3SO_3Cl. *Methyl chlorosulphonate* is obtained by dropping methyl alcohol into sulphuryl chloride in molecular proportions (Behrend, J. pr. [2] 15, 32). It is an oily liquid with pungent smell; decomposed by water into methyl sulphuric and hydrochloric acids.

2. *Dimethyl sulphate* $(CH_3)_2SO_4$; b.p. 188°; sp.gr. $\frac{22°}{-}$ = 1·324. By distilling wood spirit with 8 or 10 pts. of sulphuric acid (Dumas and Péligot, A. Ch. 58, 54) or by distilling anhydrous methyl sulphuric acid, best *in vacuo* (Claesson, J. pr. [2] 19, 244). A colourless liquid with odour like that of peppermint.

Methyl Sulphides.

1. *Hydrogen methyl sulphide* CH_3HS, *methyl mercaptan, methyl sulphydrate* (Gregory, A. 15, 239); b.p. 5·8° at 752 mm. (Klason,

B. 20, 3407). By heating potassium hydrosulphide with potassium methyl sulphate (Dumas and Péligot). It is a colourless liquid with a disagreeable odour and forms a crystalline hydrate with water. By the action of chlorine upon carbon bisulphide containing a little iodine, *Perchlormethyl mercaptan* CCl_3ClS, a liquid (b.p. 146°–148° cor.; sp.gr. $\frac{12·8°}{0°}$ 1·712) is obtained (Rathke, A. 167, 195). This substance is decomposed by heating to 200° into carbon tetrachloride and sulphur chloride.

2. *Dimethyl sulphide* $(CH_3)_2S$; b.p. 37·1°–37·3° at 754·7 mm. (Beckmann, J. pr. [2] 17, 453); b.p. 37·2° at 758 mm. (Klason, B. 20, 3407). Sp.gr. $\frac{21°}{—}$ = ·845 (Regnault). From potassium sulphide and chloroform (Regnault, A. Ch. [2] 71, 391).

Preparation.—500 c.c. methyl alcohol are treated with 750 c.c. sulphuric acid, and a solution of 2·75 kilos. sodium carbonate (crystals) is added, and the solution concentrated until the sodium sulphate crystallises out. To the solution of sodium methyl sulphate 500 grams of potash dissolved in water and half saturated with sulphuretted hydrogen are added. The yield is about 150 grams (Klason, B. 20, 3407; C. J. 54, 356). Methyl sulphide is a colourless liquid with an unpleasant smell. It combines directly with chlorine to form oily substitution products $(CH_2Cl)_2S$, $(CHCl_2)_2S$, and $(CCl_3)_2S$ (Riche, A. Ch. [3] 43, 283). Bromine unites with it to form a crystalline bromide $(CH_3)_2SBr_2$ (Cahours, A. 135, 355). It also forms many crystalline compounds with various salts, *e.g.* $(CH_3)_2S.HgCl_2$; $2(CH_3)_2S.PtCl_4$) &c. (Loir, A. Ch. 39, 448; 54, 42). It combines at ordinary temperatures with methyl iodide to form *trimethyl sulphine iodide* $(CH_3)_3SI$, which crystallises in prisms.

By the action of moist silver oxide upon this compound we get *trimethyl sulphine hydroxide* $(CH_3)_3S.OH$, an oily liquid which possesses strongly basic properties and forms characteristic salts with the acids. By the action of sulphuretted hydrogen upon the base we get the sulphide $[(CH_3)_3S]_2S$ which resembles in its reactions the sulphides of the alkalis (Brown and Blackie, C. N. 37, 130; 39, 51).

Methyl sulphite $(CH_3)_2SO_3 = SO(OCH_3)_2$; b.p. 121·5°; sp.gr. $\frac{16·2°}{4°}$ = 1·0456. Obtained from methyl alcohol and sulphur chloride (Carius, A. 110, 209). Is isomeric with ethyl sulphurous acid $OH.SO.OC_2H_5$, and ethyl sulphonic acid $C_2H_5SO_2.OH$.

Methyl sulphonic acid $CH_3SO_2.OH$, a syrupy liquid decomposed at about 130°. By the action of nitric acid upon methyl thiocyanate or disulphide (Muspratt, A. 65, 261). Also by heating methyl iodide with sodium sulphite solution to 120° (Collmann, A. 148, 105). It forms stable crystalline salts which are very soluble in cold water but almost insoluble in alcohol. The potassium compound $CH_3SO_2.OK$, is decomposed by heating with caustic potash—

$$CH_3SO_2OK + 3KOH = H_6 + K_2CO_3 + K_2CO_3$$

(Berthelot, J. 1869, 336).

Methyl sulphonic chloride $CH_3.SO_2.Cl$; b.p. 150°–153° (Carius); 160° (Nithack); sp.gr =1·51 (Gowan, J. pr. [2] 30, 281). By the action of phosphorus pentachloride upon methyl sulphonic acid (Carius, A. 114, 142). It is not acted upon by sulphuretted hydrogen or potassium cyanide in alcoholic solution. Ammonia forms an amide $CH_3.SO_2.NH_2$ which crystallises in long prisms (Gowan, *l.c.*, also C. J. 48, 367).

Chlormethyl sulphonic acid $CH_2Cl.SO_2.OH$, an acid syrup obtained by the action of nascent hydrogen upon trichlormethyl sulphonic acid (Kolbe, A. 54, 168).

Dichlormethyl sulphonic acid $CHCl_2.SO_2.OH$, an unstable body formed by the action of zinc upon trichlormethyl sulphonic acid (Kolbe, A. 54, 164); also by heating chloroform with a solution of potassium sulphite to 180° (Strecker, A. 148, 92). The *chloride* $CH.Cl_2.SO_2.Cl$ (b.p. 170°–180°, sp.gr. 1·71) is formed by the action of phosphorus pentachloride upon the acid (Gowan, J. pr. [2] 30, 399), or by reducing, by means of sulphur dioxide or stannous chloride, trichlormethyl sulphonic chloride (Kolbe).

Trichlormethyl sulphonic acid

$$CCl_3SO_2OH + H_2O;$$

m.p. 130°. The free acid is obtained from the chloride by treatment with baryta, and precipitation of the dissolved barium by means of sulphuric acid, the excess of sulphuric acid is then removed by means of lead carbonate and excess of lead by means of sulphuretted hydrogen (Gowan, J. pr. [2] 30, 284).

It forms small prisms which are very stable and insoluble in water, but soluble in alcohol or ether. It has strong acid properties and is not affected by nitric acid, aqua regia, or chromic trioxide. The *chloride* $CCl_3SO_2.Cl$ (m.p. 135°, b.p. 170°) forms camphorlike crystals, and is obtained by the action of moist chlorine upon carbon bisulphide (Berzelius and Marcet, Gilb. Ann. 48, 161). Bassett (C. N. 54, 79) recommends the following process—100 grams of powdered potassium chlorate, 200 c.c. hydrochloric acid, 400 c.c. water and 50 c.c. carbon bisulphide are mixed together and allowed to stand for some days until the carbon bisulphide becomes solid; the white solid is then removed by filtration and washed, the yield is as high as 63 grams from the 50 c.c. carbon bisulphide.

Methyl thiocyanate $CH_3.S.CN$; b.p. 132·9° at 757·2 mm.; sp.gr. $\frac{0°}{—}$ = 1·088 (Pierre, J. 1851, 51). H.C. = 398·95 cals. (Thomsen, Th. 4, 196). By heating methyl sulphide with cyanogen bromide to 100° (Cahours, J. 1875, 257). By distilling a concentrated solution of equal parts of potassium thiocyanate and calcium methyl sulphate (Cahours, A. 61, 95).

If heated to 180°–185° it is partially converted into the isothiocyanate. By the action of chlorine in daylight cyanuric chloride $Cl_3(CN)_3$, thiocarbonyl chloride $CSCl_2$ and thiocarbonyl tetrachloride $CSCl_4$ are obtained (James, C. J. 51, 272). By heating with methyl iodide to 100° trimethyl sulphine iodide $(CH_3)_3SI$ is produced (Cahours, J. 1875, 257).

Methyl isothiocyanate $CH_3.NCS$, *methyl mustard oil*; m.p. 34°; b.p. 119° (Hofmann, B. 1, 172). By heating the silver salt of methyl thiocarbamic acid $CS(NH.CH_3)SH$ with water. This acid is formed by the action of carbon disulphide upon methylamine. Methyl mustard oil forms white crystals which have a smell resembling that of horseradish.

Methyl selenide $(CH_3)_2Se$; b.p. 58·2°. Obtained by distilling a solution of sodium selenide (prepared from phosphorus pentaselenide and caustic soda), with potassium methyl sulphate (Jackson, A. 179, 1). A disagreeably smelling liquid; with platinum tetrachloride forms a yellow compound $2(CH_3)_2Se.PtCl_4$, soluble in alcohol. It also unites with chlorine and bromine $(CH_3)_2SeCl_2$, m.p. 59·5°; $(CH_3)_2SeBr_2$, m.p. 82°.

Methyl diselenide $(CH_3)_2Se_2$, a heavy, reddish yellow liquid with very unpleasant odour, formed when potassium diselenide is heated with potassium methyl sulphate (Wöhler and Dean, A. 97, 5; Rathke, A. 152, 211).

METHYLAMINES. These are bodies with strongly marked basic properties, derived from ammonia by the replacement of one, two, or three atoms of hydrogen by an equal number of methyl groups.

Methylamine $NH_2(CH_3)$, *monomethylamine*; b.p. −6° to −5·5° at 768·35 mm. sp.gr. $\frac{-10{\cdot}8^{\circ}}{} = {\cdot}699$ (Hofmann, B. 22, 699).

Occurrence.—In the oil yielded by the dry distillation of bone (Anderson, A. 88, 44). In the plants *Mercurialis annua* and *M. perennis* (Reichardt, J. 1865, 457). In herring brine (Tollens, Z. 1866, 516). In crude wood spirit (Commaille, J. 1873, 686; Vincent, A. Ch. [5] 1, 444). In the products of the dry distillation of the residues from beet-sugar 'vinasses' (Duvillier and Buisine, A. Ch. [5] 23, 317).

Formation.—By the action of caustic potash upon methyl isocyanate or isocyanurate (Wurtz, A. Ch. [3] 30, 443). From ammonia and methyl iodide (Hofmann, Tr. 1851, 381) or methyl nitrate (C. Lea, C. N. 6, 46; Juncadella, C. R. 48, 342). By heating wood spirit with sal ammoniac to 300° (Berthelot, A. Ch. [3] 38, 69).

By heating caustic potash with certain alkaloids—*e.g.* morphine, codeïne, creatine, &c. (Wertheim, A. 73, 210; Dessaignes, J. 1855, 331). By the action of chlorine upon caffeïne or theobromine (Rochleder, J. 1850, 435). By the action of nascent hydrogen, from zinc and sulphuric acid, upon hydrocyanic acid (Mendius, A. 121, 139); or by passing a stream of hydrogen and hydrocyanic acid gas over platinum black, heated to 110° (Debus, C. J. 16, 249).

Preparation.—Equal molecules of methyl nitrate and ammonia dissolved in methyl alcohol are heated to 100°. The product is decomposed by caustic soda, and the base combined with hydrochloric acid, the dried chloride is then heated with caustic soda, and the liberated methylamine passed into sulphuric acid, the sulphate is dried at 110° and treated with absolute alcohol in which the di- and tri-methylamine salts are soluble, the insoluble monomethylamine sulphate is then decomposed by potash, and the free methylamine passed into a cooled solution of oxalic ether. The resulting di-methyl oxamide is dissolved in hot water, filtered and recrystallised, then decomposed by caustic potash, and the gas received in absolute alcohol (Duvillier and Buisine, A. Ch. [5] 23, 324; *v.* also Muller, Bl. 42, 202; C. J. 48, 501).

A mixture of 1 molecule of acetamide and 1 molecule of bromine is digested with a 10 p.c. solution of caustic potash in the cold until the liquid becomes yellow, then a 30 p.c. solution of caustic potash (3 molecules) is slowly added, the temperature being kept at 60–70°. The mixture is digested at this temperature until colourless, and the methylamine distilled off. In this way the product is obtained almost free from ammonia (Hofmann, B. 15, 765; 18, 2741).

Properties.—Methylamine is a colourless gas with a strong ammoniacal smell. It is very inflammable and burns with a yellow flame; it is decomposed at a red heat into ammonia, hydrocyanic acid, hydrogen, and marsh gas. It is very soluble in water, 1 volume of water at 12·5° dissolving 1,150 volumes and 959 volumes at 25°. The solution behaves like *liquor ammoniæ* and yields crystallisable salts on neutralisation with acids.

Heat of neutralisation with hydrochloric acid = 25·9 cals. (Muller, A. Ch. 15, 517). For salts of methylamine, which, as a rule, resemble those of ammonia, *v.* Wurtz, A. Ch. [3] 30, 443; Topsoë, J. 1883, 618; Bailey, C. J. 45, 692).

Methylamine, like ammonia, in aqueous solution precipitates metallic hydroxides from solutions of many salts; but, unlike ammonia, dissolves when in excess the hydroxide of aluminium, whereas it fails to dissolve the hydroxides of cadmium, nickel, and cobalt.

By leading chlorine into aqueous methylamine, *methyl dichloramine* CH_3NCl_2, a golden yellow liquid b.p. 59–60°, is produced (Köhler, B. 12, 771).

Dimethylamine $N(CH_3)_2H$; b.p. 7·2°−7·8° at 764·1 mm.; sp.gr. $\frac{-5{\cdot}8^{\circ}}{} = {\cdot}6865$ (Hofmann, B. 22, 699). From methyl iodide and ammonia (Hofmann, J. 1862, 329). In small quantity by distilling the compound of aldehyde ammonia with sulphurous acid with caustic lime (Petersen, A. 102, 317). In the putrefaction of fishes; occurs in herring brine (Bocklish, B. 18, 87, 1924).

Preparation.—The product of the action of ammonia upon methyl iodide (consisting of hydriodides of mono- di- and tri-methylamine and tetramethylammonium iodide) is treated with alcohol in order to remove the last-mentioned compound. The residue on treatment with caustic potash yields the free bases which can be partially separated by condensation, the more volatile monomethylamine escaping condensation may be received in hydrochloric acid.

The mixture of the free bases is then treated with ethyl oxalate, the trimethylamine remains unacted upon, the di- compound is converted into the ethyl ether of methyl oxamic acid, while the mono- base is converted into dimethyl oxamide. The latter is difficultly soluble in cold water, and is thus separated from the dimethylamine compound which is then distilled with potash.

$$(CH_3)_2N.C_2O_2.(OC_2H_5) + 2KOH$$
$$= (KO)_2C_2O_2 + C_2H_5OH + N(CH_3)_2H.$$

The alcoholic solution is then neutralised with hydrochloric acid, evaporated to dryness, and decomposed by caustic potash. The hydrochlorate of dimethylamine can be freed from admixed ammonium chloride by treatment with chloroform, in which the latter is insoluble (Behrend, A. 222, 119).

Properties.—Dimethylamine is a colourless, inflammable liquid with a strong ammoniacal smell. Bromine acts upon an aqueous solution forming hypobromite and bromide of dimethylamine $N(CH_3)_2H.HBrO$ and $NH(CH_3)_2.HBr$, or, if the bromine be in excess, the unstable tribromide $N(CH_3)_2Br_3$, a yellow flocculent precipitate, is obtained (Raschig, B. 18, 2250).

Dimethylamine forms salts resembling those of ammonia, the hydrochlorate, however, is deliquescent, and very soluble in chloroform (*v.* also Topsoë, J. 1883, 618).

Trimethylamine $N(CH_3)_3$; b.p. 3·2–3·8° at 764·6 mm., sp.gr. $\frac{-5{\cdot}2^{\circ}}{} = {\cdot}662$ (Hofmann, B. 22, 699); b.p. = 9–10°, sp.gr. $\frac{0^{\circ}}{} = {\cdot}673$ (Bleunard). Does not solidify at −75° under a pressure of 10 mm.; forms a crystalline hydrate with 7 molecules of water, melting at 4·3°. Occurs in certain plants, *e.g. Chenopodium vulvaria, Arnica montana*, hawthorn blossom, pear and wild cherry blossom, and in ergot (Dessaignes, J. 1857, 481; Walz, J. 1852, 552). It also occurs in various animal fluids, *e.g.* in calves' blood (Dessaignes), and in human urine. Also in large quantities in herring brine (Wertheim, J. 1851, 480).

It is obtained by treating methyl iodide with ammonia (Hofmann), by the distillation of tetramethylammonium hydrate (Hofmann, A. 93, 325); by distillation of narcotine (Wertheim, A. 73, 208), or codeïne (Anderson, A. 77, 376), with potash.

By the putrefaction of yeast or of wheat meal (Hesse, J. 1857, 403). Also by the dry distillation of 'vinasses' from the beetroot sugar manufacture (Vincent, Bl. 27, 150).

Preparation.—The crude methylamine from the distillation of the 'vinasse' is treated with sulphuric acid, the solution evaporated to a syrup and treated with absolute alcohol, the monomethylamine sulphate is thus precipitated. The filtrate is treated with the proper amount—1 molecule for every 2 molecules of primary amine present—of oxalic ether, and allowed to stand for twenty-four hours. The precipitate, consisting of a mixture of di-isobutyl oxamide and di-isopropyl oxamide, is filtered off and the filtrate distilled; the residue is then decomposed by potash, the free bases received in alcohol, and the alcoholic solution mixed at 0° with oxalic ether (1 molecule to each molecule of free base) and allowed to stand for a day. The mixture is then distilled, and the triethylamine obtained pure. The non-volatile residue is made slightly alkaline with milk of lime and evaporated, calcium isopropyl oxamate first crystallises out, and then calcium ethyl oxamate. The mother-liquor, on addition of alcohol, gives a precipitate of calcium methyl oxamate while calcium dimethyl oxamate remains in solution (Duvillier and Buisine, A. Ch. [5] 23, 299).

Trimethylamine can more readily be obtained in a pure state by the distillation of tetramethylammonium hydrate.

Properties.—Trimethylamine is a volatile liquid with a strong, fish-like smell. It is very soluble in water, and possesses strong basic properties, though it can be displaced from its compounds by either mono- or dimethylamine.

When passed through a hot tube with hydrogen it decomposes, forming dimethyl dimethylene diamine $(CH_2)_2(CH_3)_2N_2$, ammonia, cyanogen, and other products (Romeny, B. 11, 835). It forms salts with acids, of which the hydrochlorate is of some importance; it is now employed in the manufacture of potassium carbonate from potassium chloride by a process analogous to the Solvay ammonia soda process. Ammonia cannot be employed in this process, since ammonium chloride has only about the same solubility as potassium hydrogen carbonate, while trimethylamine hydrochlorate is very much more soluble.

Trimethylamine combines with carbon disulphide to form a colourless crystalline compound $N(CH_3)_3.CS_2$, m.p. 125°, which is somewhat unstable; it is soluble in chloroform, and combines with dilute acids, but is decomposed by the strong acids into its constituents.

Tetramethylammonium $N(CH_3)_4$, *tetramethylium.* The base $N(CH_3)_4OH$ *tetramethylammonium hydrate* is obtained by the action of moist silver oxide upon the iodide. It forms a crystalline mass which eagerly absorbs water and carbon dioxide upon exposure to the air; has a strong alkaline reaction, and decomposes on heating into methyl alcohol and trimethylamine. The *iodide* $N(CH_3)_4I$ is the main product of the action of ammonia upon methyl iodide (Hofmann, Pr. 1851, 381). It forms quadratic prisms soluble in hot water, but only slightly in cold water. Sp.gr. 1·84 (Schröder, B. 12, 562).

Tetramethylammonium forms many salts which have the power of forming crystalline double compounds with many metallic salts (*v.* Topsoë, J. 1883, 619; Risse, A. 107, 223; Lossen, A. 181, 374).

Methyl hydroxylamine $CH_3.NH.OH$, obtained by treating the methyl salt of ethyl benzhydroxamic acid with hydrochloric acid (Lossen and Zanni, A. 182, 225). The hydrochlorate forms prisms which melt at 149°.

Methyl hydrazine $CH_3HN.NH_2$. A colourless liquid with ammoniacal smell. The sulphate $NHCH_3.NH_2.H_2SO_4$, a crystalline body, is obtained from methyl hydrazine carbamide which results from the action of nascent hydrogen upon nitroso-methyl carbamide $NH_2.CO.N.CH_3NO$ (Brüning, B. 21, 1809).

Dimethyl hydrazine $(CH_3)_2N.NH_2$; b.p. 62·5° at 717 mm.; sp.gr. $\frac{11^{\circ}}{} = {\cdot}801$; from nitroso-dimethylamine and nascent hydrogen (zinc-dust and acetic acid) in alcoholic solution (Renouf, B. 13, 2171). It has a strong ammoniacal smell, and is very soluble in water, alcohol, and ether. It is decomposed by nitrous acid into nitrous oxide and dimethylamine.

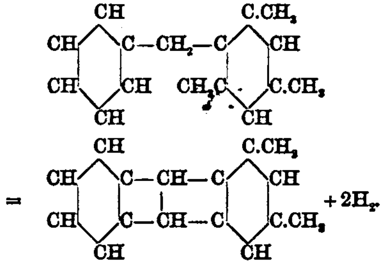
Tetramethyl tetrazone $(CH_3)_2N.N{:}N.N(CH_3)_2$; b.p. 130°; a yellow explosive oil, slightly soluble in water. It is a strong base, and its salts are very soluble in water; it reduces silver solution with formation of a mirror (Renouf).

METHYL-ANTHRACENE AND OTHER ALKYL DERIVATIVES OF ANTHRACENE. In order to obtain the higher homologues of anthracene, it has been found necessary in most cases to resort to synthetical methods, as very few of these substances have been met with in coal tar.

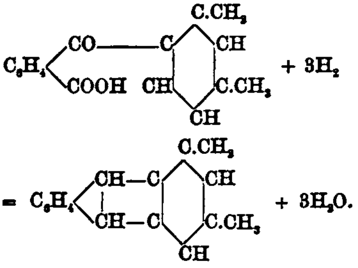
The methods usually employed are the following:—

(1) Elimination of hydrogen from the hydrocarbons of the C_nH_{2n-14}, or C_nH_{2n-16} series, by passing them through red hot tubes.

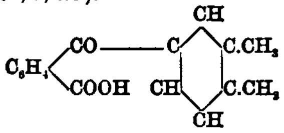
Benzyl mesitylene is thus converted into dimethylanthracene.



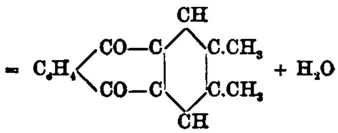
(2) By distilling *o*-ketonic acids with zinc-dust (Gresly, A. 234–238), *m*-xyloyl-*o*-benzoic acid yields *m*-dimethylanthracene.



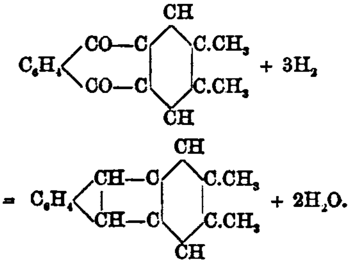
(3) By the action of sulphuric acid on *o*-ketonic acids (at about 125°), and subsequent reduction with zinc-dust and ammonia (Elbs, J. pr. 1890, 1, &c.).



o-Xyloyl-*o*-benzoic acid



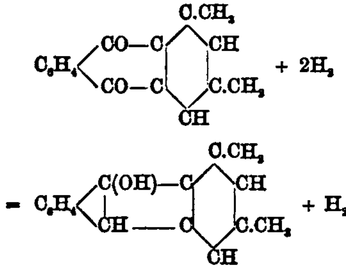
o-Dimethylanthraquinone



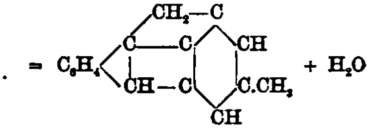
o-Dimethylanthracene

This reaction cannot be successfully employed in a number of cases where one of the methyl groups is attached to the carbon atom next to the CO, as under these conditions anthracylene derivatives frequently result (*v.* Elbs, *l.c.* p. 15–18).

Thus *m*-dimethylanthraquinone, on reduction with zinc-dust and ammonia, yields *m*-dimethylanthracylene and not *m*-dimethylanthracene.



m-Dimethylanthranol

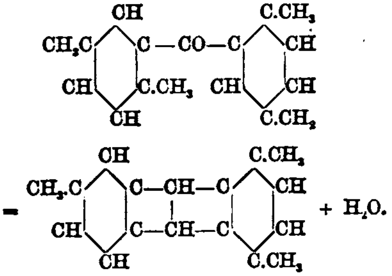


m-Dimethylanthracylene

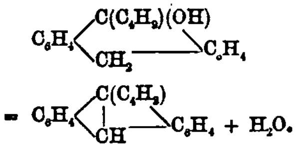
and similarly in a number of other cases.

It should, however, be remarked that the results of a number of Elbs' analyses of these anthracylene derivatives agree only so very approximately that this explanation can scarcely be looked on as completely satisfactory.

(4) By the prolonged boiling of some ketones. Thus di-*p*-xylylketone, when boiled for 6 hours on a reversed condenser yields (1,4,2) trimethylanthracene (Elbs, Olberg, B. 19, 409).

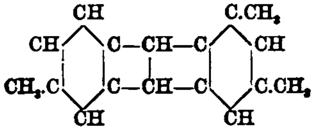


(5) The homologues of anthracene of the formula $C_6H_4(C_2HC_nH_{2n+1})C_6H_4$ are produced by boiling the alkylhydroanthranole with alcohol, hydrochloric acid, or picric acid. Thus isobutyl hydranthranol yields isobutylanthracene.

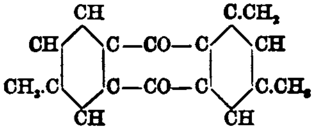


In their properties and reactions the homologues of anthracene behave very similarly to anthracene itself. On oxidation with chromic acid they yield corresponding anthraquinone derivatives, but in most cases the oxidation goes further and converts a portion of the anthraquinone into mono-, di-, or tricarboxylic acid, according to the number of side chains present, thus

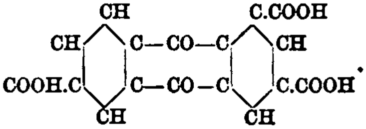
(1,3,3') Trimethylanthracene



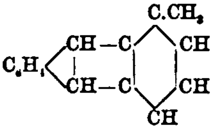
on oxidation yields first trimethylanthraquinone



and ultimately trimethylanthraquinone (1,3,3') tricarboxylic acid



***o*-Methylanthracene**



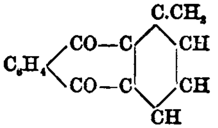
(Birukow, B. 20, 2069). This hydrocarbon is best prepared by distilling methylerythrooxyanthraquinone $C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_2(CH_3)(OH)$ with zinc-dust.

8 grams methylerythrooxyanthraquinone yield 4 grams methylanthracene.

The distillate is purified by recrystallisation from alcohol.

o-Methylanthracene crystallises from alcohol in colourless plates, which melt at 199-200°. The alcoholic solution possesses a beautiful blue fluorescence. The picrate crystallises in red needles.

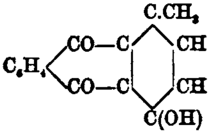
***o*-Methylanthraquinone**



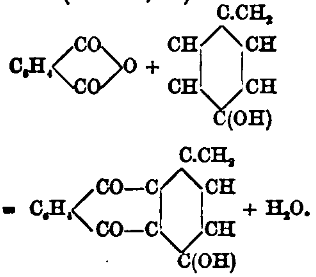
is readily prepared by oxidising *a*-methylanthracene with chromic acid in acetic acid solution, only small quantities of anthraquinone carboxylic acid being produced.

o-Methylanthraquinone crystallises from dilute acetic acid in small white needles, which, when exposed to light, become reddish-coloured. It melts at 166-167°, is very readily soluble in alcohol and benzene, but difficultly soluble in glacial acetic acid.

Methylerythrooxyanthraquinone



is produced when a mixture of phthalic anhydride and *p*-kresol is heated with concentrated sulphuric acid (Birnkoff, *l.c.*).



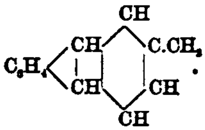
Preparation.—5 parts of phthalic anhydride, 2 parts of *p*-kresol, and 15 parts of concentrated sulphuric acid are heated to 160° for ten minutes, the product poured into water, the precipitate well washed with boiling water, and extracted with boiling dilute caustic potash solution. Methylerythrooxyanthraquinone is obtained from the alkaline solution by the addition of hydrochloric acid in yellow flocks, which are readily purified by recrystallisation from glacial acetic acid. The pure substance is thus obtained in beautiful dark-brown needles, which melt at 169-170°.

Methylerythrooxyanthraquinone is almost insoluble in ammonia and carbonate of soda solution, readily soluble in caustic potash solution with a red colouration; with baryta or lime-water insoluble brick-red lakes are produced. It dissolves in sulphuric acid with an orange-yellow colour, sublimes very easily, and in all its reactions, and also in its absorption spectrum, shows great similarity with erythrooxyanthraquinone.

Fusion with potash converts it with difficulty into a colouring matter which is probably *a*-methylalizarine.

The *acetate* crystallises from acetic acid in yellow needles, which melt at 179-180°.

***m*-Methylanthracene**

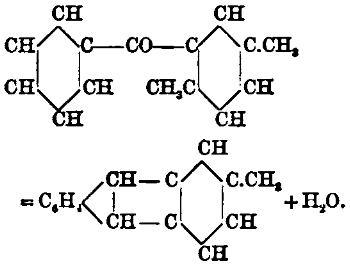


This hydrocarbon is found in varying quantities, together with anthracene and phenanthrene, in the fraction of coal tar which distils above 340°.

It may be synthetically prepared by the following reactions.

1. By passing the vapours of ditolylmethane (Weiler, B. 7, 1185) $CH_2(C_6H_4CH_3)_2$, ditolylethane (Fischer, B. 7, 1195), $CH_3{\cdot}CH(C_6H_4CH_3)_2$, or of oil of terpentine (Schultz, B. 10, 117) through a red-hot tube.

2. By boiling *p*-xylylphenylketone for several days on a reflux apparatus (Elbs, J. pr. 1890, 3).

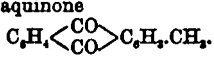


3. By the distillation of chrysophanic acid $C_{15}H_{10}O_4$, emodin $C_{15}H_{10}O_5$ (Liebermann, A. 183, 163), colophonium, benzoe resin (Ciamician, B. 11, 273), chrysarobin $C_{30}H_{26}O_7$ (Liebermann, Seidler, A. 212–34) and methylquinizarine $C_{15}H_{10}O_4$ (Nietzki, B. 10, 2013) with zinc-dust.

Preparation (Japp, Schultz, B. 10, 1049).—The high boiling distillate of coal tar, known as crude phenanthrene, is freed from the greater part of the anthracene it contains by oxidation with bichromate of potash and sulphuric acid. The dark-brown mass is extracted with hot alcohol, the well-cooled solution allowed to deposit as much anthracene and phenanthrene as possible, the mother-liquors which contain the methylanthracene evaporated and the residue repeatedly recrystallised from alcohol.

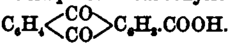
Methylanthracene crystallises from alcohol in yellow needles which melt at 199-200°. It sublimes readily when heated continuously at 100°. It is difficultly soluble in ether, alcohol, glacial acetic acid, acetone, and light petroleum, readily soluble in benzene, chloroform, and carbon bisulphide.

Oxidation with nitric acid converts it into methylanthraquinone



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3.CH_3.$$

Chromic acid oxidises it for the most part direct to β-anthraquinone carboxylic acid



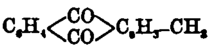
$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3.COOH.$$

Methylanthracene combines with picric acid, forming a compound which crystallises in large red needles; alcohol and water decompose this compound.

Dibrommethylanthracene $C_{15}H_{10}Br_2$ is produced by treating methylanthracene in CS_2 with bromine; it crystallises from glacial acetic acid in yellow needles, m.p. 156°.

Tetrabrommethylanthracene $C_{15}H_8Br_4$ is formed when dibrommethylanthracene is treated with bromine. It crystallises from toluene in yellow needles. Oxidation with nitric acid converts this compound into dibrommethylanthraquinone $C_{15}H_8Br_2O_2$.

m-**Methylanthraquinone** (O. Fischer, B. 8, 675)



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3\text{—}CH_3$$

is obtained by boiling methylanthracene in alcoholic solution with nitric acid, or by carefully oxidising the hydrocarbon with CrO_3, in which latter case, however, considerable quantities of anthraquinone and anthraquinone carboxylic acid are also formed.

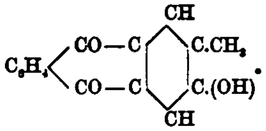
Sublimes in yellow needles, m.p. 162°-163°: moderately soluble in ether, acetone, chloroform, and hot alcohol; difficultly soluble in glacial acetic acid and benzene.

Dibrommethylanthraquinone (Liebermann, Seidler, B. 11, 1606) $C_{15}H_8Br_2O_2$ is obtained by oxidising dibrommethylanthracene with nitric acid. Sparingly soluble in organic solvents. (Other properties not given.)

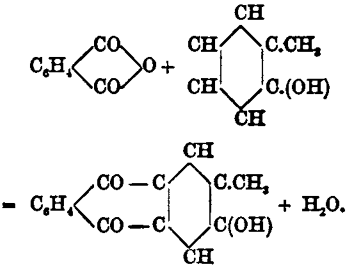
Methylanthraquinone disulphonic acid (O. Fischer, *l.c.*) $C_{15}H_8(HSO_3)_2O_2$.

Preparation. — Methylanthraquinone is heated with 5–6 parts of fuming sulphuric acid for several hours at 250°–270°. The alkali salts and the barium and calcium salts of this acid are soluble in water. Fusion with potash converts the acid into methylalizarine.

Oxymethylanthraquinone

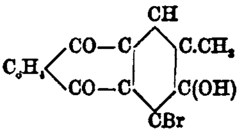


Preparation (Fraude, A. 202, 163).—By heating 2 parts of *o*-cresol, 3 parts phthalic anhydride, and 100 parts of sulphuric acid at 160° for two days. The product is poured into water, extracted repeatedly with ether; the ether distilled off, the residue divided in dilute soda, acidified with HCl, and the precipitate purified by sublimation and recrystallisation from alcohol.



Oxymethylanthraquinone melts at 260°-262°, is readily soluble in alcohol, ether, and acetic acid; it dissolves in alkalis, also in lime and baryta water, forming a dark reddish-brown solution. When strongly heated it sublimes in golden-yellow leaflets.

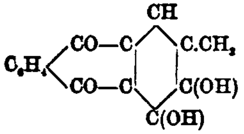
Bromoxymethylanthraquinone



is obtained by heating 4 parts of dibromo-*o*-cresol phthaleïne ($C_{22}H_{16}Br_2O_4$) with 1 part of phthalic anhydride and 200 parts of sulphuric acid at 150° for five hours.

Small yellow needles, m.p. 205°. Fusion with potash converts this substance into *a*-methylalizarine.

Dioxymethylanthraquinone (α-methylalizarine)



is readily prepared by fusing methylanthraquinone disulphonic acid (O. Fischer, *l.c.*), oxymethylanthraquinone or bromoxymethylanthraquinone (Fraude, A. 202, 166) with potash. The melt is dissolved in water, acidified with HCl, and the precipitate purified by sublimation. Orange-yellow needles, m.p. 250°-252°, moderately soluble in alcohol, ether, and acetone. The calcium and barium salts are insoluble blue precipitates.

The absorption spectrum of a solution of this substance in concentrated sulphuric acid is

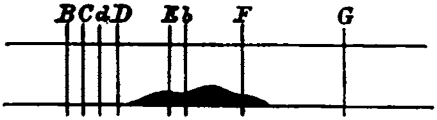
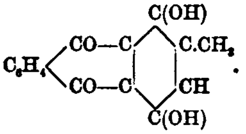


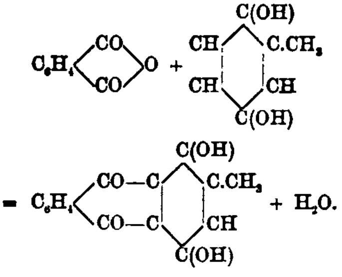
Fig. 1.

which corresponds very closely with that of alizarine itself (Liebermann, Kostanecki, B. 19. 2330). Methylalizarine dyes mordanted cloth similarly to alizarine, but according to some authorities the tinctorial power of methylalizarine is much inferior to that of alizarine, hence the introduction of this substance into artificial alizarine is avoided by the alizarine manufacturer as much as possible.

Methylquinizarine (Nietzki, B. 10, 2012)



This isomeride of methylalizarine is produced by heating a mixture of hydrotoluquinone and phthalic anhydride with 8–10 parts of sulphuric acid at 130°-150° for two to three hours. The product is treated with water, the precipitate repeatedly extracted with boiling water, and purified by recrystallisation from benzene.



Methylquinizarine crystallises in long fine bent needles which melt at 160° and sublime with slight decomposition. The solutions in ether and alcohol are fluorescent. Distilled with zinc-dust methylanthracene is formed.

The absorption spectrum of methylquinizarine dissolved in sulphuric acid is represented as follows:

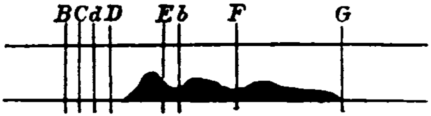
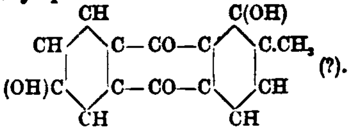


Fig. 2.

and is very closely allied to that of quinizarine itself.

Methylquinizarine when treated with acetic anhydride yields a *diacetate* $C_{15}H_8(C_2H_3O)_2O_4$, which crystallises in yellow needles, m.p. 185.

Chrysophanic acid



Occurrence.—In Lichens, *Parmelia parietana*, *Squamaria elegans*, in the root of *Rumex obtusifolius*. and in senna leaves.

Preparation (Liebermann, Seidler, A. 212, 36). Chrysarobin is mixed with dilute potassium hydrate solution and a current of air passed until the liquid has acquired a deep and even reddish hue. HCl is then added and the precipitate extracted with light petroleum. Chrysophanic acid crystallises from alcohol in golden-yellow needles which melt at 162°, and on strongly heating sublime in needles. It is almost insoluble in water, but soluble in ether, benzene, and glacial acetic acid. It is difficultly soluble in ammonia and alkaline carbonates, but readily so in potassium hydrate, forming a deep-red solution. It does not dye mordanted cloth. Distilled with zinc-dust chrysophanic acid yields methylanthracene (Liebermann, A. 183, 169).

The absorption spectrum of a solution of chrysophanic acid (Liebermann, Kostanecki, B. 19, 2330) in sulphuric acid, which resembles very closely that of chrysazin, is

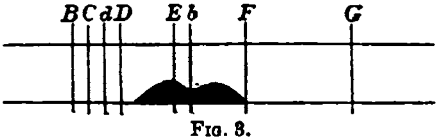


Fig. 3.

Tin and hydrochloric acid, reduce chrysophanic acid to *chrysophanhydranthron*

$$OH.C_6H_3{<}\substack{CH_2\\CO}{>}C_6H_2(CH_3)(OH),$$

light-yellow microscopic needles, m.p. 200°-206°.

Acetic anhydride converts chrysophanic acid into a *diacetate* (Liebermann, Seidler, B. 11, 1607) $C_{15}H_8(C_2H_3O)_2O_4$, light-yellow plates, m.p. 202°-204°.

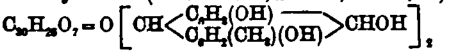
The corresponding *dibenzoate* (W. de la Rue, H. Müller, J. 1862, 323), $C_{15}H_8(C_7H_5O)_2O_4$ crystallises from a mixture of alcohol and benzene in long irregular six-sided prisms, m.p. 200°.

Tetranitrochrysophanic acid (Liebermann, Giesel, A. 183, 175) $C_{15}H_6(NO_2)_4O_4$ is the product of the action of fuming nitric acid on chrysophanic acid. It crystallises in yellow plates, which decompose on melting.

Amidochrysophanic acid (Liebermann, A. 183, 218) $CH_3C_{14}H_5(OH)(NH_2)O_2$ is formed when chrysophanic acid is heated to 200° with strong ammonia. Crystallises from alcohol in small brownish-coloured plates. HCl decomposes it into ammonia and chrysophanic acid.

Diamidochrysophanic acid (Liebermann, *l.c.*) $CH_3C_{14}H_5(NH_2)_2O_2$ separates in the form of a crystalline precipitate when chrysophanic acid is heated with ammonia to 150°.

Chrysarobin (Liebermann, Seidler, A. 212, 34)



$$C_{30}H_{26}O_7 = O\left[CH<\begin{matrix}C_6H_3(OH)\\C_6H_2(CH_3)(OH)\end{matrix}>CHOH\right]_2$$

occurs in the powder which separates out in the pith hollows of certain trees (*Arraroba*, *Angelim amargosa*) in Brazil and India. The powder is extracted with beuzene, the solution evaporated, and the residue repeatedly recrystallised from glacial acetic acid. Small yellow needles, m.p. 170–178. Insoluble in water and ammonia, difficultly soluble in alcohol and ether, more readily soluble in benzene, glacial acetic acid, and chloroform. Insoluble in very dilute potassium hydrate, but soluble with a dark-green fluorescence in strong solutions. This solution is readily oxidised by the oxygen of the air, yielding chrysophanic acid:

$$C_{30}H_{26}O_7 + 4O = 2C_{15}H_{10}O_4 + 3H_2O.$$

Distilled with zinc-dust, chrysarobin yields methyl anthracene.

The **Tetraacetate** $C_{30}H_{22}(C_2H_3O)_4O_7$ crystallises in yellow prisms, m.p. 228–230°.

Trioxymethylanthraquinone.

(*a*) **Emodin** $C_{15}H_{10}O_5 = C_{14}H_4(CH_3)(OH)_3O_2$ (position of OH groups unknown, but probably the same as those in flavopurpurine).

Occurrence.—In rhubarb root and the bark of the alder tree.

Preparation.—Alder bark is extracted with dilute sodium hydrate, the solution precipitated with HCl, and the precipitate purified by repeated recrystallisation from absolute alcohol.

Orange-red, silky needles, m.p. 245°–250° (Liebermann, A. 183, 161).

Moderately soluble in benzene, more readily so in alcohol and acetic acid; soluble in dilute ammonia, forming a cherry-red solution. Does not dye mordanted cloth. Distilled over zinc-dust, methylanthracene results. The absorption spectrum of a solution in concentrated sulphuric acid is (Liebermann, Kostanecki, B. 19, 2330):

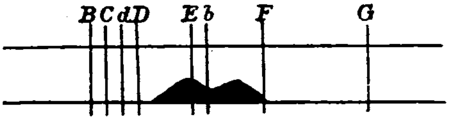
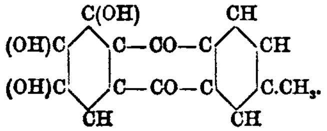


FIG. 4.

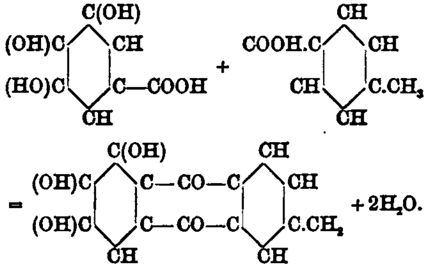
and closely resembles that of flavopurpurine.

The **Triacetate** (Liebermann, *l.c.*) $C_{15}H_7(C_2H_3O)_3O_5$ crystallises from glacial acetic acid in yellow needles, m.p. 190°.

(*b*) **β-Methylanthragallol**



Formation.—By heating a mixture of gallic acid and *p*-toluylic acid to 130° (Cahn, A. 240–284):



Sublimes in orange-red needles, m.p. 275°. Its other properties are very similar to those of anthragallol itself. The absorption spectrum of its solution in sulphuric acid is (Cahn, *l.c.*):

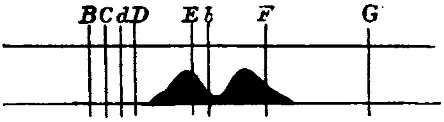
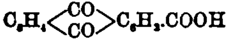


FIG. 5.

β-Anthraquinone carboxylic acid



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_3.COOH$$

is produced by oxidising methylanthracene or β-anthracene carboxylic acid (Liebermann, Rath, B. 8, 248) with chromic acid and acetic acid, or $K_2Cr_2O_7$ and H_2SO_4.

Preparation.—Methylanthraquinone (1 part) is dissolved in concentrated sulphuric acid (6 parts), mixed then with water (1 part), and $K_2Cr_2O_7$ (2½ parts) slowly added. The mass is warmed to 110°–120° for a short time, filtered, the precipitate washed with water, and boiled out with dilute ammonia. The excess of ammonia is evaporated off, the solution filtered, and precipitated with HCl (Börnstein, B. 16, 2609; *v.* also Liebermann, Glock, B. 17, 888).

β-Anthraquinone carboxylic acid crystallises from alcohol in yellow prisms, which melt at 282°-284°, and sublime when carefully heated undecomposed. It is almost insoluble in ether, benzene, chloroform, and excess of caustic soda, difficultly soluble in glacial acetic acid and absolute alcohol, readily soluble in acetone. Gives with zinc-dust and KOH the anthraquinone reaction; reduction with zinc-dust and ammonia converts it into γ-anthracene carboxylic acid. Distillation over red-hot asbestos decomposes it into CO_2 and anthraquinone. It dissolves in sodium acetate and ammonium oxalate, and is not reprecipitated on the addition of acetic acid. Fusion with soda converts it into oxyanthraquinone carboxylic acid $C_{15}H_8O_5$.

The calcium salt $Ca(C_{15}H_7O_4)_2$ and the barium salt $Ba(C_{15}H_7O_4)_2$ are sparingly soluble.

Ethyl salt (Liebermann, Glock, B. 17, 890) $C_{15}H_7O_4.C_2H_5$ is formed by the action of alcohol on the chloride. It crystallises in needles, melts at 147°, and is readily soluble in alcohol.

Chloride $C_{15}H_7O_3Cl$ is produced by treating the acid with PCl_5. Crystallises from benzene in needles which melt at 147°.

Amide $C_{14}H_7O_2CONH_2$ is obtained by passing NH_3 into a benzene solution of the chloride. It crystallises from a mixture of glacial acetic acid and benzene in needles, which melt at 280°, and are difficultly soluble in alcohol and benzene.

Anilide crystallises from xylene in needles, m.p. 258°–260°.

Nitroanthraquinone carboxylic acid

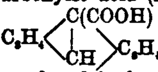
$C_{14}H_6(NO_2)O_2.COOH$

is produced by mixing the solution of the acid in concentrated sulphuric acid with nitric acid. Crystallises from glacial acetic acid in small needles, which melt above 300°. Gives with sulphuric acid a violet colouring matter.

γ-Anthraquinone carboxylic acid (Liebermann, Bischoff, B. 13, 49) $C_{14}H_7O_2COOH$ is formed by dissolving γ-methylanthracene in boiling glacial acetic acid, and adding an aqueous solution of chromic acid.

It crystallises from glacial acetic acid in long, pale-yellow needles, which melt at 285°. Gives with zinc-dust and caustic soda solution a red colouration.

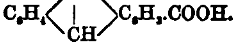
The **Barium salt** is very sparingly soluble in water.

α-Anthracene carboxylic acid (Liebermann, Graebe, B. 2, 678)  $C_6H_4\left\langle\begin{matrix}C(COOH)\\|\\CH\end{matrix}\right\rangle C_6H_4$. The chloride of this acid is produced by heating anthracene with $COCl_2$ to 180°-200°.

The acid crystallises from alcohol in long, silky, pale-yellow needles, which melt at 206° with decomposition. It is almost insoluble in cold water, readily soluble in alcohol. On distillation with soda lime it decomposes into CO_2 and anthracene. The salts are mostly soluble in water.

β-Anthracene carboxylic acid. The nitrile of this acid is produced by distilling potassium anthraquinone sulphonate (from anthracene and H_2SO_4) with potassium ferrocyanide (Liebermann, Rath, B. 8, 246). The acid crystallises from acetic acid in lemon-yellow needles, which melt at about 260°, but become soft at 220°–230°. It sublimes undecomposed in needles, is sparingly soluble in benzene and ether, readily soluble in alcohol and glacial acetic acid, insoluble in water. Distillation with soda lime decomposes it into CO_2 and anthracene. Chromic acid oxidises it to anthraquinone carboxylic acid $C_{15}H_8O_4$ (m.p. 282°–284°). The acid and its salts possess a blue fluorescence; the latter are mostly readily soluble in water. The Ba and Ca salts dried at 130° are yellow amorphous powders. The Pb salt is a flocky precipitate.

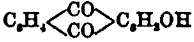
γ-Anthracene carboxylic acid



$C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_3.COOH.$

The nitrile of this acid is obtained (together with a small quantity of the nitrile of the β acid) by distilling sodium anthracene sulphonate (from the acid obtained by the reduction of anthraquinone sulphonic acid) with potassium ferrocyanide (Liebermann, Bischoff, B. 13, 47). The nitriles are decomposed by boiling with KOH, and the acids separated by means of their barium salts; that of the β-acid being readily soluble in water, whereas barium γ-anthracene carboxylate is very sparingly soluble.

The same acid is produced by the reduction of β-anthraquinone carboxylic acid



$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle C_6H_3OH$

with zinc-dust and ammonia (Börnstein, B. 16, 2610).

γ-Anthracene carboxylic acid crystallises from alcohol in small yellow plates, which melt at about 280°, and sublime at a higher temperature in plates. It is sparingly soluble in $CHCl_3$, almost insoluble in CS_2 and benzene, less soluble in alcohol and glacial acetic acid than the β-acid. The alcoholic solution possesses an intense blue fluorescence. Reduction with sodium amalgam or hydriodic acid converts this acid into three acids, $C_{15}H_{12}O_2$, $C_{15}H_{14}O_2$, and $C_{15}H_{16}O_2$. Chlorine led into the solution in $CHCl_3$ produces first γ-chloranthracene carboxylic acid and then dichloranthracene (m.p. 209°). Bromine behaves similarly.

The **Sodium salt** is difficultly soluble in cold water, and crystallises in glittering flakes. The solutions fluoresce blue.

The **Barium salt** is almost insoluble in cold water, and only very sparingly soluble in hot.

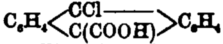
Methyl salt (Behla, B. 20, 703) $C_{15}H_9O_2CH_3$ crystallises in yellow prisms; m.p. 111°.

Ethyl salt (Liebermann, Bischoff, B. 13, 49) $C_{15}H_9O_2C_2H_5$ melts at 134°, and is readily soluble in alcohol. Both these salts distil without decomposition.

Chloride (Börnstein, *l.c.*) $C_{15}H_9OCl$ crystallises from benzene in yellow warts; m.p. not given. Readily soluble in alcohol ether, $CHCl_3$ and CS_2. Decomposed only by boiling water.

Amide $C_{15}H_9ONH_2$ crystallises from glacial acetic acid in plates; m.p. 293°–295°. Insoluble in water, CS_2, $CHCl_3$, and benzene. Difficultly soluble in alcohol. The solutions fluoresce blue.

γ-Chloranthracene carboxylic acid (Behla, *l.c.*)

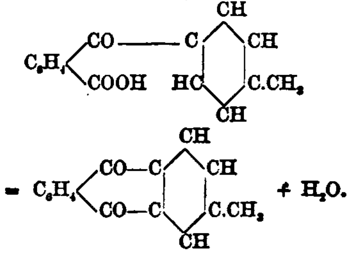


$C_6H_4\left\langle\begin{matrix}CCl—\\C(COOH)\end{matrix}\right\rangle C_6H_4$

(*v. supra*) crystallises from benzene in needles; m.p. 258°–259°, being at the same time decomposed into chloranthracene and CO_2.

γ-Bromanthracene carboxylic acid (Behla, *l.c.*) crystallises from alcohol in long, greenish-yellow needles; melts at 266°, being converted into CO_2 and bromoanthracene.

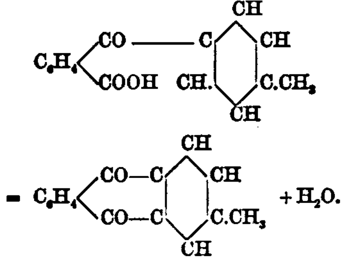
A second *m*-**Methylanthraquinone** which should be identical with the *m*-methylanthraquinone just described, has been isolated from the by-products which accumulate in the manufacture of anthraquinone (Wachendorff, Zincke, B. 10, 1485; Börnstein, B. 15, 1820). This substance is identical with the methylanthraquinone which is obtained synthetically by heating *p*-toluenephthalylic acid with concentrated sulphuric acid to 160–180° (Gresly, A. 234, 239).



The melting-point of this substance is 177°, or about 15° higher than Fischer found for his methylanthraquinone. In most other respects these substances have almost identical properties, except that Fischer's methylanthraquinone is difficultly soluble in benzene and glacial acetic acid, whereas the above substance dissolves readily in these solvents.

Fischer's methylanthraquinone is prepared by the oxidation of a methylanthracene melting at 199-200°, whereas the above supposed isomer yields on distillation with zinc-dust a methylanthracene of almost identical melting-point, *i.e.* 203°.

This methylanthraquinone (m.p. 176–177°) is conveniently prepared by the action of sulphuric acid on *p*-toluyl *o*-benzoic acid (Elbs, J. pr. 1890, 4; Gresly, A. 234, 239).



The powdered acid is slowly added to 7 or 8 times its weight of concentrated sulphuric acid, and the mixture gradually heated until at the end of half an hour the temperature has risen to 120–125°.

The clear dark brownish-red coloured solution is kept at this temperature for about an hour, allowed to cool and poured into much water. Steam is passed through the liquid for some time, the precipitate collected, washed well first with water, and lastly with dilute ammonia, dried, and the greenish-yellow mass purified by recrystallisation from a mixture of xylene and alcohol. Yield 70–75° p.c. of theory.

The following derivatives of this methylanthraquinone have been prepared:—

Nitromethylanthraquinone

$C_{15}H_9NO_4 = CH_3.C_{14}H_6(NO_2)O_2$.

Preparation.—Methylanthraquinone (2 parts) is dissolved in concentrated H_2SO_4 (12–14 parts), and to the resulting solution KNO_3 (1 part) is slowly added. The product after standing 24 hours is carefully mixed with water, the precipitate collected, and extracted repeatedly with alcohol until the filtrate is only slightly yellowish-coloured. The resulting nitromethylanthraquinone is purified by recrystallisation from acetic acid (Römer, Link, B. 16, 695), from which solvent it is obtained in yellow needles melting at 269–270°. It is difficultly soluble in alcohol, ether, benzene, chloroform, glacial acetic acid, and ethylacetate, readily soluble in nitrobenzene. It dissolves in sulphuric acid, producing a yellow solution which on warming turns brown. Water precipitates from this solution a purple precipitate, which dissolves in alkalis with a violet-blue colour. Nitromethylanthraquinone sublimes in small almost colourless needles. It is not decomposed by boiling caustic potash solution.

Amidomethylanthraquinone

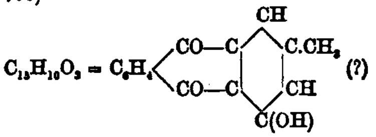
$C_{15}H_{11}NO_2 = CH_3.C_{14}H_6(NH_2)O_2$

is readily produced by the reduction of nitromethylanthraquinone with $SnCl_2$ (Römer, Link, *l.c.*). The freshly precipitated nitro- substance is added in small quantities at a time to a dilute solution of $SnCl_2$ in KOH, and the product heated nearly to boiling. The resulting precipitate, which must dissolve completely in excess of cold HCl, is purified by recrystallisation from dilute HCl.

Amidomethylanthraquinone crystallises in glittering red needles which melt at 202°, and sublime on heating in long dark-red needles. It is almost insoluble in water, readily soluble in alcohol, ether, chloroform, benzene, and glacial acetic acid. Boiling with hydriodic acid and phosphorus converts it into amidomethylanthranole $C_{15}H_{13}NO$; at 150°, however, amidomethylanthracenedihydride $CH_3.C_{14}H_{10}NH_2$ results.

The *acetyl-derivative* $CH_3.C_{14}H_6O_2NH(C_2H_3O)$ crystallises from glacial acetic acid in yellow needles, m.p. 176-177°.

Oxymethylanthraquinone (Römer, Link, B. 16, 700)



is produced from amidomethylanthraquinone by the replacement of the amido- group by the hydroxyl group.

Preparation. — Amidomethylanthraquinone is dissolved in sulphuric acid, the solution mixed with small quantities of water until the resulting precipitate becomes reddish-coloured.

The well-cooled product is slowly mixed with a solution of KNO_2 until the precipitate becomes light yellow and free nitrous acid is evolved, then an equal volume of water is added and the whole heated to boiling.

The precipitate is collected, dissolved in boiling dilute caustic potash solution, precipitated with HCl, and recrystallised from alcohol.

Oxymethylanthraquinone crystallises from alcohol in orange-yellow needles which melt at 177-178°, and sublime in long thin yellow plates when carefully heated. It is almost insoluble in water, difficultly soluble in alcohol, readily soluble in ether and benzene. Cold caustic potash solution dissolves it sparingly.

Fused with potash a small quantity of a colouring matter is produced which dissolves in alkalis with colourations similar to those produced by alizarine. Oxymethylanthraquinone, if freshly precipitated, dissolves in boiling lime or baryta water, but is insoluble in sodium carbonate or solution of alum. Its alcoholic solution is not precipitated by alcoholic lead acetate.

The *acetate* $C_{17}H_{12}O_4 = CH_3.C_{14}H_6O_2(C_2H_3O_2)$ crystallises from alcohol in orange-yellow plates which melt at 177°.

Under the heading methylanthracene, besides *o*- and *m*-methylanthracene two other substances are to be found in chemical literature.

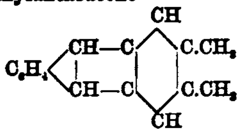
Isomethylanthracene (Börnstein, B. 15, 1821) obtained by digesting isomethylanthraquinone with zinc-dust and ammonia, and by distilling *p*-toluene phthaloylic acid (Gresly, A. 234, 238), with zinc-dust, is evidently identical with *m*-methylanthracene.

Methanthrene $C_{15}H_{12}$ (Oudemans, J. pr. [2] 9, 416), obtained by distilling podocarpinic acid $C_{17}H_{22}O_3$ with zinc-dust, is probably not an anthracene derivative at all. It melts at 117°, and gives on oxidation with CrO_3 and acetic acid, methanthraquinone $C_{15}H_{10}O_2$ which crystallises from 70 p.c. alcohol in orange-red needles melting at 187°.

It therefore possesses more the properties of a phenanthrene than of an anthracene derivative.

DIMETHYLANTHRACENES.

***o*-Dimethylanthracene**

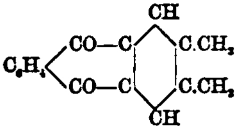


(Elbs, J. pr. 1890, 5–12) is readily prepared by the reduction of the corresponding (2, 3) dimethylanthraquinone with zinc-dust and ammonia.

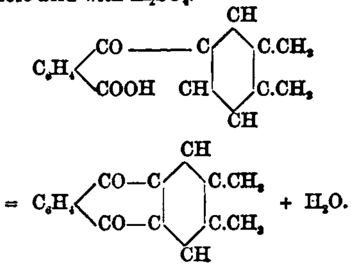
5 grams of the quinone, 30 grams zinc-dust, and 500 c.c. aqueous ammonia (equal parts of concentrated ammonia solution and water), are heated to boiling until the red liquid which is produced at first has become colourless. The mass is then filtered, the residue washed with hot water, dried in a water oven, and repeatedly extracted with boiling alcohol. The clear alcoholic extract deposits on cooling yellowish plates of dimethylanthracene. *o*-Dimethylanthracene melts at 246°, and sublimes in colourless plates which possess a bluish-green fluorescence. It is readily soluble in benzene and hot alcohol, but difficultly soluble in cold alcohol.

The picric acid compound crystallises in long garnet-red needles; it is readily decomposed by alcohol.

o- or (2, 3) **Dimethylanthraquinone**

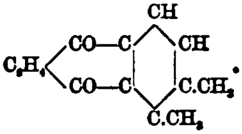


is obtained synthetically by heating *o*-xyloyl-*o*-benzoic acid with H_2SO_4.



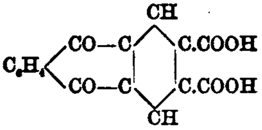
1 part of *o*-xyloyl-*o*-benzoic acid is dissolved in 6 parts of warm concentrated H_2SO_4, and the mixture heated at 128° for a quarter to half an hour, the dark-coloured solution poured into a dish, and placed next a dish of water. As the solution becomes dilute the quinone crystallises out, the operation being complete in 3–4 days.

The precipitate is collected, washed with water and dilute ammonia, and purified either by sublimation or recrystallisation from xylene; *o*-dimethylanthraquinone is thus obtained in long yellow needles which melt at 183°. It is readily soluble in hot xylene, benzene, and alcohol, and is readily reduced by zinc-dust and ammonia to *o*-dimethylanthracene, hence its constitution is probably that given above, and not

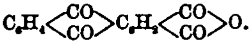


(Compare action of zinc-dust and ammonia on dimethylanthraquinones with a CH_3 group in the 1 or 4 position.)

Anthraquinone-*o*-dicarboxylic acid



is produced by heating *o*-dimethylanthraquinone (3 grams) with 20–25 c.c. of nitric acid (sp.gr. 1·1) in a sealed tube at 210–220° for five hours. It crystallises in yellow needles, melts at 340°, and when strongly heated sublimes in yellow plates, which melt at 290°, and consist now of anthraquinone dicarboxylic anhydride.



$$C_6H_4{<}{\substack{CO\\CO}}{>}C_6H_2{<}{\substack{CO\\CO}}{>}O.$$

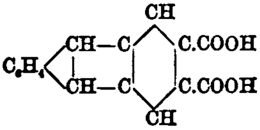
Ammonium salt. Red amorphous mass, easily soluble in water.

Calcium salt. Light red precipitate, almost insoluble in water.

Lead salt. Light red precipitate, almost insoluble in water.

Ag salt. Light red precipitate; is decomposed on heating into CO_2, Ag, and ordinary anthraquinone.

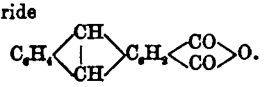
Anthracene-*o*-dicarboxylic acid



is readily prepared by treating the solution of the ammonium salt of anthraquinone dicarboxylic acid with zinc-dust and ammonia until the red solution becomes yellowish-green coloured; and then precipitating the clear solution with HCl.

Anthracene-*o*-dicarboxylic acid crystallises from alcohol in small yellowish-green crystals, which melt at 345°. It is insoluble in water, readily soluble in alcohol. The solution in dilute ammonia fluoresces blue-green, that in dilute NaOH blue.

The acid, if carefully heated, gives a yellowish-red sublimate of anthracene-*o*-dicarboxylic anhydride



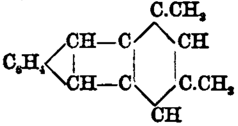
$$C_6H_4{<}{\substack{CH\\|\\CH}}{>}C_6H_2{<}{\substack{CO\\CO}}{>}O.$$

Calcium salt. Brownish-green precipitate, almost insoluble in water.

Lead salt. Yellowish precipitate, insoluble in water.

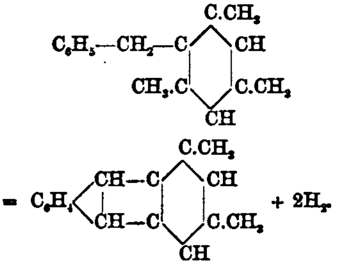
Silver salt. Yellowish-brown precipitate, insoluble in water; decomposes on distillation into CO_2, Ag, and anthracene.

***m*-Dimethylantaracene**

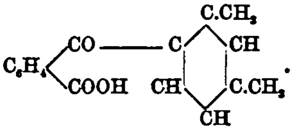


(Elbs, J. pr. 1890, 13-27). This hydrocarbon cannot be produced by the reduction of *m*-methylanthraquinone with zinc-dust and ammonia.

It is obtained by passing mesitylphenyl methane (Louise, A. Ch. [6] 6, 187, 193) through a red-hot tube



Or by distilling *m*-xyloyl-*o*-benzoic acid

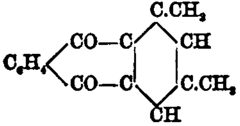


with zinc-dust (Gresly, A. 234, 238).

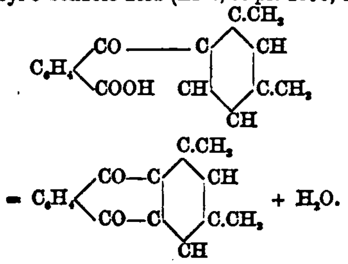
m-Dimethylanthracene crystallises from alcohol in colourless plates, which melt at 202–203°. Gives with bromine γ-brom-*m*-dimethyl anthracene tetrabromide

(m.p. 175–180°).

***m*-Dimethylanthraquinone**

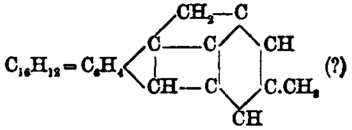


is prepared by the action of sulphuric acid on *m*-xyloyl-*o*-benzoic acid (Elbs, J. pr. 1890, 13).



1 part of the pure acid is dissolved in 7–10 parts of concentrated sulphuric acid, the clear solution heated to 110–125° for half an hour, the product poured in a thin stream into water, and the precipitate treated as described under *m*-methylanthraquinone. Yield 60–70 p.c. of theory. *m*-Dimethylanthraquinone crystallises in small needles which melt at 162°. It dissolves with difficulty in alcohol and benzene. Zinc-dust and ammonia reduces it to *m*-dimethylanthracylene $C_{16}H_{12}$, and not to dimethylanthracene.

***m*-Dimethylanthracylene**

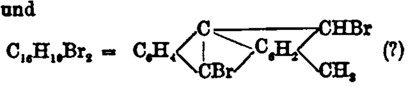


Preparation.—*m*-Dimethylanthraquinone (5 grams), finely powdered, is mixed with zinc-dust (30 grams) and concentrated aqueous ammonia (200 c.c.), and a solution (5 c.c.) of basic copper carbonate in ammonia added. The product is well agitated, and gently warmed until it has assumed a light green colour, then boiled for six hours with the addition from time to time of small quantities of copper carbonate dissolved in ammonia. The mass is filtered, the precipitate washed with water, dried at the ordinary temperature, and extracted with boiling alcohol. The alcoholic solution on cooling deposits a small quantity of crystals, which are filtered off. The mother liquor is partially evaporated, again allowed to stand, filtered from the crystals which form, and this operation repeated until oily drops appear. The remainder of the hydrocarbon present in the mother liquor is purified by conversion into the picric acid compound and decomposing this with ammonia or sodium hydrate solution (Elbs, *l.c.*).

m-Dimethylanthracylene crystallises from alcohol in groups of colourless plates which melt at 85°. It is readily soluble in hot alcohol and glacial acetic acid, difficultly soluble in cold alcohol.

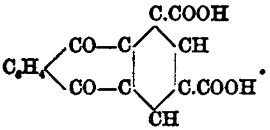
With picric acid it forms a deep garnet-red compound $C_{16}H_{12}\text{-}C_6H_2(NO_2)_3OH$, which is not decomposed by alcohol. M.p. 135°.

Treated with bromine in CS_2 solution (4 at. Br to 1 mol. $C_{16}H_{12}$) an unstable dibromo- compound



is produced, which crystallises from CS_2 in sulphur-yellow prisms, which melt at 175° with decomposition.

Anthraquinone-*m*-dicarboxylic acid



This acid is produced quantitatively by the oxidation of *m*-dimethylanthraquinone with dilute nitric acid (for details, *v.* the *o-dicarboxylic acid*). It crystallises in fine yellow needles, which sublime above 330° without melting. It is almost insoluble in water, and difficultly soluble in the ordinary organic solvents.

Ammonium salt. Reddish warty masses, easily soluble in water.

Potassium salt. Reddish gelatinous mass, which becomes crystalline on standing, and contains then 2 mol. of water of crystallisation.

Sodium salt. Reddish crystalline crusts, contains 9 mol. of water of crystallisation.

Calcium salt. Light-red powder, insoluble in water and alcohol.

Barium salt. Light-violet powder, contains 1 mol. of water of crystallisation.

Lead salt. Red powdery precipitate, insoluble in water and alcohol.

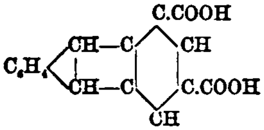
Copper salt. Dark-green crystalline powder, contains 1 mol. of water of crystallisation, insoluble in water and alcohol.

Silver salt. Pinkish precipitate, almost insoluble in water and alcohol. Decomposes on heating into CO_2, Ag, and anthraquinone.

Anthraquinone-*m*-dicarboxyl chloride is obtained by warming the acid (5 grams) with phosphorus pentachloride (7·5 grams), distilling off the phosphorus oxychloride at 140°, and shaking the residue with water and chloroform. The chloroform solution is dried over $CaCl_2$ and evaporated, when the acid chloride remains behind as a reddish mass, which showed little tendency to crystallise.

The *acid amide* prepared by treating the chloride with ammonia is also difficult to obtain in a crystalline condition.

Anthracene-*m*-dicarboxylic acid



is prepared by reducing anthraquinone-*m*-dicarboxylic acid with zinc-dust and ammonia (for details *v.* the *o*-dicarboxylic acid). Crystallises in brownish-yellow masses, which do not melt at 330°. It is almost insoluble in water, difficultly soluble in most other solvents.

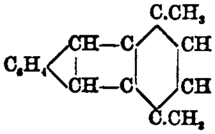
Ammonium salt. Greyish-green crystalline powder, readily soluble in water, difficultly soluble in dilute alcohol.

Copper salt. Dirty-green precipitate, almost insoluble in water and alcohol. Dissolves in ammonia, producing a yellow solution with a strong blue fluorescence (characteristic).

Silver salt. Light-brown powder. Dissolves in ammonia, producing a yellow solution with a blue fluorescence.

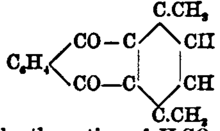
The chloride of the acid has the same properties and is produced in the same manner as the chloride of anthraquinone-*m*-dicarboxylic acid.

***p*-Dimethylanthracene**

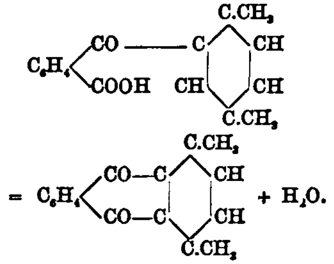


has not yet been prepared.

***p*-Dimethylanthraquinone**

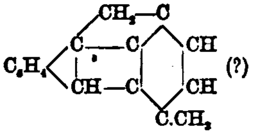


is produced by the action of H_2SO_4 on *p.*-xyloyl-*o*-benzoic acid, at a temperature of 125° (Elbs, J. pr. 1890, 27–32; Gresly, Ann. 224–240).



The details of the preparation and purification are the same as those of the ortho-derivative. Yield 50–65 p.c. of the theoretical. *p*-Dimethylanthraquinone crystallises from xylene in yellow needles, which melt at 118–119°. It is readily soluble in benzene and xylene, sparingly soluble in alcohol.

***p*-Dimethylanthracylene**

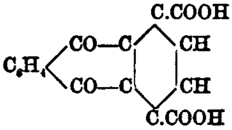


is produced when *p*-dimethylanthraquinone is reduced with zinc-dust and ammonia (*v. m*-dimethylanthracylene).

It crystallises from alcohol in plates which melt at 63°.

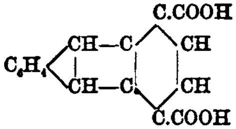
The picrate $C_{16}H_{12}.C_6H_2(NO_2)_3OH$ crystallises from alcohol in dark-red needles, which melt at 129°.

Anthraquinone-*p*-dicarboxylic acid



is prepared by oxidising *p*-dimethylanthraquinone with dilute nitric acid (for details *v.* the *o*- and *m*- derivatives). Yield nearly quantitative. It crystallises in small yellow crystals, which are difficultly soluble in water, but readily soluble in alcohol. The melting-point lies above 300°. The salts are similar to those of the *o*- and *m*- derivatives.

Anthracene-*p*-dicarboxylic acid



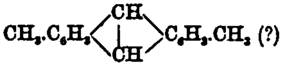
is obtained in the same way as its isomers, by reducing anthraquinone *p*-dicarboxylic acid with zinc-dust and ammonia.

It crystallises from alcohol in the form of a light-brown crystalline powder which melts at about 320°. It is readily soluble in alcohol, but almost insoluble in water.

The salts are similar to those of the *o*-acid.

DIMETHYLANTHRACENES OF UNKNOWN CONSTITUTION.

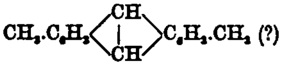
α-Dimethylanthracene



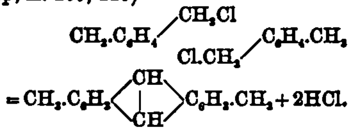
is produced when a mixture 3 parts toluene, 3 parts CS_2, and 1 part $CHCl_3$ is treated with 2 parts of aluminium chloride (Elbs, Wittich, B. 18, 348). It melts at 215–216°, and gives, on oxidation with CrO_3 and acetic acid, a quinone melting at 161–162°.

It would thus appear to be identical with γ-dimethylanthracene, which melts at 225° and gives a quinone melting at 155°.

β-Dimethylanthracene

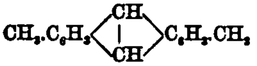


is prepared by heating (*m*?) xylylchloride with water to 210–220°, and distilling the product (Dorp, A. 169, 210)



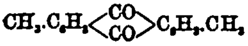
It sublimes in large plates like anthracene, melts at 200°, and gives, on oxidation with CrO_3 and acetic acid, two substances, one of which melts at 153° and is probably a dimethylanthraquinone. With bromine it forms a dibromo-compound $C_{16}H_{12}Br_2$, which crystallises in yellow needles, melting at 154°.

γ-Dimethylanthracene



has been isolated from the higher fractions of coal tar (Zincke, Wackendorff, B. 10, 1481). It is formed further (1) together with ditolylmethane $C_{15}H_{16}$ and *m*- and *p*-xylene, by treating a mixture of toluene and methylene chloride with aluminium chloride (Friedel, Crafts, Bl. 41, 323); (2) by treating xylyl chloride $CH_3.C_6H_4.CH_2Cl$ with aluminium chloride (Friedel, Crafts, Bl. 41, 326); (3) by treating toluene and acetylene tetrabromide with aluminium chloride (Anschütz, Immendorff, B. 17, 2816; A. 235, 172). It crystallises in glittering yellowish plates, which melt at 224–225°; sublimes readily, is moderately soluble in hot alcohol, benzene, or glacial acetic acid, and gives, on oxidation with CrO_3 and acetic acid, dimethylanthraquinone (m.p. 155), methylanthraquinone, carboxylic acid, anthraquinone dicarboxylic acid, and eventually even anthraquinone.

γ-Dimethylanthraquinone (Zincke, Wackendorff, *l.c.*)

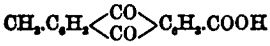


$$CH_3.C_6H_3\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_3.CH_3$$

is produced by the oxidation of the above hydrocarbon with CrO_3 and acetic acid; it crystallises from dilute alcohol in small straw-yellow needles, which melt at 155°.

It sublimes in almost colourless flat needles, is moderately soluble in alcohol, ether, benzene, glacial acetic acid, and hot light petroleum.

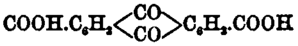
Methylanthraquinone carboxylic acid



$$CH_3.C_6H_3\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_3.COOH$$

is produced by the oxidation of γ-dimethylanthracene (m.p. 224–225°) with CrO_3 and acetic acid. It crystallises in flocks, which melt at 244–246°, and sublime, when strongly heated, in small needles.

Anthraquinone dicarboxylic acid



$$COOH.C_6H_3\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_3.COOH$$

is formed, together with dimethylanthraquinone and methylanthraquinone carboxylic acid, by oxidising γ-dimethylanthracene with CrO_3. It crystallises in small warty masses (m.p. not given). It is readily separated from methylanthraquinone carboxylic acid by treatment with concentrated NaOH, in which the sodium salt of the dicarboxylic acid is readily soluble, but that of the monocarboxylic acid sparingly soluble. The solution of the acid in KOH becomes violet on exposure to the air. The Ba and Ca salts are gelatinous and insoluble.

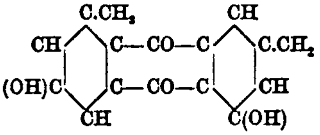
δ-Dimethylanthracene (Anschütz, A. 235, 319) is obtained by distilling tetramethylanthracene tetrahydride with zinc-dust. It crystallises from benzene in greenish-yellow plates, which melt at 243–244°, and are readily soluble in benzene, but difficultly so in alcohol.

δ-Dimethylanthraquinone is produced by the oxidation of δ-dimethylanthracene with CrO_3 in acetic acid solution. It crystallises from alcohol in long silky needles, which melt at 236°. It is very sparingly soluble in alcohol and glacial acetic acid.

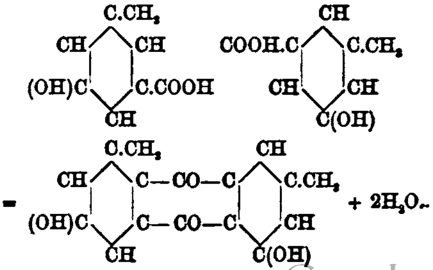
FURTHER DIMETHYLANTHRACENE DERIVATIVES.

Dioxydimethylanthraquinones (Kostanecki, Niementowski, A. 241, 276–278).

(1) **Dimethylanthrarufin**



is obtained, together with small quantities of two other isomers, by heating symmetrical *m*-oxytoluylic acid with sulphuric acid.



The crude product is poured into water, the precipitate collected, washed with water, and treated with baryta water, which leaves the dimethylanthrarufin undissolved. The baryta extract is precipitated with HCl, the precipitate extracted with alcohol. Dimethylbenzdioxyanthraquinone dissolves, whereas dimethylanthraflavic acid is insoluble (*v. infra*).

Dimethylanthrarufin crystallises from benzene in yellow silky needles, which melt at 300° and sublime in orange-red needles. It does not dye mordanted cloth. The solution in sulphuric acid is cherry-red coloured, and similar to that of anthrarufin in H_2SO_4. The *diacetate*

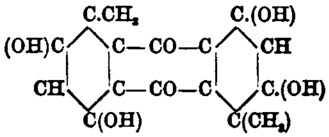
$$C_{16}H_{12}O_2(C_2H_3O_2)_2$$

crystallises in yellow plates, m.p. 236–237°.

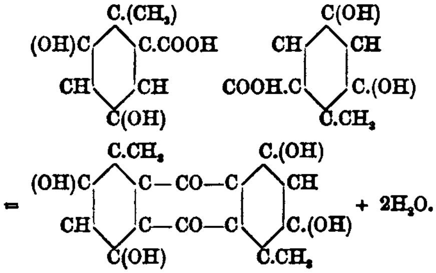
(2) **Dimethylanthraflavic acid** (for preparation, *v. Dimethylanthrarufin*). It sublimes in yellow needles which do not melt at 300°. It is insoluble in benzene, difficultly soluble in alcohol and glacial acetic acid; it dissolves in alkalis and sulphuric acid with a yellow colour like anthraflavic acid. It does not dye mordanted cloth. The *diacetate* crystallises in needles which melt at 223°.

(3) **Dimethylbenzdioxyanthraquinone** (for preparation, *v. Dimethylanthrarufin*). It crystallises from alcohol in yellow needles which melt at 213°. It dissolves in glacial acetic acid, but is sparingly soluble in alcohol and benzene. It does not dye mordanted cloth. The *diacetate* melts at 188°.

Dimethylanthrachryson (Cahn, A. 240, 280)



is prepared by heating cresorsellinic acid (1 part) with concentrated sulphuric acid (10 parts) to 100°.

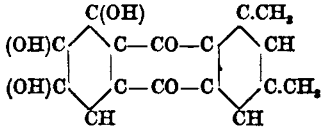


It crystallises from alcohol in bronze-coloured needles which do not melt when heated to 360°. It sublimes with difficulty, and then with considerable decomposition. It is insoluble in water, benzene, and light petroleum, sparingly soluble in alcohol and CS_2, readily soluble in $CHCl_3$, acetone, and glacial acetic acid. It is soluble in solutions of the alkalis and alkaline earths with a yellowish-red colour. The solution in sulphuric acid is magenta-coloured, and shows two absorption bands in the green. It does not dye mordanted cloth.

The *tetraacetyl derivative* $C_{16}H_8O_2(C_2H_3O_2)_4$ crystallises in yellowish needles which melt at 234° and are readily soluble in hot alcohol, glacial acetic acid, and benzene.

Dimethylanthragallol (Birnkow, A. 240, 287)

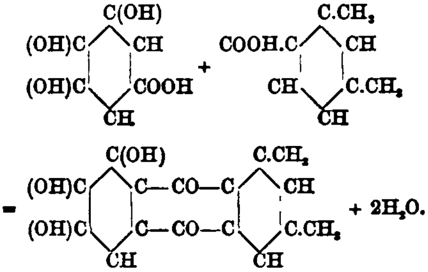
$C_{16}H_{12}O_5$ =



is obtained by heating a mixture of 5 parts xylylic acid

$$C_6H_3.(COOH)(CH_3).(CH_3)(COOH:CH_3:CH_3 = 1, 2, 4).$$

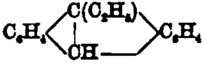
with 3 parts of gallic acid and 40 parts H_2SO_4.



The product is mixed with water, the precipitate collected, washed with water, dissolved in absolute alcohol (in which small quantities of accompanying rufigallic acid are insoluble); evaporated and the residue extracted with benzene; again evaporated, and the product recrystallised from acetone. Glittering reddish-yellow needles (no m.p. given). Distilled with zinc-dust, dimethylanthracene (m.p. 224°) results. The absorption spectrum of a solution of dimethylanthragallol in concentrated sulphuric acid is almost identical with that of anthragallol itself.

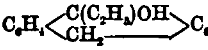
This substance should, from its method of preparation, be a derivative of *m*-dimethylanthracene, which, however, melts at 202–203°, whereas the dimethylanthracene obtained from dimethylanthragallol melts at 224°, and is evidently identical with that obtained from coal tar by Zincke and Wackendorff. This point requires investigation.

Ethylanthracene (Liebermann, A. 212, 109)



$$C_6H_4\left<\begin{matrix}C(C_2H_5)\\CH\end{matrix}\right>C_6H_4$$

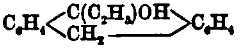
is formed by boiling ethylhydranthranol with alcohol and hydrochloric or picric acid.



$$C_6H_4\left<\begin{matrix}C(C_2H_5)OH\\CH_2\end{matrix}\right>C_6H_4 = C_{16}H_{14} + H_2O.$$

It crystallises from alcohol in large concentrically grouped plates which melt at 60–61°. The picrate melts at 120°.

Ethylhydranthranol

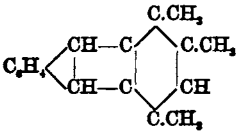


$$C_6H_4\left<\begin{matrix}C(C_2H_5)OH\\CH_2\end{matrix}\right>C_6H_4$$

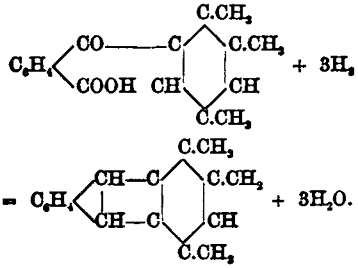
is produced by heating together anthraquinone (3 parts) with zinc-dust (10 parts), caustic soda solution (10 p.c.), and ethyl bromide (2–4 parts).

Trimethylanthracenes (Elbs, J. pr. 1890, 121–140).

(1, 2, 4) **Trimethylanthracene**



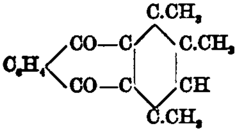
is produced by the distillation of pseudocumoyl-*o*-benzoic acid with zinc-dust (Gresly, A. 234, 241).



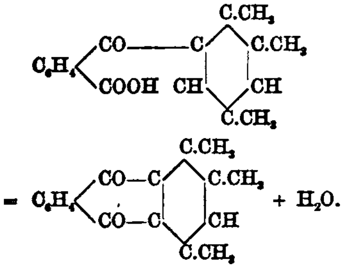
Preparation.—5 grams of the powdered acid are intimately mixed with 10 grams of zinc-dust, and distilled from a retort, the temperature being raised very gradually. The greenish-coloured oil which first passes over is separated from the reddish-coloured oil, which distils last and crystallises on cooling; the latter is dissolved in boiling light petroleum, and the crystals which separate out on cooling purified by recrystallisation.

Trimethylanthracene crystallises in white plates, possessing a blue fluorescence, and which melt at 244°. The picrate crystallises from benzene in brownish-red needles, which melt at 145° and are decomposed by alcohol.

(1, 2, 4) **Trimethylanthraquinone**



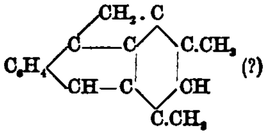
is obtained by the action of dehydrating agents on pseudocumoyl-*o*-benzoic acid.



In order to obtain a good yield of this substance, the following directions must be carefully observed.

10 grams of powdered pseudocumoyl-*o*-benzoic acid are dissolved in 100 c.c. of concentrated sulphuric acid, and the product gently warmed. The solution, which becomes clear and cherry-reddish coloured at 60°, is heated at 115° for one hour, allowed to cool to 70–80°, and then mixed with 10 grams of phosphorous pentoxide, the temperature being allowed to rise gradually to 115–120° during the addition, at which temperature it is kept for further two hours. The well-cooled product is poured in a thin stream into water, the precipitate collected, washed with water, and then with cold carbonate of soda solution; dried at 100°, and recrystallised from a mixture of alcohol and xylene. Trimethylanthraquinone crystallises in long yellow needles which sublime readily and melt at 162–163°. It is readily soluble in ether, benzene, and xylene; sparingly soluble in alcohol.

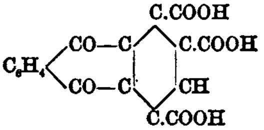
(1, 2, 4) **Trimethylanthracylene**



results from the action of zinc-dust and ammonia on trimethylanthraquinone (for details, *v.* dimethylanthracylene). It crystallises from alcohol in colourless plates which melt at 64° and resemble naphthalene in appearance. The picrate $C_{17}H_{14}.C_6H_2(NO_2)_3OH$ melts at 134°, and is decomposed by alcohol.

Bromine converts the hydrocarbon into its unstable dibromo-trimethylanthracylene.

Anthraquinone 1, 2, 4 Tricarboxylic acid



is produced by the oxidation of (1, 2, 4) trimethylanthraquinone with dilute nitric acid (*v. Anthraquinone dicarboxylic acids*). It crystallises from alcohol in yellowish-white warty masses, which do not melt at 320°. It is almost insoluble in water.

The *ammonium salt* separates from its solution in reddish amorphous crusts, which dissolve in water with a deep-red colour.

The *primary sodium salt*

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H(COOH)_2(COONa)+2H_2O$$

crystallises in yellow plates, readily soluble in hot, but difficultly in cold water.

Secondary sodium salt

$$C_6H_4{<}\substack{CO\\CO}{>}C_6H(COOH)(COONa)_2+3H_2O$$

crystallises in yellowish-red plates, more soluble in water than the primary salt.

Tertiary sodium salt is very readily soluble in water, and difficult to obtain in a crystalline form.

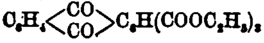
Neutral calcium salt. Rose-red plates from water.

Neutral copper salt. Light-green precipitate, very difficultly soluble in water.

Neutral lead salt. Yellow powdery precipitate insoluble in water.

Neutral silver salt. Reddish powdery precipitate which, when heated to a high temperature, decomposes into CO_2, Ag, and anthraquinone.

The *triethyl salt*



$$C_6H_4{<}\substack{CO\\CO}{>}C_6H(COOC_2H_5)_3$$

crystallises from alcohol in glittering white plates, which melt at 125°.

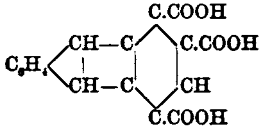
When treated with nitric acid and sulphuric acid trimethyl anthraquinone yields three nitro-derivatives which, on oxidation, yield two mononitro- and one dinitro-anthraquinone tricarboxylic acids.

I. *Mononitro-anthraquinone* (1, 2, 4) *tricarboxylic acid*, $C_{12}H_4(CO)_2(COOH)_3(NO_2)$, crystallises in small yellow crystals which melt at 308–310°. It is soluble in alcohol, ether, acetone, glacial acetic acid, and benzene, insoluble in water.

II. *Mononitro-anthraquinone tricarboxylic acid* crystallises in small crystals, which melt at 360–370° with decomposition, is readily soluble in alcohol, ether, and benzene, insoluble in water. The copper salts of these two acids differ very distinctly. That of acid I. crystallises in green needles, which dissolve in ammonia with a green colour; that of acid II. crystallises in red needles which dissolve in ammonia, forming a red solution.

Dinitro (1, 2, 4) *anthraquinone tricarboxylic acid*, $C_{12}H_2(NO_2)_2(CO)_2(COOH)_3$, melts at 340–360° with decomposition.

Anthracene (1, 2, 4) Tricarboxylic acid

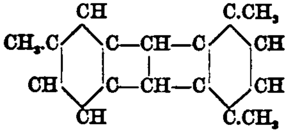


is readily obtained by reducing anthraquinone (1, 2, 4) tricarboxylic acid with zinc-dust and ammonia (for details see the corresponding dicarboxylic acids). It is readily soluble in benzene and light petroleum, still more readily in alcohol, with a yellowish-green colour, insoluble in water. No sharp m.p. was observed, as the acid sublimed above 260°, being converted probably into the anhydride.

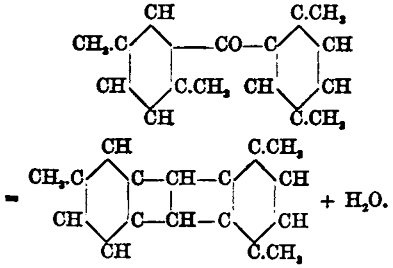
The *alkali salts* are very readily soluble in water, and do not crystallise readily.

The *silver salt* is a yellowish-green precipitate which, on heating, is decomposed, yielding a sublimate of anthracene.

Trimethylanthracene (1, 4, 2^1)

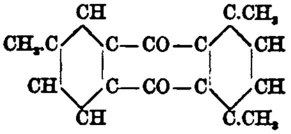


is readily obtained by boiling di-*p*-xylylketone on a reflux apparatus for 6 hours (Elbs, *l.c.* 140).



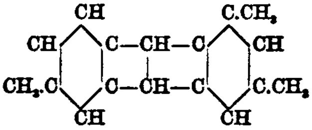
The yield is about 20–25 p.c. of the theoretical. It crystallises in thin colourless plates, which fluoresce bluish-green, melt at 227°, and sublime with great readiness, even at 100°. It is difficultly soluble in cold alcohol, more readily soluble in hot alcohol, benzene, and ether.

(1, 4, 2^1) **Trimethylanthraquinone**

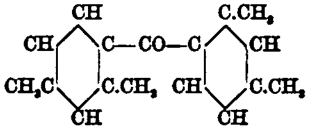


is obtained by oxidising (1, 4, 2^1) trimethylanthracene with the theoretical quantity of CrO_3 in glacial acetic acid solution. The yield is almost quantitative. It crystallises in yellow needles, which melt at 184°, and sublime with great readiness. It dissolves readily in glacial acetic acid, but is only sparingly soluble in alcohol. With zinc-dust and KOH it gives the anthraquinone reaction. On further oxidation this substance yields a mixture of carboxylic acids which could not be satisfactorily separated.

(1, 3, 3^1) **Trimethylanthracene**



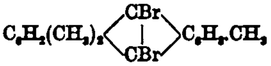
is synthetically prepared by the action of heat on di-*m*-xylylketone (Elbs, *l.c.* 142)



(*v. supra*).

The yield is 20–25 p.c. of the theoretical. It crystallises from a mixture of alcohol and acetone in plates which melt at 222°, is difficultly soluble in alcohol and light petroleum, more readily in ether and glacial acetic acid, very readily in CS_2, acetone, and benzene.

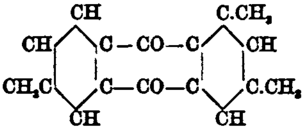
γ-Bibrom (1, 3, 3^1) *Trimethylanthracene*



$$C_6H_2(CH_3)_2 < \underset{CBr}{\overset{CBr}{|}} > C_6H_3.CH_3$$

results when trimethylanthracene (1 mol.) dissolved in CS_2 is treated with bromine (2 mol.). On evaporation a brownish-yellow crystalline mass is obtained, which crystallises from acetone in yellow rosettes of plates which melt at 142°.

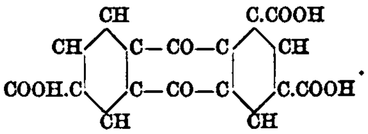
(1, 3, 3^1) **Trimethylanthraquinone**



is produced by oxidising (1, 3, 3^1) trimethylanthracene with the calculated quantity of chromic acid in acetic acid solution.

It crystallises in yellow needles which melt at 190°, are readily soluble in glacial acetic acid, difficultly soluble in alcohol. It sublimes readily and gives with zinc-dust and potash a deep-red solution.

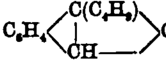
Anthraquinone (1, 3, 3^1) Tricarboxylic acid



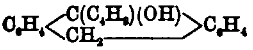
To prepare this substance 0·5 grams (1, 3, 3^1) trimethylanthracene are heated with 15 grams HNO_3 (sp.gr. 1·1) in a sealed tube 10 hours to 180°, then 10 hours to 210–220°. The tricarboxylic acid crystallises out in yellow plates. It is scarcely soluble in water, and very difficultly soluble in other solvents; it does not melt when heated to 300°.

The *ammonium salt* is readily soluble in water, and crystallises in flesh-coloured plates.

The *barium salt* is a cherry-red crystalline precipitate, very sparingly soluble in water.

Isobutylanthracene (Liebermann, A. 212, 107)  is obtained by boiling an alcoholic solution of isobutyl hydranthranol ($C_{18}H_{19}OH$) with picric acid or hydrochloric acid. It crystallises from alcohol in fluorescent needles; m.p. 57°. The picrate crystallises in long brownish-red needles.

Isobutylhydranthranol

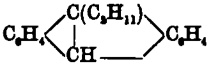


$$C_6H_4{<}{\textstyle{C(C_4H_9)(OH) \atop CH_2}}{>}C_6H_4$$

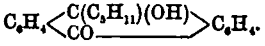
is prepared by boiling together 3 parts anthraquinone with 10 parts of zinc-dust, 50 parts of caustic soda solution (10 p.c.), and 2·4 parts of isobutyl bromide. It crystallises in needles, which melt at 71–72°.

Tetramethylanthracene (Anschütz, A. 235, 174) $C_{14}H_6(CH_3)_4$ is formed in small quantity, together with toluene and trimethylbenzene, by the action of aluminium chloride on a mixture of acetylenetetrabromide and *m*-xylene; m.p. 280°. If *o*-xylene be used in the place of *m*-xylene in the above reaction, a tetramethylanthracene, which melts above 280°, is obtained; in the case of *p*-xylene being used the tetramethylanthracene obtained melts at about 280°.

Isoamylanthracene (Liebermann, *l.c.*)

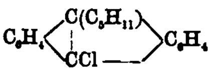


is prepared from isoamylhydranthranol (*v. Isobutylanthracene*). Long, colourless sea-green needles; m.p. 59°. Very soluble in benzene, $CS_2.CHCl_3$, light petroleum, and hot alcohol; difficultly soluble in cold alcohol. The solutions fluoresce blue. The solution in sulphuric acid is green; on warming it becomes red. Chromic acid oxidises it to isoamyloxanthranol



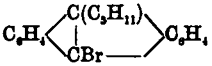
$$C_6H_4{<}{\textstyle{C(C_5H_{11})(OH) \atop CO}}{>}C_6H_4.$$

Chlorisoamylanthracene



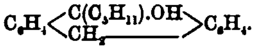
is obtained by passing chlorine into a solution of isoamylanthracene in chloroform. It crystallises from alcohol in pale-yellow needles, which melt at 70–71°. The solutions fluoresce blue. The picrate crystallises in red needles, which melt at 108°.

Bromisoamylanthracene



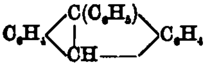
is obtained by adding the calculated quantity of bromine to the solution of the hydrocarbon in 20 to 30 parts of CS_2. Orange-yellow needles, m.p. 76. The picrate crystallises in orange-yellow needles, which melt at 110°.

Isoamylhydroanthranol

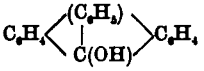


$$C_6H_4{<}{\textstyle{C(C_5H_{11}).OH \atop CH_2}}{>}C_6H_4.$$

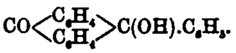
(*v. Isobutylhydranthranol*). Needles; m.p. 73–74°. Very readily soluble in alcohol; insoluble in water.

Phenylanthracene  is obtained by distilling phenylanthrol (Baeyer, A. 202, 61) $C_{20}H_{13}(OH)$ with zinc-dust; also, but in very small quantity, by distilling diphenylphthalid $C_6H_4{<}{\textstyle{C(C_6H_5)_2 \atop CO}}{>}O$ or triphenylmethane carboxylic acid $C_{20}H_{16}O_2$ with zinc-dust. It is also produced, together with anthracene and other hydrocarbons, by the action of aluminium chloride on a mixture of chloroform and benzene (Friedel, Crafts, A. Ch. [6] 1, 495). It crystallises from alcohol in plates which melt at 151–153, and boil at 417°. It is readily soluble in hot alcohol, ether, CS_2, $CHCl_3$, and benzene, the solutions possessing a blue fluorescence. Oxidation with CrO_3 and acetic acid converts it into phenyloxanthranol $CO{<}{\textstyle{C_6H_4 \atop C_6H_4}}{>}C(C_6H_5)OH$. The *picrate* crystallises in red needles. Reduction with hydriodic acid converts it into a dihydride $C_{20}H_{16}$, which melts at 120–120·5.

Phenylanthranol (Baeyer, *l.c.*)



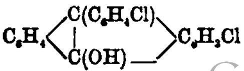
is formed by dissolving triphenylmethane carboxylic acid $(C_6H_5)_2.CH.C_6H_4.COOH$ in 3 parts of sulphuric acid and pouring the mass into water. The precipitate is collected, washed with dilute sodium carbonate, and recrystallised from alcohol. Yellow needles, which melt at 141–144°, with slight decomposition. It dissolves readily in ether, forming a yellowish solution, which possesses a greenish-yellow fluorescence. It dissolves also in hot alcohol, petroleum spirit, and acetone. Oxidation with CrO_3 converts it into phenyloxanthranol

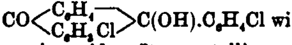


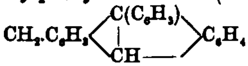
$$CO{<}{\textstyle{C_6H_4 \atop C_6H_4}}{>}C(OH).C_6H_5.$$

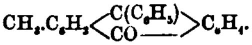
The *acetate* $C_2H_3O_2.C_{20}H_{13}$ crystallises from alcohol in yellow needles which melt at 165–166°.

Dichlorphenylanthranol

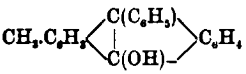


is formed by boiling phenolphthalideïn chloride  $CO<^{C_6H_4}_{C_6H_3Cl}>C(OH).C_6H_4Cl$ with zinc-dust and acetic acid. It crystallises from alcohol in needles, which melt at 170°. It is very sparingly soluble in alcohol, moderately soluble in acetone and ether, readily soluble in benzene and CS_2, forming bluish-green fluorescent solutions.

Methylphenylanthracene (Haemilian, B. 16, 2367)  $CH_3.C_6H_3<^{C(C_6H_5)}_{CH}>C_6H_4$ is formed by the distillation of methylphenylanthranol with zinc-dust (*v. infra*). It crystallises from alcohol in yellow crystalline masses (melting-point not given). The alcoholic solution fluoresces greenish-blue. It is readily oxidised by CrO_3 and acetic acid to methylphenyl oxanthranol


$$CH_3.C_6H_3<^{C(C_6H_5)}_{CO}>C_6H_4.$$

Methylphenylanthranol

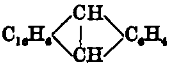

$$CH_3.C_6H_3<^{C(C_6H_5)}_{C(OH)}>C_6H_4$$

is similarly prepared by heating methyltriphenylmethane carboxylic acid

$$(C_6H_5)_2.CH.C_6H_3(CH_3)COOH$$

with sulphuric acid to 100°. It crystallises from alcohol in glittering plates, which on heating become brown at 130°, and melt at 156–157°. It is readily soluble in ether, boiling alcohol, and glacial acetic acid.

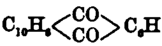
Naphthanthracene (Elbs, B. 19, 2209)


$$C_{10}H_6<^{CH}_{CH}>C_6H_4$$

is formed by boiling naphthanthraquinone with zinc-dust and ammonia.

It crystallises from a mixture of alcohol and glacial acetic acid in broken plates which melt at 141°, and possess an intense yellowish-green fluorescence. It sublimes in plates.

The *picrate* $C_{18}H_{12}2C_6H_2(NO_2)_3OH$ crystallises in red needles which melt at 133°, and are decomposed by alcohol.

Naphthanthraquinone  $C_{10}H_6<^{CO}_{CO}>C_6H_4$ results from treating naphthoyl-*o*-benzoic acid with sulphuric acid, $C_{18}H_{12}O_3 = C_{18}H_{10}O_2 + H_2O$.

It crystallises from toluene in deep-yellow prisms which melt at 168°, and sublime, on further heating, in deep-yellow needles.

It is sparingly soluble in alcohol and ether, more readily soluble in acetone and glacial acetic acid, still more readily so in $CHCl_3$ and benzene, but insoluble in light petroleum. It does not combine with picric acid. W. H. P. jun.

METHYLATED SPIRIT *v.* ALCOHOL.

METHYLBUTYL ACETIC ACID *v.* FATTY ACIDS.

METHYLDIBUTYL ACETIC ACID *v.* FATTY ACIDS.

METHYLDIETHYL ACETIC ACID *v.* FATTY ACIDS.

METHYLDIPHENYLAMINE *v.* DIPHENYLAMINE.

METHYLENE CH_2, a dibasic radicle not known in the free state.

Methylene diacetate $CH_2.(C_2H_3O_2)_2$. B.p. 170°; from methylene iodide and silver acetate (Butlerow, A. 107, 111); from chlormethyl acetate $C_2H_3O_2.CH_2Cl$ and potassium acetate (Henry, B. 6, 739). A liquid decomposed by water at 100° into acetic acid and trioxymethylene.

Methylene bromide CH_2Br_2, *Dibrommethane.* B.p. 80–82°; sp.gr. $\frac{11\cdot5}{} = 2\cdot084$ (Steiner, B. 7, 507); b.p. 96·5–97·5° cor.; sp.gr. $\frac{15°}{15°} = 2\cdot4985$, $\frac{25°}{25°} = 2\cdot47745$; M.M. at 15·9° = 8·11 (Perkin, C. J. 45, 520). Obtained by the action of bromine upon methylene iodide under water (Butlerow, A. 111, 251); from methyl bromide and bromine at 250° (Steiner).

A liquid which, by the action of water and excess of lead oxide at 150° gives ethylene glycol (Eltekow, B. 6, 558).

Methylene chloride CH_2Cl_2, *Dichlormethane.* B.p. 41·6° cor.; sp.gr. $\frac{0°}{4°} = 1\cdot37777$ (Thorpe, C. J. 37, 195); b.p. 40°; sp.gr. $\frac{15°}{15°} = 1\cdot33771$, $\frac{25°}{25°} = 1\cdot32197$; M.M. at 11·9° = 4·313 (Perkin, C. J. 45, 527); H.C. p. = 106·8 cals. (Berthelot and Ogier, Bl. 36, 68). From methane and chlorine (Regnault, A. 33, 328); from methylene iodide and chlorine (Butlerow, A. 111, 251).

Preparation.—A mixture of chloroform (1 vol.), zinc and alcohol (3 vols.) is gradually treated with hydrochloric acid and distilled; the distillate, consisting of chloroform and methylene chloride, is rectified, and the residue boiling above 58° is again treated with zinc (Greene, C. N. 50, 75).

Properties.—A colourless liquid with a pleasant smell, resembling that of chloroform. When heated to 200° with water, hydrochloric and formic acids and methyl chloride are formed, the latter, on further heating, forming methyl alcohol and hydrochloric acid. With aqueous ammonia at 140° it forms ammonium chloride, methylamine hydrochlorate, and formic acid (André, C. R. 102, 1474).

Methylene chlorobromide CH_2ClBr, *Chlorobrommethane.* B.p. 68–69° at 765 mm.; sp.gr. $\frac{19°}{19°} = 1\cdot9907$; V.D. = 4·43 (Henry, C. R. 101, 599). Obtained by the action of bromine upon chloriodomethane. A mobile colourless liquid, with agreeable smell.

Methylene chlorofluoride CH_2ClF, *Chlorfluormethane.* A gas, sp.gr. 34·18 (calc. 34·25). From methyl fluoride and chlorine in sunlight. Is colourless, and slightly soluble in, and slowly decomposed by, water; burns with difficulty in air (Collie, C. J. 55, 112).

Methylene chloroiodide CH_2ClI, *Chloriodomethane.* B.p. 109–109·5° at 760·4 mm.; sp.gr. $\frac{11°}{11°} = 2\cdot447$, $\frac{14\cdot5°}{14\cdot5°} = 2\cdot444$; V.D. 88·14. An oily liquid obtained by the action of iodine monochloride upon methylene iodide (Sakurai, C. J. 47, 198); also by action of iodine in potassium iodide solution upon monomercuric methylene chloriodide (S., C. J. 41, 362).

Methylene iodide CH_2I_2, *Diiodomethane.* M.p. 4°; b.p. 180°, with partial decomposition;

sp.gr. $\frac{5^\circ}{} = 3{\cdot}342$; b.p. 151–153° at 350 mm.; sp.gr. $\frac{15^\circ}{15^\circ} = 3{\cdot}28528$, $\frac{25^\circ}{25^\circ} = 3{\cdot}26555$; M.M. at 15° $= 18{\cdot}827$ (Perkin, C. J. 45, 464). From iodoform and sodium alcoholate (Butlerow, A. Ch. [3] 53, 319); by heating iodoform either alone or with iodine (Hofmann, A. 115, 267); from chloroform or iodoform and hydriodic acid (Leben, Z. 1868, 712). A yellow liquid which, when heated with water and copper to 100°, yields ethylene (Butlerow, A. 120, 356). With zinc ethyl it forms butane. With silver acetate yields methylene acetate; combines with mercury to form mercuric methylene iodide CH_2IHgI.

Methylene oxide CH_2O, *Formaldehyde:* Known only in the gaseous state and in aqueous solution. Formed by passing the vapour of methyl alcohol and air over heated platinum (Hofmann, Pr. 16, 156). By heating calcium formate (Mulder, Z. 1868, 265). By heating excess of ethylene with oxygen to 400° (Schützenberger, Bl. 31, 482). By the action of the electric discharge upon a mixture of marsh gas and oxygen (Maquenne, Bl. 37, 298), or upon a mixture of hydrogen and carbon monoxide (Brodie, Pr. 22, 172).

Preparation.—A mixture of the vapour of methyl alcohol and air is led through a heated glass tube filled with platinised asbestos, and the product received in a cooled vessel, from which it is afterwards distilled at as low a temperature as possible into another vessel cooled by ice (Kablukoff, J. R. 14, 194); *v.* also Hofmann, B. 11, 1686, and Tollens, B. 16, 917. The aqueous solution of methylene oxide has a strong odour, and reduces ammoniacal silver solution with formation of a mirror. Sulphuretted hydrogen causes the separation of crystals of *parathioformaldehyde* $(CH_2S)_3$.

On standing, a solution of formaldehyde deposits *trioxymethylene* $(CH_2O)_3$, a white, slightly crystalline mass melting at 152°, but subliming easily below 100°; the sublimed products melt at 171–172° (Tollens, B. 16, 919).

This body can also be prepared by the action of silver oxide upon methylene iodide, or by heating methylene acetate and water together to 100° (Butlerow, A. 111, 242). Also by heating anhydrous calcium glycollate with 6 or 8 parts of sulphuric acid to 170° (Heintz, A. 138, 43). Heated with water to 140°, it dissolves, being split up into the simpler molecule. The vapour density, 1·06 (Hofmann), shows that its vapour also is dissociated into methylene oxide. By heating in a tube with a trace of sulphuric acid, an isomer is obtained, which crystallises in needles melting at 60–61° (V.D. = 44·9); and is soluble in water and ether (Pratesi, G. 14, 140). A polymer $(C_6H_6O_2)$, a brownish-yellow syrup which blackens on heating to 100°, is obtained by electrolysing an acid (sulphuric) solution of glycerine (Renard, A. Ch. [5] 17, 311). It is identical with methylenitan.

METHYLENE SULPHIDES.

Trimethylene sulphide $(CH_2S)_3$, *Parathioformaldehyde.* B.p. 216°; sublimes without decomposition. Formed by the action of sulphuretted hydrogen upon a solution of methylene oxide or of trioxymethylene. Also by reducing by means of zinc and hydrochloric acid, carbon disulphide (Girard, A. 100, 306) or potassium thiocyanate or allyl mustard oil (Hofmann, B. 1, 176). It crystallises from benzene, carbon disulphide, or chloroform in quadratic prisms which are insoluble in water and possess a penetrating odour. It forms crystalline compounds with many salts, *e.g.* $C_3H_6S_3.HgCl_2$, needles, insoluble in water; $2C_3H_6S_3.PtCl_4$, golden-yellow needles.

Methylene hydrogen sulphide $CH_2(HS)_2$, *thiomethylene glycol*, is not known in the free state. The diethyl ether, $CH_2(SC_2H_5)_2$, b.p. 184°, sp.gr. $\frac{20^\circ}{} = {\cdot}987$, is obtained by the treatment of sodium mercaptide with methylene oxide (Claesson, J. pr. [2] 15, 176).

Methylene sulphonic acid $CH_2(SO_3H)_2$, *Methylene disulphonic acid*, forms very unstable needle-like crystals. Produced in small quantity by the action of sulphur trioxide upon ether (Liebig, A. 13, 35; Strecker, A. 100, 199); by the oxidation of methylene thiocarbonate (Husemann, A. 126, 293); from chloroform and potassium sulphite solution at 180° or from iodoform and potassium sulphite at 150° (Strecker, A. 148, 92).

Preparation.—Lactic acid or calcium lactate is heated with fuming sulphuric acid until sulphur dioxide begins to be evolved; the mixture is then neutralised with barium carbonate. It can also be prepared by heating 2 volumes of acetamide with 1 volume of fuming sulphuric acid (Buckton and Hofmann, A. 100, 133). For salts *v.* Hofmann, Strecker, *l.c.*, also Monari (B. 18, 1343).

Trimethylene disulphonic acid $(CH_2)_3(SO_3H)_2$ forms a thick syrup, but can be obtained in amber-coloured needle-like crystals. It is very soluble in water and alcohol (Monari, *l.c.*).

METHYLENE AMINES.

Hexamethylene tetramine $(CH_2)_6N_4$. Forms rhombohedrons which sublime about 100°. It is obtained by the action of ammonia upon trioxymethylene $(CH_2O)_3$.

$$2C_3H_6O_3 + 4NH_3 = (CH_2)_6N_4 + 6H_2O$$

(Butlerow, A. 115, 322). It has an alkaline reaction, is very soluble in water, slightly in cold alcohol, and almost insoluble in ether. With methyl iodide at 170° forms tetramethylammonium iodide (Tollens, B. 17, 656).

It forms crystalline salts with acids—$C_6H_{12}N_4.HCl$ long prismatic needles very soluble in water—$(C_6H_{12}N_4.HCl)_2PtCl_4$.

Methylene tetraethyl diamine $CH_2[N(C_2H_5)_2]_2$, b.p. 166°–169°. Formed by the action of trioxymethylene, 6·5 parts, upon diethylamine, 29·2 parts (Kolotoff, J. R. 17, 244). It is an unpleasant-smelling liquid, insoluble in water but very soluble in alcohol.

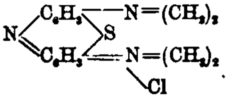
Methylene thiocarbonate CH_2CS_3. A yellowish white, amorphous powder insoluble in water, almost insoluble in alcohol, ether, and carbon disulphide, obtained by the action of methylene iodide upon sodium thiocarbonate in alcoholic solution (Husemann, A. 126, 292). Is decomposed by ammonia into ammonium thiocyanate and methylene sulphide $(CH_2S)_x$.

Methylene thiocyanate $CH_2(CSN)_2$, m.p. 102°. From methylene iodide and potassium thiocyanate in alcoholic solution (Lermontow, B. 7, 1282). It forms needles or prisms which are almost insoluble in cold, moderately soluble in warm water, and easily soluble in alcohol and ether. By oxidation, e.g. by nitric acid, it yields methylene disulphonic acid.

Dimethylene dimethyl diamine
$(CH_2)_2N_2(CH_3)_2$.
A crystalline non-volatile body obtained by passing triethylamine and hydrogen through a heated tube (Romeny, B. 11, 835).

Dimethylene diethyl diamine
$(CH_2)_2N_2(C_2H_5)_2$.
b.p. 205°-208°. Obtained by heating in a sealed tube a mixture of trioxymethylene with ethylamine (Kolotoff, J. R. 17, 231). An oily liquid with an unpleasant odour, soluble in cold water or in alcohol. Is decomposed by hydrochloric acid into trioxymethylene and ethylamine.

METHYLENE BLUE



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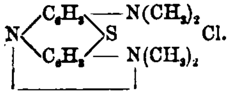
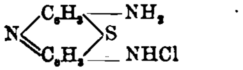


A colouring matter first obtained by Caro in 1876 by the oxidation of dimethyl-*p*-phenylenediamine in presence of sulphuretted hydrogen. By treating *p*-phenylenediamine with sulphuretted hydrogen and oxidising agents, or by heating the same body with sulphur and subsequently oxidising, Lauth obtained a violet basic colouring matter containing sulphur, known as 'Lauth's violet' or thionine.



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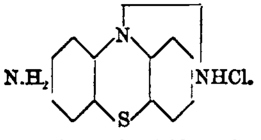
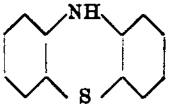
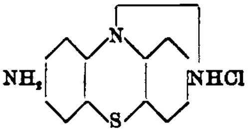


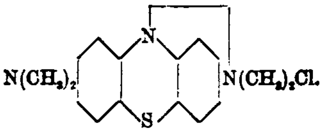
The comparatively small yield of the colouring matter (15-20 p.c. of the *p*-phenylenediamine taken), together with the difficulties attending the preparation of the materials required, prevented its manufacture on the large scale. Lauth's reaction, however, became of industrial importance through Caro's discovery of the method of manufacture of nitrosodimethylaniline, whereby it was readily possible to obtain dimethyl-*p*-phenylenediamine. This compound, when treated by Lauth's reaction, gave rise to a methylated Lauth's violet, which differed from the parent substance in being of a pure blue colour, and also in being more easily obtained and in much larger quantity. The new colouring matter came into commerce under the name of *Methylene blue*. Its constitution, together with its relation to Lauth's violet (thionine), was first established by Bernthsen (A. 230, 77 *et seq.*). He showed that both these substances were derived from a sulphuretted diphenylamine (thiodiphenylamine), from which by nitration, reduction, and subsequent oxidation, Lauth's violet could be obtained. Methylene blue is the tetramethyl derivative of Lauth's violet, and the relation of these several substances may be thus formulated:



Thiodiphenylamine



Thionine



Methylene blue

The method of manufacturing methylene blue adopted by the Badische Aniline und Sodafabrik (Eng. pat. 3,751, Oct. 9, 1887; Ger. pat. 1886, &c.) consists in reducing nitrosodimethylaniline $C_6H_4{<}^{NO}_{N(CH_3)_2}$, made by the action of sodium nitrite on dimethylaniline, by means of zinc or sulphuretted hydrogen; the dimethyl *p*-phenylenediamine so obtained is treated in dilute acid solution with sulphuretted hydrogen and some oxidising agent (*e.g.* ferric chloride)

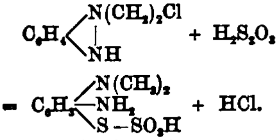
$$2C_8H_{12}N_2 + H_2S + 3O + 2HCl$$
$$= C_{16}H_{18}N_3SCl + NH_4Cl + 3H_2O.$$

By the gradual addition of the ferric chloride the liquid becomes deep blue, and the resulting colouring matter is 'salted out' by adding common salt and zinc chloride, and purified by re-solution in water and 're-salting out.' This double salt, which constitutes the methylene blue of commerce, crystallises in copper-coloured crystals, readily soluble in pure water, but sparingly soluble in solution of zinc chloride.

Tetramethyldiamidodiphenylamine when oxidised in presence of sulphuretted hydrogen yields only traces of methylene blue. Similarly in the simultaneous oxidation of dimethyl-*p*-phenylenediamine and dimethylaniline in presence of sulphuretted hydrogen, the dimethylaniline enters but slightly into the reaction. On the other hand, if the tetramethyldiamidodiphenylamine, or the mixture of dimethyl-*p*-phenylenediamine and dimethylaniline, is oxidised in presence of sodium thiosulphate, a peculiar sulphoacid results, which on boiling with acids decomposes into sulphur dioxide and *leuco-methylene blue*. By the oxidation of this body methylene blue is readily obtained (Ulrich, Ger. pat. 38,573, 39,757, 1885). According to Ger. pat. 38,573 a mixture of the neutral salts of amido-dimethylaniline and dimethylaniline is oxidised in presence of the thiosulphate; in No. 39,757 a solution of nitrosodimethylaniline hydrochlorate is heated with dimethylaniline and sodium thiosulphate.

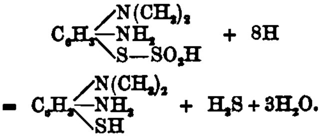
By the action of thiosulphuric acid upon the red oxidation product of dimethylphenylene green there is obtained a thiosulphonic acid of amidodimethylaniline $C_8H_{12}N_2S_2.O_3$. By reduction this yields the mercaptan of amidodimethylaniline $C_8H_{12}N_2S$, which under the influence of oxidising agents combines with dimethylaniline to form a green indamine containing sulphur. This indamine $2C_{16}H_{19}N_3SHCl.ZnCl_2$ is a green colouring matter readily soluble in water, and on warming quickly passes into methylene blue.

(1)



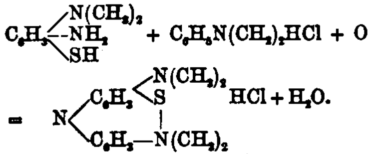
Amidodimethylaniline-thiosulphonic acid

(2)



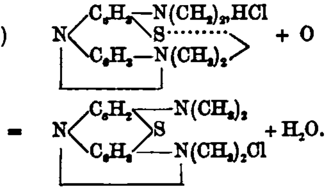
Amidodimethylaniline mercaptan

(3)



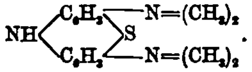
Tetramethylindamine sulphide

(4)



Methylene blue

Concentrated sulphuric acid dissolves methylene blue with a green colour. By reducing agents it is readily transformed into its leuco- base, *tetramethyldiamidothiodiphenylamine*



This body forms colourless plates; it rapidly oxidises on exposure to air, and is transformed into methylene blue. By the methylisation of the leuco- base Lauth's violet is obtained.

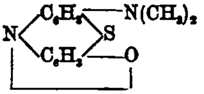
Methylene blue is, with the exception of Victoria blue, the only basic blue colouring matter which has any technical importance, and it is preferable to Victoria blue on account of its greater fastness to light. It resists the action of neutral soaps and dilute solutions of chloride of lime. It is largely used in cotton-yarn dyeing and in calico-printing with tannin, or with tannin and tartar emetic mordants. It gives a greenish-blue inclining to indigo, and is frequently shaded with methyl violet, malachite green, and other basic colouring matters. It has no special applications in silk or wool dyeing. For pure blue the oiled goods are mordanted with alum and the alumina fixed in a chalk bath with sodium arsenate, heated in a weak tannin bath, and the mordanted goods dyed in a bath containing methylene blue, sodium phosphate, and soda, at a gradually increasing heat. For indigo blue, the oiled goods are mordanted in acetonitrate of iron, aged, and the mordant fixed in a chalk bath, treated with tannin, and dyed with methylene blue. For method of detection on dyed fabrics *v.* vol. i. p. 594.

Methylene blue is of considerable value as a staining material in bacteriological research; *v.* Ehrlich, Centralb. f. Medic. Wissensch. 1885; Dresser, Zeits. f. Biol. 1885, 41.

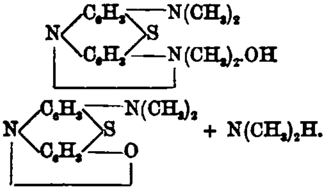
METHYLENE GREEN. A body obtained by treating methylene blue with nitrous acid. Dyes cotton a fine dark-green colour. Appears to be a nitro- derivative of methylene blue.

METHYLENE RED $C_{12}H_{18}N_4S_4$ is obtained as a by-product in the manufacture of methylene blue, and is found in the mother-liquors after salting out the methylene blue, and may be obtained from them by evaporation, or by treatment with phenol, from which it may be extracted by ether-alcohol. It crystallises from alcohol in green prisms, and readily dissolves in water and alcohol with a fine, fiery, purple colour. The solution is decolourised by alkalis, and by sodium acetate and phosphate, and the colour is not restored by acids. By reducing agents it is transformed into leuco- base, apparently different from methylene blue (Bernthsen, A. 230, 165).

METHYLENE VIOLET or **DIMETHYLTHIONOLINE**



is best obtained by boiling a solution of the hydrochlorate or hydriodate of methylene blue with silver oxide whereby dimethylamine is evolved, and silver chloride or iodide formed together with the methylene violet. Its formation from the base of methylene blue may be thus expressed:



Methylene violet is almost insoluble in cold water and but sparingly soluble in hot water, with blue colour and a reddish-brown fluorescence. It crystallises in needles. It is readily soluble in alcohol, acetone, chloroform, and aniline, but slightly soluble in ether and benzene. Its hydrochlorate crystallises readily, and is almost insoluble in cold dilute hydrochloric acid. Its aqueous solution dyes silk and cotton of a violet colour, somewhat bluer than thionine, and with a greyish shade. Bernthsen, *l.c.* 169 (*cf.* ANILINE BLUE, vol. i. p. 167).

METHYL-ETHYL ACETIC ACID *v.* FATTY ACIDS.

METHYL-ETHYLBENZENE *v.* CUMENES.

METHYL GREEN *v.* TRIPHENYL METHANE COLOURING MATTERS.

METHYLHEXYL ACETIC ACID *v.* FATTY ACIDS.

METHYL INDOLE *v.* Indoles.

METHYLISOPROPYL ACETIC ACID *v.* Fatty acids.

METHYLISOPROPYL PROPIONIC ACID *v.* Fatty acids.

METHYL KETOLE *v.* Indoles.

METHYL ORANGE *v.* Azo- colouring matters.

METHYLPHENYL HYDRAZINE *v.* Hydrazines.

METHYLPROPYL ACETIC ACID *v.* Fatty acids.

METHYLPROPYLBENZENE *v.* Cymenes.

METHYLPYROGALLOL. *Methylpyrogallic acid v.* Phenol and its homologues.

METHYLPYRROL *v.* Bone oil.

METHYL VIOLET *v.* Triphenyl methane colouring matters.

METTERNICH GREEN. A double salt of zinc chloride with the chlormethyl-hexamethyl rosaniline chlorhydrate. Known also as *iodine green* or *night green.* Obtained by the action of the iodide or chloride of methyl upon rosaniline (Hofmann and Girard, B. 2, 442; Appenzeller, B. 6, 965).

MEXICAN ELEMI *v.* Oleo- resins.

MEZEREON RESIN *v.* Resins.

MIARGYRITE, *Silver sulphantimonite,* $Ag_2S.Sb_2S_3$. Found near Freiburg, in Saxony, associated with arsenical pyrites. Forms tabular pyramidal or short prismatic crystals belonging to the monoclinic system. Of an iron-black colour, with sub-metallic adamantine lustre; thin splinters appear blood-red by transmitted light. H = 2. Sp.gr. 5·2 to 5·4.

MICA (Ger. *Glimmer*). A name applied to a group of minerals characterised by the facility with which they split into thin laminæ, which are flexible, and more or less elastic. It is now believed that all micas belong to the monoclinic system, but the crystals often affect a hexagonal habit. The perfect cleavage, on which the micaceous structure depends, is parallel to the basal plane. A similar structure is seen in the group of chlorites, but their laminæ, though flexible, are not elastic. The hardness of the micas is between 2 and 3; while their sp.gr. ranges from 2·76 to 3·2. The optical characters and chemical composition are subject to considerable variation in different species. Broadly speaking, there is a group of potash-micas, generally of pale colour, and having the optic axes separated by wide angles; and a group of magnesian, or ferro-magnesian, micas, usually of dark colour, with the optic axes in some cases so close that the mineral becomes apparently uniaxial. On sharply striking a plate of mica with a needle-point, a six-rayed star is produced (*Schlagfigur*); while pressure with a blunt instrument develops a similar figure (*Druckfigur*), having each ray at right angles to one in the percussion-figure.

All the micas are complex silicates, containing aluminium and potassium, generally with magnesium, but rarely with calcium. The potassium is frequently replaced in part by lithium and sodium, while iron may be substituted for the magnesium and aluminium. Water is always present, and many micas, as first determined by H. Rose, contain fluorine. The chemical constitution of the group of micas has been discussed by Rammelsberg (Min. Chem.) and by Tschermak (Z. f. Min. 2, 1878, 14; 3, 1879, 122, and later by F. W. Clarke, Am. J. 38, 1889, 384). The following analyses will serve to illustrate the composition of the principal species:—

—	I	II	III	IV
Silica . .	46·74	50·43	44·81	40·91
Alumina . .	35·10	28·07	10·87	17·79
Ferric oxide .	4·00	—	—	11·02
Manganese oxide	—	0·88	—	—
Ferrous oxide .	1·53	—	0·31	—
Magnesia. .	0·80	1·42	28·90	19·04
Potash . .	9·63	10·59	8·40	9·96
Soda . .	—	1·46	0·38	—
Lithia . .	—	1·23	0·08	—
Fluorine . .	1·05	4·86	—	—
Water . .	3·36	—	5·42	—
	102·21	98·94	99·17	98·72

I. Muscovite from Easton, Pennsylvania, by Rammelsberg. II. Lepidolite from Rozena, Moravia, by Reuter. III. Phlogopite from Edwards, St. Lawrence Co., New York, by Penfield. Notable for the absence of fluorine. IV. Biotite from Vesuvius, by Chodnew.

Muscovite, or potash-mica, is the common species widely distributed as a constituent of granite, gneiss, and mica-schist. It is usually white, grey, or yellow; and the angle of the optic axes may be as much as 70°. Some forms of muscovite have been mistaken for talc, as in the granitic rock of the Alps called protogine, and in certain so-called talc-schists. *Sericite* is a silky talc-like mica, occurring in the schists of the Taunus. The *paragonite* of St. Gothard, closely related to muscovite, is a soda-mica. The Tyrolese mineral called *margarite* is characterised by a nacreous lustre, whence its name *Perlglimmer*; it is apparently identical with the *emerylite,* occurring with deposits of emery in Naxos, Asia Minor, and the United States. A white micaceous mineral, similar to margarite, found in Tyrol, has been described as a baryta-mica (*Oellacherite*), since its analysis has yielded nearly 6 p.c. of baryta with a little strontia.

Lepidolite, or lithia-mica, is generally of peach-blossom colour, but sometimes grey or white, with a pearly lustre. It occurs in certain granites, especially with minerals containing fluorine, like topaz and tourmaline. Rubidium, cæsium, and thallium may be present in lepidolite. The best-known locality for the typical kind is near Rozena in Moravia, where it forms a beautiful rock, occasionally polished as an ornamental stone. *Zinnwaldite* is a greyish lithia-bearing mica, occurring in the tin-mining districts of Saxony, Bohemia, and Cornwall.

Certain magnesian micas, usually of reddish or bronze colour, occurring in crystalline limestone and in serpentine, are distinguished as *phlogopite.* The angle of the optic axes ranges from 0° to 17°. It is notable that certain phlogopites exhibit by transmitted light luminous stars, due to the presence of multitudes of included acicular crystals definitely orientated; the best examples of this asteriated mica being yielded by some of the Laurentian limestones of Canada.

The *biotite* group includes a number of magnesian and ferro-magnesian micas, generally of dark colour, and transparent only in thin laminæ. Frequently occurring in six-sided plates, and having a very small optic angle, they were formerly referred to the hexagonal system. In thin sections they exhibit strong pleochroism. They are generally denser than muscovite, and their cleavage-laminæ are less elastic. Biotite is often found, in association with muscovite, in granite, gneiss, and mica-schist, and the two micas are sometimes closely intergrown. The biotitic micas also occur in mica-syenite, mica-porphyry, and trachyte; while crystals are not uncommon in the ejected blocks of Monte Somma. The Vesuvian dark micas were termed by Breithaupt *meroxene*, and this name has been revived by Tschermak for all the true biotites, while he uses the term *anomite* to distinguish a similar mica, differing only in optical characters. *Rubellan*, an opaque red mica from certain volcanic rocks, is merely an altered biotite which has lost its elasticity. In *lepidomelane*, the aluminium of an ordinary biotite is largely replaced by iron, and the mica becomes black and is attracted by a powerful magnet. Heddle's *Haughtonite*, of the Scottish granites, differs from biotite by containing less magnesium, and from lepidomelane by having most of its iron in the condition of FeO, the average percentage of this oxide being 17·22. *Fuchsite* is a magnesian mica of bright-green colour, containing about 4 p.c. of chromium oxide, and occurring at Schwarzenstein in Tyrol. The vanadium-mica of California, termed by Blake *Roscoelite*, yields as much as 28·85 p.c. of vanadic anhydride.

Of the various micas, muscovite is the only one of commercial importance; and this, strangely enough, often passes in trade under the name of 'talc.' Muscovite was formerly called 'Muscovy glass,' in allusion to its use in Russia as a substitute for window-glass. At the present day it is employed chiefly as a transparent fire-resisting medium in the doors of stoves and furnaces, and for lamp-shades and gas covers. It is also used for the dial-plates of compasses, while in the East, especially in India, it is applied to various ornamental purposes. Paintings on mica, executed by native artists, are well known to collectors. Sheets of mica, used as a decorative material, have been found in the prehistoric mounds of the Mississippi Valley. The mica of commerce comes mostly from the United States, Canada, India, and Russia. Large sheets of sufficient purity to be profitably worked are of very limited occurrence; they are usually found in veins of giant granite, where the constituents crystallise on a large scale, and are often associated with rare minerals such as beryl and columbite. A single mica crystal from North Carolina has been known to weigh nearly 2,000 pounds. This State takes the lead in the production of mica, though the industry was only started in 1868. Mica has been worked for the last forty years at Alstead, in New Hampshire, where sheets have been found measuring 4 feet across. Mining for mica has also been carried on in the Black Hills of Dakota; in Virginia and in New Mexico.

The preparation of mica for the market is very simple. The blocks of rough mica, having been freed from associated minerals, or dressed, are split into plates, which are then 'scribed,' or marked out into patterns, and along this scribing the mineral is cut by means of shears. A good deal of refuse is necessarily produced. This mica-waste is ground and used as a lubricating agent, and as an absorbent for nitroglycerin in the preparation of certain explosives; it has also been employed in the ornamentation of wall-papers, and to a limited extent as a substitute for asbestos. (For the mica industry in America, *v.* F. W. Clarke in Min. Res. U.S., 1885, 906; and W. B. Phillips, do., 1888, 660.)

F. W. R.

MICA POWDER *v.* EXPLOSIVES.

MICACEOUS IRON ORE *v.* IRON.

MICROCLINE *v.* FELSPAR.

MICROCOSMIC SALT. *Ammonium sodium hydrogen phosphate*, $NH_4.NaHPO_4.4H_2O$, used as a flux in blow-pipe tests.

MIDDLETONITE *v.* RESINS.

MIEMITE. A dolomite of an asparagus-green colour found in Tuscany, *v.* DOLOMITE.

MIKADO ORANGE *v.* STILBENE COLOURING MATTERS.

MILK. Milk is the term usually restricted to the liquid secreted by the mammary glands of the class of animals called mammalia. Certain secretions, however, which are produced by birds and by some species of plants more or less resemble ordinary milk in their general physical and chemical characters.

Milk is generally white in colour, with a faint yellow or bluish tinge; it is homogeneous and opaque, the opacity being due to particles of fat (milk globules); of milk caseïn (Cameron, C. N. 21, 54) and probably of calcium phosphate in suspension. When fresh it has a characteristic aroma. Immediately after drawing, it has in addition a faint odour of an exhalation from the skin which disappears on exposure to the atmosphere. The sp.gr. of milk in general varies between 1·018 and 1·045 (Scherer); that of human milk averages 1·032 (Simon), 1·03267 (1·02561–1·04648) (Vernois and Becquerel), 1·0313 (1·0353–1·0260) (Leeds, C. N. 50, 263); that of cow's milk varies between 1·029 and 1·033 (Bouchardat and Quevenne). The average of English cows is 1·0322 (Vieth), of German cows 1·031 (Fleischmann).

The specific heat of milk is ·847 (·80–·89) and it attains its maximum density between 0° and 1° (Fleischmann, L. V. S. 17, 251). The refractive index of cow's milk was found by Valentin (P. Arch. 1879, 78) to average 1·35 with Abbe's refractometer. The refractive index of human milk varies from 1·3475 to 1·3494, maximum 1·3518. Jorgenssen (L. J. 11, 699) found the refractive index of 23 samples of milk to vary from 1·347–1·3515; on the other hand 29 samples of whey gave indices varying from 1·3465–1·3433.

The viscosity of milk depends upon the temperature, but the diminution in viscosity with rise of temperature is much more rapid in milk than in water.

The reaction with litmus varies according to the species. Human milk is normally alkaline, whilst that of the carnivora is generally acid; cow's milk may appear faintly alkaline or faintly acid, or show both reactions (amphoteric).

Abnormally, milk may be bluish-white, deep-yellow, brown, pinkish-red, blue, or black in colour, watery, slimy, stringy, sandy, or heterogeneous in consistency, putrid or otherwise offensive in odour, and salty, sour, bitter, or astringent in taste.

The liquid secreted by the female immediately before or after parturition is termed colostrum or beastings, and differs considerably from normal milk in both physical and chemical characters.

Reaction.—The reaction of cow's milk with litmus has occasioned considerable controversy. Soxhlet (J. pr. 6, 1) has shown that cow's milk, in common with all liquids containing both neutral and acid phosphate in solution, is amphoteric—*i.e.*, it will exhibit both acid and alkaline reactions. To test cow's milk it is necessary to prepare a very carefully neutralised solution of litmus, spread it on papers, and turn them barely red or blue with an extremely dilute solution of acid or ammonia. A drop of the milk is then brought on the paper and quickly shaken off, a blue or red spot will be respectively seen.

It is still better to use Liebreich's gypsum plates coated with the solution of litmus, as the drop of milk can sink into the gypsum and produce a deeper colouration.

Composition.—The ancients were acquainted with only three of the constituents of milk, viz., fat, caseïn, and water. Bartoletus of Bologna (1619) discovered a fourth constituent, the 'nitrum seri lactis,' afterwards renamed by Testi (1698) *succhero di latte* (sugar of milk). Geoffrey (1737) separated the soluble salts and identified sodium chloride among them.

Scheele (1780) found calcium phosphate in the ash.

At the present time the following substances are stated to be normal constituents of fresh milk.

(*a*) *Albuminoids:* Caseïn, nucleïn (Lubawin, B. 10, 2073), albumin (lactalbumin); globulin (Sebelien, Z. 9, 445); a peptone? (Radenhausen, Z. 5, 29; Schmidt-Muhlheim, P. Arch. 28, 287); lactoproteïn? (Millon and Commaille); hemialbumose?

(*b*) *Extractive matters:* Urea (Lefort, C. R. 62, 190); creatinin (Weil, B. 11, 2175); traces of lecithin, cholesterin, and hypoxanthin (Schmidt-Muhlheim, P. Arch. 30, 379).

(*c*) *Organic acids:* Lactic acid (Marchand, J. Ph. [4] 29, 311; Hoppe-Seyler, Virch. Arch. 17, 443; Manetti and Musso, Z. 16, 397); citric acid (Häckel and Soxhlet, B. C. 17, 787); acetic acid (Béchamp, C. R. 76, 836).

(*d*) *Carbohydrates:* Sugar of milk, and a second carbohydrate discovered by Ritthausen (J. pr. 157, 348).

(*e*) *Other organic bodies:* Alcohol (Béchamp, C. R. 76, 836); lactochrome, an organic colouring matter (Blyth, Trans. C. S. 1879, 531), and a bitter principle (Blyth, *supra*).

(*f*) *Inorganic acids (in combination):* Phosphoric, hydrochloric, sulphuric (Musso and Schmidt, B. C. 1179, 865); sulphocyanic (Musso, J. 7, 168).

(*g*) *Bases:* Potash, soda, lime, ferric oxide, magnesia, and ammonia (Latschenberger, J. 14, 222).

(*h*) *Gases (in solution)* CO_2.O.N.

Microscopic characters.—Viewed under the microscope fresh milk appears as a clear colourless liquid in which are suspended—(*a*) milk globules and more rarely (*b*) granular bodies, the so-called colostrum corpuscles. Haidenhain (Handb. der Phys.) states that the following morphological structures have been observed in human and to a less extent in cow's milk:—

(1) Semiglobular fat drops with a finely granular substance.

(2) Clear cells containing one or two fat drops and an eccentric nucleus.

(3) Round clear bodies easily coloured by eosin and picrocarmine, supposed to be free nuclei.

(*a*) The milk globules may vary in diameter from ·01 to ·0015 mm., but generally range from ·005 to ·0033 mm.

According to Bohr (J. 1880, 183) the diameter may vary from ·0063 to ·00014 mm.

Under the highest powers of the microscope they appear merely as more or less irregularly shaped globules of fat, without the faintest trace of a limiting membrane; nevertheless, all the earlier observers (Henle, Mitscherlich, Lehmann, Moleschott, &c.) believed in the existence of an external envelope, principally because ether, when shaken up with milk, will not dissolve out the fat unless acetic acid or potash is previously added. These substances were supposed to dissolve the enveloping membrane of the globules and release the fat. This view has of late been again advocated by Struve (J. pr. [2] 27, 249), who thinks the globules have a coat of insoluble casein; by Babcock (Milchz. 17, 809), who states they are covered with an envelope of milk-fibrin, and by Béchamp (C. R. 107, 772).

The weight of evidence appears, however, to be against the existence of a solid membrane. Soxhlet (J. 76, 111) holds that the milk is a simple emulsion of fat particles with casein, calcium phosphate, &c., and that the addition of acetic acid or sodium carbonate deprives the casein of its emulsifying power. He found that when a small quantity of ether was added it also entered into an emulsion with the fat and casein, &c., and only separated out with extreme slowness. If a large excess of ether or a mixture of ether and alcohol is shaken up with milk, the fat is completely extracted, without any previous addition of acid or alkali, whereas benzol and chloroform, which are equally good solvents for fat will not extract it from the globules even after the addition of potash. If acetic acid is added to the milk in quantity just sufficient to convert the phosphates present into acid phosphates, but not to coagulate the milk, the fat cannot be extracted with ether. If a current of CO_2 is then passed through the milk, coagulation ensues and the fat can very readily be extracted with ether. The CO_2 cannot be supposed to be capable of dissolving any membrane (L. V. S. 19, 118). If milk be dried in a vacuum over H_2SO_4 the fat can easily be extracted from the residue with ether, but if the residue is redissolved in water, the solution resists the action of the ether.

Duclaux (Ch. Biol. 667) finds that if the globules are kept warm whilst under the microscope, they may be squeezed out and broken by pressing on the cover glass, the altered globules only differing in size from the original ones. Babcock (Milchz. 15, 393) also found that if milk be heated to 100° and whipped, the globules are doubled in number but present the same microscopic outline as before. Taking into consideration the somewhat viscous character of the milk solution or serum, it appears highly probable that the envelope of the globules (if any) consists of nothing more than the merest film of liquid (*serumhülle*) resembling the envelope of a soap-bubble. Refer also to De Sinety (Arch. de Phys. 1874, 479), Herer (J. 1871, 120), Hoppe-Seyler (Arch. Path. Anat. 17, 417). The milk globules consist mainly of various fats, but analysis shows the presence of traces of cholesterin, lecithin, and of a yellow colouring matter spectroscopically identical with luteïn.

(*b*) The colostrum cells or corpuscles occur very sparingly in normal milk, but abundantly in the colostrum. They consist of irregular conglomerations of very small fat vesicles embedded in a granular protoplasmic matrix; occasionally one or more eccentric nuclei may be observed. They are about four or five times as large as the milk globules, the diameter varying from ·014 to ·055 mm. Heidenhain (Handb. der Phys.) finds that if a drop of warm perfectly fresh milk be examined on a Strecker's warm stage, and the temperature regulated to 38°C. amœboid movements of these cells can be observed resembling in all respects those of the white blood corpuscles, from which indeed Heidenhain considers them to be derived by a process of infiltration with milk fat.

The fat of these corpuscles is much more readily dissolved by ether than that of the milk globules. They are disintegrated by potash or acetic acid, iodine water colours them intensely yellow, hence they consist of very small globules of fat embedded in an albuminous substance.

Abnormal milk may contain hematin, biliary colouring matters, mucin, blood corpuscles, pus, mucus, fibrous clots, and many varieties of fungi and bacteria.

Changes in milk.—Milk commences to undergo change from the moment it is drawn. If left exposed to the air it very soon loses its dissolved CO_2 and takes up oxygen. Cow's milk, in which the alkaline reaction is said to be more distinct whilst in the udder, soon shows the acid reaction markedly. On standing for a time a thick yellowish-white stratum, rich in fat, collects on the surface (cream), whilst the lower portion becomes bluish-white, poorer in fat, and increases in sp.gr. If the temperature is then not too low the milk-sugar undergoes lactic and even a slight alcoholic fermentation; the liquid then becomes acid, remains homogeneous for a time, but afterwards curdles. Recknagel (C. C. 83, 716) finds that 2 or 3 hours after the milk has been drawn the sp.gr. commences to rise, the milk attaining its maximum density in 6 hours if the temperature is kept down to 5°, but only after the lapse of 2 or 3 days at 15°C. This property he considers to be due to the swelling up of the casein suspended in the milk. Vieth (Milchz. 18, 141) found the average sp.gr. of 15 samples to be 1·0296, half an hour after milking, and 1·0309, 16 hours later.

If milk is cooled to 10°C. it acquires a viscous consistency which increases rapidly as the temperature falls. Hoppe-Seyler (Ph. C. 723) states that on standing the quantity of albumen falls and that of casein increases.

On boiling, CO_2 is expelled, and it is stated that H_2S is also given off (Schreiner, J. 10, 203). Arnold (B. C. 1882, 131) states that unboiled milk colours tincture of guaiacum blue. but that boiled milk does not; potassium iodide and starch are rapidly turned blue by unboiled milk, but only slowly by boiled milk.

As in all fairly alkaline liquids, the alkaline reaction in cow's milk becomes more evident whilst hot (Soxhlet, J. pr. [2] 6, 1), but recovers its previous intensity on cooling. Boiled milk also coagulates less readily, and (Richet, C. R. 88, 750) is less sensible to the action of ferments and bacilli. Very considerable chemical change must therefore have taken place, but it is still not very clear what is the nature of this change.

If heated over 60°C. milk acquires a slimy consistency, which has also been attributed to a change in the state of the suspended casein; this sliminess retards the subsequent separation of cream.

When milk is evaporated in a vacuum at the ordinary temperature, or at the ordinary pressure at a temperature of 50°C., a skin gradually forms on the surface and is renewed as often as it is removed. This skin is due to the desiccation of the albuminoids by the surface evaporation. It was formerly thought to consist of albumen only (Hoppe-Seyler, Virch. Arch. 17, 417), and the statement was made that, on boiling milk, the albumen separated out; but Sembritzki (P. 37, 460) found that by continually removing the skin, he could obtain 1·023 p.c. of the milk in that form. Since the albumen is not present in such quantity, it follows that some other body such as caseïn must enter into its composition.

On slowly freezing milk, the ice first formed contains a greater proportion of fat, but the mother liquor contains more casein, milk-sugar, and salts, but if the freezing takes place quickly the fat is equally distributed (Kaiser and Schmeider, B. C. 267).

If, however, the milk is agitated, the milk-ice is richer than the mother-liquor in slow freezing, but more watery and poorer in both solids and fat when quickly frozen (Henzold, Milchz. 15, 461).

Coagulation of milk.—Under certain circumstances, the homogeneous structure of milk undergoes a change, and the greater part of the contained solids is thrown down in the form of a flocculent or compact precipitate. This change is termed curdling or coagulation, and usually takes place either (1) spontaneously on standing, (2) by the action of acids &c., (3) by the action of rennet. The cause of coagulation in the first two cases is substantially the same, the casein is thrown down and carries many other substances with it as soon as the solution becomes distinctly acid. In spontaneous coagulation the acid (lactic acid) is derived from the oxidation of the milk sugar by the action of an organism—the *Bacillus acidi lactici*—which is constantly present in the milk even when drawn from the udder with every precaution against contact with the atmosphere (Hueppe, B. C. 85, 408). The action of acids upon milk depends upon the very peculiar unstable character of that liquid (*v. Constitution of milk*).

Spontaneous coagulation is characterised by the gradual souring and thickening of the milk; it takes place more readily when the temperature is raised, and when the atmosphere is charged with electricity.

Soxhlet found fresh milk to coagulate in 19 hours at 39°C.; in 29 hours at 25°; in 48 hours at 20°; in 63 hours at 17·5°; in 88 hours at 15°C.; in 99 hours at 10°; and he kept milk for fourteen days without much change in taste at 1-2°C. When milk is boiled for some time, *most* of the organisms contained in it are destroyed, and spontaneous coagulation cannot occur unless it is again impregnated by contact with the air. A temperature of 100° is, however, insufficient to destroy all the organisms present in milk.

Duclaux (Le Lait, Paris, 1887) kept milk unchanged for five years by removing all the air from the vessel, and subsequently by heating to 120°C. for some time.

Spontaneous coagulation is retarded by the addition of antiseptics, which inhibit the action of the bacilli themselves, and also by alkaline substances which merely neutralise the acid formed by their action. As antiseptics the following substances are sometimes added to milk, viz. boric acid, salicylic acid, mustard oil, glycerin, thymol, &c.

Coagulation by acids.—Most acids coagulate milk in the cold, more readily when heated. 1 p.c. of acetic acid is required to precipitate milk fully at the ordinary temperature, but ·4 p.c. is sufficient at 35°C. and ·2 p.c. at 100°C. Even carbonic acid will coagulate milk at an elevated temperature. Duclaux (*Le lait*) found that on saturating milk in the cold with CO_2 and heating it in a closed vessel to 115-120°C., coagulation ensued.

Many salts such as NaCl, $MgSO_4$, &c. coagulate milk, probably by dehydrating the milk-casein (*v. Constitution*). Alcohol acts in a similar manner.

Coagulation by rennet.—This is by far the most important of all the methods of coagulating milk, and the phenomena merit the closest attention. Unfortunately the action is very complex, and there exists very considerable divergence of opinion as to its nature. The old theory, that coagulation was in this case also preceded by the formation of lactic acid, held by Simon, Liebig, Soxhlet, &c., is now entirely abandoned, and it is generally admitted that the action of rennet depends upon the specific property of a chemical ferment present in it. This was first isolated by Deschamps (D. P. J. 1840, 445), who termed it *chymosin*. Hammersten (Bl. 22, 352) fully investigated the properties of this ferment. He found that it does not give the xanthoproteic reaction, is not precipitated by nitric acid, alcohol, iodine, tannin, nor by neutral acetate of lead, but it is precipitated by basic lead acetate. It is not coagulated at 100°C., but its efficiency is destroyed. It is soluble in water and glycerin; the latter solution is precipitated by alcohol.

Hammersten (J. 5, 267) further proved that it could coagulate milk even in the absence of acids or of milk sugar, and that the precipitate obtained differed in many important particulars from that thrown down by acids. Heintz showed that rennet could produce coagulation even in solutions rendered alkaline with sodium carbonate, provided the temperature were raised to 65°C.

The ferment is inactive in the cold, and when present in only very small quantity. Hammersten has proved that it cannot precipitate a solution of casein unless a small amount of certain soluble salts is present; the salt may be phosphate or chloride or sulphate, but it is essential to have it in solution; calcium phosphate in suspension is entirely useless. Small quantities of sodium phosphate, potassium chloride, the soluble barium, strontium, calcium, and magnesium salts promote the action of the ferment; larger quantities have, however, an adverse influence. The great majority of the sodium, potassium, and ammonium salts invariably retard the action of rennet.

Duclaux finds (Le Lait) that milk to which 1 p.c. of calcium chloride has been added coagulates five times as fast as ordinary milk, whereas ·01 p.c. of soda reduces the rate of coagulation to one-half, ·01 p.c. of lime to one-fourth, ·1 p.c. of sodium carbonate to one-tenth, and ·2 p.c. of borax to one-sixteenth of the normal.

The presence of alkalis and alkaline carbonates either delays or entirely prevents coagulation. Small quantities of acids on the other hand (except boric) hasten the action. 1 p.c. of lactic acid greatly accelerates coagulation (Engling, L. V. S. 31, 391).

Both alkalis and acids, however, if present in any quantity effect the destruction of the ferment, when they act upon rennet itself, though acids act less powerfully. ·025 p.c. of soda was sufficient to destroy the ferment in 24 hours at 15-17°C., whereas ·3 p.c. of HCl required 48 hours at 37-40°C. to produce the same result. Mayer (D. P. J. 240, 224) found that rennet acts slowly at 33°C., best at 39°C., and ceases to act altogether at 45°C. He also noticed that at the commencement of the action there is a regular fall in temperature of ·04-·06 p.c. per minute, which ceases as soon as the action is somewhat advanced. Hoppe-Seyler (Phys. Chem. 81, 754) asserts, however, that heat is developed during coagulation.

Constitution of milk.—Chemists have hitherto been unable to agree with regard to the constitution of milk. According to some it is a solution, according to others an emulsion, and others consider it to be a mere mixture.

On filtering milk through a porous cell, the following substances occur in the filtrate in solution:—

Albumen and extractive matters, soda, potash, hydrochloric and citric acids (in combination), the greater part of the magnesia, about one-third the lime, and one-half the phosphoric acid present in the milk. The bulk, however, of the milk solids—viz., the fat, casein, lime, and phosphoric acid fail to pass through.

The question whether the fat exists in an emulsified state, or in morphologically differentiated structures has already been noticed (*v. Microscopic character*). The state of the casein, lime, and phosphoric acid, now claims our attention.

Hammersten (J. Ph. 5, 267) found that perfectly pure casein is insoluble in water, and possesses a strongly acid character. It dissolves in the phosphates and carbonates of the alkalis; in the latter case CO_2 is expelled. It also dissolves in a solution of caustic soda, in lime water, and in baryta water. If the solution in lime water is neutralised with phosphoric acid and kept for some time at about 40°C., it becomes milk-white in appearance, behaves on filtration like natural milk, and is coagulated by acids or rennet. Other solutions of casein were not affected by rennet, unless calcium and phosphoric acid or a few other substances were introduced.

Hammersten also observed that milk-casein precipitated by rennet constantly contained 4-5 p.c. of tricalcium phosphate, whilst that precipitated by acids contained a lesser and more variable percentage; the serum obtained from rennet also contained more albuminoids than that obtained from other precipitants.

From these facts he concluded that casein was held in solution in milk by the neutral phosphates of the alkalis, and that the casein thus dissolved was able to take up the insoluble di- and tri-calcium phosphates and enter with them into a turgid, highly hydrated, and colloid condition which he considered the characteristic state of milk-casein, both in his artificial compound and in natural milk.

Coagulation by acids is according to this theory due to the conversion of the neutral phosphates of the alkalis into acid phosphates, which are unable to hold the casein in solution, but at the same time the acids convert part of the insoluble di- and tri-calcium phosphates, into the soluble mono-calcium salts. The milk-casein precipitated by acids is therefore poor in calcium phosphate.

Coagulation by rennet is due, according to Hammersten, to the decomposition of the milk-casein into two albuminoids, one of which passes into perfect solution, whilst the other forms an insoluble compound with tricalcium phosphate (cheese). The approximate constancy of the percentage of calcium phosphate in the coagulum, and the excess of albuminoids in the serum, are thus accounted for.

Engling (L. V. S. 31, 391) found that ammonium oxalate does not readily precipitate calcium from milk, but if calcium chloride is added to it calcium oxalate is readily thrown down.

He also found that alcohol or common salt precipitates a milk-casein which contains approximately constant quantities of tricalcium phosphate. Rennet serum was also found to be more acid than the alcohol or salt serum, and to contain more albuminoids. These observations, in conjunction with those of Hammersten, led Engling to conclude that milk-casein was *a chemical compound* of casein and tricalcium phosphate which normally exists in milk, partly swollen up (by hydration) in the solution of alkaline phosphates and chlorides, and partly dissolved. Milk-casein, or according to Engling, casein-tricalcium-phosphate, is completely decomposed by acids, casein being precipitated and more or less of the calcium phosphate taken up into solution. Rennet again only partially decomposes the casein-tricalcium-phosphate. A portion of the albuminate is detached and goes into perfect solution as acid albuminate, and as soon as a certain quantity of this is formed its acid character determines the precipitation of the bulk of the casein and tricalcium phosphate as a *basic* salt (cheese).

Boiled milk is found to have become more or less insensible to the action of rennet, but resumes its normal condition on addition of acids. Engling observed that milk serum obtained from boiled milk contained 10 p.c. less P_2O_5 than that from unboiled milk. And he therefore asserts that on boiling milk the phosphates of the alkalis in the serum lose part of their acid, which attaches itself to part of the *base* in the casein-tricalcium-phosphate. Some alkali is thus set free in the serum and some casein; these combine, forming alkali albuminate, which like other alkaline bodies retards the action of rennet (*supra*).

The addition of acid of course restores the previous condition. Söldner (L. V. S. 35, 351) made the observation that although the reaction of milk is amphoteric, the bases in the ash of milk were very largely in excess of the acids. It seemed to him *à priori* improbable that a strongly acid body like casein should exist in milk in combination with neutral tricalcium phosphate, and that a quantity of base should be simultaneously present with no acid to neutralise it, and without imparting a basic reaction to the liquid. Soxhlet (J. Ph. 1873, 1) held milk-casein to be identical with alkali-albuminate, but besides differences in the action of rennet and acids, and in the rotatory power of these bodies, Engling found that soda and potash salts could be completely separated from milk-casein by dialysis, and further that alcohol precipitates milk-casein quite free from salts of the alkalis. Hammersten (*supra*) had found that casein was soluble in lime-water and Söldner found he could obtain two compounds of casein and lime; one containing 2·36 p.c. CaO reacts alkaline with litmus, but not with phenolphthaleïn, and dissolves in water to form an opalescent fluid which is not coagulated by rennet. The other compound containing 1·55 p.c. CaO, has a slight acid reaction; its solution in water forms after some time a milk-white fluid which is coagulated by rennet. Hammersten had observed that pure casein contains ·847 p.c. of phosphorus, and Söldner has proved that a solution of pure casein in lime water leaves on ignition a residue of calcium pyrophosphate. Söldner therefore concludes that milk-casein is the *unsaturated compound of casein and lime* (1·55 p.c. CaO), and that it does not enter into combination with, nor has any specific solvent power for the insoluble di- and tri-calcium phosphates as such, these salts merely existing *in suspension* in the milk.

The power that *free casein* possesses of dissolving di- and tri-calcium phosphates is due to the acid nature of free casein. Just as it expels CO_2 from carbonates &c., like other acids, so it abstracts part of the base from the insoluble phosphates, forming a soluble lime-casein compound, whilst *mono*-calcium phosphate passes into solution.

The salt-like mass which casein forms with lime may be regarded as existing in a turgid colloidal state liquefied by hydration. On addition of acids or acid phosphates to milk, the base is removed from the lime-casein, and the casein itself (which is incapable of existing in the colloid state) falls out of solution. Söldner attributes coagulation by rennet to some specific property of the ferment itself (probably of a dehydrating nature) which as Hammersten proved (*v. Coagulation*) only acts in the presence of certain soluble salts.

On boiling milk Söldner finds that phosphoric acid passes out of solution in association with lime. There is, therefore, no cause for the formation of alkali-albuminate, since it is not the alkaline phosphates that have lost any part of their acid, but simply the monocalcium phosphate in solution that has taken up some base from the suspended tricalcium phosphate, and thus been rendered insoluble. The same effect is produced by adding alkali drop by drop to milk serum; an increase in the amount of insoluble phosphates takes place. A small amount of acid on the contrary increases the amount of soluble salts, and since the action of rennet depends upon the amount of the latter, it is evident that boiling or the addition of alkali must be prejudicial, and that the normal condition should be restored by the addition of acid.

Analysis of Milk.

The methods in use may be divided into two classes—1st, Approximate; 2nd, Scientific.

(1) *Approximate methods.*

(*a*) **Chevallier's cremometer.** A rough indication of the value of milk may be obtained by unskilled persons by means of this instrument. It consists of a glass cylinder containing 100 c.c. up to a certain mark, from which the cylinder is graduated downwards for 50 c.c. It is filled to the upper mark with milk and let stand for 24 hours, and the depth of the cream observed. Pure milk gives a layer of 10–14 c.c. Half skimmed about 6–8 c.c. The indications of this instrument are not very trustworthy.

(*b*) **The lactometer** or **lactodensimeter.** This is merely a special form of hydrometer with a very large bulb and a very slender tube, which is graduated from 15-45° corresponding to specific gravities of 1·015 to 1·045. The milk is supposed to be at 60°F., otherwise an addition or subtraction of 1° of sp.gr. must be made for every 10°F. the temperature is respectively above or below 60°F.

The milk should be stirred, and the instrument very gently lowered till it sinks no further. The reading of the upper edge of the meniscus should be taken. The specific gravity of pure cow's milk is usually taken to vary from 1·030 to 1·034. If no cream has been removed, the addition of 10 p.c. of water lowers the sp.gr. to 1·027-1·030, of 20 p.c. water to 1·024–1·027, of 30 p.c. water to 1·021–1·024 &c. If the whole of the cream is removed the milk rises in density to 1·033-1·037. Subsequent addition of water occasions a decrease in density of about 3 units for every 10 p.c. of water. Tables have been constructed from which the amount of sophistication can be found from the readings of the cremometer and lactometer.

(*c*) **Feser's lactoscope.** This instrument gives fairly approximate indications of the amount of fat in the milk. It consists of a glass cylinder provided with two scales, one graduated to c.c. the other to percentages of fat. In the lower end of the instrument is a contraction in which is placed a cylindrical piece of white glass marked with well-defined black lines. 4 c.c. of milk are introduced, water added with shaking until the black marks are just visible. The percentage of fat can then be read off.

(*d*) **Marchand's lactobutyrometer.** This instrument consists of a glass tube provided with three graduations each indicating 10 c.c. content. The interval between the two upper marks is graduated to one-tenth c.c. 10 c.c. of milk are introduced, 10 c.c. of ether added and well shaken; 10 c.c. of alcohol (90–92 p.c.) are then added and the shaking repeated. The tube is then tightly corked and placed in a water-bath heated to 40°C. In about 15 minutes the mixture separates into three layers; the upper one contains the fat and its volume is read off. Every one-tenth c.c. represents 2 p.c. of fat in addition to 1·2 p.c. of fat which always remains in solution and must be added on. The results are more accurate than those obtained from the preceding methods; they are almost correct in dealing with milk which is not too rich.

(2) *Exact methods.*

(*a*) *Specific gravity.*—This may be determined by the lactodensimeter (*v. supra*), the pyknometer, the Westphal balance, or by the sp.gr. bottle.

In practice, bottles are used containing exactly 50 grs. of water at 15°C.; these are filled with milk at 15°, weighed, and the weight multiplied by ·02. The Westphal balance consists of a counterpoised thermometer of exactly 5 or 10 c.c. displacement, suspended by a fine platinum wire from one end of a graduated lever. The thermometer or plummet is immersed in the milk at 15° and equilibrium restored by suspending a series of riders from the lever, which is graduated for the direct reading of the sp.gr.

(*b*) *Determination of the total solids.*—About 10 grams of milk are rapidly weighed out into a tared platinum dish, and dried on a water-bath to constant weight. This generally occupies 2½–3½ hours.

Richmond (A. Ch. 14, 121) states that the most satisfactory results are obtained by taking not more than 2 grams of milk, and drying for 1½ hours in a wide, flat-bottomed basin.

Some analysts measure out the quantity of milk, say 10 c.c., and determine the weight from the sp.gr.

Determination of the ash.—The total solid matter obtained by evaporating a portion of the milk to dryness is ignited at the lowest possible temperature till the ash is perfectly white; a dark-red heat should be employed. If the temperature is raised to a visible red heat, serious loss may be incurred owing to the volatility of the chlorides in the ash. In a series of experiments Vieth (A. 12, 60) found that the ash lost 25 p.c.

in weight after heating at a bright red heat for half an hour. On heating for 5, 10, and 20 minutes respectively, the ash lost 6, 19, and 24 p.c. in weight. The percentage of chlorine in the ash was simultaneously reduced by 15½, 69, and 96 p.c. of its total amount, so that over two-thirds of the chlorides volatilise in 10 minutes, and nearly the whole in 20 minutes. The ash must not be kept even at the lower temperature longer than necessary. Vieth found that it lost 6 p.c. in weight in 30 minutes when kept at a dark-red heat.

Determination of the milk-fat.—The fat is the most valuable and important constituent of milk, and its determination with exactness is therefore indispensable for commercial and analytical purposes. Formerly the dried milk solids were exhausted with ether or petroleum, the ether evaporated from the solution obtained and the fat weighed. This method is almost entirely abandoned, as 20–25 p.c. of the fat is left unextracted, and concordant results are unattainable.

The following methods are now in use:—

(1) *Soxhlet's areometric process.*—This process depends upon the variation of the sp.gr. of a solution of fat in ether at a constant temperature (17·5°C.) with the amount of fat dissolved. The milk-fat from a definite quantity of milk is brought into solution in ether, and the sp.gr. noted. On reference to the tables the percentage of fat is known.

The apparatus required consists of a tube surrounded by a water jacket, and inclosing an areometer (graduated from 43 to 66) combined with a thermometer (reading to one-third of a degree), a flask fitted with a cork and two glass tubes at right angles, caoutchouc tubes with clip and bulbs, are arranged as in fig. 1. The process is carried out as follows. 200 c.c. of milk are run into the flask, 10 c.c. of potash solution (prepared by dissolving 400 grams KHO in 1 litre water) are mixed with the milk, 60 c.c. of ether are added. (The ether must be thoroughly saturated with water.) The flask is firmly closed and violently shaken for half a minute. It is then placed in a water-bath heated to 17–18°C. and gently shaken every half minute for ten minutes. The flask is then left in a slightly inclined position in the water until a clear solution has collected on the surface. This consists of a solution of milk-fat in ether. The stopper is now removed from the flask, and the cork with the tubes inserted, the longer tube dipping well into the ether, and connection is made with the lower end of the jacketed tube. This jacket is previously filled with water at 17–18°C. By gently working the caoutchouc bulbs, enough of the ethereal solution is forced up into the tube to float the areometer. The tube is then corked to prevent evaporation of the ether, and connection with the ether-flask cut off with the clamp. If the temperature of the ether is exactly 17·5°C. the sp.gr. is given by prefixing ·7 to the reading (the lowest edge of the meniscus is read; thus 48·1 would mean ·7481), otherwise as many units must first be added to or subtracted from the reading as the number of degrees of temperature respectively exceeds or falls short of 17·5 (*e.g.* if the reading is 58·9 at 16·3°C. then 1·2 = (17·5° − 16·3°) must be subtracted from it, and it becomes (58·9 − 1·2) = 57·7, and the sp.gr. = ·7577). The percentage of fat is found from the following table:—

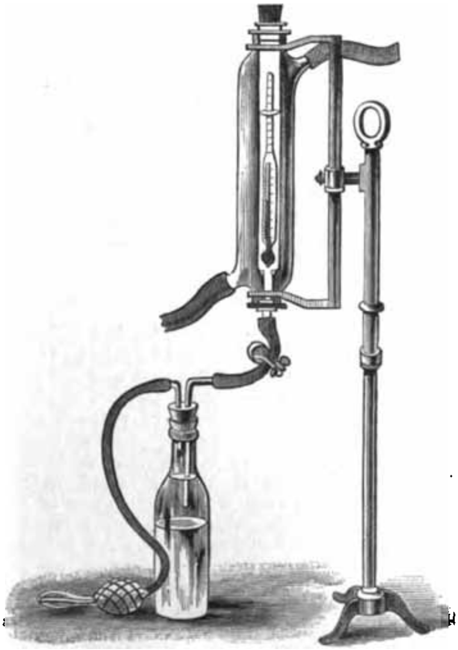


Fig. 1.

Sp.gr.	Fat p.c.	Sp.gr.	Fat p.c.	Sp.gr.	Fat p.c.
43	2·07	46·1	2·42	49·2	2·78
43·1	2·08	46·2	2·43	49·3	2·79
43·2	2·09	46·3	2·44	49·4	2·80
43·3	2·10	46·4	2·45	49·5	2·81
43·4	2·11	46·5	2·46	49·6	2·83
43·5	2·12	46·6	2·47	49·7	2·84
43·6	2·13	46·7	2·49	49·8	2·86
43·7	2·14	46·8	2·50	49·9	2·87
43·8	2·16	46·9	2·51	50	2·88
43·9	2·17	47	2·52	50·1	2·90
44	2·18	47·1	2·54	50·2	2·91
44·1	2·19	47·2	2·55	50·3	2·92
44·2	2·20	47·3	2·56	50·4	2·93
44·3	2·22	47·4	2·57	50·5	2·94
44·4	2·23	47·5	2·58	50·6	2·96
44·5	2·24	47·6	2·60	50·7	2·97
44·6	2·25	47·7	2·61	50·8	2·98
44·7	2·26	47·8	2·62	50·9	2·99
44·8	2·27	47·9	2·63	51	3·00
44·9	2·28	48	2·64	51·1	3·01
45	2·30	48·1	2·66	51·2	3·03
45·1	2·31	48·2	2·67	51·3	3·04
45·2	2·32	48·3	2·68	51·4	3·05
45·3	2·33	48·4	2·70	51·5	3·06
45·4	2·34	48·5	2·71	51·6	3·08
45·5	2·35	48·6	2·72	51·7	3·09
45·6	2·36	48·7	2·73	51·8	3·10
45·7	2·37	48·8	2·74	51·9	3·11
45·8	2·38	48·9	2·75	52	3·12
45·9	2·39	49	2·76	52·1	3·14
46	2·40	49·1	2·77	52·2	3·15

Sp.gr.	Fat p.c.	Sp.gr.	Fat p.c.	Sp.gr.	Fat p.c.
52·3	3·16	56·9	3·74	61·5	4·39
52·4	3·17	57	3·75	61·6	4·40
52·5	3·18	57·1	3·76	61·7	4·42
52·6	3·20	57·2	3·78	61·8	4·44
52·7	3·21	57·3	3·80	61·9	4·46
52·8	3·22	57·4	3·81	62	4·47
52·9	3·23	57·5	3·82	62·1	4·48
53	3·25	57·6	3·84	62·2	4·50
53·1	3·26	57·7	3·85	62·3	4·52
53·2	3·27	57·8	3·87	62·4	4·53
53·3	3·28	57·9	3·88	62·5	4·55
53·4	3·29	58	3·90	62·6	4·56
53·5	3·30	58·1	3·91	62·7	4·58
53·6	3·31	58·2	3·92	62·8	4·59
53·7	3·33	58·3	3·93	62·9	4·61
53·8	3·34	58·4	3·95	63	4·63
53·9	3·35	58·5	3·96	63·1	4·64
54	3·37	58·6	3·98	63·2	4·66
54·1	3·38	58·7	3·99	63·3	4·67
54·2	3·39	58·8	4·01	63·4	4·69
54·3	3·40	58·9	4·02	63·5	4·70
54·4	3·41	59	4·03	63·6	4·71
54·5	3·43	59·1	4·04	63·7	4·73
54·6	3·45	59·2	4·06	63·8	4·75
54·7	3·46	59·3	4·07	63·9	4·77
54·8	3·47	59·4	4·09	64	4·79
54·9	3·48	59·5	4·11	64·1	4·80
55	3·49	59·6	4·12	64·2	4·82
55·1	3·51	59·7	4·14	64·3	4·84
55·2	3·52	59·8	4·15	64·4	4·85
55·3	3·53	59·9	4·16	64·5	4·87
55·4	3·55	60	4·18	64·6	4·88
55·5	3·56	60·1	4·19	64·7	4·90
55·6	3·57	60·2	4·20	64·8	4·92
55·7	3·59	60·3	4·21	64·9	4·93
55·8	3·60	60·4	4·23	65	4·95
55·9	3·61	60·5	4·24	65·1	4·97
56	3·63	60·6	4·26	65·2	4·98
56·1	3·64	60·7	4·27	65·3	5·00
56·2	3·65	60·8	4·29	65·4	5·02
56·3	3·67	60·9	4·30	65·5	5·04
56·4	3·68	61	4·32	65·6	5·05
56·5	3·69	61·1	4·33	65·7	5·07
56·6	3·71	61·2	4·35	65·8	5·09
56·7	3·72	61·3	4·36	65·9	5·11
56·8	3·73	61·4	4·37	66	5·12

(2) *De Laval's lactocrite.*—This is a very speedy method adapted for the simultaneous analysis of a considerable number of samples. The results are of very considerable accuracy.

It is especially useful for the technical examination of butter-fat in whole milk, but less so for skimmed or separated milk. The process depends upon the solution of the casein in the milk by a mixture of acetic and sulphuric acids, and subsequent separation of the fat by centrifugal force.

The lactocrite (fig. 2) consists of a thick steel disc, mounted on a spindle, which can be rotated either by hand or by fixing in the frame of a Swedish cream separator, or by a Rabe's turbine. On the upper surface of the disc there is a shallow cylindrical cavity, in the circumference of which a number of recesses (generally 12) are sunk in an outward and slightly downward direction. The test vessel consists of a cylindrical cup (*a*), into which fits accurately a plug (*b*) turned and bored out conically so that the hollow tapers towards the top into a fine hole. Directly over this hole a narrow graduated tube (*c*) is fastened to the plug by means of the outer case (*e*) and a perforated nut (*d*). The aperture in the plug, tube, and nut are thus continuous, so that the whole constitutes a vessel open at both ends. 10 c.c. of milk are run into a test-tube and 10 c.c. of glacial acetic acid containing 5 p.c. of its volume of concentrated H_2SO_4 are added, the tube is closed with a perforated cork through which a piece of fine glass-tubing is passed to allow for expansion; the whole is placed in hot water for 7–8 minutes. The steel disc is now heated to about 50°C. (by filling the cavity with hot water and covering up), the test-tube is shaken, and its contents transferred to the cup, the plug pressed down upon the liquid, and the excess allowed to flow away through the hole in the nut. A definite quantity of liquid is thus obtained in the apparatus. The case is inserted in one of the recesses in the disc, allowed to rotate for 3–5 minutes at about 6,000 revolutions per minute; it is then removed and the depth of the fat in the graduated tube read off at once before cooling. Each division = ·1 per cent. of fat.

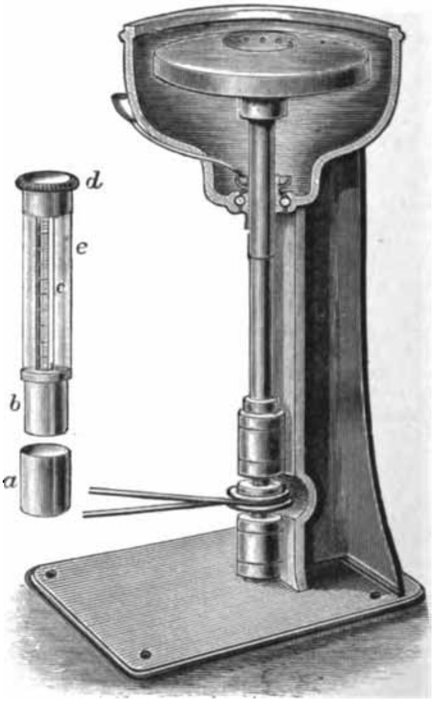


FIG. 2.

Gravimetric methods.—In consequence of the discrepancies between the results obtained by different analysts by processes in general use in 1884–5 (Wanklyn, or modifications), the Society of Public Analysts appointed a committee to compare the principal methods then known. The report of the committee, presented in 1886, and adopted by the Society, stated that 283 comparative analyses had been made, and that the most concordant, and most trustworthy results had been obtained by the use of *Adams's process.* It was accordingly resolved that public analysts should use that process in preference to any other.

Adams's process.—The original method (A. 85, 48) as modified by Allen and Chattaway (A. 86, 74) is carried out as follows. A strip of blotting paper 22 inches long, 2½ inches wide, is thoroughly exhausted with ether and dried at 100°C. to constant weight. It is then rolled up into a coil of about 1 inch diameter with a piece of thin string (previously boiled with sodium carbonate) placed in a cap of (fat free) filter paper, and attached to it by means of the ends of the string. 5 c.c. of milk are distributed with a pipette over the upper surface of the coil, it is then transferred to the water oven and roughly dried on a glass plate. The dry coil is transferred to a 'Soxhlet's extractor,' and exhausted with ether, light petroleum, or carbon bisulphide for 1½ to 3 hours, the fat solution evaporated to dryness and weighed.

If the milk is sour it is preferable to mix it well, transfer a portion into a tared basin, weigh, pour it on to the coil, wash out the basin with 2 or 3 drops of water, adding these also to the coil, then proceed as above.

Sour milk may also be rendered homogeneous by adding a few drops of ammonia. A definite volume may then be used (the sp.gr. being known).

There is some difficulty in completely exhausting the blotting paper before use. Richmond (A. 14, 123) states that this can be very perfectly done by treating for 3 or 4 hours with alcohol containing 10 p.c. of acetic acid, in a large Soxhlet's extractor.

Soxhlet's plaster of Paris method.—This method is generally used in Germany. It consists in adding to the milk 1 or 2 parts by weight of powdered gypsum which is well stirred in with the milk, dried, broken up, and the powder placed in a case made of filter-paper, covered with a little cotton-wool, transferred to a Soxhlet's apparatus and then treated with solvents as usual.

If the dried mass is ground sufficiently fine and the exhaustion carried on for 3–4 hours, this method is capable of giving results that agree with those obtained by Adams's process, but if, as is commonly the case, the mass is roughly broken up and only exhausted for 1½ hours, this method gives about ·2 p.c. less fat than the blotting paper process. Richmond (A. 14, 124) recommends kieselguhr as more easily powdered and more porous than plaster of Paris.

Schmidt (Fr. 27, 464) takes a test tube of 50 c.c. capacity, graduated in the upper part to $\frac{1}{10}$ c.c., introduces 10 c.c. of milk, adds 10 c.c. of strong HCl, boils with shaking until the liquid turns dark brown, cools the tube in cold water, adds 30 c.c. of ether, shakes round, and, after standing, measures the volume of the ethereal solution and draws off 10 c.c. This he evaporates down in a weighed porcelain capsule on the water-bath, and finally in the air-bath at 100°C. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been properly conducted, the ether separates from the aqueous solution quite clear, without the slightest turbidity. The ethereal solution as it flows out from the pipette should not show any watery drops. With proper arrangements the operation can be carried out in 15 minutes. Stokes (A. 14, 30) finds the results by this method agree with those obtained by Adams's process.

Determination of milk-fat from formulæ.—It has been found that the sp.gr. of milk, the total solids, and the fat are dependent upon each other, so that if two of these quantities are known, the third can be calculated.

If F = p.c. of fat, T = p.c. of total solids, S = sp.gr. of milk at 15°C., then

$$F = \cdot 833\ T - 2\cdot 22 \left[\frac{100\ S - 100}{S}\right] (a)$$

(Fleischmann) gives results in agreement with a gravimetric estimation by Soxhlet's plaster of Paris method.

Veith (A. 8, 49) found that the average difference from this formula in 530 analyses was ·02 p.c., and the maximum difference ± ·2 p.c. It is only applicable to cow's milk. Richmond (A. 14) finds that this formula gives uniformly low figures in comparison with those obtained from direct determination by Adams's process.

If G denote the figures in the sp.gr. over 1·000, *i.e.* $G = 1000(S - 1)$, F and T as before, then $T = 1\cdot 17\ F + \cdot 263\ \frac{G}{S}$ (*b*) gives in all cases a very close approximation to the results by Adams's method. $F = \frac{5}{6}\left(T - \frac{G}{4}\right)$ gives results within ·02 p.c. of (*b*).

Claustritzer and Mayer give a somewhat similar formula. The difference between calculated and observed values becomes greater as the milk becomes richer.

Determination of the milk-sugar.—(1) *Gravimetrically, by Soxhlet's method.*—25 c.c. of milk are weighed out, diluted to 400 c.c.; 10 c.c. of a solution of copper sulphate (69·28 grams per litre) are added, then 6·5 to 7·5 c.c. of a solution of caustic soda standardised to precipitate an equal volume of the copper solution. The solution should still be slightly acid after the addition of the soda, and contain traces of copper. It is diluted to 500 c.c., filtered; 100 c.c. are transferred to a beaker, 50 c.c. of Fehling's solution are added, the whole boiled for six minutes, filtered through asbestos, washed with hot water, then twice with absolute alcohol and twice with ether. The tube containing the asbestos and precipitate is cleared of ether by blowing air through, and a stream of H passed through, whilst (a special filter is used consisting of a calcium chloride tube, the bulb half filled with asbestos and previously dried and weighed) the bulb is gently heated for five minutes. The reduced copper is allowed to cool in a stream of H, and weighed. Soxhlet gives the following table:—

Copper obtained (milligrams)	Amount of milk-sugar (milligrams)
392·7	300
363·6	275
333	250
300·8	225
269·6	200
237·5	175
204·0	150
171·4	125
138·3	100

The intermediate values are obtained by interpolation.

(2) *By polarisation.*—The albuminoids in milk affect the determination, and must first be eliminated. This may be done

(*a*) *By mercuric nitrate.*—Mercury is dissolved in double its weight of HNO_3 (sp.gr. = 1·42), and an equal volume of water added to the solution. 60 c.c. of milk are taken, 1 c.c. of the mercury solution added with shaking, then filtered in the cold, and the polarisation found. For milk-sugar $a_D = +52·53$.

It is as well to dilute the mass to 102·4 c.c. before filtering, as the precipitate occupies exactly 2·4 c.c.

The temperature during the process must be kept constant and within 15–25°C. (Wiley, A. 13, 196).

(*b*) *By basic lead acetate.*—A saturated solution of lead acetate is boiled with excess of litharge till sp.gr. = 1·97. 1 c.c. of this solution is sufficient for 60 c.c. of milk. According to Schmoeger, the milk is precipitated with acetic acid, filtered, the lead acetate added, the whole boiled, cooled down, diluted, filtered again, and polarised.

Stokes and Bodmer (A. 10, 12) recommend the use of Pavy's solution (*v.* p. 101).

100 of milk-sugar have the same reducing power as 52 of glucose or 49·4 of cane-sugar. By this method a fair determination may be made by merely diluting the milk so that 6–12 c.c. decolourise about 40 c.c. of Pavy's solution.

Determination of the total Albuminoids.—*Ritthausen's method.*—The albuminoids are precipitated by copper sulphate and soda solution (*v. Determination of milk-sugar*). The precipitate is collected on a weighed filter, washed with a little of the clear filtrate, allowed to drain, washed with 80–100 c.c. of hot water, dried, the fat extracted, dried again at 125°, and weighed. The copper is calculated to CuO and its weight deducted. Sebelien (Z. 13, 135) points out that this method is not exact, since copper hydroxide does not give up all its water at 125°, but only on ignition. This error is avoided if at least ·6 gram of albuminoid is present in solution, and the ratio between the copper oxide used and the amount of albuminoid falls between 1·3 to 1·35.

Pfeiffer dries the precipitate for 8–10 hours at 100° and calculates the copper as hydroxide.

Pfeiffer determines the small amount of salts retained by the precipitate by igniting with sulphur in a stream of hydrogen, and deducting any excess in weight over the copper sulphide calculated.

Almen's method.—This method gives very exact results, and is particularly recommended by Sebelien. 3 to 5 grams of milk are taken (2 grams of colostrum, 10 of whey), diluted with 3–4 vols. water; a few drops of solution of some salt (NaCl, $MgSO_4$, &c.), then excess of solution of tannin, is added in the cold. (The tannin solution consists of 4 grams tannin added to 8 c.c. of 25 p.c. acetic acid and 190 c.c. of 40–50 p.c. alcohol.) The precipitate is thoroughly washed with *cold* water, and the nitrogen in the filter and precipitate estimated by Kjeldahl's process. The result, after subtraction of the N in the filter, gives the albuminoid N, and this × 6·37 = total albuminoids (since both casein and albumin contain 15·7 p.c. N).

Total albuminoids in human milk.—Hoppe-Seyler proceeds as follows. 20 c.c. of milk are taken, dilute acetic acid is added to slightly acid reaction, then 4 vols. strong cold alcohol, the whole shaken, and, after standing for one hour, passed through a weighed filter. The precipitate is washed 6 or 8 times with 60 p.c. alcohol, then with ether, and dried at 120–125°. The filtrate, which still contains albuminoids, is evaporated to a small bulk and treated with 60 p.c. alcohol. The filtrate from this is again concentrated, treated with tannin, and the precipitates dried at 120°, &c.

Christenn takes 10 grams human milk, adds 10 c.c. ether and 20 c.c. alcohol, shakes, and filters till the filtrate is perfectly clear. The precipitate, consisting of albuminoids and salts, is dried, weighed on the filter-paper, ignited, and the ash deducted. The fat, milk-sugar, and soluble salts may be determined in the filtrate by (1) evaporating to dryness and extracting the fat, (2) drying the residue and weighing (milk-sugar and soluble salts), (3) igniting for salts.

Total nitrogen.—The total nitrogen in milk is best determined directly by Kjeldahl's method. The digestion must be somewhat prolonged to obtain the best results (Kreusler, L.V. S. 31, 248). In absolutely accurate determinations it is not advisable to calculate the total albuminoids from total N by multiplication by 6·37, because of the presence of nitrogenous extractive matters in the milk. Schmidt-Muhlheim found an average of ·04–·05 p.c. of extractive N. This is confirmed by Sebelien (J. Ph. 13, 135), who finds the same average, with a minimum of ·03 p.c. and an exceptional maximum (in colostrum) of ·08 p.c.

(N − 0·4) 6·37 gives a very close approximation (Sebelien).

Separate determination of the albuminoids (casein, albumin, globulin, &c.).—Hoppe-Seyler (Handb. der Phys. Chem. Anal.) proceeds as follows. 20 c.c. of milk are diluted with water to 400 c.c., transferred to a deep beaker, and very dilute acetic acid added till a flocculent precipitate just appears. CO_2 is then passed for ¼–½ hour, and the precipitate allowed to subside for 12 hours. The solution, which should be perfectly clear, is passed through a weighed filter, the precipitate washed on with a little of the clear filtrate, allowed to drain, and washed once with distilled water. The precipitate = casein + fat. The latter is extracted as usual. The filtrate is boiled for a few minutes, when the albumin separates out; if the precipitate is not very flocculent, a few drops of very dilute acetic acid may be added. It is collected on a weighed filter, washed with cold water, and dried at 120–125°.

The filtrate and wash-water are evaporated to the consistency of a thin syrup, the precipitate which settles out gathered on a small weighed filter, well washed with cold water, and weighed.

If peptone or albumose is to be estimated, 100 c.c. of milk must be taken, and after treatment as above, or preferably by Almen's method, using an excess of tannin, the filtrate is treated with a solution of phosphotungstic acid (the crystallised acid is dissolved in 5 parts of water and 2 p.c. concentrated H_2SO_4 added), the precipitate washed with water, acidulated with H_2SO_4, decomposed with baryta water, dried, and weighed; otherwise the N may be directly determined in the phosphotungstic precipitate.

This method cannot be used for human milk nor for that of the mare and ass, because on dilution and treatment with acetic acid and CO_2 the caseïn separates in such a finely divided condition that it cannot be filtered. Blyth (Food: Lond. 88) uses the following modification for human milk; 100 c.c. are diluted to 400 c.c., acidified with dilute acetic acid, saturated with CO_2, and transferred to a tall beaker. A small cylindrical porous battery cell, closed by a perforated plug connected with a mercury pump, is immersed in the liquid. A good vacuum is maintained, and ultimately the whole of the solution passes through. The caseïn is left behind, and is washed, dried, and weighed. The albumin is precipitated by boiling &c.

Pfeiffer and Schmidt (Z. 23, 445) modify Hoppe-Seyler's method in the following way for human milk: 20 c.c. of milk are diluted to 400 c.c., heated to 40°C., acetic acid added drop by drop till a granular precipitate commences to form; CO_2 is then passed in for half an hour and the precipitate allowed to subside for 24 hours. The casein is then weighed, and the filtrate treated in the ordinary way.

Tolmatscheff's method.—(1) *Casein.* 20 cc. of milk are saturated in the cold with crystallised $MgSO_4$ (it is best to make the crystals into a paste with water), 100 c.c. of a very concentrated solution of $MgSO_4$ are added, the precipitate filtered off, well washed with a concentrated solution of $MgSO_4$, the fat extracted, and the residue dried, weighed, and the ash deducted.

(2) *Albumin.* The filtrate and wash-water from the casein are acidified with dilute acetic acid, heated to boiling, filtered, washed with water and alcohol, dried at 120–125°, and weighed. Sebelien (Z. 13, 135) advises that in each case the N should be determined in the precipitate by Kjeldahl's process, and the albuminoid found by multiplication by 6·37. The results are accurate.

Tolmatscheff estimates casein + albumin in human milk thus. To 20 c.c. of milk 4 vols. of cold alcohol are added, the precipitate filtered off, washed with 60 p.c. alcohol, extracted with ether, dried and weighed. It is then ignited and the ash deducted. Albumin is afterwards determined as above.

The following scheme is recommended for scientific purposes (Sebelien):—

(1) Determine total N by Kjeldahl's method.

(2) Total albuminoids by precipitation with tannin (N by Kjeldahl).

(3) Casein + globulin by precipitation with $MgSO_4$ (N by Kjeldahl).

(4) Casein by precipitation with dilute acetic acid (N by Kjeldahl).

The difference between (2) and (3) gives the albumin, between (3) and (4) the globulin, between (1) and (2) the non-albuminoid or extractive N. The latter may also be determined directly by Kjeldahl's method, in the filtrate from the tannin (2).

Average composition of milk (König).

—	Sp.gr.	Water	Caseïn	Albumin	Fat	Milk sugar	Ash	In the dry solids Caseïn	Albumin	Fat	Total N
Human	1·0270	87·41	1·03	1·26	3·78	6·21	0·31	18·15		30·02	2·90
Cow	1·0315	87·17	3·02	0·53	3·69	4·88	0·71	23·51	4·15	28·75	4·42
Ewe	1·0341	80·82	4·97	1·55	6·86	4·91	0·89	33·98		35·78	5·44
Goat	—	85·71	3·20	1·09	4·78	4·46	0·76	22·36	7·63	33·46	4·80
Mare	1·0347	90·78	1·24	0·075	1·21	5·67	0·35	21·62		13·16	3·46
Ass	—	89·64	0·67	1·55	1·64	5·99	0·51	21·22		15·49	3·39
Sow	—	84·04	7·23		4·55	3·13	1·05	46·44		27·68	7·33
Bitch	—	75·44	6·10	5·05	9·57	3·09	0·73	45·48		38·49	7·27
Buffalo	—	81·41	5·85	0·25	7·47	4·15	0·87	32·96		40·49	5·27
Camel	—	86·57	4·0		3·07	5·59	0·77	29·80		22·82	4·77
Elephant	—	67·85	3·09		19·57	8·84	0·65	9·61		60·89	1·54
Cat (A)	—	81·63	3·12	5·96	3·33	4·91	0·58	49·44		18·13	7·91
Mule (B)	—	91·50	1·64		1·59	4·80	0·38	19·29		18·71	3·08
Lama (C)	—	86·55	3·0	0·90	3·15	5·60	0·80	29·0		23·42	4·64
Hippopotamus (D)	—	90·43	—	—	4·51	4·51		—		47·13	—
Porpoise (E)	—	41·11	11·19		45·80	1·33	0·57	—	—	—	—

(A) Commaille, C. R. 63, 692. (B) E. F. Ladd, Agric. Science 1, 108. (C) Doyère, A. a. 1852, 251. (D) F. W. Gunning, C. C. 1871, 149. (E) Purdie, C. N. 52, 170.

Constituents of milk.—The proportions of the constituents of cow's milk vary within certain limits, dependent upon the race, constitution, and age of the individual, upon the period of lactation, sexual excitement, &c., and to a certain extent upon the character of the food, and especially the amount of water supplied. The influence of food is confined to the regulation of the ratio of solids to water in the milk, but has little effect upon the relative proportion of the solids (fat, casein, &c.) to each other. This is proved by the fact that milk poor in fat does not show a very high, nor milk rich in fat a very low sp.gr., as they would do if the other solids were not proportionately diminished or increased (*v.* Dietrich, Zusammensetzung und Verdaulichkeit der Futter). Succulent fodder increases the percentage of water.

Severe exertion may cause a change in the chemical character of the milk; the percentage of fat and total solids may fall, and the ash rise largely. Calving and sexual excitement merely occasion a temporary disturbance; the yield falls suddenly, the milk often coagulates on boiling, &c. The quality of the milk varies with the season of the year and the time of day. The poorest milk is received in April, the richest in November; a fall in quality also occurs in July. In autumn the cows are stale, and give a limited quantity of milk which is of high quality. In spring they are mostly new-calved and the fresh grass forms a succulent fodder, and a larger quantity of poor milk is given. In summer the cows frequently suffer from excessive heat, which burns up the pasture, or from continuous rain; the milk then becomes inferior in both quality and quantity.

Milk drawn in the evening is universally richer than that drawn in the morning. Nilsson (B. C. 88, 171) found an average of 3·33 p.c. of fat in the morning, and 3·82 p.c. in the evening. This is due to the unequal interval between two successive milkings. If drawn at equal intervals no difference is observed. The milk obtained from the first part of the milking is poorer than that drawn at the end (fore milk).

For analyses and details respecting the influence of food, season, &c., see König (Chemie der menschlichen Nahrungs und Genussmittel, Berlin); Dietrich (*l.c.*); also Vieth (J. R. Agric. S. 25, 180).

Fat (*v. Microscopic characters*). The butter of cow's milk is a very pale yellow substance, solidifying at 26·5, whereupon the temperature rises to 32°. It melts between 29° and 41°; melted fat, however, begins to harden at 23°. It is soft and sticky above 18° The sp.gr. varies from ·9221 to ·9370 (Fleischmann, J. 33, 251). It consists of a mixture of glycerides of fatty acids; the amount of volatile acid (butyric) distinguishes it from all other fats. Blyth (Foods) gives as its composition: oleïn 1·477, stearin + palmitin 1·750, butyrin 0·270, caproïn, caprylin, and rutin ·003. Total, 3·5 p.c.

The amount of glycerides of volatile acids is at a maximum 5–7 days after calving, and then decreases during lactation (Nilsson, B. C. 17, 171).

Proteids. A considerable number of these bodies are found in milk. Milk curd, obtained by the action of rennet or acids, consists chiefly of casein. The clear whey gives on boiling a precipitate of another proteid—albumin. On adding mercurous nitrate to the clear filtrate from this body Millon and Commaille obtained a precipitate of another proteid, termed by them 'lactoprotein.' This is, however, generally considered to be a mixture of the other proteids which have escaped precipitation, or of the decomposition products of casein and albumin produced by the action of acids, heat, &c. Blyth (C. T., 1879, 530) believes it to be a mixture of (1) galactin, (2) lactochrome, (3) traces of albumin, (4) traces of urea. The existence of peptone and hemialbumose is very doubtful; they can only be present in minute traces if at all. Sebelien found that the albumin precipitate consisted of a mixture of two distinct bodies, one of which resembles the paraglobulin of the blood; this he calls lactoglobulin.

Lubawin found that pure casein contained a molecule of nuclein in combination. The whole of the phosphorus in casein appears to belong to this body.

Casein. The views held with regard to the state in which casein exists in milk have been fully set forth (*v. Constitution*). When milk is filtered through a porous cell the albumin which is in solution passes through, but the casein remains behind.

Casein is completely precipitated from neutral or amphoteric milk by excess of common salt, by alcohol, acids, many metallic salts, &c. For other properties *v. Proteids.* The amount of casein in cow's milk varies from 2-4½ p.c.; the mean is 3·2 (Kirchner), 3·98 (Blyth).

Nuclein. Lubawin (B. 10, 2073) found that on digesting a solution of casein in hydrochloric acid with pepsin, nuclein gradually separated out. Hammersten found nuclein in the free state in the scum produced in Laval's cream separator (Milchz. 1879, 663). Perfectly pure casein contains ·831-·883 p.c. of phosphorus constantly; in all probability this is entirely contained in the nuclein molecule.

Globulin. Sebelien (Z. 9, 445) isolated this body in milk. He precipitated the casein with common salt, heated the filtrate to 35°, filtered off a very slight flaky precipitate which was thus formed, and saturated the filtrate with $MgSO_4$. The precipitate thus formed was found to resemble the paraglobulin of the blood. It contains 15·72 p.c. of N.

It is an essential constituent of colostrum in which Sebelien (J. 18, 102) found 10·12 p.c.; it diminishes, however, very rapidly in a few days. It is imperfectly precipitated by NaCl, but completely by $MgSO_4$.

Albumin. As usually obtained, *i.e.* by precipitating the casein with acetic acid and CO_2 and boiling the filtrate, it contains the globulin and traces of casein. Sebelien prepared lactalbumin by treating the filtrate from the globulin (*q. v.*) with ¼ p.c. acetic acid, redissolving the precipitate in water, carefully neutralising, filtering and reprecipitating the filtrate with ¼ p.c. acetic acid. The albumin thus prepared was redissolved in water, the salts separated by dialysis, the remaining solution precipitated by alcohol, washed with ether and alcohol, pressed and dried. It is a white powder, perfectly soluble in water, from which solution it is precipitated by ammonium sulphate but not by magnesium sulphate. The solution in water free from salts becomes opalescent at 62-67°, and coagulates at 72°; in presence of NaCl the temperature of coagulation may be raised to 82–84°.

Ultimate analysis gives C = 52·19 p.c., H = 7·18 p.c., N = 15·77 p.c., S = 1·73 p.c.; lactalbumin closely resembles serum-albumin, but its sp.rotn. is $\alpha_D = -36{\cdot}4$ to $-36{\cdot}98$, whereas for serum-albumin $\alpha_D = -62{\cdot}6$ to $-64{\cdot}6$.

Peptone. This body was found in milk by Schmidt-Muhlheim (P. 28. 287), by Radenhausen (Z. 5, 29), and by many older investigators. Its presence is, however, denied by Sebelien (Z. 13, 135), Hammersten (J. 6, 13), Dogiel (Z. 9, 591), and Hoffmeister (Z. 2, 288). Schmidt-Muhlheim found ·08–·10 p.c. of peptone in milk.

Lactoprotein. Obtained by Millon and Commaille by precipitating casein and albumin and adding $HgNO_3$. It is soluble in excess of $HgNO_3$, and turns red when warmed with it. Lactoprotein is not precipitated by heat, acetic acid, mercuric chloride, or nitric acid.

After removing the Hg with H_2S, lactoprotein gives the biuret reaction for peptone (Kirchner).

Milk contains from ·1–·4 p.c. of lactoprotein.

Hemialbumose was found in the milk by Schmidt (J. 14, 175). It differs from peptone only in being diffusible through an animal membrane.

Extractive matters.—These are partly nitrogenous; their total amount is very small. Liebermann (A. 181, 90) found ·035–·045 p.c. of non-albuminoid nitrogenous bodies; Schmidt-Muhlheim (P. 30, 379) found ·040–·050 p.c.; Sebelieu (Z. 9, 445) finds a mean of ·04 p.c. and variations of from ·03–·08 p.c.

Urea. Small quantities of this body are nearly always present. Schmidt-Muhlheim (P. 30, 379) found an average of ·0091 p.c. (·0079–·0103) in whey. Lefort obtained 1·5 gram nitrate of urea from 8 litres of whey = ·0073 p.c. Vogel (J. 67, 932) found ·07 p.c. of urea in milk.

Creatinin. Traces have been found by Schmidt-Muhlheim (P. 30, 379) and Weil (B. 11, 2175).

Lecithin, cholesterin, and **hypoxanthin.** These bodies are mentioned by Bouchardat and Quevenne. Schmidt-Muhlheim found ·0038 p.c. lecithin in whey, ·174–·153 p.c. in butter.

Organic acids. There is little doubt that more of these bodies exist in milk than have been discovered up to the present, since the excess of base is so considerable in the milk ash.

Lactic acid. Marchand (J. Ph. 29, 311) found ·082–·422 p.c. of lactic acid. Varying amounts have been observed by different chemists. Soxhlet has shown that lactic acid never occurs normally in milk as taken from the udder; but by the time analyses are generally made, from ·01 p.c. is generally present.

Citric acid. Henkel (B. C. 17, 787) found that on saturating the serum left after removing albuminoids &c. with calcium salts, and slowly evaporating, a crystalline deposit of calcium citrate was formed. The amount of citric acid was estimated from this as ·08–·12 p.c. As no method is at present known for estimating citric acid in milk, the quantity present is probably considerably greater.

Söldner (L. V. S. 35, 351) estimates it as ·25 p.c.

It evidently exists as a soluble salt, since the same quantity separates out from whey and from serum (by cell filtration). The concretions in condensed milk consist of pure calcium citrate.

Carbohydrates. Milk-sugar (*q. v.*) is one of the principal constituents of milk. In cow's milk it varies in amount from 3–6 p.c., averaging 4·5 p.c. (Kircher), 4 p.c. (Blyth). It readily undergoes lactic fermentation in milk, and after some time a slight alcoholic fermentation. The latter is, however, more readily set up by a peculiar ferment contained in kephir grains.

Ritthausen's carbohydrate (J. pr. 15, 329) was obtained by evaporating the ethereal solution of milk-fat and separating the less soluble portion. It solidifies to a brown mass, soluble in water. It will only reduce an alkaline solution of copper oxide if it has been previously boiled with dilute H_2SO_4.

It will not reduce a mixture of $Bi(NO_3)_3$ and KHO.

Alcohol added to its solution causes a precipitate uncrystallisable from water.

Other organic bodies.—Traces of alcohol and acetic acid are stated to occur in fresh milk by Béchamp (C. R. 76, 836). Lactochrome is a peculiar colouring matter found by Blyth (Tr. C. S. 1879, 530) in the lactoprotein precipitate by decomposing it with H_2S, precipitating the solution with lead acetate; the filtrate gave with a solution of $HgNO_3$ a precipitate of a compound of Hg with an alkaloidal colouring matter $HgO,C_6H_{13}NO_6$. On decomposing this with H_2S, lactochrome was obtained in solution. It forms bright-red orange, resin-like masses, soluble in water, very soluble in hot alcohol, less so in cold; softens at 110°C.

The amount present in milk was not estimated.

Glucoside? A bitter principle isolated by Blyth (*supra, q. v.*) in the filtrate from lactochrome by precipitation with ammonia and tannin. It is a dark-brown mass, hygroscopic and soluble in water, insoluble in strong alcohol, reduces solution of copper on boiling, bitter taste, neutral reaction.

Salts. These consist principally of phosphates, chlorides, and citrates of the alkalis and alkaline earths. Musso (J. 14, 222) also found ·0391–·0831 grams of sulphuric acid per litre. This would amount to ·558–1·19 p.c. of SO_3 in the ash.

Musso (J. 7, 168) also found ·0021–·0046 gram NaCNS per litre of milk.

The amount of ash in cow's milk varies from ·65–·85 p.c.; generally from ·7–·8.

The ratio of ash : proteids : sugar is very constantly 1 : 5 : 6 in cow's milk, 1 : 5 : 10 in human, 1 : 6 : 23 in mare's milk (Vieth, A. 13, 49). The following are average analyses of milk-ash:

	Percentage in milk	Percentage in ash
K_2O	·1228	24·5
Na_2O	·0868	11
CaO	·1608	22·5
MgO	·0243	2·6
Fe_2O_3	·0005	0·3
P_2O_5	·1922	26
Cl	·1146	15·6
SO_3	·0061	1·0

(Fleischmann).

More sulphuric acid is actually found in the ash than that shown, but it is due to the oxidation of the sulphur in the albuminoids; only that determined by Musso is taken into account. On the other hand, a deduction must be made for increase of weight by oxidation. Fleischmann deducts 3·5 p.c. of the weight of the ash for this error.

Söldner has lately shown (L. V. S. 35, 351) that, owing to the excess of base present in milk-ash, the whole of the phosphorus in the nuclein is oxidised to phosphoric acid, and appears in the ash as calcium pyrophosphate. From 25–40 p.c. of the P_2O_5 in the ash may be due to this source. The composition of the ash therefore still requires revision.

Söldner (*supra*) has made an estimate of the amounts of salts as actually existing in the milk. Assuming the presence of ·25 p.c. citric acid, he calculates:

Sodium chloride	·962
Potassium chloride	·830
Monopotassium phosphate .	1·156
Dipotassium phosphate . .	·835
Potassium citrate	·495
Dimagnesium phosphate . .	·336
Magnesium citrate	·367
Dicalcium phosphate . . .	·671
Tricalcium phosphate . . .	·806
Calcium citrate	2·133
Lime (in combination with casein)	·465

Latschenberger (J. 14, 222) found ·02016 p.c. of ammonia in milk.

Schrödt and Hansen (L. V. S. 31, 55) found the amount of chlorine in the ash to be greater at the end than at the beginning of the period of lactation (17·63 p.c.). There was also relatively more soda than potash, though the total alkalis were the same.

The ash is almost always 8 p.c. of the solids—not fat (Vieth, A. 13, 63).

Gases in milk.—Pflüger (P. Arch. 2, 166) found:

	O	CO_2 pumped out)	CO_2 (expelled by phosphoric acid)	N
1.	·1	7·6	·00	·7
2.	·09	7·4	·02	·8

V. also Hoppe-Seyler (Virch. Arch. 17, 417); Setchenow (Zeit. rat. Med. 1861, 285).

Colostrum is, immediately after parturition, a yellow or brownish-yellow dirty-looking liquid, slimy, viscous, and often heterogeneous in consistency. It has a peculiar smell, a stale salty taste, and generally a slight acid reaction. It coagulates on boiling. The sp.gr. at 15° varies from 1·040 to 1·080.

The presence of colostrum corpuscles is characteristic (*v. Microscopic characters*).

Analyses of Colostrum (cor.).

—	I sp.gr. 1·046	II
Solids . . .	25·47	25·33
Fat . . .	6·98	3·59
Milk sugar . .	—	2·67
Total N . . .	2·506	11·10
Extractive N . .	·237	—
Total albuminoids	14·45	17·64
Casein + globulin .	12·87	—
Casein . . .	3·57	4·04
Globulin . .	1·58 9·30	—
Albumin . .	1·59	13·60

I. Sebelien (L. V. S. 3, 51); II. König.

The albuminoids in colostrum vary greatly. Casein is always somewhat greater than in normal milk; albumin varies from a little above that of ordinary milk to over three times that amount. Globulin is always an essential constituent. Extractive N is a little higher than in ordinary milk. Engling (*l.c.* 96) states that at first colostrum contains no milk sugar, but only carbohydrates, resembling grape sugar. The colostrum fat differs from ordinary butter in smell, taste, consistency, and melting-point. It melts at 40–44°. This is due, according to Nilsson (B. C. 17, 171), to the smaller quantity of volatile acids. Nuclein has been found up to 2 p.c. Cholesterin and lecithin also occur in some quantity. Urea is higher than in ordinary milk.

Engling found the ash of colostrum to consist of

K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	SO_3	Cl
7·23	5·72	34·85	2·06	·52	41·43	·16	11·25

The higher percentage of phosphoric acid and lime, and the low alkalis, are particularly noteworthy.

ABNORMAL MILK.

Blue milk. This is characterised by the appearance of blue, yellow, and red spots, which gradually increase till the whole surface is covered. It is due to a bacillus (*B. cyanogenus*). If the reaction of the milk is acid the colouration is deep blue; in other cases it is a slaty blue, changing to deep blue on addition of acids. The colouring matter is identical with triphenylrosaniline (Martiny and Fürstenberg, Milchz. 10, 594).

Stringy milk. Some milk, on standing for a short time, becomes thick and stringy. It is due to a special ferment, which sets up mucic fermentation. Sound milk is infected by addition of a little of the stringy milk, but the ferment can be destroyed by heating to 65°C. or by the addition of strong antiseptics.

Red milk is due either to colouring matter in the food of the animal or to some disease, as 'red murrain' or inflammation of the udder.

Bitter milk is principally due to the food, but it is occasionally obtained from cows just before the end of lactation.

For particulars of other abnormalities in milk *v.* Kirchner's Milchwirthschaft. For milk in disease *v.* Blyth's Foods, where other references will be found.

ADULTERATIONS.

The principal adulteration practised is the addition of water, or partly skimmed milk; starch is sometimes added to impoverished milk to thicken it. Carbonates of the alkalis and borax, or boric acid, and more rarely, salicylic acid, are also introduced to keep milk from souring.

The addition of water or removal of cream is shown by the analysis.

Soxhlet has proposed the following direct test for the addition of water, based upon the presence of nitrates in water and their total absence in milk.

The milk is coagulated by a solution of calcic chloride free from nitrate; the serum is now treated with a solution of diphenylamine in concentrated H_2SO_4, in the same way as with the ferrous sulphate test. Szilasi (A. Ch. 33) measures out 1 c.c. of a solution of diphenylamine sulphate into a porcelain dish, and adds a few drops of milk; nitrates gradually give a blue colouration. These tests are not sufficiently delicate for pure water.

Carbonates of the alkalis are best determined by taking 500 grams of milk and determining the CO_2 in the ash. The ash of pure milk should not contain more than 2 p.c.

Boric acid is detected by Meissl as follows. 100 c.c. are made alkaline with milk of lime, evaporated and incinerated. The ash is dissolved in as little concentrated HCl as possible, filtered, the filtrate evaporated to dryness, and the HCl expelled. The residue is moistened with a drop or two of extremely dilute HCl, saturated with 'tincture of curcuma,' and evaporated on the water-bath. Mere traces of boric acid give a cinnabar or cherry-red colouration.

Salicylic acid is detected by Pellett by mixing 100 c.c. of milk, 100 c.c. of water at 60°C., 5 drops acetic acid, 5 drops of a solution of mercuric nitrate, filtering off the albuminoids, shaking with 50 c.c. of ether, allowing to settle, removing the ether, evaporating to dryness, dissolving the residue in a few drops of water, and adding ferric chloride. The quantity of salicylic acid can be approximately known by comparing the violet colouration produced with a series of standard solutions.

PRESERVATION OF MILK.

To preserve milk for any length of time at the ordinary temperature it must be sterilised. This may be done either by means of antiseptics, such as salicylic acid, borax, or boric acid, &c. —the presence of which is highly undesirable in food—or, as is more generally practised, by the agency of heat. For the action of drugs *v.* Soxhlet, J. 6, 118; Mayer, Milchz. 1882, 321. A temperature of 100°C. is insufficient to sterilise milk completely. Dietzell found that milk heated for twenty minutes to 105–110° only kept sweet for a few weeks, whilst that heated to 100–115° for twenty minutes (five minutes at 115°) was perfectly sweet three years later.

Duclaux kept milk unchanged for five years by exhausting the air from the containing vessel and subsequently heating to 120°.

Milk can, however, be preserved unchanged by mixing it with a considerable percentage (not less than 12 p.c. of its weight) of sugar, evaporating to a semi-solid mass, and excluding the air.

Fleischmann gives the following account of the process of manufacture of condensed milk *with* addition of sugar. The milk on delivery is weighed, filtered through a wire sieve, and thrown into a reservoir communicating with the tank A (fig. 3), tapped into cans 20 to 30 inches deep. A number of these are placed in the water-bath B, which is heated by steam from a perforated coil at the bottom, communicating with the steam-pipe F. (Beside each water-bath is a smaller bath for cleaning the cans.) When the milk has attained a temperature of 87–94°C. it is transferred to the vats C or D, which have false copper bottoms, into which steam can be introduced to prevent the milk from cooling. The vat E contains the necessary quantity of *cane-sugar*—12 p.c. of the weight of the milk, hot milk is thrown in, stirred, and passed back to C through a filter, and this is repeated till all the sugar is dissolved.

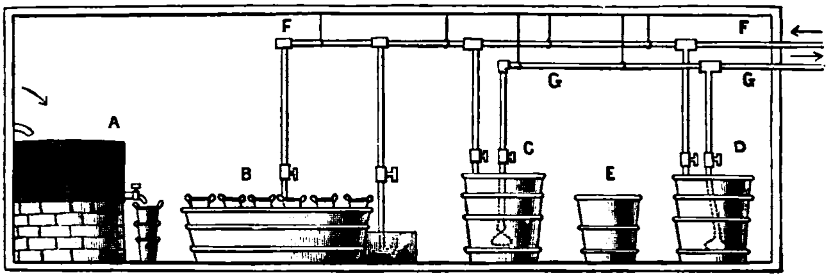


FIG. 3.

The milk in C is then sucked up by the pipe G, which terminates in a sieve, into the vacuum V (fig. 4). This is a spherical copper vessel, with a wooden jacket round the middle and with a false bottom, into which either steam or cold water can be introduced. There is also a copper coil inside the vacuum, into which steam and cold water can be passed. A (fig. 4) is the pipe through which the sugared milk is introduced; B is a sight-hole, hermetically closed with a thick glass plate; C is a thermometer; D a manometer; E a condenser; F the cold-water pipe for the condenser; G the pipe leading to the air-pumps; H an air-cock; I is an exhaust pipe for the condensed water; K and L are cold-water pipes for clearing the vacuum; M an

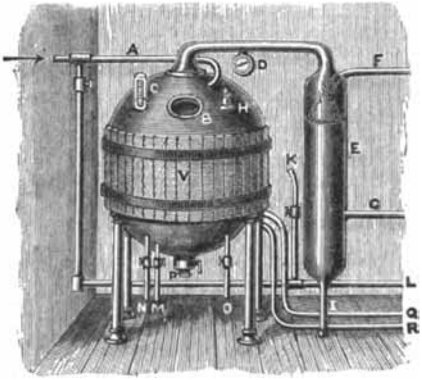


FIG. 4.

exhaust pipe for the waste water from the space between the two bottoms; N an exhaust pipe for the coil inside the vacuum; O a pipe for drawing samples of milk, P the delivery pipe for the condensed milk; Q a steam pipe for supplying the space under the false bottom; R a supply pipe for the coil. On the other side of the vacuum there is another sight-hole resembling B, behind which a light is placed, whilst the progress of the operation is continually watched through B. The air-pumps are set to work, but no steam is passed in until the milk is seen to be *boiling briskly*; the temperature is then regulated to 60°C. The pressure inside the vacuum is generally 60 to 100 millim.

When a sample taken out and cooled is of the right consistency, cold water is turned on in both the coil and false bottom, and after a short time the milk is run out and quickly cooled to 15°C. It is then tapped into canisters; the covers, which are pierced with a fine hole, are soldered on—the heat of the operation causes the greater part of the residual air to be expelled; the hole is then quickly soldered over.

Various modifications of the above process are adopted. In some places, for instance, special precautions are taken to regulate the temperature of the water-bath, and the heat is not allowed to rise above 60–75°; in others a series of ledges are arranged in the vacuum, so that the milk trickles down from one to the other and is more quickly condensed, &c., &c. Grandeau and Kramer (J. Ph. 16, 267) state that at Zurich the addition of sugar is made to the milk heated to 35°C., and the temperature in the vacuum is not allowed to rise above 52°C.

In many cases part of the cream is removed before condensation.

Analysis of condensed milk (sweetened).

—	Nestlé	Nestlé	Anglo-Swiss Company	Anglo-Swiss Company	Cham	Gerber & Co.
Water	15·30	24·48	24·94	25·63	27·67	23·68
Fat	8·85	11·33	8·90	6·13	9·33	9·74
Albuminoids	9·98	10·97	9·68	12·65	16·53	9·80
Milk-sugar	13·62	11·19	13·29	12·50	13·20	12·93
Cane-sugar	50·08	39·95	41·24	41·21	30·65	41·80
Ash	2·17	2·08	1·95	1·88	2·20	2·05

MILK CONDENSED WITHOUT ADDITION OF SUGAR.

In America the milk is filtered, heated to 60 or 70°C., filtered again and condensed in a vacuum at 40–45°C. to about ⅓ of its bulk. A portion of the cream is often abstracted before condensation.

This milk will not keep for more than a few days. The milk prepared at Romanshorn (Switzerland) keeps better, but the process of manufacture is not known. It is believed that the milk is heated to about 120°C. in its preparation, as about ⅔ of the albumen is coagulated, whilst in ordinary (sweetened) condensed milk only about half the albumen is coagulated. A portion of the cream is abstracted before condensation on account of the rancidity which a large amount of fat quickly occasions.

Scherff's process, which is in use at Stendorff, consists in first sterilising the milk by heating it to 100–113° for 1–2 hours in sealed vessels under a pressure of 2 to 4 atmospheres. It is then condensed to either ½ or to ⅓ of its bulk in a partial vacuum at a temperature of 65–70° and a pressure of 11 m.m.

Voelcker gives the following analyses of unsweetened milk:

	I	II
Water	57·96	51·72
Fat	16·02	14·33
Casein	8·50	11·69
Milk-sugar	16·32	19·51
Ash	2·20	2·75

KEPHIR.

Milk does not readily undergo the alcoholic fermentation by the action of yeast, though a small amount of alcohol is formed during the lactic fermentation.

In the Caucasus a special ferment (kephir grains) is used which has the property of speedily inducing alcoholic fermentation in milk. Kern (Biol. Centbl. 2, 137) found in the grains two of the organisms of ordinary yeast (*Saccharomyces cerevisiæ*) and a bacillus (*Dispora caucasica*)

For the manufacture of kephir *v.* Krannhals (J. 14, 191), Haeccius (Milchz. [14] 19, 209).

The milk-sugar is changed by the action of the grains partly into CO_2 and alcohol and partly into lactic acid; small quantities of glycerin, acetic, succinic, and butyric acids are also formed. The casein and albumen are partly peptonised.

Kephir is an agreeable nourishing drink with a slightly sour taste. It is best relished when two days old, and three days after preparation it is decidedly sour and stronger in alcohol.

König gives the following average composition of kephir:

Water	91·21
Alcohol	0·75
Fat	1·44
Sugar	2·41
Lactic acid	1·02
Casein	2·83
Albumin	0·36
Hemialbumose	0·26
Peptone	0·039
Total proteids	3·49
Ash	0·68

A simple method of making kephir consists in taking some of the good three days old product, adding 4–5 parts of cow's milk, and allowing it to ferment for two days with occasional shaking. The consumption of kephir in Russia has made considerable progress recently. In Tiflis also it is now the custom to take kephir medicinally, although its preparation in reference to the production and significance of the so-called kephir grains is still obscure. In the Caucasus kephir is prepared from milk, particularly sheep and goat's milk, in peculiar leather pipes (*burdinks*) by adding to it kephir grains as ferment. Struve has investigated the formation of this ferment and studied its properties. Since the augmentation of the kephir grains takes place when the milk is kept in leather pipes their growth must necessarily be affected by the milk constituents, and although it was *à priori* impossible to determine what changes the ingredients consumed during this process undergo, it was assumed that the substance belonging to the group of proteids would maintain their general type to a greater or less degree. 100 parts of the grain dried in the air gave:

Water	11·21
Fat	3·99
Peptones soluble in water . .	10·98
Proteids soluble in ammonia .	11·32
Proteids soluble in potash .	30·39
Insoluble residue	33·11

On digesting the insoluble residue in a dilute solution of potash and subjecting it to microscopical examination, it showed an intimate mixture of yeast fungi with the bacteria described by Kern under the name of *Dispora caucasica.* Struve concludes that only 33·11 p.c. of the total substance of the grains constitutes the active ferment. With kephir grains of the above composition a drink is prepared which, according to Podwisozky, contains only traces of alcohol after 24 hours' bottling, whilst in 48 hours it becomes brisk and contains a considerable amount of alcohol, the latter increasing still further after the lapse of another 24 hours. On subjecting the three drinks characterised by the difference in the duration of the fermentation to analysis it was found that although the percentage of casein was the same in each case, the latter was not completely soluble in a mixture of dilute ammonia and potash. In the solution of the casein of the kephir of one day's fermentation only traces of a precipitate were observed; the kephir two days old gave 0·05 p.c. and that three days old 0·22 p.c. of residue. Microscopical examination of the residues showed that yeast fungi only were present, bacteria or other forms of fungi being entirely absent. From this Struve infers that the fermentation of the milk is dependent upon the growth of the yeast fungus (*Saccharomyces mycoderma, Mycoderma cerevisiæ et vini*) contained in the kephir grains, whilst the bacteria *Dispora caucasica* take no active part in the fermentation. This conclusion is confirmed by the fact that the finished kephir is capable of fermenting fresh portions of milk. From the results of this investigation Struve concludes (1) During the fermentation the yeast fungus, under the influence of the power of vegetation and of osmotic laws, enters into animal as well as vegetable tissues, and disposes them to a variety of changes. (2) The development of the yeast fungus in the interior of organic tissues may, under favourable conditions, assume the character of a special process of fermentation. (3) The effects of such a process are increased when the evolution of carbonic anhydride is retarded. (4) Animal tissues into which the yeast fungus has entered exhibit in sugar solutions as well as in milk all appearances of vinous fermentation. They can therefore be used instead of kephir grains for the preparation of kephir. (5) The formation of the kephir ferment is the cause of a peculiar growth of the yeast fungus within the tissues of the leather pipes during the process of fermentation, its fungoid form being due to the development of carbonic anhydride. (6) The bacteria *Dispora caucasica* must be regarded as residues of fibrils of the tissues of the leather pipes (B. 17, 1364; S. C. I. 3, 493).

Human Milk.

Human milk differs very little from cow's milk. It is a little bluer, contains rather more sugar, less albuminoids and less salts than cow's milk. It undergoes spontaneous coagulation less readily, acids precipitate the casein more imperfectly, and the precipitate is more soluble in excess. Acetic acid and CO_2 also throws the casein down in a very finely divided state, but these differences are due, according to Dogiel (Z. 9, 591), to the small amount of salts present in human milk. If the salts are raised to the standard of cow's milk the casein falls out in thick flakes. For effects of salts (*v. Coagulation*).

Human milk shows, however, a very wide variation in composition due to the individual constitution, health, and nutrition. Leeds (C. N. 50, 263) obtained the following figures from 84 samples from healthy subjects:—

—	Maximum	Minimum	Average	Average of milk of English cows (Blyth)
Specific gravity	1·0358	1·0260	1·0313	1·032
Albuminoids	4·86	0·85	1·995	4·93
Sugar	7·92	5·40	6·936	4·00
Fat	6·89	2·11	4·131	3·5
Solids, not fat	12·09	6·57	9·137	—
Ash	0·37	0·13	0·201	·7
Total solids (by addition) . . .	16·79	10·92	13·268	—
,, (by evaporation) . .	16·66	10·91	13·267	—
Water	89·08	83·21	86·732	86·87

In the colostrum the albuminoids are higher and more variable, the average is about 4·2; this falls to the normal in about 10–14 days. The percentage of milk-fat rises with the length of the period of lactation. Pfeiffer (J. 13, 163) found 2·87 p.c. in milk taken during the first six months, 3·28 p.c. in the succeeding six months. The last portions drawn from the breast are richer in fat than those preceding. Forster (B. 14, 591) obtained from samples successively drawn 1·71 p.c., 2·77 p.c., and 4·5 p.c. of fat respectively.

They also decrease in specific gravity (Rodenhausen, Z. 5, 13). Human milk fat is stated to be richer in olein than butter fat. It contains small quantities of lecithin and cholesterin. Tolmatscheff found ·0252–·0385 p.c. cholesterin and ·0569–·0266 p.c. lecithin.

The milk-sugar from human milk is identical with that from cows (Radenhausen, Z. 5, 13).

Pfeiffer (J. 13, 163) states that it increases in amount with the duration of the period of lactation; thus he found in the first week an average of 4 p.c.; second week, 4·8 p.c.; third week, 5·2 p.c.; a gradual rise then took place from 5·7 p.c. to 6·2 p.c. to the end of lactation. In the colostrum it is very low. Pfeiffer found on the first day 2·7 p.c., second day 3·5 p.c. (*v. Colostrum*).

The total N varies from ·13 to ·38 p.c. (Forster, B. 14, 591; Dogiel, Z. 9, 591; Christenn, L. V. S. 20, 439; Liebermann, A. 181, 90).

Struve (J. pr. 27, 249) found ·41 p.c. of peptone in human milk; his results are contradicted by Dogiel (*supra*) and Hofmeister.

The casein in human milk is stated by Dogiel to be identical with that from other animals. On digestion with pepsin, nuclein is left behind and a peptone formed of the same rotative power as that from bovine casein. In the colostrum the albuminoids vary greatly in amount, but rapidly decrease to the normal. Pfeiffer (J. 13, 163) found 8·6 p.c. in the first two days. Kemmerich (P. 2, 401) found 7·4 p.c.

Urea is nearly always present in small quantities. Picard obtained ·0118 p.c. from human milk.

The principal qualitative differences between human and cow's milk are first its difficult coagulation by acids (2 p.c. HCl will not coagulate it even on heating); secondly, the absence of citrates (Soxhlet).

The ash of human milk is richer in potash and chlorine, and poorer in lime and phosphoric acid than cow's milk. The following analyses are given by Bunge:—

—	K_2O	Na_2O	CaO	MgO	Fe_2O_3	P_2O_5	Cl
I. Percentage in milk .	·0779	·0231	·0828	·0064	·0004	·0473	·0437
II. „ „ .	·0703	·0257	·0843	·0065	·0006	·0468	·0445
I. Percentage in the ash	35·15	10·43	14·79	2·87	0·18	21·30	19·73
II. „ „	32·14	11·75	15·67	2·99	0·27	21·42	20·35

Milk of other Animals.

Healthy children of both sexes discharge, from their seventh to their twelfth day from birth, a white secretion from the breast (*Haeenmilch*), which has pretty much the composition of human milk.

Mare's milk is white, sp.gr. 1·035 (1·034–1·036). It is much sweeter than cow's milk, but contains less fat and proteids. Mare's milk is distinguished from all others by its small amount of fat.

Koumiss is a vinous liquor made by the Tartars by the fermentation of mare's milk. It is a white, sweetish, effervescing liquid, somewhat sour when old. The sugar gradually diminishes with age, whilst the alcohol and the lactic acid increase.

It is prepared by adding 1 part of old koumiss to 10 of fresh milk, and warming for 2–3 hours to 20–25°C. CO_2 then comes off, and the liquid is bottled and left to mature. (For manufacture and analyses *v.* Vieth, A. 13, 2; L. V. S. 31, 353; Biel, J. 4, 166.) A similar preparation in imitation of the true Russian koumiss is made in Switzerland and in this country from cow's milk by adding a small quantity of sugar and yeast to skim milk; it contains more sugar and less lactic acid than old Russian koumiss, and on account of the much greater proportion of casein contained in cow's milk differs considerably from that prepared from mare's milk (Ph. T. [3] 1, 861, 888).

H. Suter-Naef (B. 5, 286) gives the composition of Swiss koumiss (sp.gr. 1·1286), manufactured at Davos, as follows:

	In 100 grams	Per litre
Water . .	90·346 .	1019·64 grams.
Alcohol . .	3·210 .	36·23 „
Lactic acid .	0·190 .	2·14 „
Sugar . .	2·105 .	23·75 „
Albuminates .	1·860 .	20·99 „
Butter . .	1·780 .	20·09 „
Inorganic salts	0·509 .	5·74 „
Free carbonic acid	0·177 .	2·00 „

For observations on the changes and action of Russian koumiss *v.* Jaqielski (Ph. [3] 1, 861, 885); J. T. George (Ph. T. [3] 3, 544).

Ass's milk is white, and sweeter than cow's milk. Sp.gr. between 10·23–10·35.

It readily turns acid, and easily undergoes fermentation. For composition *v.* Table.

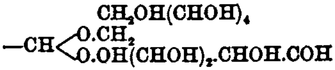
Goat's milk is white, of insipid, sweetish, taste and peculiar odour. It is a little richer in solids than cow's milk. Sp.gr. 1·030–1·035. On coagulation its casein forms thick clots. For composition *v.* Table.

Ewe's milk is a thick yellowish-white liquid of agreeable taste and smell. Sp.gr. 1·035–1·041. Reaction with litmus is amphoteric (Fleischmann).

Ewe's milk is remarkable for its high percentage of fat.

References: Martiny, Die Milch, Danzig, 1871; Kirchner, Die Milchwirthschaft, Berlin, 1882; König, &c.

MILK-SUGAR $C_{12}H_{22}O_{11}$ (Tollens and Mayer, B. 21, 1566; Brown and Morris, C. J. 1888, 618). According to Fischer (B. 22, 361) it is an anhydride, and possesses the structural formula



$$\begin{array}{l}\qquad CH_2OH(CHOH)_4\\ -CH\left\langle\begin{array}{l}O.CH_2\\ O.OH(CHOH)_2.CHOH.COH\end{array}\right.\end{array}$$

(*v. Oxidation*). This compound was first separated from whey by Fabrizio Bartoletti in 1619, and termed *nitrum seri lactis*. Testi gave it its present name. It is found in the milk of the mammalia, and, according to Bouchardat (C. R. 73, 462), in the juice of the fruit of *Achras sapota*.

In Switzerland it is manufactured on the large scale in the following manner (Jour. fab. Sucre, 28, 44). 50,000 litres of whey are directly evaporated to dryness; the residue weighing about 1,250 kilos. is dissolved in water at 65° in copper pans, ¾ to 1 kilo. of alum is added, the solution is filtered through animal charcoal, boiled down to a syrup, and allowed to crystallise on wooden rods. The yield is 55–60 p.c. of the crude sugar.

It is purified by recrystallisation and repeated precipitation from its aqueous solution by alcohol.

Human milk contains from 5 to 8 p.c. of milk-sugar, cow's and ewe's milk from 4½ to 5 p.c., mare's and ass's milk about 6 to 7 p.c.

Milk-sugar is deposited from its aqueous solutions in hemihedral rhombic crystals, exhibiting the combinations $\infty\breve{P}\infty.\frac{P}{4}.OP.2\breve{P}.\infty$.

The angle $OP:2\breve{P}\infty = 109° 39'$; $OP:\frac{P}{4} = 101° 41'$.

Ratio of axes $a:b:c = 0{\cdot}6215:1:0{\cdot}2193$ (Schabus).

The crystals are white, semi-transparent, hard, and grate between the teeth; their sp.gr. = 1·53–1·54. They contain 1 molecule of water ($C_{12}H_{22}O_{11}.H_2O$), which they retain at 100°C. over H_2SO_4, but give up completely at 130°, leaving a colourless melted mass of anhydrous milk-sugar, which solidifies in the crystalline state on cooling, and is strongly hygroscopic.

If a solution of milk-sugar is evaporated to dryness on the water-bath, an anhydrous milk-sugar remains behind, which is not hygroscopic.

Hydrated milk-sugar is slightly hygroscopic, soluble in 5 or 6 parts of cold or 2½ of boiling water; from the latter solution the crystals only separate out slowly on cooling. An aqueous solution saturated at 10° has a density of 1·055, and contains 14·55 p.c. of hydrated milk-sugar; when left to evaporate it begins to deposit crystals as soon as the density = 1·063, and the solution contains 21·64 p.c. of sugar. It is insoluble in alcohol or ether, but readily dissolves in distilled vinegar, crystallising out unaltered on evaporation.

Polarisation.—All solutions of milk-sugar are dextrorotatory. The average normal specific rotation of a solution of milk-sugar is $\alpha_D = 52{\cdot}5$, at a temperature of 15–25° (Miley, A. 13, 174) $+52{\cdot}53$ at 20° (Schmœger, B. 13, 1927). The rotatory power is not affected by the concentration of the solution, but diminishes very rapidly on a rise of temperature.

A recently prepared cold aqueous solution of hydrated milk-sugar, or of the hygroscopic anhydride (obtained at 130°), shows a strong *birotation* = $\frac{8}{5}$ the normal. A fresh solution in cold water of the anhydride obtained at 100° shows *semirotation* = $\frac{5}{8}$ the normal. A solution in hot water shows only the normal rotation. All solutions show the normal rotation on standing for 4–24 hours, or on boiling (Schmoeger, B. 13, 1915).

The rotatory dispersive power $\alpha_D:\alpha_0 = 1{\cdot}259$ is constant during all these changes.

Action of heat.—At 130° hydrated milk sugar loses its water of crystallisation, at 160° it turns brown, at 175° it loses another molecule of water, and yields lactocaramel $C_{12}H_{20}O_{10}$, at 203° it melts, and at a higher temperature yields humus-like products. In oxygen it colours at 105–110°, oxygen being absorbed and carbon dioxide given off. In the cold neither O nor ozone have any effect (Gorup-Besanez, A. Ch. 100, 264). Oxygen gas passed over a mixture of milk sugar and platinum black heated to 250° yields water and carbon dioxide. Heated with water in a sealed tube to 170° it is decomposed with separation of carbon, carbon dioxide, formic acid, and humic acid (Loewe, Bl. 8, 429).

Munk (J. 1877, 1024) states that an easily fermentable sugar (galactose) is also formed, and at 180° a small quantity of pyrocatechin.

Oxidation.—By the slow action of bromine water and moist silver oxide, *lactobionic acid* $C_{12}H_{22}O_{12}$ was obtained (Fischer, B. 22, 361). It is a colourless, strongly acid syrup, very soluble in water, slightly soluble in alcohol, insoluble in ether. It expels carbon dioxide from carbonates, does not reduce Fehling's solution on boiling. Dilute acids convert it into galactose and gluconic acid.

On heating to 100° for some hours with bromine and water, and then treating with moist silver oxide, *lactonic acid* $C_6H_{12}O_7$ is formed (Barth and Hlasiwetz, A. 119, 281).

A solution of milk-sugar mixed with potash or soda dissolves copper hydroxide, forming a deep-blue solution, which deposits cuprous oxide on warming. 1 molecule of milk-sugar reduces 14–16 molecules of copper hydroxide according to the duration of the heating (Fehling, A. Ch. 104, 79). The solution contains lactic and glycollic acids (Habermann, B. 17, 351). According to Bödeker and Struckmann (A. 264), the solution contains *gallactic* and *pectolactic acids*. Metallic silver is thrown down from solutions of silver salts; other easily reduced metallic oxides also oxidise milk sugar.

On heating with potassium bichromate and sulphuric acid or with chromic acid, aldehyde is formed (Guckelberger, A. 64, 98). Potassium permanganate in alkaline solution oxidises milk-sugar on boiling to carbon dioxide and water (Laubenheimer, A. 144, 283). On distillation with MnO_2 and H_2SO_4, formic acid is formed. Nitric acid first inverts the milk-sugar (*v. Action of acids*), then forms mucic acid from the galactose and saccharic acid from the dextrose; small quantities of tartaric, racemic, and on prolonged treatment oxalic acid, are also formed (Dubrunfaut, C. R. 42, 228).

Action of acids.—Organic acids have but little effect on milk-sugar in the cold or when gently warmed with it, but on prolonged boiling they either invert it or form compound ethers. On boiling milk-sugar with dilute HCl or H_2SO_4, it is inverted, *i.e.* it is split up into two sugars, dextrose and galactose, both of which, however, are dextrorotatory:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6.$$

To separate these the solution is neutralised with calcium carbonate, mixed with baryta water, treated with CO_2, concentrated, left to crystallise slowly, and finally mixed with alcohol. Galactose separates out as a crystalline mass, and on addition of excess of absolute alcohol to the mother liquor, dextrose is thrown down. The separation may also be effected by means of alcohol of 95-98 p.c., in which dextrose is more soluble than galactose. On prolonged boiling with HCl, milk-sugar is converted into formic, acetopropionic, and humic acids (Conrad and Gutzeit, B. 19, 1575).

Concentrated H_2SO_4 does not blacken milk-sugar in the cold, but rapidly chars it on warming.

Very strong nitric, or a mixture of concentrated nitric and sulphuric acids, forms an amorphous ethereal tri-nitrate $C_{12}H_{19}(NO_2)_3O_{11}$, and a pentanitrate (Gé, B. 15, 2238) $C_{12}H_{17}(NO_2)_5O_{11}$.

The tri-nitrate melts at 36·8, sp.gr. at 0° = 1·479, on treatment with more acids forms $C_{12}H_{18}(NO_2)_4O_{11}$, melting at 80–81°.

The pentanitrate crystallises in semitransparent colourless laminæ. Sp.gr. at 0° = 1·684; melts at 1·392°; explodes on concussion or on heating to 155·5°.

Chlorosulphonic acid (SO_3HCl) dissolves anhydrous milk sugar with formation of crystallisable $C_6H_7O(SO_4H)_4Cl$ (dextrose chloride tetrasulphate?), and the uncrystallisable isomer of dextrose sulphate, viz. galactose sulphate (Claesson, J. pr. 20, 29).

On heating with acetic anhydride, three compounds are formed:

(1) Milk-sugar tetra-acetate $C_{12}H_{18}O_7(C_2H_3O_2)_4$, which forms deliquescent grains, soluble in water, sp. rotation $\alpha = +50°$ (Schutzenberger, Bl. 1869, 243).

(2) Hexacetate $C_{12}H_{16}O_5(C_2H_3O_2)_6$, a crystalline salt.

(3) Octacetate $C_{12}H_{14}O_3(C_2H_2O_2)_8$, a viscid ether, insoluble in water, dissolves in alcohol and acetic acid. Softens at 52°. Sp. rotn. $\alpha_D = +31$.

Action of alkalis.—Alkalis impart to milk-sugar a very light yellow tinge. It dissolves in strong caustic potash, forming a thick liquid from which alcohol throws down white flakes of $C_{12}H_{22}O_{11}KHO$; with soda a similar compound $C_{12}H_{22}O_{11}NaOH$ is formed. They are readily decomposed even by CO_2, milk-sugar separating out unchanged. The solution in milk of lime gives on concentration and addition of alcohol a precipitate containing, when washed and dried, from 11·2–15·7 p.c. of CaO. Dubrunfaut obtained two compounds of lime and milk-sugar by rubbing the two together, one of them ($C_{12}H_{22}O_{11}CaO$) is soluble in water, the other is an insoluble basic salt.

Baryta forms a similar compound

$$2(C_{12}H_{22}O_{11}) + 3BaO$$

containing 40·1 p.c. of pure baryta.

Milk-sugar heated gently with lead oxide gives off water. On digesting the aqueous solution with lead oxide at a temperature below 50°, part of the oxide dissolves and an insoluble compound remains suspended, which contains when dry 63·5 p.c. of lead oxide. The dissolved portion evaporated in a vacuum leaves a gummy soluble mass containing 18·1 p.c. lead oxide.

Milk-sugar absorbs about 12·5 p.c. of ammonia gas, forming a brown amorphous nitrogenous mass, which is decomposed on exposure to the air (Thenard, C. R. 52, 444).

It forms no compound with chloride of sodium.

By the prolonged action of alkalis on milk-sugar, lactic acid and pyrocatechin are formed (Hoppe-Seyler, B. 4, 347; Nencki and Lieber, J. pr. 34, 503).

The prolonged action of lime results in the formation of isosaccharin and metasaccharin (Kiliani, B. 16, 2625). On fusing with KHO, oxalic acid is formed.

Other reactions.—By the action of sodium amalgam on milk-sugar, mannite and dulcite are formed (Bouchardat, C. R. 83, 1008).

A solution heated with aniline may yield two products, or only one, according to the equations

$$2C_{12}H_{22}O_{11} + C_6H_7N = H_2O + C_{30}H_{49}NO_{21}$$
$$2C_{12}H_{22}O_{11} + 2C_6H_7N = 2H_2O + C_{36}H_{54}N_2O_{20}.$$

Both these bodies are very soluble in water, very sparingly so in absolute alcohol, nearly insoluble in pure ether. They reduce alkaline cupric solutions, bromine added to their solutions disappears immediately (Sachsse, B. 4, 834). On heating with phenylhydrazin (1 pt. milk-sugar + 1½ pts. phenylhydrazin chloride + 2 pts. sodium acetate + 30 pts. water) for 1½ hours, phenyllactosazon $C_{24}H_{32}N_4O_9$ is formed, and separates out in yellow needles *on cooling*. The needles melt at 200°, dissolve in 80–90 pts. hot water. With very dilute H_2SO_4 they form an anhydride $C_{24}H_{30}N_4O_8$, which melts at 223–224°, and is almost insoluble in water (Fischer, B. 20, 830).

Metallic derivatives.—Potassium and sodium derivatives $C_{12}H_{22}O_{11}K$ and $C_{12}H_{22}O_{11}Na$, are obtained by mixing alcoholic solutions of milk-sugar and of potash or soda. Otherwise by precipitating a mixture of their aqueous solutions with absolute alcohol. They are amorphous salts, and easily decomposed (Fremy, A. Ch. 15, 278).

Ca, Pb, and Ba derivatives may be obtained in the same manner.

Compounds of milk-sugar with copper and iron probably exist, since the oxides of these metals are held in solution by milk-sugar in presence of an excess of alkali.

Synthesis of milk-sugar.—Demole (B. 12, 1935) states that on boiling a mixture of dextrose and galactose with acetic anhydride, and adding water, the octoacetate of milk-sugar is precipitated as a viscid body identical with Schutzenberger's ether, and yielding on saponification with alkalis a substance identical with milk-sugar. This is, however, denied by Berthelot (Bl. 34, 82) and by Hertzfeld, who state that no milk-sugar is obtained on decomposition of the octoacetate.

Reactions.—Milk-sugar is distinguished from other sugars by its ready crystallisation and by the formation of mucic acid when oxidised by nitric acid.

Characteristic reactions are the precipitation of the yellow needles of phenyllactosazon *on cooling*, and the formation, on boiling milk-sugar with lead acetate and adding a little ammonia, of a yellow colouration changing to a cinnabar-coloured precipitate (Deon, Bl. 32, 123). In other respects—reactions with Fehling's solution, metallic salts, &c.—milk-sugar only shows differences of degree with dextrose, &c.

PRODUCTS OF DECOMPOSITION.

Lactonic acid $C_6H_{12}O_6$ is a very hygroscopic crystalline body, is not volatile, has a strongly acid taste, dissolves readily in water and alcohol, but is insoluble in ether. The aqueous solution has the sp. rotn. $a = -25°$. It forms soluble and crystallisable salts with the alkalis and alkaline earths, the solutions of which are not precipitated by the neutral salts of Cu, Pb, Hg, or Ag; but ammonia with lead acetate precipitates a basic salt. Concentrated solutions of the alkali salts form a gelatinous precipitate with silver salts, which is readily coloured brown by light, and is decomposed on solution in water. The ammonium salt gives a mirror with solution of silver nitrate (Barth a. Hlasiwetz, 122, 96).

Gallactic acid $C_{14}H_{18}O_8$? is a light-yellow odourless syrup, miscible with water, soluble in alcohol but not in ether, does not reduce alkaline solutions of copper; the alkaline salts are amorphous and deliquescent. Its solution precipitates the salts of copper, mercury, and lead.

Pectolactic acid $C_8H_8O_8$? is an odourless syrup, reduces alkaline copper solutions on warming and gives a mirror with an ammoniacal silver solution. It is soluble in alcohol but not in ether, and forms soluble salts with the alkalis and alkaline earths. Ferric salts throw down a red precipitate soluble in soda; silver, and mercury salts are reduced in the presence of alkalis.

Lactocaramel $C_6H_{10}O_5$ is produced when milk-sugar is heated for some time to 180°C. It is a dark-brown substance, soluble in water and capable of combining with the oxides of lead and copper (Lieben, Wien. Akad. Ber. 18, 180).

For determination of milk-sugar (*v.* MILK and SUGAR).

Fermentation.—Milk-sugar does not readily undergo alcoholic fermentation, but when left for some time in contact with a large quantity of yeast at a temperature of 15°–25°C., fermentation gradually sets in. With kephir grains milk-sugar readily undergoes alcoholic fermentation. In presence of cheese or gluten the lactic fermentation is easily set up. A small amount of alcohol is, however, always formed at the same time, especially if no chalk is added to neutralise the acid as it is formed; the quantity of alcohol is greater in very dilute solutions.

MILK-TREE WAX *v.* WAX.

MILLERITE. Native nickel sulphide, found at Lancaster, Pa., United States. Occurs in brass-yellow capillary crystals *v.* NICKEL.

MILLON'S REAGENT *v.* ALBUMINOIDS.

MILORY GREEN. *Chrome green v.* PIGMENTS.

MINARGENT. *Aluminium bronze v.* ALUMINIUM.

MINERAL ACIDS. Acids of inorganic origin, *e.g.* sulphuric, nitric, hydrochloric, phosphoric, &c.

MINERAL ALKALI. A term originally given to soda in contradistinction to potash, which was termed the *vegetable alkali.*

MINERAL BLUE. *Antwerp blue v.* PIGMENTS.

MINERAL CAOUTCHOUC. Syn. with *Elaterite* (*q. v.*).

MINERAL CARBON. *Anthracite v.* FUEL.

MINERAL CHAMELEON. *Sodium* or *potassium manganate v.* MANGANESE.

MINERAL COTTON. A name given to slag-wool.

MINERAL GREEN. *Scheele's green, Hydrocupric arsenite* $CuHAsO_3$ *v.* ARSENIC, vol. i. 201.

MINERAL INDIGO. A name given to the blue oxide of molybdenum *v.* MOLYBDENUM.

MINERAL KERMES. Amorphous antimony sulphide containing the trioxide (*v.* vol. i. p. 180).

MINERAL OILS *v.* PETROLEUM.

MINERAL PURPLE. *Purple of Cassius v.* GOLD, PURPLE.

MINERAL TALLOW. *Hatchettine.* A variety of fossil resin or wax resembling dysodil, ozokerite, &c.

MINERAL TURPETHUM. *Mercuric sulphate v.* MERCURY.

MINERAL WATERS *v.* AERATED WATERS; also WATER.

MINERAL YELLOW. A term occasionally given to the oxychlorides of lead when used as pigments *v.* LEAD.

MINIUM *v.* LEAD.

MINJAK-LAQAM *v.* OLEO-RESINS.

MINJAK TENGKAWANG. This substance, known in commerce as Borneo tallow, appears to be particularly suitable for the manufacture of soap and candles. It is obtained from the fruit of a number of plants belonging to the family of Dipterocarpus. Its original colour is light green, which changes to yellow, then white, on prolonged exposure to the air. In consistency at ordinary temperatures, and in its taste, it resembles cocoa butter. It has a crystalline granular structure, and is covered with numerous fine white needles of stearic acid. It melts at 35°–42°. The quantity of free fatty acids present in this substance calculated as stearic acid amounts to 9·5–10 p.c. A closer examination of the nature of these acids proved that they consist almost entirely of oleic and stearic acids in the proportion of 34 p.c. of the former to 64 p.c. of the latter. The fat is saponified very readily (A. C. Geitel, J. pr. 36, 515; S. C. I. 7, 391).

MIRBANE, ESSENCE OF. A trade name for nitrobenzene as used in perfumery.

MISPICKEL. *Arsenical pyrites, White mundic, Danaite.* Silver-white to steel-grey mineral occurring in trimetric crystals, sp.gr. 6 to 6·4. Found in Cornwall, Germany, Sweden, and in various localities in the United States.

MITIS GREEN. *Aceto-arsenate of copper, Schweinfurth green v.* ARSENIC, vol. i. 201.

MITTLER'S GREEN. Syn. with *Guignet's green*, vol. i. p. 554, art. CHROMIUM.

MOCHA STONES *v.* AGATE.

MOIRÉE MÉTALLIQUE. The term given to the variegated arborescent or crystalline appearance given to the surface of tin plate produced by heating the plate and applying to it some dilute aqua regia for a few seconds, washing it with water, drying and coating it with lacquer.

MOLASSES *v.* SUGAR.

MOLYBDENITE. *Molybdenum sulphide* MoS_2.

MOLYBDENUM. Symbol Mo. At. w. 95·9 (Debray, Liechti, and Kempe, Rammelsberg).

Molybdenum occurs as sulphide MoS_2 in *molybdenite* in the older metamorphic rocks of Sweden, Norway, Cumberland, the United States, Newfoundland, and other localities, in micaceous ductile plates which closely resemble graphite. As *molybdic ochre* or *molybdine* the oxide MoO_3 occurs rarely with molybdenite, being produced by the oxidation of that mineral. Molybdenum occurs also as *wulfenite* $PbMoO_4$ and *pateraite* $CoMoO_4$, and is found in traces in iron ores, pig iron, and iron slags.

Molybdenum may be prepared by heating one of the chlorides or the trioxide to redness in a current of hydrogen. It is a silver-white metal harder than silver, of sp.gr. 8·6 (Debray) which does not fuse completely at a white heat. It oxidises when heated in air, and decomposes water at a red heat. It dissolves readily in nitric acid or hot concentrated sulphuric acid, but not in hydrofluoric or dilute hydrochloric or sulphuric acids.

Molybdenum forms four oxides MoO, Mo_2O_3, MoO_2, MoO_3, the three first being basic, while trioxide is an acid oxide forming salts like those of chromium. Two blue oxides which may be regarded as combinations of the dioxide and trioxide are also known, $MoO_2{\cdot}MoO_3$ and $MoO_2 2MoO_3$.

Molybdenum trioxide. Molybdic anhydride MoO_3 may be prepared on the small scale by heating the native sulphide in a combustion tube in a current of air. The sulphur is oxidised and passes away, while the oxide sublimes and condenses on the cooler parts of the tube in colourless rhombic crystals, which become yellow when heated and melt at a red heat to a dark-yellow liquid.

When an equal bulk of nitric acid (1·16 gr.) is added to a solution containing 3 parts ammonium molybdate in 20 parts water, *molybdic acid* $H_2MoO_4H_2O$ is slowly precipitated as a yellow crust. A soluble and a colloidal molybdic acid are also known.

Ammonium molybdate Am_2MoO_4. This, the most important of the molybdates, is prepared by heating molybdenum trioxide with concentrated ammonia. It crystallises in four-sided prisms decomposed by water. On evaporating the ammoniacal solution, colourless six-sided monoclinic crystals are produced, which form the ordinary ammonium molybdate of commerce $(NH_4)_6Mo_7O_{24}4H_2O$. A di- and tri-molybdate are also known.

When the ammoniacal solution of this salt is added to a nitric acid solution containing phosphoric acid, a canary-yellow powder of ammonium phosphomolybdate

$$2(NH_3)_3PO_4 22MoO_3 12H_2O$$

is obtained, insoluble in water and dilute acids, easily soluble in alkalis. This reaction forms a most delicate test for phosphoric acid, precipitation taking place in presence of the most minute traces of that acid after standing in a warm place for some hours. The presence of hydrochloric acid, chlorides, and many organic acids retards, and excess of phosphoric acid prevents the precipitation.

When ammonium phosphomolybdate is dissolved in aqua regia and evaporated, yellow triclinic crystals of phosphomolybdic acid $2H_3PO_4 22MoO_3$ are obtained, the acid solution of which is used as a precipitant for many alkaloids.

Six sodium molybdates are known, ranging from the normal salt Na_2MoO_4 to the decamolybdate $Na_2Mo_{10}O_{31}13H_2O$. Molybdates of potassium, barium, calcium, magnesium, and lead, are also known.

Molybdenum forms four chlorides $MoCl_2$, Mo_2Cl_6, $MoCl_4$, $MoCl_5$, three bromides $MoBr_2$, Mo_2Br_6, $MoBr_4$, and oxychlorides, oxybromides, oxyfluorides, chlorobromides, and a bromofluoride and bromosulphate. Three sulphides MoS_2, MoS_3, MoS_4, and thiomolybdates of potassium and ammonium and a molybdenum phosphide Mo_2P_3 have been prepared.

MONAZITE *v.* THORIUM.

MONOBROMO-CAMPHOR *v.* CAMPHORS.

MOONSTONE *v.* FELSPAR.

MORDANT ROUGE. *Aluminium acetate v.* ACETIC ACID.

MORIN *v.* FUSTIC.

MORINDIN. A glucoside found in *Morinda citrifolia* and *M. tinctoria* which are extensively employed in various parts of India under the general trade name of Suranji as a dyestuff, more especially for dyeing reds, purples, and chocolates (*v.* A'L, vol. i.). Morindin was first isolated by Anderson, and was considered by Rochleder (W. A. B. 7·806) and subsequently by Stenhouse (C. J. 1864, 17, 333) to be identical with ruberythric acid. Morindin is, however, distinguished from ruberythric acid by the violet colour of its barium compound, and by its behaviour with potash. Both give bright-red solutions with potash, but on boiling that of ruberythric acid at once changes to a dark purple, whilst that of morindin does not alter even after long-continued boiling.

Morindin forms silky-yellow needles, soluble in hot water and in alcohol, m.p. 245°. On analysis it gives numbers agreeing with the formula $C_{28}H_{30}O_{15}$, or $C_{26}H_{28}O_{14}$. On hydrolysis it yields 48·4 p.c. *morindon* (*q. v.*) (Thorpe a. Greenall, C. J. 51, 52).

MORINDON. A trihydroxymethyl anthraquinone $C_{15}H_{10}O_5$ obtained by sublimation from morindin or by its hydrolysis (Thorpe a. Smith, C. J. 53, 171). Forms long red needle-shaped crystals, insoluble in water, soluble in alcohol and ether; soluble in caustic alkalis and strong sulphuric acid with an intense violet colour. With alum an ammoniacal solution gives a red lake, and with baryta water a cobalt-blue precipitate. With ferric chloride morindin gives a sage-green colour. These properties serve to distinguish morindon from alizarin, with which it was formerly thought to be identical.

MORPHINE *v.* VEGETO-ALKALOIDS.

MORTAR *v.* CEMENTS.

MORTAR, HYDRAULIC, *v.* CEMENTS.

MOSAIC GOLD. *Ormolu.* An alloy of equal parts of zinc and copper.

MOSANDRIUM *v.* Cerium metals.

MOTHER OF PEARL. This is the nacreous lining of the shell of various molluscs, notably that of the large pearl oyster *Avicula* (*Meleagrina*) *margaritifera*, Lam. The nacre is secreted by the mantle of the mollusc, and consists mainly of calcium carbonate associated with organic matter. An analysis of mother of pearl gave about 66 p.c. of $CaCO_3$, 2·5 of organic matter, and 31·5 of water. On digesting the nacre in a dilute acid, all the calcareous salt may be dissolved, leaving a coherent pellicle of connective tissue which retains the iridescence until disturbed by pressure. The iridescence is due to the interference of light reflected from the microscopic corrugated edges of the delicate layers of nacre. In consequence of its pleasing lustre, mother of pearl is largely employed for buttons, counters, card-cases, knife-handles, and a great variety of trivial ornaments. Large quantities are used by the manufacturers of Birmingham and Sheffield. An important use is that of inlaying papier-maché work, while it is also used in the ornamentation of Moorish and other Oriental furniture. Mother of pearl is sometimes decorated by engraving, especially by the Chinese, or by having a pattern etched upon it by means of acid. In trade three varieties of shell are recognised—namely, the white, the gold-edged, and the black-edged. Dark shells are known generally as 'smoked pearl.' The principal fisheries for pearl-shell are in Torres Straits, off the coast of North-west Australia, in the Sooloo Archipelago, in the Persian Gulf and Red Sea, and round Tahiti and some other islands of the South Pacific. The shell is commonly known in the market by the name of its place of shipment, such as 'Manila' and 'Egyptian' shells. In the Bay of California and the Gulf of Panama mother of pearl shell is obtained from the *Meleagrina californica*, Cpr., and passes in trade as 'bullock shell.' The brilliant shells of the *Haliotis* and certain species of *Turbo* are also used for inlaid papier-maché and other ornamental purposes; *v.* W. H. Dall, Amer. Nat. 27, 1883, 579; and E. W. Streeter, Pearls and Pearling Life, London, 1886. F. W. R.

MOTHER-LIQUOR. The liquid which remains after the crystallisation of a salt or other solid.

MOTTRAMITE *v.* Vanadium.

MOUNTAIN BLUE. Syn. with *Azurite* $Cu(HO)_2.2CuCO_3$, *v.* Copper.

MOUNTAIN CORK. Syn. with *Asbestos* (*q.v.*).

MOUNTAIN FLAX. Syn. with *Asbestos* (*q.v.*).

MOUNTAIN GREEN. Syn. with *Malachite* (*q.v.*, also *v.* Copper). The term is also applied to a mixture of Schweinfurth green with gypsum or heavy spar; *v.* Arsenic.

MOUNTAIN LEATHER. A variety of *Asbestos* (*q. v.*).

MOUNTAIN SOAP. *Steatite* (*q. v.*).

MOUNTAIN WOOD. A variety of *Asbestos* (*q. v.*).

MUCIC ACID $C_6H_{10}O_8$. A dibasic acid, isomeric with saccharic acid, obtained in 1780 by Scheele, by the action of nitric acid on milk-sugar. Scheele also found that this acid may be obtained from gum tragacanth, and Fourcroy and Vauquelin discovered that it may also be obtained from a number of gums and mucilages. Is formed by the oxidation of dulcitol, melitose, and galactose. Is best prepared by heating 1 part of milk-sugar with 4 parts of nitric acid (Schwanert, A. 116, 265). Forms a white pulverulent powder consisting of minute oblique rhombic prisms. Sparingly soluble in cold water, more readily in hot water; insoluble in alcohol. By further action of nitric acid is converted into racemic acid, whereas saccharic acid by similar treatment seems to yield mainly tartaric acid. Mucic acid on being heated yields *pyromucic acid* $C_4H_3O(CO_2H)$, together with *dehydromucic acid* $C_4H_2O(CO_2H)_2$. The latter acid may be obtained more easily by heating mucic acid with equal weights of fuming hydrochloric and hydrobromic acids. It crystallises from hot water in lustrous needles, which may be sublimed.

MUCIC FERMENTATION GUM *v.* Gums.

MUCILAGE. The older writers made a distinction generally between gums which, like arabic and tragacanth, are obtained as a solid exudate, and the gum which is almost a universal constituent of plants, especially of some seeds and roots, and may be extracted by treatment with water (*cf.* Gm. 15, 209). The latter was termed *mucilage*, or *vegetable mucilage*, or *pflanzenschleim* (Ger.). Among the more important sources of this gum are marshmallow, salep, fleawort, linseed, and quince; *v.* Gums. A. S.

MULBERRY PAPER. The inner bark of *Broussonetia papyrifera*, used in China for the preparation of a kind of paper, and in Polynesia for the manufacture of a fabric.

MULHOUSE BLUE *v.* Triphenylmethane colouring matters.

MUNDIC. The name given by the Cornish miners to iron or arsenical pyrites.

MUNJEET or **MANJEET.** The *Rubia cordifolia* was formerly extensively cultivated in various parts of India, particularly in the mountainous districts, for the sake of the colouring matters contained in its stem and roots. In the Dárjiling district it occurs as a small climber, common all over the hills at elevations varying from 3,000 to 7,000 feet, but most abundant between 5,000 and 6,000 feet, and is found either creeping along the ground or climbing the trunks of trees in large festoons. In Bengal it would seem that the dye of munjeet is extracted mainly from the stem, and only occasionally from the root, as is the case in the North-West Provinces and elsewhere in India. The munjeet of Bengal is apparently rather the *Rubia munjista* of Roxburgh than the *Rubia cordifolia*. This species of Roxburgh is, however, reduced to *Rubia cordifolia* in Hooker's Flora of British India. To prepare the dye the wood of the munjeet is first dried, then crushed and pounded, and then generally boiled with water, but sometimes merely left to steep for two or three hours in cold water. The solution obtained is of a deep red, and is used generally to dye coarse cotton fabrics, or the thread which is to be woven into such fabrics. Alum seems to be generally employed as a mordant, although myrabolams are used in the Dárjiling district, and other astringents in the Maldah district. In the latter district munjeet is used in conjunction with iron salts to produce a deep purple, and in the Dárjiling district the liquor is mixed with indigo to form a maroon (McCann, Dyes and Tans of Bengal). The reds and chocolates of East Indian chintzes were formerly entirely obtained from munjeet. The colours produced from munjeet are bright, but not so durable as those from ordinary madder, the inferiority being due, according to Stenhouse (Pr. 13, 148), to the presence of purpurin and an orange dye munjistin. Runge, who first examined the tinctorial power of munjeet, concluded that it contained twice as much available colouring matter as madder; but later experiments have shown that the colouring power is actually less. Stenhouse found that munjeet-garancin had only half the colouring power of garancin made from Naples roots, but that munjeet yields (according to Higgin) from 52 to 55 p.c. of garancin, whereas madder yields only 30–33 p.c.

MUNJISTIN *Purpuroxanthin carboxylic acid* $C_{14}H_5(OH)_2O_2 \cdot CO_2H$ (Stenhouse, Pr. 12, 633; 13, 86, 145; Schunck and Römer, B. 10, 790). An orange colouring matter contained in considerable quantity, and associated with purpurin, in munjeet (East Indian madder) from which it may be best extracted by the following process.

To every pound of finely powdered munjeet is added 16 pounds of water and 2 pounds aluminium sulphate. On boiling these together for 4 or 5 hours, a red liquid is obtained which after being filtered whilst hot through cloth filters is saturated with hydrochloric acid. A bright-red precipitate is formed consisting of the colouring matter of the munjeet together with a quantity of resinous matter. The precipitate increases on standing, and after 12 hours is washed on cloth filters with cold water, dried, powdered, and digested in a percolator with boiling carbon disulphide, the extract thus obtained consisting chiefly of purpurin and munjistin. The excess of carbon disulphide being removed, the purpurin is precipitated by boiling water and separated by filtration. On acidifying the filtrate with hydrochloric or sulphuric acid, the munjistin is deposited in large yellow flocks, these are then washed with cold water, dried by pressure and dissolved in boiling alcohol to which a little hydrochloric acid is added to remove any alumina still present. On evaporating off about three-quarters of the spirit, the munjistin crystallises out in large yellow scales. It can be obtained in a state of purity after 2 or 3 crystallisations from spirit.

It may also, with less advantage, be extracted by boiling munjeet with water, acidifying the filtrate with hydrochloric acid, and proceeding as above.

Boiling solutions of alum may also be used for the same purpose, but the tendency of the alum to crystallise out renders filtration difficult.

The process given by E. Kopp for the extraction of colouring matters from madder by means of sulphurous acid is not applicable to munjeet (J. 1861, 938).

Munjistin dissolves slightly in cold, more readily in boiling alcohol, from which it precipitates on cooling in brilliant golden-yellow plates.

It dissolves slightly in cold, more readily in hot water, to a yellow solution, from which it is thrown down in yellow flocks on cooling. The alcoholic solution is not precipitated by water. In *soda* it dissolves to a rich crimson colour; in *ammonia* and *sodium carbonate* to a red solution. In cold *sulphuric acid* it forms a bright orange solution which is not decomposed on heating to boiling-point, and from which the munjistin may be precipitated apparently unchanged on the addition of water. *Bromine-water* yields a substitution-product as a pale yellow precipitate when added to an aqueous solution of munjistin. *Baryta-water* gives a yellow precipitate and *copper acetate* a brown one. *Lead acetate* gives a bright crimson precipitate with either the aqueous or the alcoholic solution. *Alumina* removes all the munjistin from solution in water or alcohol as an orange lake. This lake dissolves to a crimson solution in caustic potash. Strong *nitric acid* decomposes it, converting it into phthalic acid and some oxalic acid.

This reaction is analogous to the action of nitric acid on alizarin and purpurin, to which two colouring matters munjistin is very nearly related.

It sublimes more readily than either purpurin or alizarin, and appears in unaltered yellow scales. It melts at 231° on the careful application of heat, and recrystallises on cooling. At 233° it decomposes into carbon dioxide and purpuroxanthin.

It also resembles the rubiacin of Schunck (Runge's madder-orange), but a distinction is afforded by the different colours of their solutions in sodium carbonate, a highly dilute solution of munjistin being red inclining to pinkish-orange, whilst rubiacin of the same dilution is claret-red (Stokes, Pr. 12, 637).

Another distinction lies in the difference in the absorption bands of the spectra of these solutions, that of rubiacin extending from D to F, whilst that of munjistin extends from beyond D to beyond F. The fluorescence afforded by their ethereal solutions is also different, that of rubiacin being orange-yellow, and that of munjistin yellow inclining to green. A solution of munjistin in ammonia is decomposed on standing in a warm place exposed to the air, a brown body resembling humus being thrown down, the solution containing a non-crystalline colouring substance analogous to purpurein (which is formed in a similar manner from purpurin). This substance dyes unmordanted cloth of a brownish yellow. With alumina mordants munjistin dyes cloth of an orange colour, with iron-salts a brownish purple, and with Turkey-red mordants a deep orange. These dyes are tolerably permanent, and are not affected by the application of bran or soaps.

MUNTZ METAL *v.* Zinc.

MUREX. A name applied by Linnæus to a genus of Vermes. Testaceæ having a univalve spiral shell with oval aperture ending in an entire, straight, or slightly ascending canal.

The celebrated Tyrian purple was obtained partly from this shell-fish and partly from Buccinum, both of which species were found close to the shore and in the deep waters about the Phœnician coast. The dye is contained in a receptacle situated in the neighbourhood of the stomach (B. 9, 84).

A. and G. de Negri, state that the purple obtained from *Murex trecuculus* consists of two distinct colouring matters, one of which is indigo, which they have succeeded in preparing in a state of purity from it. The dye obtained from *Murex brandaris* contains in all probability different colouring matters, as the sap of the latter is coloured only on exposure to light, whereas the former is changed in the dark.

MUREXAN *Dialuramide* or *Amido-malonyl-urea* $C_4H_5N_2O_3$. Discovered by Prout (A. Ch. 48), who called it purpuric acid; also examined by Kodweiss (P. 19, 12), Liebig and Wöhler (A. 26, 327).

Formed by the action of strong acids, or of sulphuretted hydrogen or potash upon murexide. When sulphuric or hydrochloric acid is added to a boiling solution of murexide in water or potash, murexan is obtained as a crystalline precipitate, which is purified either by dissolving in cold sulphuric acid and reprecipitating with water, or by dissolving in potash and precipitating by an acid. It is a heavy, white, lustrous powder like uramil, infusible, tasteless, and without action on litmus; almost insoluble in cold water, quite insoluble in alcohol, ether, dilute sulphuric, hydrochloric or phosphoric, acetic, tartaric or citric acids. It is dissolved in aqueous alkalis, with which it forms colourless solutions when air is excluded. Subjected to dry distillation, cyanic acid, amongst other products, is formed.

Chlorine water decomposes it, no cyanic acid being formed. It dissolves in strong nitric acid with effervescence, nitrous and carbonic anhydrides being given off and murexan oxalate formed. The same compound is formed when murexan is dissolved in oxalic acid containing a little nitric acid.

In warm dilute nitric acid it is soluble without effervescence, murexan nitrate being obtained in crystals on evaporation.

Strong sulphuric acid also decomposes it, evolving carbonic acid and some nitrogen, and forming a brown solution containing free ammonia, which gives no precipitate on the addition of water.

Ammonia dissolves it to a colourless solution, which is turned purple when exposed to the air or when boiled with mercuric oxide, murexide being formed:

$$2C_4H_5N_3O_3 + HgO = C_8H_8N_6O_6 + H_2O + Hg.$$

The same body is formed whenever a solution of murexin is exposed to air containing ammonia.

Oxygen destroys the colour of this solution, forming oxalurate of ammonia.

Gerhardt (Chim. Org. 1, 1517) was the first to consider murexan as identical with dialuramide $C_4H_5N_3O_3$, which view was supported by Beilstein (A. 107, 191). Its true constitution was ascertained by Baeyer, who obtained it by reduction of nitroso- and nitro-malonyl-urea.

MUREXIDE *Acid ammonium purpurate* $C_8H_4N_5O_6(NH_4)H_2O$. A body at one time extensively used for producing red, purple, and yellow shades in dyeing and calico-printing. The superiority of aniline dyes has, however, caused it to be almost entirely superseded by them. The colours obtained by murexide are exceedingly brilliant and unaffected by light, but are immediately tarnished by sulphurous acid, rendering them unfit for use where coal-gas is employed. With mercuric salts red and purple dyes are obtained on silk, wool, cotton, and leather, and with zinc salts the same substances are dyed orange and yellow colours.

Grimaux (B. 8, 545, 1352) has prepared murexide by synthesis from urea and asparagin. When these bodies are heated together to 125°C., the following reaction takes place:

$$C_4H_8N_2O_3 + CH_4N_2O = C_5H_7N_3O_3 + H_2O + NH_3.$$

The amide of malylureidic acid thus obtained yields ammonium chloride and malylureidic acid on boiling with hydrochloric acid. From the barium-salt of one of the bromine derivatives of this acid, $2(C_8H_2Br_4N_4O_4) + H_2O$, he obtained murexide by heating with nitric acid and subsequent treatment with ammonia.

For commercial purposes it was obtained from guano. For this purpose the guano was treated with caustic soda and slaked lime, and the precipitate allowed to subside. On the addition of hydrochloric acid to the clear fluid, uric acid was precipitated (Elsner, Chem. Tech. Mittheilung. 1864, 123). The uric acid thus obtained was added gradually to nitric acid surrounded by water, heat was evolved, and, on cooling, ammonia or ammonium carbonate was added in small quantities at a time until the liquid was neutral. It was then heated to 60-70°, and, on cooling, impure murexide separated out, which was washed with dilute ammonia and dried. Murexide was formerly made by the late Mr. Rumney to the extent of 12 cwt. weekly, and its cost, in the form of paste, was originally 30*s*. per lb.

It can be prepared also by heating dialurate of ammonium, by acting on dialuramide with oxides of silver or mercury, by exposing a solution of dialuramide in ammonia to the air, and by adding ammonia to alloxantin. By this latter process it can also be prepared on the manufacturing scale, ammonia being added to a solution of uric acid in dilute nitric acid; this solution containing both alloxan and alloxantin.

Beilstein (A. 107, 176) gives the following method as the best. 30 or 40 parts of water are added to 4 parts of dialuramide and 3 parts of mercuric oxide, ammonia is added to the solution, which is then boiled and filtered, murexide crystallising out on cooling. The addition of ammonium carbonate to the solution when nearly cool increases the quantity of the crystals.

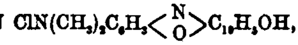
Gregory dissolves 4 parts alloxantin and 7 parts tetrahydrated alloxan in 240 parts boiling water, adding 80 parts of a cold saturated solution of ammonium carbonate.

Gmelin prepared it by the continued action of dry ammonia upon alloxantin in fine powder; the brown-red mass which is formed is repeatedly pulverised and exposed to the action of the gas. On expelling the excess of ammonia, murexide is obtained by crystallising out the solution of this compound in as little water as possible. It is to be noted that the formation of murexide by the addition of ammonium carbonate upon a boiling solution of alloxan (Fritzsche, J. pr. 16, 380; 17, 42) is probably due to the previous action of heat upon the alloxan solution which converts it into alloxantin, no murexide being formed under similar circumstances with pure alloxan.

Murexide crystallises in four-sided prisms, which are garnet-coloured by transmitted light, and gold-green by reflected light. At 100°C., or dried *in vacuo*, they lose their water of crystallisation, of which they contain 1 mol. (6·54 p.c.), and are changed into a brownish powder, which assumes a green metallic lustre when rubbed. They form a purple solution with cold, more readily with hot, water; insoluble in alcohol or ether. Nitric acid converts murexide into alloxan.

Hydrochloric or sulphuric acid precipitates murexan from its solution in water, a mixture of alloxantin, alloxan, urea, and ammonia remaining in solution. Sulphuretted hydrogen also precipitates murexan from the solution. In this case alloxantin and dialuric acid remain in solution. Potash dissolves it, forming an indigo solution, ammonia being liberated. This colour is discharged by heat, and murexan is precipitated from the colourless solution on the addition of sulphuric acid.

MURIATIC ACID *v.* CHLORINE.



MUSCARIN $ClN(CH_3)_2C_6H_3 < \substack{N \\ O} > C_{10}H_5OH$, the chloride of dimethyl phenyl-*p*-ammonium-*β*-oxynaphthoxazine obtained by the action of nitrosodimethylaniline hydrochloride on *α*-dioxynaphthalene. A colouring matter introduced by Durand and Huguenin. Is a brownish violet powder, sparingly soluble in cold water but readily soluble in hot water with a bluish-violet colour. Alkalis precipitate the base as a yellow-brown powder. Dyes cotton mordanted with tannin and tartar emetic a blue colour *v.* OXAZINE COLOURING MATTERS.

MUSCARINE *v.* PTOMAÏNES.

MUSCOVADA. The unrefined brown or raw sugar of commerce *v.* SUGAR.

MUSCOVITE GLASS. A term occasionally applied to mica (*q. v.*).

MUSK. (*Moschus*; *Musc*, Fr.; *Moschus*, Ger.) Musk consists of the dried secretion of the preputial follicles of the musk deer, *Moschus moschiferus* (Linn.), which inhabits the mountainous districts of Central Asia. *Cf.* Pereira (Mat. Med. [3] 2, 2251). An analysis by Geiger and Reimann, quoted by Gmelin (Handb. Chem. 2, 1449) shows that it contains cholesterin together with fatty, waxy, and albuminous substances. The well-known odour of musk is not due to the presence of a volatile oil, but probably to the slow decomposition of some hitherto undetermined constituent. Besides its use as a perfume, musk is employed in medicine as a nervous stimulant.

A. S.

MUSK-ROOT *v.* OLEO-RESINS.

MUSTARD. The plants which furnish mustard are *Sinapis nigra* or black, and *Sinapis alba* or white mustard, belonging to the family *Cruciferæ*.

The seeds of *S. nigra* are reddish or blackish brown; those of *S. alba* are of a pale yellow. Both species are indigenous to Great Britain. A large quantity of seed is, however, imported. In strength of pungency the black is superior to the white, which yields no volatile oil. The seeds of both black and white mustard are first crushed between rollers and then pounded in mortars. The pounded seeds are then sifted. The residue in the sieve is called *dressings* or *siftings*; what passes through is *impure flour of mustard*. The latter by a second sifting yields *pure flour of mustard* and a second quality of *dressings*. By pressure the dressings yield a fixed oil, which is used for mixing with rape and other oils.

Formerly it might be said with certainty that no mustard as supplied to the public was sold in a pure state; such ingredients as wheat flour, turmeric, cayenne pepper, *Sinapis arvensis* or charlock, clay, plaster of Paris, &c., being frequently present. A large proportion of the mustard sold is still more or less mixed with flour or other starchy matter under names devised to keep within the law. The use of the microscope, as in many other cases of adulteration, detects many of the foreign substances so employed.

The following analyses of black or brown and white mustard were made by Piesse and Stansell. The results given are for the whole seed from different sources and three qualities of farina obtained by crushing and sifting. The numbers are averages:—

—	Whole seed		Farina	
	White	Brown	White	Brown
Moisture . . .	8·66	8·52	6·04	4·83
Fat . . .	26·53	25·54	35·16	37·05
Cellulose . .	9·69	9·01	5·79	2·80
Sulphur . . .	0·96	1·28	1·27	1·43
Nitrogen . . .	4·51	4·38	4·73	4·75
Albuminoids . .	28·21	26·50	29·56	28·71
Myrosin & albumin	4·91	5·24	6·70	6·46
Soluble matter .	26·83	24·22	33·94	31·94
Volatile oil . .	0·07	0·47	0·03	1·44
Ash, total . .	4·63	4·98	4·28	4·93
Ash, soluble . .	0·65	1·11	0·44	0·92
Potassium myronate	—	1·69	—	5·15

The *volatile oil*, consisting of allyl isothiocyanate is formed from the brown mustard on addition of water; but admixture of some white causes a greater yield to be obtained. The mixture was allowed to stand with ten times its weight of cold water for about five or six hours, this time giving the maximum production of the oil, the amount of which decreases by longer standing. The oil is distilled off into strong ammonia as long as the escaping steam has a pungent odour; and the mixture of ammonia solution and distillate is put by in a closed vessel until the oily drops have disappeared; the liquid is then boiled for a few minutes and the thiosinamine in solution is weighed after evaporation in a platinum dish and drying at 100°C. Its weight multiplied by 0·85344 gives the weight of allyl isothiocyanate, or if multiplied by 3·5775 the weight of potassium myronate from which it is derivable.

The following is the average percentage composition of the ash of mustard seed; the numbers in columns 3, 4, 5 being calculated after charcoal and sand have been deducted:—

—	White	Brown	White	Brown	White seed. Way and Ogston, 1850
Potash . . .	20·08	21·41	23·81	23·59	25·78
Soda . . .	0·19	0·35	0·23	0·38	0·33
Lime . . .	11·40	13·57	13·49	14·95	19·10
Magnesia . . .	9·33	10·04	11·13	11·06	5·90
Iron oxide . .	1·10	1·06	1·30	1·16	0·39
Sulphuric acid . .	7·11	5·56	8·48	6·12	2·19
Chlorine . . .	0·11	0·15	0·13	0·16	trace
Phosphoric acid .	33·87	37·20	40·22	40·99	44·97
Silica . . .	1·06	1·41	1·25	1·55	1·31
Sand . . .	1·88	1·38	—	—	—
Charcoal . . .	13·98	7·57	—	—	—

MUSTARD OIL *v.* OILS, ESSENTIAL.

MYOSIN *v.* ALBUMINOIDS.

MYRICIN. The more difficultly soluble portion of beeswax, consisting mainly of myricyl palmitate *v.* WAX.

MYRISTIC ACID *v.* FATTY ACIDS.

MYRISTICA SURINAMENSIS. The fruit of the *Myristica surinamensis*, is imported into Germany under the name of 'oil nut.' The nuts have the size and form of a cherry, with a dark-grey brittle shell inclosing a hard kernel. The kernels freed from shell, ground to powder, and extracted with ether, give 73 p.c. of fatty extract. The crude fat contains resin and a free acid. 100 parts of crude fat contain therefore 87 parts of pure substance. The pure fat has the formula $C_{45}H_{86}O_6$, which agrees with that of trimyristin. Like tristearin and tripalmitin, this body exists in different modifications with different melting-points. The trimyristin, saponified with alcoholic potash, yields myristic acid $C_{14}H_{28}O_2$. No other glycerides exist in this fat. The free acid in the crude fat was found to be myristic acid. Owing to the purity of the fat, and the absence of other glycerides, Reimer and Will recommend it as a source of pure myristic acid (S. C. I. 4, 746).

MYRISTICOL *v.* CAMPHORS.

MYRISTIN *Trimyristyl Glyceride v.* FATTY ACIDS.

MYRRH *v.* GUM RESINS.

MYRRHIN *v.* MYRRH.

MYRRHOL *v.* MYRRH.

MYRTLE BERRY WAX *v.* WAX.

MYRTLE OIL and **MYRTOL.** This oil as used medicinally begins to boil at 160° and about 80 p.c. distils over up to 240°C. The residue consists of high-boiling terpenes partly resinised and partly polymerised. From the portion boiling between 160° to 240°C., by repeated fractional distillation the following constituents can be separated:

A terpene, $C_{10}H_{16}$, boiling between 158° and 160°, and having a specific rotation $[\alpha]_D = +36{\cdot}8°$. Its properties led Jahns to believe it to be right-handed pinene.

Cineol $C_{10}H_{18}O$, which, purified by Wallach's method, boiled constantly at 176°.

A camphor, probably of the formula $C_{10}H_{16}O$, in small quantity, boiling at 195° to 200°C. The therapeutic value of the myrtle oil is to be traced to the amount of cineol present in it, the latter substance being identical with cajeputol and eucalyptol (E. Jahns, Ar. Ph. 27 [3] 174; S. C. I. 8, 721).

N

NADORITE $Sb_2O_3PbCl_2$ (Pisani, C. R. 71, 319), or SbOClPbO (Flajolot, C. R. 71, 406), a mineral found near the hot spring of Hammam-Nbaïl-Nador, in the province of Constantine, Algeria.

NAGYAGITE. Native telluride of lead and gold, containing more or less sulphur, and occasionally antimony (*v.* TELLURIUM).

NAPHTHA. This term was originally applied to a number of volatile, more or less mobile, inflammable liquids, usually ethers obtained by distillation, e.g., *Naphtha vitrioli* (ethyl ether), *N. nitri* (nitrous ether), *N. aceti* (acetic ether). The term was subsequently restricted to the naturally occurring liquid hydrocarbons, but was afterwards extended to other hydrocarbons obtained by the destructive distillation of shale, coal, bone, &c.

Boghead or **Bathgate Naphtha** *v.* PARAFFIN.

Bone Naphtha *v.* BONE OIL.

Caoutchouc Naphtha *v.* INDIA-RUBBER.

Coal Naphtha *v.* GAS, COAL.

Mineral Naphtha *v.* PETROLEUM.

Miscible Naphtha *v.* WOOD, DISTILLATION OF.

Shale Naphtha or **Shale Oil** *v.* PARAFFIN.

Solvent Naphtha *v.* WOOD, DISTILLATION OF.

NAPHTHALENE $C_{10}H_8$.

History.—The production of naphthalene in the manufacture of coal-gas seems to have been noticed first by Clegg (*cf.* Brande, Quart. Journ. Sci. 8 (1820), 287); the discovery of its presence in coal-tar, however, was made simultaneously in 1819 by Garden (Annals of Philos. 15 (1820), 74) and Brande (*l.c.*), the latter regarding it as a hydrocarbon (*cf.* Thomson, Schweig. 47, 337).

It was further examined by Kidd (Phil. Trans. 1821, 209), who named it 'naphthaline,' and first analysed by Ure (Phil. Trans. 1822, 473); its true composition being determined by Faraday in the course of his investigation of its isomeric monosulphonic acids (Phil. Trans. 1826, 159) and later by Laurent (A. 3, 11). A bibliography of the early history of the subject is given in Gmelin (Eng. ed. 14, 1).

Formation and sources.—Naphthalene is, in innumerable cases, a constituent of the products obtained by submitting organic substances to the action of comparatively high temperatures. It is, for example, formed in small quantity, together with other aromatic hydrocarbons, when vapours of alcohol, acetic acid (Berthelot, A. Ch. [3] 33, 295), marsh gas, acetylene (Berthelot, Bl. 7, 306), toluene, xylene, or cumene, are passed through porcelain tubes filled with pumice and heated to redness, and when the vapours of benzene, cinnamene, anthracene, or chrysene, mixed with ethylene, are similarly treated (Berthelot, C. R. 63, 790, 834; Bl. 6, 268; 7, 218, 278, 285). It occurs, also, to the extent of 2–3 p.c. in the products obtained by passing the vapours of toluene, or ethylbenzene, or of a mixture of toluene and ethylene through an iron tube heated to redness (Ferko, B. 20, 660). Berthelot's results have not, in certain instances, been confirmed by later investigators (*cf.* Graebe, B. 7, 49; Lorenz, B. 7, 1097; Carnelley, C. J. 37, 705; Ferko, *l.c.*), but this is hardly surprising in view of the fact that everything depends on the conditions, and in particular on the temperature employed, in reactions of this character. Naphthalene is a constituent of the tar produced when turpentine vapour is led through a red-hot iron tube (Schultz, B. 10, 116), and is formed on distilling colophony or gum benzoin with zinc-dust (Ciamician, B. 11, 269).

Berthelot's experiments on the pyrogenic formation of aromatic hydrocarbons led naturally to laboratory experiments being instituted with the object, primarily, of obtaining benzene, toluene, and anthracene from the comparatively valueless high-boiling oils of wood tar and brown coal tar, and from petroleum residues, by passing these through red-hot tubes filled with charcoal, pumice, &c. The tars formed under these conditions from the residues of Baku petroleum (Letny, B. 11, 1210; D. P. J. 229, 353; Lissenko, B. 11, 342; Rudnew, D. P. J. 239, 72), and from the high-boiling oils of brown coal tar (Liebermann and Burg, B. 11, 723; Salzmann and Wichelhaus, B. 11, 1431), and pinewood tar (Atterberg, B. 11, 1222) contain considerable quantities of naphthalene, and possess such a general resemblance to coal tar that the production of aromatic hydrocarbons on the large scale from the first of these sources was at one time undertaken (*cf.* Greiff, Chem. Ind. 2, 185; Liebermann, D. P. J. 246, 429; S. C. I. 2, 128; Redwood, S. C. I. 4, 79), but has now been abandoned on account of the wastefulness of the process (Smith, S. C. I. 3, 65), and finds no mention in Engler's more recent paper on the Baku petroleum industry (D. P. J. 260, 337, 433, 481, 525). In this connection it may be noted that naphthalene is present in but small quantity in the benzenoid hydrocarbons obtained from oil-gas tar (Armstrong and Miller, C. J. 49, 80).

Hlawaty (Germ. pat. 51553, of Aug. 11, 1888) has patented a process for obtaining naphthalene and other aromatic hydrocarbons from petroleum residues, petroleum, coal tar, coal tar oil, shale tar, shale tar oil, brown coal tar, brown coal tar oil, paraffin, or vaseline, on somewhat similar lines. The method consists in passing steam, superheated at 400°, into a mixture of 150 parts of any of these substances with 50–60 parts of sawdust and 25 parts of caustic alkali heated at 400°, and leading the mixed steam and petroleum vapours through red-hot iron or porcelain tubes filled with charcoal. The yield of benzene and its homologues from the tar is said to be twice as great as that from any known tar, but no details have as yet transpired as to the commercial value of the process.

Naphthalene is a constituent of the principal varieties of tar produced from coal in the manufacture of gas and coke. The proportion in gas tar varies considerably with the varieties of coal employed (*cf.* Smith, S. C. I. 8, 951), and is greater the higher the temperature used during carbonisation (Smith, S. C. I. 3, 64), amounting usually to 4–6 p.c., but in some cases to as much as 10 p.c. (Lewis, Journ. Gas Lighting, 47, 1248; Smith, S. C. I. 9, 446). It is frequently a source of considerable inconvenience to the gas engineer owing to the impossibility of completely removing it from the gas in the coolers and purifiers, for it crystallises out in the gas mains, and in course of time accumulates to such an extent as to seriously impede the passage of the gas (*cf.* S. C. I. 3, 158; Smith, S. C. I. 8, 949). The proportion of naphthalene, as of other aromatic hydrocarbons, in coke-oven tars seems to depend on the type of coke-oven used, or, in other words, on the temperature at which carbonisation is effected. The tar, or tar-oil, from Jameson's coke-ovens is destitute of naphthalene (Smith, S. C. I. 2, 498), and that from Pauwel's coke-oven contains only a small proportion of the hydrocarbon (Behrens, J. pr. [2] 6, 278). Watson Smith found 0·39 p.c. of naphthalene in a tar from a Carvès oven (S. C. I. 3, 104), from 1–10·17 p.c. in tars from Simon-Carvès ovens working with different kinds of coal (S. C. I. 2, 500; 3, 508; Journ. Iron and Steel Inst. 1885, 103), and about 'the same proportion as in gas tar' in the tar from an Otto oven (S. C. I. 3, 508); Knublauch obtained from 4·27–5·27 p.c. in tars from Otto-Hoffmann ovens (D. P. J. 254, 37), and Lunge found 7·69 p.c. of the crude hydrocarbon in tars from Otto-Hoffmann ovens, and 1·53 p.c. in tars from a modified form of bee-hive coke-oven provided with external heating flues and recuperators (S. C. I. 6, 583). Gartsherrie blast-furnace tar contains only a very small proportion of naphthalene (Smith, S. C. I. 2, 495), and none could be detected in Sutherland gas-producer tar (Smith, S. C. I. 3, 10).

Synthetical methods of preparing naphthalene have been described by Aronheim (B. 6, 67), Wreden and Znatowicz (B. 9, 1606), Brunner and Brandenburg (B. 11, 698), and Baeyer and Perkin jun. (B. 17, 448).

Isolation and purification (Lunge, Coal Tar and Ammonia, ed. 1887, 407 *et seq.*).—Naphthalene occurs in the coal tar fraction boiling at 180–250°, and is present, therefore, in the 'light oil' (b.p. *circa* 110–210°), and 'creosote oil' (b.p. *circa* 240–270°), but most abundantly in the 'carbolic oil' (b.p. *circa* 210–240°) of the tar distiller. Large quantities separate in the crystalline form from the first portions of the creosote oil, and can be freed from the greater portion of the oily impurities by filtration and subsequent hot-pressing. The hot-pressing of crude naphthalene is, perhaps, the most important process for refining it, and is carried out in presses with hollow plates heated by steam like the anthracene refining presses. Much depends on the regulation of the temperature, for the higher this is kept the more complete will be the removal of the impurities, but at the same time a good deal of the naphthalene itself will also be removed as the temperature approaches its melting-point (79°), since its solubility in the accompanying oils increases rapidly with rise of temperature.

The crude naphthalene is then extracted with aqueous caustic soda to remove phenolic constituents. The treatment is effected in closed iron vessels, heated above the fusing-point of naphthalene by a steam-jacket or coil, and preferably provided with a mechanical agitator, and the caustic liquor may be of any convenient strength. The fused naphthalene is stirred up for some time with the liquor, and, after the latter has been run off, is washed with hot water. As the washing with caustic soda solution is an essential part of the process adopted for the extraction of phenol and its homologues from the carbolic oil, large quantities of naphthalene are made from the residual oil drawn off from the sodium carbolate (*v.* CARBOLIC ACID), either by fractionally distilling it in order to remove the small proportion of light oil present, or by allowing it to cool and crystallise. It is advisable to hot-press the naphthalene from this source also, otherwise impurities might be retained which would render it unfit for use in the preparation of naphthols.

The next stage of the purification consists in washing the hydrocarbon with 5–10 p.c. of sulphuric acid heated at about 100°, which not only removes basic substances, but in the concentrated state converts any residual phenols into soluble sulphonic acids. Lunge states (*l.c.*) that acid of at least sp.gr. = 1·7 should be employed, and that the strongest oil of vitriol (sp.gr. = 1·84) is even better, though it has the disadvantage of dissolving much naphthalene at the temperature employed. The washing is effected in steam-jacketed cast-iron vessels lined with lead and provided with stirring apparatus, and is continued for about an hour. In order to obtain naphthalene which will remain permanently white an addition of about 5 p.c. of finely-ground pyrolusite, or, preferably, Weldon-mud may be added to the contents of the vessel (Lunge, C. N. 44, 65). The purified naphthalene is washed several times with hot water, then with weak alkali to remove all acid, again washed with hot water, and finally sublimed or distilled. A sublimation plant, suitable for use in a small works, has been described by Hirsch (Ch. Z. 8, 839, with sketch; S. C. I. 3, 474).

Far preferable to sublimation, according to Lunge, is the distillation of naphthalene, both because it permits larger quantities to be dealt with, and because fractionation is in this case much more easily effected. The stills are shallow, wrought-iron vessels holding a ton or upwards, heated by a direct fire, but protected against its first action by a curtain arch; they are provided with a man-hole, a safety valve, and a very high head (up to 7 feet), which can be furnished with contrivances for dephlegmation, but which already acts in this direction by the cooling effect of the air. Condensation is effected by a simple iron worm free from sharp elbows and the like, where, at the end of the operation, solid naphthalene might accumulate and in the next distillation cause a dangerous pressure in the still, or, ultimately, an explosion. The water in the tub surrounding the worm is maintained at 80° at least, so that the naphthalene may run out of the condenser and be collected in the liquid form. If, after all, the worm should become choked, the safety valve will blow out, whereupon the fire must instantly be drawn and the still, if necessary, cooled from above by pouring water upon it. In the distillation, a small quantity of water and light oil at first passes over and is collected in a separate receiver, pure naphthalene being collected between 210–235°, as indicated by a thermometer immersed in the vapour. Then either the still is stopped and the residue run to the creosote oil, or the distillation continued into another receiver, and the impure naphthalene so collected again purified.

Link (Germ. pat. 35168 of Oct. 30, 1885, expired June 1886) agitates pressed and distilled naphthalene with soap solution heated at about 85°, and afterwards distils the washed hydrocarbon.[1]

According to Dehnst (Germ. pat. 47364 of Oct. 3, 1888, taken over by Bayer & Co.,[2] Jan. 1890), the impurities in crude naphthalene, which, though amounting only to a small percentage, render it unfit for use in the preparation of naphthols and naphthylamines, are converted into substances of high boiling-point, with the evolution of sulphuretted hydrogen, when heated with sulphur, whilst naphthalene is not affected. About 0·5–2 p.c. of sulphur is required in the process, which is carried out by heating 1000 kilos. of crude naphthalene in a still at 120–125°, adding 5 kilos. of sulphur and rapidly distilling. The

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[1] It is not easy to see what advantage this method could have over the ordinary process, as the soap solution could only play the part of the less costly caustic soda, and would not in any way tend to remove basic substances from the naphthalene, whilst there is the further objection that two distillations are necessary as against the one required in the ordinary process.

[2] The following abbreviations are employed in this article:—

Actieng. f. A. .	Actiengesellschaft für Anilinfabrikation in Berlin.
B. A. S. F. . .	Badische Anilin- und Sodafabrik in Ludwigshafen.
Bayer & Co. . .	Farbenfabriken vorm. F. Bayer & Co. in Elberfeld.
Cassella & Co. .	Anilinfarbenfabrik von L. Cassella & Co. (Frankfurter Anilinfarbenfabrik F. Gans & Co. in Mainkur bei Frankfurt a. M.).
M. L. B. .	Farbwerke vorm. Meister, Lucius & Brüning in Höchst a. M.
Schöllkopf Co. .	Schöllkopf Aniline and Chemical Co., Buffalo (U.S.A.).
Ver. Chem. Fab. .	Verein Chemischer Fabriken in Mannheim.

sulphuretted hydrogen, which begins to come off at about 170°, can be absorbed by milk of lime. The distillation is continued until the product begins to come over yellow, which is usually the case with the last 5 p.c., and this is worked up in the next operation. The chief fraction may then be submitted to a second distillation over 0·5–1 p.c. of caustic soda, and is then perfectly snow-white. The chief advantages claimed for the process are that it avoids the production of the large quantities of sulphur dioxide generated in the ordinary process and the unavoidable loss of naphthalene which ensues, estimated by the patentee to amount to 25 p.c. of that employed.

Properties.—In the pure state naphthalene forms white crystalline masses or thin scales. It crystallises from alcohol in scales or monoclinic tables (Groth, B. 3, 453), melts at 79–80°, and has a boiling-point, according to Crafts (Bl. 39, 282), of:

215·9°	at	723·69	mm.	217·5°	at	750·50	mm.
216·1°	,,	727·00	,,	217·6°	,,	752·20	,,
216·3°	,,	730·31	,,	217·8°	,,	753·90	,,
216·5°	,,	733·65	,,	217·9°	,,	755·31	,,
216·7°	,,	736·99	,,	218°	,,	759·02	,,
216·9°	,,	740·35	,,	218·1°	,,	760·74	,,
217·1°	,,	743·72	,,	218·3°	,,	764·18	,,
217·3°	,,	747·10	,,	218·5°	,,	767·68	,,

Its specific gravity is 1·1517 at 18·75° (15° R.) (Vohl, J. pr. 102, 30), 0·9774 in the liquid state at 79·2° (Kopp, A. 95, 335), and is given for any temperature t° above its fusing-point by the formula $0·9777 - 0·0_{3}2676\,(t-80) - 0·0_{6}59538(t-80)^2$ (Schiff, A. 223, 261). Naphthalene has a characteristic, penetrating, tarry odour, a pungent taste, and burns with a very smoky flame. It is insoluble in cold and very slightly soluble in hot water, appreciably soluble in strong caustic soda solution, sparingly soluble in petroleum spirit, very soluble in benzene and ether, and miscible in all proportions with hot toluene or absolute alcohol. According to Bechi (B. 12, 1978), 100 parts of toluene dissolve 31·94 parts of naphthalene at 16·5°, and 100 parts of absolute alcohol dissolve 5·29 parts at 15°. Naphthalene volatilises at temperatures considerably below its boiling-point, and is readily volatile with steam, alcohol vapour, and the vapour of low-boiling tar oils, occurring therefore with the last-named in crude tar oils. Naumann (B. 10, 2016; 11, 33) has determined the vapour-tension of naphthalene to be 2 mm. at 15°, 9 mm. at 78°, and 20·5 mm. at 100°, and finds that naphthalene and water distil over in the ratios given in the following table when steam is passed into naphthalene:—

Barometer (cor.)	Temperature of liquid	Temperature of vapour	Ratio of naphthalene to water in distillate
mm.			
759·5	97·8°	99·2°	100 : 520
757	97·7°	99·1°	100 : 570
733	—	98·2°	100 : 555

Reactions.—1. When heated with amorphous phosphorus and hydriodic acid for periods varying from 6 to 56 hours, naphthalene yields a series of hydrides which have been examined chiefly by Wreden and Znatowicz (Beilstein, Handb. der organ. Chem. 2nd ed. 2, 137), and Graebe and Guye (B. 16, 3028).

2. When its vapour is passed through a red-hot iron tube, naphthalene yields about 15 p.c. of $\beta\beta$- (iso-)dinaphthyl, and, when mixed with ethylene, gives in addition minute proportions of acenaphthene and phenanthrene (Ferko, B. 20, 662). All three isomeric dinaphthyls are produced when naphthalene vapour mixed with gaseous antimony trichloride or tin tetrachloride is passed through a red-hot porcelain tube (Smith, C. J. 32, 553; 35, 225). When heated with 20 p.c. of aluminium chloride at 100–160°, naphthalene yields $\beta\beta$-dinaphthyl together with other compounds, but with excess of the chloride is converted into a mixture of naphthalene hydrides and benzene (Friedel and Crafts, Bl. 39, 195).

3. By interaction with alkyl bromides or iodides in the presence of aluminium chloride, naphthalene is converted into a series of alkyl derivatives (Roux, A. Ch. [6] 12, 289).

4. Naphthalene combines with a large number of nitro- derivatives, forming molecular compounds of varying stability. Of these, the compound with picric acid $C_{10}H_8,C_6H_3(NO_2)_3O$ (Fritzsche, J. 1857, 456) is the most important, and serves occasionally as a means of recognising naphthalene in a mixture of hydrocarbons, since naphthalene is the only solid hydrocarbon which is precipitated from a saturated alcoholic solution by the addition of picric acid. The picric acid compound crystallises in golden-yellow needles, melts at 149°, and dissolves in alcohol, ether, and benzene without decomposition.

5. On oxidation with potassium permanganate, chromic acid mixture (Lossen, A. 144, 71), or dilute nitric acid, naphthalene is converted into phthalic acid, the yield amounting to 40 p.c. of the theoretical when it is heated with 20 parts of nitric acid (sp.gr. = 1·15) at 130° (Beilstein and Kurbatow, A. 202, 215). When oxidised with chromic acid in acetic acid solution, it yields [α-]naphthaquinone (Groves, C. J. 26, 209) and phthalic acid (Beilstein and Kurbatow, *l.c.*).

6. Chlorine initially forms addition compounds, [α-] di- and [α-] tetra- chloride, with naphthalene, and these by elimination of hydrogen chloride can subsequently be converted into mono- and di-chloronaphthalenes (Laurent, A. 8, 13; Faust and Saame, A. 160, 66; Krafft and Becker, B. 9, 1088; Widman, B. 15, 2162; Armstrong and Wynne, C. J. Proc. 1890, 85). Bromine, on the contrary, converts naphthalene into mono-, di-, and tri-bromonaphthalenes, or, in other words, forms substitution derivatives (Laurent, A. Ch. [2] 59, 216; Glaser, A. 135, 40; Guareschi, A. 222, 265; Armstrong and Wynne, *l.c.*).

7. Fuming nitric acid or a mixture of nitric and sulphuric acids converts naphthalene into mono-, di-, tri-, and tetra-nitro- derivatives and sulphuric acid yields mono-, di-, and tri-sulphonic acids or sulphones according to the quantity, concentration, or temperature employed. The nitronaphthalenes and naphthalene-sulphonic acids are dealt with in a later portion of this article.

Tests.—Commercial naphthalene is required to be almost chemically pure. It should be perfectly white, melt at 79°, boil at 216–217°, volatilise without leaving a residue, and be free from phenols and quinoline bases. When heated with pure concentrated sulphuric acid at 170–200° it ought not to give a black or red solution, and at the most colour the acid grey (Witt, Chem. Ind. 10, 216).

The presence of phenols can be detected by boiling the sample with dilute caustic soda solution, cooling, filtering off the solidified naphthalene and adding to the filtrate bromine water and hydrochloric acid, when any phenols present will be precipitated in the form of brominated compounds. Quinoline bases are detected by dissolving the sample in warm concentrated sulphuric acid, pouring the solution into water, filtering from the separated naphthalene, rendering the filtrate alkaline and steam-distilling. Any quinoline bases present will pass over with the steam, and are readily recognised in the distillate by their characteristic odour.

Uses.—Until recently naphthalene had but a limited use, and was either mixed with coal and employed as a fuel, or burned for soot. Innumerable attempts were made with the object of using it in the production of artificial dyes, but with little success, except in the two instances of Martius yellow (dinitro-α-naphthol) and Magdala red (*v.* Azines), until the discovery of the eosins about 1874, and the azo-colours about 1878. At the present time considerable quantities of naphthalene are used in the manufacture of the phthalic acid required in the production of the former, and of the naphthols and naphthylamines extensively used in the preparation of the latter.

Naphthalene is now also employed on the large scale for carburetting gas in the special form of apparatus known as the albo-carbon burner (Livesey and Kidd, Eng. pat. 244 of 1878; Germ. pat. 2075 of Feb. 1, 1878; Eng. pat. 38 of 1879; 2682 of 1879; Germ. pat. 8644 of July 8, 1879; Vale, Germ. pat. 9840 of Oct. 30, 1879; Eng. pat. 83 (prov. spec.) of 1880; 1546 (prov. spec.) of 1880; Kidd and Vale, Eng. pat. 2135 of 1880; Livesey, Eng. pat. 1331 of 1881; Vale, Germ. pat. 19012 of Jan. 29, 1882; 32255 of Sept. 20, 1884; Livesey and Whitehouse, Eng. pat. 9473 of 1886; D. P. J. 236, 237). The apparatus is principally adapted to small flames, and, with reference to the economy effected by its use, Pattinson states that 1,000 cubic feet of gas burned with 4·63 lbs. of naphthalene in an albo-carbon lamp gave as much light as 2,700 cubic feet of gas burned in flat-flame burners, or 1,780 cubic feet of gas in Argand burners (Trans. Newcastle Chem. Soc. 1882, 137). A machine for moulding naphthalene into small spheres or ovals of convenient size to suit the carburetting vessels is described and figured in the specification of Eng. pat. 14085 of 1887.

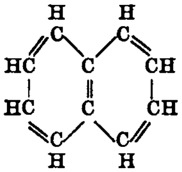
Homologues.—The isomeric methyl-, dimethyl-, ethyl-, phenyl-, and naphthyl-naphthalenes and acenaphthene (*q. v.*) have hitherto found few technical applications and, consequently, are not described in this article. α- and β-methylnaphthalene occur to the extent of about 6 p.c. in the 'creosote oil' of commerce boiling at 200–300° (Schulze, B. 17, 842, 1527), and have been employed, doubtless to a very limited extent, as sources of orange- and brown-red azo- dyes (Actieng. f. A., Germ. pat. 15649 of Feb. 17, 1881, expired June 1884).

Constitution of Naphthalene and Naphthalene Derivatives.

A very large number of derivatives of naphthalene have been prepared, and a description of each would naturally find a place in a monograph of the subject. Those dealt with in this article are restricted to substances which are either of actual or possible value to the colour chemist. For an account of other naphthalene derivatives Watts' Dictionary, Beilstein's Handbuch der organischen Chemie, or Ladenburg's Handwörterbuch der Chemie should be consulted.

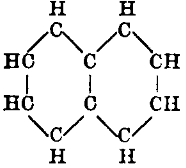
The naphthalene compounds of greatest technical importance are the naphthols, naphthylamines, and the derived isomeric sulphonic acids. These substances are by no means equally valuable as sources of dyes; some, for example, are incapable of forming azo- dyes, others yield azo- dyes which are not fast to soap, changing their shade according as they are dipped in weak acid or alkaline baths, whilst a third class yield azo- dyes which answer all the requirements of the dyer as far as fastness is concerned, but (apart from the question of cost compared with that of dyes from other sources giving similar shades) have unequal commercial value on account of peculiar differences of shade. In view of the increasing amount of evidence pointing to the intimate connection between constitution and colour in the case of organic compounds, it is of importance that the constitution of the various naphthalene derivatives which find employment in the colour industry should be known.

Constitution of naphthalene.—The view put forward by Erlenmeyer (A. 137, 346 (foot-note)), but first shown probable on the basis of experimental evidence by Graebe (A. 149, 22), that the naphthalene molecule contains two benzene nuclei having two carbon atoms in common

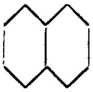


has at the present time a very considerable number of supporters. Several proofs have been given of the fact that phthalic acid, or substituted phthalic acids, unquestionably benzene derivatives, are formed on partial destruction of either 'ring' by oxidation (Graebe, *l.c.*; Atterberg, B. 10, 547; Widman, Bl. 28, 511), the most elegant being that in which it is shown, on the one hand, that α-nitronaphthalene yields nitrophthalic acid (Beilstein and Kurbatow, A. 202, 217), and, on the other, that α-naphthylamine, obtained from the α-nitro- compound by reduction, yields phthalic acid (Monnet, Reverdin and Nölting, B. 12, 2306) by oxidation with chromic acid.

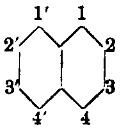
The arrangement of the carbon atoms in two rings has, with one exception (Wreden, B. 9, 590; *cf.* Bamberger, A. 257, 44; C. J. 58, 1299), been adopted in all formulæ since proposed, the Erlenmeyer-Graebe symbol being modified only so far as the distribution of the fourth affinity of each carbon atom is concerned with a view of accounting for selected peculiarities exhibited by naphthalene derivatives (*cf.* Wichelhaus, B. 2, 199; Wreden (2nd formula) B. 9, 590; Claus, B. 15, 1409 [in criticism of Claus's formula *cf.* R. Meyer, B. 15, 1827; Widman, B. 15, 2163 (foot-note)]; Armstrong, B. A. Report, 1889, 175; C. J. Proc. 1890, 102; Bamberger, *l.c.*). All that can be said at the present time with any approach to certainty is that the naphthalene molecule contains two similar systems of six carbon atoms having two carbon atoms in common. Each system is *similar* to but not *identical* with that of benzene, becoming identical with it only when either the second system is destroyed by oxidation or its influence is removed by reduction. Three affinities of each carbon atom are employed in effecting union either with contiguous carbon atoms or with contiguous carbon atoms and hydrogen or other monad radicle, the distribution of the fourth affinity being unknown. To the influence exerted by each ring on the second (due beyond doubt primarily to these 'spare affinities') is to be referred the peculiar properties which distinguish derivatives of naphthalene from those of benzene, for when this influence is removed by saturating the four spare affinities of one ring with, for example, hydrogen, the compound ceases to exhibit these characteristic properties, and assumes those of a benzene derivative containing two side chains attached to contiguous carbon atoms (*v. infra*). It is preferable, therefore, to employ as a symbol for naphthalene one which expresses the symmetry of the molecule but makes no assumption as to the distribution of the fourth affinity of each carbon atom; such a symbol is



or conventionally



carbon atoms being supposed, in the latter symbol, to be placed at the angles of the hexagons, and, with the exception of the two 'central' carbon atoms, associated each with an atom of hydrogen. The position taken up by any radicle in the molecule is indicated by writing its symbol at the angle marking the position of the carbon atom to which it is attached. To save the labour of writing the symbol each time it is desired to indicate the orientation of a substituent, the positions have been numbered



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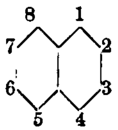
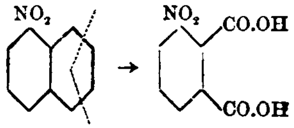
and



II

in order that the substituent's position may be indicated by use of the corresponding numeral. Unfortunately two systems of notation are in general use, and a certain amount of confusion is thereby entailed. System II. was originally proposed by Graebe (A. 149, 26), but met with no support until adopted recently by Schultz (Chemie des Steinkohlentheers, ed. i. 792) and Erdmann (A. 247, 310). System I., on the contrary, has been employed in this country for a number of years, and is adopted in the Chemical Society's publications and in Watts' Dictionary (1st ed. 8, 1374); also in Beilstein's Handbuch (2nd ed.) and Ladenburg's Handwörterbuch; it has, moreover, the distinct advantage of expressing the similarity of the two rings, corresponding positions being similarly numbered, and will, on these grounds, be employed in this article.

Constitution of mono-derivatives.—Ever since Faraday, in his investigation of the action of sulphuric acid on naphthalene, described the calcium salts of two isomeric monosulphonic acids (Phil. Trans. 1826, 140), two series of corresponding mono- derivatives have been known, termed α- and β-derivatives as first suggested by Merz (Z. [2] 4, 394). The formula admits of the existence of two distinct mono-derivatives according as the radicle is substituted for hydrogen in any one of the four similar positions 1, 4, 1', 4', and 2, 3, 2', 3' respectively. The designations α and β were assigned by Merz to the isomeric monosulphonic acids and corresponding derivatives without reference to the naphthalene symbol, and although a general consensus of opinion was in favour of regarding the positions 1, 4, 1', 4' as α-, and 2, 3, 2', 3' as β- positions, no entirely satisfactory evidence of the truth of this conjecture was forthcoming until Reverdin and Nölting pointed out (B. 13, 36) that the nitrophthalic acid (m.p. = 212°) obtained from α-nitronaphthalene by oxidation (Beilstein and Kurbatow, A. 202, 217) must by exclusion be the 1:2:3-acid, since the only theoretically possible isomeride, the 1:3:4-acid (m.p. = 161° [1]) discovered by Miller (B. 11, 393; A. 208, 229), had been shown by Miller (B. 11, 1191) to correspond in constitution with Baeyer's hydroxyphthalic acid (B. 10, 1083) which, as Schall showed, had the constitution [OH:COOH:COOH = 1:3:4] (B. 12, 834). It followed, therefore, that in α-nitronaphthalene, and similarly in any α- derivative, the radicle must be associated with one of the four carbon atoms contiguous to the two central carbon atoms, thus:



As already stated, the existence of two, and only two, mono-derivatives finds expression in the symbol which indicates that four α- and four β- positions are existent; a satisfactory proof of the presence in the molecule of four similarly situated α- positions based on the existence of three isomeric αα-dichloronaphthalenes has been given by Atterberg (B. 10, 547; *cf.* also B. 9, 1736), and the presence of four similarly situated β-

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[1] Given as 165° in Reverdin and Nölting's paper.

positions follows from the existence of three isomeric ββ-dichloronaphthalenes (Armstrong and Wynne, C. J. Proc. 1890, 83).

Constitution of di- and tri- derivatives.—The formula admits of the existence of ten 'uniform' di- and fourteen 'uniform' tri- derivatives of naphthalene, and in the case of one set of compounds—the chloronaphthalenes—all the theoretically possible isomerides have been prepared. With dissimilar substituents, the number of isomeric di- and tri- derivatives is much greater; thus, for example, fourteen (seven α- and seven β-) naphthylaminemonosulphonic acids and forty-two (twenty-one α- and twenty-one β-) naphthylaminedisulphonic acids are theoretically possible, and as a reference to the sections dealing with the nitro-, amido-, and hydroxy-naphthalenes will show, a considerable proportion of the expected number of isomeric di- derivatives has in several instances been obtained.

The constitution, melting-point, and crystalline character of each of the ten dichloro-[1] and fourteen trichloro-naphthalenes are given in the following tables since the chloronaphthalenes form a set of standard compounds to which reference can be made when the constitution of any di- or tri- derivative is in question:—

Dichloronaphthalenes.

Old and trivial name	Constitution	Melting-point	Character of crystallisation from alcohol
—	1:2	35°	Prisms.
—	1:3	61°	Long, flat, thin needles.
[β-]	1:4	67·5°	Long, flat, thin needles.
[ξ-]	1:1′	82°	Rhombohedra.
[θ-]	1:2′	62·5°	Small aggregates.
[η-]	1:3′	48°	Long, flat, thin needles.
[γ-]	1:4′	107°	Short, flat needles.
[ι-]	2:3	119·5°	Thin, lustrous scales.
[δ-]	2:2′	114°	Thin laminæ.
[ε-]	2:3′	135°	Long, flat, thin needles.

Trichloronaphthalenes.

Old and trivial name	Constitution	Melting-point	Character of crystallisatio from alcohol
[α-]	1:2:3	81°	Groups of long needles.
—	1:2:4	92°	Tufts of flat needles.
—	1:2:1′		
—	1:2:2′	84°	Microscopic needles.
—	1:2:3′	92·5°	Slender needles.
—	1:2:4′	78·5°	Short, flat needles.
?[β-]	1:3:1′	90°	Large, flat prisms.
[η-]	1:3:2′	113°	Short, thin needles.
[θ-]	1:3:3′	80°	Tufts of thin needles.
[γ-]	1:3:4′	103°	Long, flat needles.
[δ-]	1:4:1′	131°	Very long needles.
[ε-] and [ξ-]	1:4:2′	66°	Needles, becoming opaque.
—	2:3:1′	109·5°	Long, thin needles.
—	2:3:2′	91°	Minute plates.

As is evident from the tables, many of the dichloro- and trichloro-naphthalenes exhibit differences in melting-point and other characters sufficient to ensure their ready identification. The remaining members of the series cannot readily be distinguished in this way; for example, two dichloronaphthalenes melt at about 61°, and no fewer than three trichloronaphthalenes melt at about 80°, and four at about 91°; and in these cases some further criteria are obviously necessary before the individual compound can be identified. The sulphonic acids derived from the dichloro- and trichloro-naphthalenes have been found to afford a ready means of discriminating between the various isomerides, inasmuch as two additional melting-points, apart from other distinguishing properties, are furnished by the chloride and amide of each sulphonic acid. A description of these derivatives and an account of the methods by which the constitution of the chloronaphthalenes have been determined lie outside the scope of this article, but find a place in the art. NAPHTHALENE in the new edition of WATTS' DICTIONARY OF CHEMISTRY, which, together with the papers of Armstrong and Wynne (*cf. inter alia*, C. J. Proc. 1888, 106; 1889, 5, 34, 48; 1890, 76, 77), and Erdmann (A. 247, 366; B. 21, 3446) should be consulted for details.

The problem of the determination of the constitution of any naphthalene mono-, di- or tri- derivative, whether a technical product or otherwise, resolves itself into converting that derivative by any of the known methods into the corresponding chloronaphthalene or in the few cases where this cannot be accomplished preparing it from a compound whose constitution has been established in this manner. The practice hitherto adopted of distinguishing the various isomerides as α, β, γ, δ . . . . compounds in the order of their discovery, as, for example, the β-naphthylamine-α-, -β-, -γ-, and -δ-monosulphonic acids, has led to much confusion owing to the fact that the letters α and β were originally and are still employed in an entirely different sense to indicate the position of a substituent in the molecule. As it is eminently desirable to abandon this perplexing nomenclature in favour of one which at a glance indicates the orientation of the substituents, numerals indicating the constitution are, as far as possible, employed in this article instead of α, β, γ, ... to distinguish the isomeric naphthalene derivatives, and, in every case where it has been necessary to use the latter, the plan adopted by Ladenburg (Handwörterbuch, art. NAPHTALIN) of placing the letters in brackets (*e.g.* [α-]) to indicate that they bear no reference to the constitution of the compounds, has been followed. The isomeric acids just alluded to are respectively the 2:1′-, 2:3′-, 2:4′- and 2:2′-β-naphthylaminesulphonic acids, the β in this case referring to the position of the amido- group, and the gain in clearness is obvious when for example in speaking of one mode of preparation of the second of these acids it is stated that '2:3′-β-naphthylaminesulphonic acid can be prepared from 2:3′-β-naphtholsulphonic acid by &c.' instead of 'β-naphthylamine-β-sulphonic acid can be prepared from β-naphthol-α-sulphonic acid by &c.,' or even 'β-naphthylamine-[β-] sulphonic acid can be prepared from β-naphthol- [α-]sulphonic acid by &c.'

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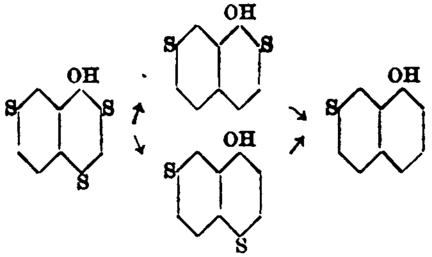
[1] Investigation has shown that two of the twelve dichloronaphthalenes at one time described have no claim to recognition as pure substances, the so-called [α-]dichloronaphthalene being a mixture of the 1:3- and 1:4-dichloronaphthalenes (Armstrong and Wynne, C. J. Proc. 1888, 106) and the so-called [κ-]derivative of Claus and Oehler (B. 15, 314) unquestionably a trichloronaphthalene (Armstrong and Wynne, C. J. Proc. 1890, 80; *v. infra* footnote to 1:2-α-naphtholsulphonic acid).

Substitution in the Naphthalene Series.

A complete discussion of the theory of substitution and of isomeric change in the naphthalene series lies outside the scope of this article, and the subject will only be dealt with incidentally in connection with the sulphonic acids of naphthalene and its amido- and hydroxy-derivatives in so far as it throws light on the conditions attending their formation. Briefly the theory is summarised in what has been termed the alpha-law of substitution, according to which naphthalene exhibits a tendency to form α- derivatives, β- derivatives only being formed either by the occurrence of secondary change or when a radicle is present in an α-position and determines the entry of the new group into the contiguous β- position. The few exceptions to this law, *e.g.* the formation of β-nitronaphthalene in small quantity in the nitration of naphthalene, will doubtless be found to be only apparent on further investigation, inasmuch as everything seems to show that an isolated β- position is never directly attacked. For a full discussion of the subject Watts' Dictionary of Chemistry, 2nd edit., article Naphthalene, should be consulted.

Action of sulphuric acid on naphthalene and naphthalene derivatives.—Unlike chlorine, bromine, nitric acid, &c., sulphuric acid readily lends itself to the formation of β- derivatives, as is exemplified in the well-known case of the production of naphthalene-β-sulphonic acid by heating naphthalene with sulphuric acid, and exhibits a large number of apparent deviations from the alpha-law of substitution. This action of sulphuric acid on naphthalene has given rise to much discussion, and the current view (*cf.* Weinberg, B. 20, 3354) seems to be that of Nölting (B. 8, 1095) and Post (B. 8, 1549), who draw attention to the liberation of a certain amount of naphthalene during the reaction, and argue that the naphthalene-α-sulphonic acid, which is known to be more readily hydrolysed than its isomeride, undergoes hydrolysis by the action of the dilute sulphuric acid formed in the reaction with the regeneration of naphthalene and sulphuric acid; and that sulphonation again ensues, but in a β- position under the influence of the high temperature and altered conditions, with the production of naphthalene-β-sulphonic acid. This theory is noteworthy if only for the fact that it recognises initial sulphonation in an α- position, and refers the production of the β-compound to the occurrence of subsequent change in the presence of the sulphuric acid; it must, however, be now regarded as distinctly less probable than the view which refers the production of the β-acid to a partial hydrolysis of a polysulphonic acid containing a sulphonic radicle in a β- position. There can be very little doubt that the *formation* as distinguished from the *isolation* of complex sulphonic acids does not require the agency of anhydrosulphuric acid, but is brought about by ordinary sulphuric acid at the higher temperatures employed in sulphonation. The dissolved anhydride of the anhydrosulphuric acid acts chiefly as a dehydrating agent, and combines with the eliminated water which is thus removed from the sphere of action as sulphuric acid (H_2SO_4). With ordinary sulphuric acid, however, the liberated water is free to hydrolyse the more complex acids as rapidly as formed, and the action proceeds in such a way that the more readily eliminated α-sulphonic groups are first removed, the extent of the hydrolysis being of course determined by the strength of acid and temperature employed and the duration of the reaction.

Di- and tri-sulphonic acids are known to be very readily formed by the action of sulphuric acid on the naphthols and naphthylamines, and there is a considerable amount of evidence proving that the β-monosulphonic acids and ββ-disulphonic acids of these substances are derived from polysulphonic acids by partial hydrolysis and elimination of the less stable α- and in certain cases β-sulphonic radicles. For example it is known (*v.* α-naphtholsulphonic acids) that the 1:2:2′- and 1:4:2′-α-naphtholdisulphonic acids and the 1:2′-α-naphtholsulphonic acid result from the action of relatively dilute sulphuric acid on the 1:2:4:2′-α-naphtholtrisulphonic acid, thus:—[1]



Everything tends to show that a like process is involved in the production of naphthalene-β-monosulphonic acid and the naphthalene-ββ-disulphonic acids, and that the former, for example, is not derived from naphthalene-α-monosulphonic acid by intramolecular change or by a process such as that suggested by Nölting and Post, but by the partial hydrolysis of a more complex sulphonic acid containing at least one of its SO_3H-radicles in a β- position.

The formation of an acid such as the 1:2:4:2′-α-naphtholtrisulphonic acid, and indeed of any β-sulphonic acid, seems at first sight to be at variance with the 'alpha-law' of substitution. Experience, however, has shown that a disulphonic acid, in which the sulphonic groups occupy either contiguous, peri-(1:1′-), or para-(1:4-) positions relatively to each other is never found in the products obtained when naphthalene, or the isomeric naphthylamines or naphthols are sulphonated under very diverse conditions. It may well be that the entering sulphonic group, in taking up an α- position in accordance with the 'alpha-law,' assumes initially one of these three positions with reference to a sulphonic group already present in the molecule, and, in consequence of what may perhaps be termed an 'invincible objection' to remain in such a position, passes immediately by intramolecular change into the nearest available β- position.

Assuming the 'alpha-law,' naphthionic acid on further sulphonation would for example be

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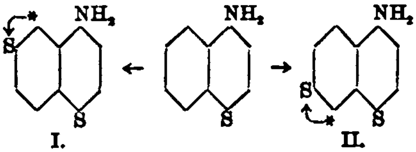
[1] In these symbols S is employed as an abbreviation of SO_3H.

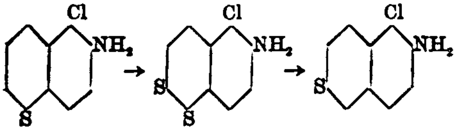
expected to yield initially both the 1:4:1′- and the 1:4:4′-disulphonic acids: the former in view of what is known of the behaviour of naphthalene-α-sulphonic acid on sulphonation, the latter in view of the behaviour of α-naphthylamine when the formation of naphthionic acid is impeded. Neither acid, however, has been detected in the product, but in their place two disulphonic acids are found which have probably been formed from them by isomeric change at the moment of formation, thus:



I. II.

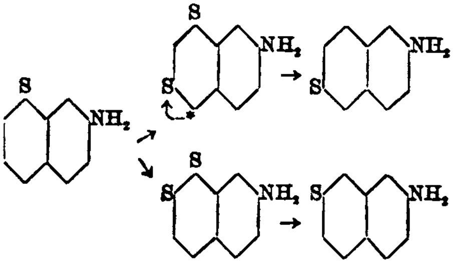
To the influence of the radicles already present in the molecule must be referred in great measure the determination of the final position of the *entering* sulpho- group; thus the change indicated in II. could be predicted from what is known of the indisposition of SO_3H-radicles to remain in, even if they initially assume, the peri- position, whilst that indicated in I. must be attributed to the influence of both the radicles present in the molecule of naphthionic acid[1] since it accords with the fact that on sulphonation α-naphthylamine does not form the 1:1′-α-naphthylaminesulphonic acid, whilst naphthalene-α-sulphonic acid is readily converted into the 1:3′-naphthalenedisulphonic acid.

In some cases it is possible that instead of the α-sulphonic group passing into the contiguous β- position, further sulphonation ensues in such a way that the entering radicle assumes the *contiguous* β- position, the resulting sulphonic acid then undergoing partial hydrolysis with the elimination of the contiguous α-SO_3H-radicle. For example, the ready conversion of 1:2:4′- into 1:2:3′-α-chloro-β-naphthylaminesulphonic acid (Armstrong and Wynne, C. J. Proc. 1889, 36) seems best accounted for by such a view, thus:



The evidence for this theory of the action of sulphuric acid on naphthalene and its derivatives cannot be discussed here, the object being simply to call attention to the fact that recent work on the subject does not support Nölting's theory of the formation of β-sulphonic acids.

To take a case in point, the examination of the β-naphthylaminedisulphonic acids has led to results which seem to show that the conversion of the 2:1′- (or 2:4′-) β-naphthylaminesulphonic acid into a mixture of the 2:2′- and 2:3′-β-naphthylaminesulphonic acids is best accounted for by the following series of reactions:



and not, as Weinberg suggests (*l.c.*), by the hydrolysis of the α-acid and resulphonation of the regenerated β-naphthylamine in β- positions.

It may be noted that whilst α- derivatives of naphthalene on sulphonation give homo- or hetero-nucleal monosulphonic acids according to the nature of the radicle, β- derivatives uniformly give heteronucleal monosulphonic acids.

REDUCTION OF NAPHTHALENE DERIVATIVES.

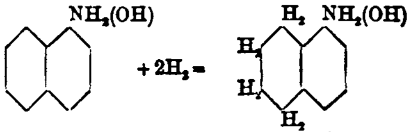
The hydrides of naphthalene have been described and their properties investigated chiefly by Wreden and Znatowicz (Beilstein, Handb. 2nd ed. 2, 137), by Graebe and Guye (B. 16, 3028), and by Bamberger and Kitschelt (B. 23, 1561), and all exhibit, as would be expected, a marked deviation in properties from the parent hydrocarbon. Of these hydrides, *tetrahydronaphthalene* $C_{10}H_{12}$, is perhaps the most interesting, since it may be regarded as the parent hydrocarbon of a series of tetrahydro- derivatives which, not improbably, may before long acquire technical importance. Tetrahydronaphthalene is a liquid which boils at 205°, and like benzene and its homologues, with which it exhibits a certain analogy, does not combine with picric acid.

This resemblance to compounds of the benzene series is much more marked in the hydroxy- and amido- derivatives of tetrahydronaphthalene. Bamberger has found that when the naphthylamines and naphthols are converted into tetrahydro- derivatives by reduction in boiling amyl alcohol solution with sodium, compounds of two kinds may result:

(1) Those in which the substituent and the four added hydrogen atoms are in one ring, termed *alicyclic* (or ac.-) derivatives.

(2) Those in which the substituent is in one and the four added hydrogen atoms in the second ring, termed *aromatic* (or ar.-) derivatives.

With α-naphthylamine and α-naphthol, 'aromatic' derivatives are exclusively formed



(ar.- derivative)

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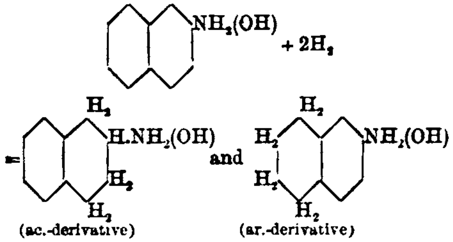
[1] The 1:4:1′-α-naphthylaminedisulphonic acid, when *isolated*, is a compound of considerable stability, but this fact does not militate with the view here taken that at the moment of formation by the sulphonation of naphthionic acid it undergoes isomeric change into the more stable 1:4:2′-acid. It may be noted that the 1:4:1′-acid is obtained either (*a*) by the reduction of 1:4:1′-α-nitronaphthalenedisulphonic acid under conditions which preclude the occurrence of intramolecular change of the SO_3H- radicles, or (*b*) by the further sulphonation of the 1:1′-α-naphthylaminesulphonic acid [NH_2:SO_3H=1:1′] when the *entering* SO_3H-radicle assumes the position '4' as would be anticipated from what is known of the behaviour of both α-naphthylamine and naphthalene-α-sulphonic acid on sulphonation.

but with β-naphthylamine and β-naphthol both 'aromatic' and 'alicyclic' derivatives are obtained, the latter forming the chief products



(ac.-derivative) (ar.-derivative)

A comparison of the properties of the tetrahydro- compounds shows that in both classes the specific properties of naphthalene derivatives are lost, since on the one hand the 'alicyclic' tetrahydro- compounds display the characters of the secondary alcohols and amines of the fatty series, and on the other the 'aromatic' tetrahydro- compounds exhibit the properties of derivatives of benzene (as distinguished from naphthalene) hydrocarbons and show a close analogy with the orthoxylenols and orthoxylidines. 'Alicyclic' tetrahydro-β-naphthylamine and its alkyl- derivatives are interesting physiologically since they act as powerful midriatic agents (Bamberger and Filehne, B. 22, 777), the first named having been introduced as a drug under the name 'Thermine' (*cf.* S. C. I. 9, 888). For further information reference should be made to the papers of Bamberger and his pupils (*cf.* A. 257, 1; C. J. 58, 1299, with bibliography).

This striking modification in properties effected by reduction, apart from its theoretical importance, is of value since it for the first time opens up the possibility of employing 'aromatic' tetrahydronaphthalene derivatives as substitutes for benzene derivatives in the production of dyestuffs, and so finding a further use for the relatively cheap naphthalene, whose production, unlike that of benzene is still very considerably in excess of the demand.

I. ADDITION DERIVATIVES.

Reference having already been made to the compounds which result when naphthalene and certain of its derivatives are reduced by means of nascent hydrogen, the only addition compound requiring description here is

Naphthalene tetrachloride $C_{10}H_8Cl_4$.

Formation.—Naphthalene tetrachloride is formed together with oily impurities containing, according to the conditions employed, varying quantities of naphthalene dichloride, α-chloronaphthalene tetrachloride, and a dichloronaphthalene tetrachloride, by the action either of chlorine (Faust and Saame, A. 160, 67; Leeds and Everhardt, Am. 2, 208), or of potassium chlorate or bleaching powder and hydrochloric acid (P. and E. Depouilly, Bl. 4, 10; E. Fischer, B. 11, 735) on naphthalene.

Preparation.—According to Salathé the chloride is prepared on the large scale by passing a rapid current of chlorine into a quantity of 15–30 kilos. of fused naphthalene contained in a large stoneware Woulffe's bottle. The leading tube dips only just below the surface of the fused hydrocarbon, and the chlorination is conducted as rapidly as possible to avoid the formation of any considerable quantity of dichloride. Owing to the great rise of temperature during the reaction, cooling with water is resorted to and the temperature carefully kept below 160–170°, since at about 180° the whole mass would undergo carbonisation (*cf.* Bolley, Chem. Technol. 5, 869).

Properties.—It crystallises from chloroform in large rhombohedra, melts at 182° and is soluble in ether, sparingly soluble in alcohol.

Reactions.—(1) When decomposed with alcoholic potash it yields a mixture of 1:3-, 1:4-, and 2:3-dichloronaphthalenes (Faust and Saame, A. 160, 69; Krafft and Becker, B. 9, 1089; Widman, B. 15, 2161; Armstrong and Wynne, C. J. Proc. 1888, 106; 1890, 80).

(2) When heated with 5–6 parts of nitric acid (sp.gr. = 1·35) it is oxidised to phthalic and oxalic acids, and as the yield of phthalic anhydride amounts to about 30 p.c. of the theoretical, naphthalene tetrachloride has been extensively used as a source of this compound.

II. NAPHTHALENESULPHONIC ACIDS.

Introductory.—Naphthalenesulphonic acids are obtained by two general methods:—

(1) Action of sulphuric acid on naphthalene.

(2) Elimination of the NH_2-radicle in naphthylaminesulphonic acids by diazotising and either boiling with alcohol, or, in cases where this is not applicable owing to the stability of the diazo- compound, reducing to hydrazine and heating this with copper sulphate solution.

On sulphonation naphthalene yields two mono-, four di-, two tri-, and one tetra-sulphonic acids, and the series of changes which probably occur in the production of several of these acids under the conditions described in connection with each is given in the table:

$$\begin{tikzcd}
C_{10}H_8 \arrow[d, "\text{(by sulphonation)}"] & \\
\alpha\text{-}C_{10}H_7.SO_3H \arrow[d, "\text{(by further sulphonation)}"] & \\
1{:}4'\text{-}C_{10}H_6(SO_3H)_2 \arrow[d, "\text{(by intramolecular change)}"] & \\
1{:}3'\text{-}C_{10}H_6(SO_3H)_2 \arrow[d, "\text{(by further sulphonation)}"'] \arrow[dr, "\text{(by partial hydrolysis)}"] & \\
1{:}3'{:}3\text{-}C_{10}H_5(SO_3H)_3 \arrow[d, "\text{(by partial hydrolysis)}"] & \beta\text{-}C_{10}H_7.SO_3H \\
2{:}2'\text{-}C_{10}H_6(SO_3H)_2 \arrow[d, "\text{(by intramolecular change)}"] & \\
2{:}3'\text{-}C_{10}H_6(SO_3H)_2 &
\end{tikzcd}$$

The conditions attending the formation of β-acids, as indicated in the table, have already been discussed (*v. Substitution in the naphthalene series*), and in connection with the questions there raised it may be noted that the 1:3'-naphthalenedisulphonic acid very readily undergoes partial hydrolysis with the production of naphthalene-β-sulphonic acid (Armstrong and Wynne, C. J. Proc. 1887, 146).

The action of sulphuric acid on naphthalene leads also to the formation of small quantities of two dinaphthylsulphones—the αβ melting at 123°, and the ββ melting at 177°. The best yield is obtained by heating 8 parts of naphthalene with 3 parts of sulphuric acid at 180°, and the sulphones occur mixed with the unattacked naphthalene, from which they can be separated by removing the latter by steam distillation (Stenhouse and Groves, B. 9, 682; C. N. 32, 151; Hofmann, B. 17, 1921; Krafft, B. 23, 2364).

Naphthalenemonosulphonic Acids.

(i) **Naphthalene-α-sulphonic acid** (sulphonaphthalic acid) $C_{10}H_7.SO_3H$.

Formation.—Naphthalene on sulphonation with about its own weight of sulphuric acid yields a product containing varying proportions of α- and β- monosulphonic acids and a small quantity of at least one disulphonic acid, according to the conditions employed. Merz and Weith (B. 3, 195) state that a mixture of naphthalene and sulphuric acid in the proportion of 10:9 gave a product containing 80 p.c. of α-acid and 20 p.c. of β-acid when heated for three hours at 100°, and 25 p.c. of α-acid and 75 p.c. of β-acid when heated for a further four hours at 160–170°, 15 p.c. of the naphthalene employed being recovered in the first case and 25 p.c. in the second. Also, that a mixture in the proportion 5:4 heated for eight hours at 160° gave 80 p.c. of β-acid, 30 p.c. of the naphthalene employed being recovered. At temperatures below the melting-point of naphthalene—*e.g.* when finely powdered naphthalene is sieved into 1½–2 times its weight of sulphuric acid of 66° Bé. at 40°, and the mixture stirred continuously for many hours until everything has dissolved—α-acid is said to be the sole product (Chem. Fabrik Grünau, Landshoff, & Meyer, Germ. pat. 50411, of Feb. 6, 1889, exp. June 1890). Naphthalene-α-sulphonic acid, mixed with a small quantity of 1:4′-naphthalenedisulphonic acid, but free from β-monosulphonic acid, is obtained, when slightly less than the theoretical quantity of chlorosulphonic acid is carefully added with continual shaking to a 10 p.c. solution of naphthalene in carbon bisulphide (Armstrong and Wynne, C. J. Proc. 1887, 146, *cf.* Armstrong, C. J. 24, 176).

Preparation.—Naphthalene is heated with slightly more than an equal weight of sulphuric acid at 90–95° for 2–3 hours in steam-jacketed cast-iron pots (*v.* β-acid), and the product poured into 6–8 times its bulk of water. The solution, separated from the 30 p.c. or so of unattacked naphthalene which solidifies on cooling, is neutralised with chalk, filtered from the precipitated calcium sulphate and concentrated by evaporation. The calcium salt of the β-acid, which crystallises out first, is filtered off, and the calcium salt of the α-acid obtained by further evaporation of the filtrate. The final mother-liquors contain the calcium salts of naphthalenedisulphonic acids in small quantity. The calcium α-sulphonate can be further purified by extraction with 85 p.c. alcohol in which the β-sulphonate is very sparingly soluble (Merz, Z. [2] 4, 394; Merz and Weith, *l.c.*; Merz and Mühlhäuser, B. 3, 710).

Salts.—The *acid* is a crystalline, deliquescent substance sparingly soluble in slightly dilute sulphuric acid; the salts crystallise in scales, having the composition and solubility given in the table:

Composition of salt	1 part of the salt dissolves in	
	parts of water at 10°	parts of 85 p.c. alcohol at 10°
Potassium salt $+\frac{1}{2}H_2O$.	13 (at 11°)	108 (at 11°)
Calcium „ $+2H_2O$.	16·5	19·5
Barium „ $+H_2O$.	87	350
Lead „ $+3H_2O$.	27	11

Reactions.—(1) Treatment with phosphorus pentachloride converts the potassium or sodium salt into *naphthalene-α-sulphonic chloride*, which crystallises from ether in scales melting at 56°.

(2) On fusion with caustic potash or soda it yields *α-naphthol* (Eller, A. 152, 275).

(ii) **Naphthalene-β-sulphonic acid.**

Formation. — *v.* Naphthalene-α-sulphonic acid.

Preparation.—Sulphonation is effected in cast-iron pots provided with mechanical stirrers and wooden or iron covers lined with lead, stout lead pipes serving to condense the naphthalene vapours. The pots are heated in sand baths or, better, baths of iron borings or fusible metal. 250 kilos. of naphthalene are heated with 230–240 kilos. of sulphuric acid of 66° Bé. at 170° for 8 hours, the melt poured into 6–8 times its volume of water, directly neutralised with caustic soda, and the separated sodium naphthalene-β-sulphonate freed from the mother-liquor in a centrifugal machine (Witt, *priv. comm.*). The mother-liquors contain sodium naphthalene-α-sulphonate.

Salts.—The *acid* forms non-deliquescent scales, the salts crystallise in small scales of the composition and solubility indicated in the table:

Composition of salt	1 part of the salt dissolves in	
	parts of water at 10°	parts of 85 p.c. alcohol at 10°
Potassium salt $+\frac{1}{2}H_2O$.	15	115
Calcium salt (anhydrous)	76	437
Barium salt $+H_2O$ . .	290	1950
Lead salt $+1\frac{1}{3}H_2O$ . .	115	305

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into *naphthalene-β-sulphonic chloride*, which is less soluble than the α- compound, and crystallises from ether in scales melting at 76° (Maikopar, Z. [2] 5, 711).

(2) On fusion with caustic potash or soda it yields *β-naphthol*, for the preparation of which it is extensively employed.

Naphthalenedisulphonic Acids.

(1) **1:4′-Naphthalenedisulphonic acid** (so-called Armstrong's naphthalenedisulphonic acid; naphthalene-[γ-]disulphonic acid of Armstrong and Wynne (C. J. Proc. 1886, 231); naphthalene-[δ-]disulphonic acid of Beilstein, Schultz, &c.).

Formation.—Naphthalene-1:4′-disulphonic acid is formed together with the 1:3′-acid when naphthalene is gradually mixed with five times its weight of 23 p.c. anhydrosulphuric acid in the cold (Actieng. f. A., Germ. pat. 45776 of March 16, 1888). It is also obtained by the action of chlorosulphonic acid on dry sodium naphthalene-α-monosulphonate, and by adding naphthalene to the theoretical quantity of sulphuric anhydride, both substances being intimately mixed with sand before admixture (Armstrong and Wynne, C. J. Proc. 1887, 42).

Preparation.—The theoretical quantity (2 mol. prop.) of chlorosulphonic acid is run into powdered naphthalene as rapidly as the rate of evolution of hydrogen chloride permits, no special attention being paid to cooling. The contents of the vessel are kept well stirred throughout the operation. When the evolution of hydrogen chloride slackens, the temperature is gradually raised to 130–140°, and maintained at this until the mass becomes solid. After cooling, the product is treated with water in not too large quantity, and the hot solution, after separation from the relatively small amount of insoluble matter, neutralised with concentrated aqueous caustic soda; this part of the operation being so arranged that the sodium salt crystallises out on cooling without evaporation of the solution being necessary. The proportion of monosulphonic acid in the product is less than 2 p.c., and is found almost entirely in the last separations of the sodium naphthalenedisulphonate.

Salts.—The *acid* crystallises in very soluble lustrous, white, non-hygroscopic scales. It does not form acid salts. The *lead* salt, $PbA + 3H_2O$, crystallises in small tufts of very slender needles, tolerably soluble in water, insoluble in alcohol; the *barium* salt, $BaA + 4H_2O$, separates from concentrated solutions in small granules consisting of microscopic needles which only dissolve again in water with great difficulty; the *calcium* salt, $CaA + 3H_2O$, crystallises in minute aggregates of needles, and separates from concentrated solutions in a pulverulent form which requires much water for its dissolution; the *potassium* salt, $K_2A + 2H_2O$, crystallises in scales or small prisms and dissolves in 8·04 parts of water at 12°; the *sodium* salt, $Na_2A + 2H_2O$, crystallises in lustrous scales or occasionally in prisms, and dissolves in 8·78 parts of water at 16·5° (Armstrong and Wynne) and in 7·99 parts at 19° (Ewer & Pick, Germ. pat. 41934).

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry sodium salt into 1:4′-*naphthalenedisulphonic chloride.* This crystallises from benzene either in needles which become opaque on drying or in small prisms, melts at 183°, and on distillation with phosphorus pentachloride at 210° yields 1:4′-*dichloronaphthalene* (Armstrong, B. 15, 205).

(2) On fusion with caustic soda, the sodium salt is converted into 1:4′-*α-naphtholsulphonic acid* and 1:4′-*dihydroxynaphthalene* (Ewer & Pick, Germ. pat. 41934; Armstrong and Wynne, C. J. Proc. 1887, 43; Bernthsen and Semper, B. 20, 938).

(3) On nitration, the sodium salt yields an *α-nitronaphthalenedisulphonic acid* which by reduction is converted into an acid identical with the α-naphthylaminedisulphonic acid-S. of the Schöllkopf Co.'s Germ. pat. 40571 (Bernthsen, B. 22, 3327; Schultz, B. 23, 77).

(ii) **1:3′-Naphthalenedisulphonic acid** (naphthalene-?-β-disulphonic acid of Armstrong and Wynne (C. J. Proc. 1886, 231); naphthalene-[γ-] disulphonic acid of Beilstein and Schultz).

Formation.—This acid is formed together with 1:4′-naphthalenedisulphonic acid when naphthalene is sulphonated with 23 p.c. anhydrosulphuric acid in the cold, and occurs in the product formed when naphthalene is heated with five times its weight of concentrated sulphuric acid at 160° for 4 hours (Armstrong, B. 15, 204).[1] A uniform acid is obtained when naphthalene is heated with five times its weight of 100 p.c. sulphuric acid at 90–110°, or with ordinary sulphuric acid at 90° and subsequently with strongly fuming acid at 110–120° (Bernthsen, B. 22, 3328, *cf.* Schultz, B. 23, 77).

Preparation. — Dry sodium naphthalene-β-sulphonate is mixed with twice its weight of 25 p.c. anhydrosulphuric acid and the reaction completed by warming the mixture on a water-bath. The product, after cooling, is poured into water, neutralised with milk of lime, and converted into sodium salt in the usual way. On concentration of the solution to a relatively small bulk, the very soluble sodium salt crystallises out in characteristic needles (Ewer and Pick, Germ. pat. 45229 of Oct. 23, 1887). A pure product is also obtained when an excess of chlorosulphonic acid is employed instead of anhydrosulphuric acid (Armstrong and Wynne, C. J. Proc. 1886, 231; Armstrong, *ibid.* 1889, 10).

Salts.—The *lead* salt, $PbA + 3\frac{1}{2}H_2O$, *barium* salt, $BaA + 4H_2O$, and *calcium* salt, $CaA + 4H_2O$, crystallise in granules consisting of microscopic needles and are readily soluble in water; the *potassium* salt, $K_2A + H_2O$, also crystallises in granules consisting of microscopic needles and dissolves in 3·4 parts of water at 16·5°; the *sodium* salt, $Na_2A + 7H_2O$, crystallises from dilute (50 p.c.) alcohol in needles soluble in 3·34 parts of water at 16·5°.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:3′-*naphthalenedisulphonic chloride*, which crystallises from a mixture of benzene and petroleum spirit in small prismatic aggregates, melts at 127°, and on distillation with phosphorus pentachloride at 200° yields 1:3′-*di-*

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[1] Some confusion has arisen with reference to the acid discovered by Armstrong in the mother-liquors of the calcium salt of Ebert and Merz's naphthalene-[α-]disulphonic acid owing to the statement that it is convertible into a dichloronaphthalene m.p. = 59° on distillation with phosphorus pentachloride (*l.c.*). The quantity of this substance obtained was too small to admit of analysis, and there can be no doubt, in view of subsequent work, that the supposed dichloro- was in reality impure 1:3′:4-trichloronaphthalene produced from the initially formed 1:3′-dichloronaphthalene owing to the pentachloride acting as a chlorinating agent under the conditions employed. The conclusion arrived at by Schultz (Steinkohlenth. 1, 499) and Ladenburg (Handwörterb. der Chemie, 7, 417) that Armstrong and Graham's 'dihydroxynaphthalene' melting at 158° (C. J. 39, 141) is obtained from this acid, although it is nowhere stated by Armstrong that such is the case, arises from a not unnatural misconception. According to a private communication from Professor Armstrong, this 'dihydroxynaphthalene' was obtained only on one occasion; all subsequent attempts to prepare it have resulted in failure, and a later analysis of a small portion of the original specimen makes it very improbable that the substance had the composition of a dihydroxynaphthalene.

chloronaphthalene (Armstrong and Wynne, C. J. Proc. 1886, 232; 1888, 106).

(2) Fusion with caustic soda converts the sodium salt into 1:3′-*dihydroxynaphthalene* (Ewer and Pick, *l.c.*).

(3) On nitration, the sodium salt yields two *nitronaphthalenedisulphonic acids*. The chief product is an *α-nitro*-acid, convertible by reduction into α-naphthylamine-[ε-]disulphonic acid (Actieng. f. A., Germ. pat. 45776; Ewer and Pick, Germ. pat. 52724; Bernthsen, B. 22, 3327; Schultz, B. 23, 77), the minor product being a *β-nitro*-acid (Schultz, *l.c.*).

(iii.) **Naphthalene-2:2′-disulphonic acid** ([α-] naphthalenedisulphonic acid of Ebert and Merz).

Formation.—Berzelius (A. 28, 9) found that naphthalene, when heated with excess of concentrated sulphuric acid at 100° is converted into a disulphonic acid, and an isomeric acid seems to have been prepared by Dusart (C. R. 64, 859) working under different conditions. The nature of the product formed by the action of sulphuric acid on naphthalene at high temperatures was first systematically investigated by Ebert and Merz (B. 9, 592) and later by Armstrong (B. 15, 204). According to Ebert and Merz two isomeric naphthalenedisulphonic acids—distinguished as the [α-] and [β-] acid—are produced on heating naphthalene with excess of sulphuric acid. About equal parts of the [α-] and [β-] acid are formed when a mixture of one part of naphthalene and 5 parts of concentrated sulphuric acid is heated at 160° for 4 hours, the product being free from naphthalenemonosulphonic acids; when heated at 180° for 24 hours, however, the same mixture gives a product consisting almost entirely of the [β-]acid, and the pure [α-]acid can be converted into [β-]acid by prolonged heating with sulphuric acid at this temperature. A repetition of these experiments led Armstrong to the conclusion that the product formed by heating at 180° for twenty-four hours contains a smaller proportion of the [β-]acid than stated by Ebert and Merz, that a third acid, subsequently recognised as the 1:3′-disulphonic acid, is present in the 160° product, and that sulphonation at 140° leads to the formation of a product differing greatly from that obtained at 160°, owing no doubt to the presence of an increased proportion of the 1:3′-acid and almost entire absence of the [β-]acid.

Preparation.—(1) To separate the two isomerides the hot aqueous solution of the product obtained by heating naphthalene with five times its weight of concentrated sulphuric acid at 160° for five hours is neutralised either with milk of lime or 'whitening,' then filtered and the filtrate evaporated down. As the solution becomes concentrated, crystalline crusts of the [β-]salt separate out on the surface of the liquid, and must be removed from time to time; ultimately the concentrated solution is strained boiling hot, and then evaporated to complete dryness. It is an advantage to heat the dry calcium salt at 200–230° for some hours to ensure the dehydration of the [β-]salt, on which the success of the subsequent extraction with water depends. The powdered salt is then added to boiling water, which readily dissolves the [α-]salt, the very sparingly soluble [β-]salt is rapidly filtered off, and the filtrate concentrated if necessary, and put aside to crystallise, when almost pure [α-]salt is deposited. This may be obtained pure and free from [β-]salt by a repetition of the process; the mother-liquors contain, in addition to [α-]salt, the very soluble calcium salt of any 1:3′-disulphonic acid which may have been present in the sulphonation product. A certain proportion of the [β-]salt remains with the calcium sulphate filtered off after neutralisation; this is extracted by prolonged boiling with large quantities of water, and the solution evaporated. The residue, together with the crude [β-]salt previously obtained, is heated at 200–230° as before, then finely powdered and carefully washed to remove any adhering [α-]salt. The pure calcium salts so obtained may be converted into potassium or sodium salts in the usual way.

(2) Advantage may be taken of the difference in solubility of the calcium salts of the [α-], [β-], and 1:3′-acids in concentrated brine to effect a separation, since the [β-]salt is practically insoluble in hot and cold, the [α-]salt tolerably soluble in hot but very sparingly soluble in cold, and the 1:3′-salt fairly soluble in cold brine. The amount of brine required varies with the proportion of [α-] and [β-]salts in the product. With the product from 200 kilos. of naphthalene at 160° either of the following two methods may be employed. (*a*) The solution of the mixed calcium salts is concentrated, if necessary, to about 3000 litres, and, after the addition of 900 kilos. of common salt, heated to boiling and filtered hot from the separated [β-]salt. On cooling to 15°, pure [α-]salt crystallises out as a thick magma of slender needles, and after filter-pressing may be converted into potassium salt in the usual way. The mother-liquor on concentration, after removal of the common salt which separates during the evaporation, yields on cooling the calcium salt of the 1:3′-acid mixed with a little [α-]salt. (*b*) The solution is concentrated to about 1000 litres, filtered from the separated [β-]salt and gypsum, and, after the addition of 200 kilos. of salt to the warm solution, allowed to cool and crystallise. The impure [α-]salt is filter-pressed, the press-cakes extracted with 7–10 times the weight of hot saturated brine, and the solution filtered hot from the insoluble [β-]salt. Pure [α-]salt crystallises from the filtrate on cooling, and the latter may be repeatedly employed for the same purpose, the common salt being finally recovered by evaporation (Chem. Fabrik Grünau, Landshoff and Meyer, Germ. pat. 48053 of Nov. 6, 1888).

Salts.—The *acid* crystallises in long, lustrous, deliquescent white needles, very soluble in water. The *lead* salt, $PbA + 2H_2O$, crystallises in long, lustrous needles, and is very soluble in water; the *barium* salt, $BaA + 2H_2O$, forms long, broad needles, soluble in 82·2 parts of water at 19°; the *calcium* salt, CaA, crystallises in needles with varying amounts of water, separating from a rapidly cooled hot saturated solution with $3H_2O$, and from a slowly cooled solution with $6H_2O$; the latter slowly effloresces on exposure to the air losing 2 mols. H_2O, and dissolves in 6·2 parts of water at 18°; the *potassium* salt, $K_2A + 2H_2O$, crystallises from a hot saturated solution in colourless transparent needles, soluble in 1·4 parts of water at 18°;

the *sodium* salt, $Na_2A + 6H_2O$, forms large lustrous needles, soluble in 2·2 parts of water at 18°, and is slightly efflorescent in the air.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 2:2′-*naphthalenedisulphonic chloride*, which crystallises from benzene in large, colourless, four- or six-sided prisms. These frequently, but not invariably, become opaque after removal from the mother-liquor, but the crystals obtained from ether or acetic acid remain transparent. The chloride dissolves in 7·5 parts of benzene at 14°, melts at 157–158°, and on distillation with phosphorus pentachloride at 210° yields 2:2′-*dichloronaphthalene* (Ebert and Merz, *l.c.*; Cleve, Bl. 26, 244).

(2) Fusion of the sodium salt with caustic soda results in the production of 2:2′-*β-naphtholsulphonic acid* ([δ-] or F-acid) or 2:2′-*dihydroxynaphthalene*, according to the conditions employed (Ebert and Merz, B. 9, 610; Cassella & Co., Germ. pat. 42112).

(3) On nitration with nitrosulphuric acid 2:2′-naphthalenedisulphonic chloride is converted into a mixture of *mono-* and *di-nitro-*acids, the former of which by reduction yields Alén's α-naphthylamine-[α-]disulphonic acid (Alén, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1883, N:o 8, 3, 13).

(iv) **2:3′-Naphthalenedisulphonic acid** ([β-] naphthalenedisulphonic acid of Ebert and Merz).

Formation and preparation.—*v.* 2:2′-Naphthalenedisulphonic acid.

Salts.—The *acid* forms small, glistening, deliquescent white scales, extremely soluble in water. The normal salts contain less water of crystallisation, crystallise less readily, and are less soluble than the corresponding salts of the 2:2′-acid; the lead, barium, and calcium salts of the 2:3′-acid are characterised, moreover, by the slowness with which they again dissolve when once separated from solution. The *lead* salt, $PbA + H_2O$, separates in microcrystalline crusts; the *barium* salt, $BaA + H_2O$, also forms microcrystalline crusts, and closely resembles the calcium salt, except that it is more soluble in hot than in cold water; the *calcium* salt, CaA, contains when air-dry from 1–1·5 p.c. of water, forms microcrystalline crusts, and, as it is equally soluble in hot and cold water, does not crystallise from a saturated solution on cooling; it is soluble to the extent of 16·2 parts of water at 18°, but dissolves with very great difficulty when it has once been dried. The *potassium* salt, K_2A, crystallises in tufts of white, anhydrous needles soluble in 19·2 parts of water at 18°; the *sodium* salt, $Na_2A + H_2O$, crystallises in aggregates of microscopic prisms soluble in 8·4 parts of water at 19°.

Reactions.—(1) When warmed with phosphorus pentachloride, the dry potassium salt is converted into 2:3′-*naphthalenedisulphonic chloride*, which crystallises from benzene in tufts of small white needles, soluble when pure in 220·7 parts of benzene at 14°, but much more soluble in the presence of the 2:2′-chloride. It melts at 226°, and on distillation with phosphorus pentachloride at 240–250° yields 2:3′-*dichloronaphthalene* (Ebert and Merz, *l.c.*; Cleve, Bl. 26, 245).

(2) Fused with caustic potash, the potassium salt is converted first into 2:3′-*β-naphtholsulphonic acid* and finally into 2:3′-*dihydroxynaphthalene* (Ebert and Merz, *l.c.*; Armstrong and Graham, C. J. 39, 141; Emmert, A. 241, 369).

(3) 2:3′-Naphthalenedisulphonic chloride, on nitration with nitrosulphuric acid, yields an α-*nitro*-acid, convertible by reduction into Alén's α-naphthylamine-[β-]disulphonic acid (Alén, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1883, N:o 8, 21).

(v) **1:3-Naphthalenedisulphonic acid.**

Formation.—This acid is obtained from 2:1′:3′-β-naphthylaminedisulphonic acid (amido-G.-acid) (Armstrong and Wynne, C. J. Proc. 1890, 13), or 2:2′:4′-β-naphthylaminedisulphonic acid (Armstrong and Wynne, C. J. Proc. 1890, 129), by conversion into the hydrazinedisulphonic acid and subsequent treatment with boiling copper sulphate solution.

Preparation.—Amido-G.-acid is diazotised at a temperature not exceeding 5°, and the resulting yellow diazo- compound pressed and then boiled with alcohol until completely decomposed. The residue left after recovery of the alcohol is converted into sodium salt in the usual way (*cf.* B. A. S. F., Germ. pat. Anm. B 10457 of 1890).

Salts.—The *barium* salt, $BaA + 4H_2O$, forms microcrystalline granules and is very soluble in water; the *potassium* salt, $K_2A + 2H_2O$, crystallises in small prisms very soluble in water; the *sodium* salt is extremely soluble in water.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:3-*naphthalenedisulphonic chloride*, which crystallises from benzene in very soluble prisms, melts at 137°, and on distillation with phosphorus pentachloride at 210° yields 1:3-*dichloronaphthalene*.

(2) Digestion with aqueous caustic soda at 200–220° converts the sodium salt into 1:3-*α-naphtholsulphonic acid* (B. A. S. F., *l.c.*), whilst fusion with caustic potash readily converts it into a *trihydroxynaphthalene* melting at 121° (Armstrong and Wynne, C. J. Proc. 1890, 136).

(vi) **1:2′-Naphthalenedisulphonic acid.**

Preparation.—This acid can be obtained from α-naphthylaminedisulphonic acid No. II. of Dahl & Co.'s Germ. pat. 41957, by the hydrazine reaction (Armstrong and Wynne, C. J. Proc. 1890, 126).

Salts.—The *potassium* salt, $K_2A + H_2O$, forms microcrystalline granules, readily soluble in water.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:2′-*naphthalenedisulphonic chloride* which crystallises from acetic acid in sparingly soluble thin lustrous scales, melts at 122°·5, and on distillation with phosphorus pentachloride at 210° yields 1:2′-*dichloronaphthalene*.

NAPHTHALENETRISULPHONIC ACIDS.

2:4:2′-Naphthalenetrisulphonic acid.

Preparation.—(1) Naphthalene in coarse powder is treated with 3½–4 times its weight of chlorosulphonic acid as in the preparation of 1:4′-naphthalenedisulphonic acid, and, after the evolution of hydrogen chloride has slackened, the mixture is heated at 150–155° for an hour.

The syrupy product is dissolved in water, freed from sulphuric acid derived from the excess of chlorosulphonic acid by neutralisation with lead carbonate, and finally converted into sodium salt (Armstrong and Wynne, C. J. Proc. 1887, 146).

(2) Dry potassium 1:3′- or 2:2′-naphthalenedisulphonate is heated with 1½ times its weight of chlorosulphonic acid at 150–155° for five hours, the product added to about twice its bulk of water, cooled, filtered from the separated acid potassium sulphate and converted into sodium salt as just described.

Salts.—The *lead* salt forms a microcrystalline powder very soluble in water; the *sodium* salt, $Na_3A + 5H_2O$, crystallises in aggregates of very slender needles extremely soluble in water.

Reaction.—Treatment with phosphorus pentachloride converts the dry sodium salt into 2:4:2′-*naphthalenetrisulphonic chloride*, which crystallises from benzene in small prisms melting at 194°.

Naphthalenetrisulphonic acid (Gürke and Rudolph, Germ. pat. 38281 of Sept. 2, 1885; Eng. pat. 15716 of 1885).

Preparation.—This acid is obtained when (*a*) 1 part of naphthalene is heated with 8 parts of 24 p.c. anhydrosulphuric acid at 180° for some hours, or (*b*) 1 part of naphthalene is mixed with 6 parts of 40 p.c. anhydrosulphuric acid at a temperature not exceeding 80°, and then heated on a water-bath until the anhydride has disappeared. It is also formed when naphthalene-mono- and- di[1]-sulphonic acids or their salts are sulphonated with a proportionately smaller quantity of anhydrosulphuric acid, and when chlorosulphonic acid is employed in place of anhydrosulphuric acid. The product after dilution is neutralised with milk of lime and converted into sodium salt which may be purified by fractional crystallisation from water or by extraction with alcohol of 80° Tralles.

Reactions.—The sodium salt yields a mixture of *naphtholdisulphonic acids* when heated with aqueous caustic soda (1:1) at 170–180° (Gürke and Rudolph, Germ. pat. Anm. G 3636), and a *dihydroxynaphthalenesulphonic acid* on fusion with caustic soda at 250° (Actieng. f. A., Germ. pat. 42261).

Gürke and Rudolph's acid is a mixed product and contains at least two naphthalenetrisulphonic acids, the chief constituent being in all probability the 2:4:2′-acid described above, and the second a derivative of 2:3′-naphthalenedi-sulphonic acid.

NAPHTHALENETETRASULPHONIC ACIDS.

Naphthalenetetrasulphonic acid.

Preparation.—(1) Naphthalene is heated with concentrated sulphuric acid and phosphoric anhydride at 260° for 3–4 hours, and the product after dissolution in water is neutralised with barium carbonate. The solution of the barium salt is evaporated at a temperature not exceeding 30–35°, and preferably at the ordinary temperature, so long as a uniform crystallisation of prisms takes place; the mother-liquor contains the barium salt of an isomeric acid. The separation may also be effected by fractional crystallisation of the copper salt, the less soluble blue prisms corresponding with the less soluble prismatic barium salt, the more soluble green crystals with the soluble isomeric barium salt Senhofer, B. 8, 1486; M. 3, 111).

(2) The acid yielding the blue copper salt is obtained when naphthalene is heated with five times its weight of 40 p.c. anhydrosulphuric acid at 160° for nine hours. The product is dissolved in water, neutralised with lime and converted into sodium salt in the usual way (Bayer & Co., Germ. pat. 40893 of Dec. 7, 1886).

Salts.—Senhofer's *acid*, yielding the blue copper salt and prismatic barium salt, crystallises in prisms which retain 4 mols. H_2O at 100° and is very soluble in water. The *copper* salt, $Cu_2A + 12H_2O$, crystallises in massive blue prisms, very soluble in hot water; the *barium* salt, Ba_2A, in thick, obliquely truncated prisms with 7, 10, 13, or 15 mols. H_2O, according to the temperature at which crystallisation occurs; the *potassium* salt, $K_4A + 2H_2O$, in tufts of slender needles very soluble in water; the *sodium* salt, $Na_4A + 10H_2O$, in four-sided, efflorescent prisms.

Reactions.—On fusion with caustic soda, the sodium salt of Bayer & Co.'s acid yields at 180° a *naphtholtrisulphonic acid*, and at 250° a *dihydroxynaphthalenedisulphonic acid* (Bayer & Co., *l.c.*)

The isomeric naphthalenetetrasulphonic acid mentioned by Senhofer has not been obtained in a state of purity.

III. NITRO-DERIVATIVES.

Introductory.—The first nitro- derivatives of naphthalene were prepared by Laurent (A. Ch. [2] 59, 376; 66, 152; *cf.* Gmelin's Chemistry, Eng. ed. 14, 82 *et seq.*) who described α-nitronaphthalene in 1835 under the name nitronaphthalase. A dinitro- and three tri-nitronaphthalenes were also obtained by him, but later investigation has shown that with one exception, the so-called nitronaphthalise now identified as [β-]trinitronaphthalene (*cf.* Lautemann and Aguiar, Bl. 8, 261), these were impure substances. It is now recognised that one mono-, two di-, three tri-, and two tetranitronaphthalenes may be obtained from naphthalene by nitration under suitable conditions (*cf.* Beilstein and Kuhlberg, A. 169, 81). Mononitro- derivatives formed by the direct nitration of naphthalene and its derivatives are α- compounds with the one possible exception of Andresen's β-nitronaphthalenedisulphonic acid produced in the nitration of 1:3′-naphthalenedisulphonic acid (Schultz, B. 23, 77). Further nitration results in the production of αα- compounds in the case of naphthalene and αβ- compounds in the case of the naphthylamines and naphthols. It is noteworthy, as an illustration of the difference between benzene and naphthalene, that whereas the former yields metadinitrobenzene as chief product by further nitration of nitrobenzene, the latter forms two *heteronucleal* αα-dinitronaphthalenes by the further nitration of α-nitronaphthalene.

The nitronaphthalenesulphonic acids are described in connection with α-nitronaphthalene in this section, the nitronaphthylamines and nitronaphthols in connection with the corresponding naphthylamines and naphthols (*q. v.*).

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[1] Presumably the 2:2′- and 2:3′-naphthalenedisulphonic acids, to judge from the date of the patent.

The nitronaphthalenes and nitronaphthalenesulphonic acids are converted by reduction, usually with iron or zinc and sulphuric acid, into the corresponding amido- derivatives, and this reaction is employed on the large scale for the production of α-naphthylamine, Cleve's α-naphthylaminesulphonic acid, and the [ε-] and [S.] α-naphthylaminedisulphonic acids.

NITRONAPHTHALENES.

(i) **α-Nitronaphthalene** $C_{10}H_7NO_2$.

Preparation.—(1) In the laboratory, α-nitronaphthalene is best prepared by Piria's method (A. 78, 82; *cf.* Beilstein and Kuhlberg, A. 169, 81). Powdered naphthalene is gradually mixed with five to six times its weight of nitric acid (sp.gr. = 1·33), and the action allowed to continue in the cold with frequent stirring. After an interval of three weeks or more, the product is filtered off, washed from acid, dried, ground up with a little alcohol, pumped dry, and finally extracted with cold carbon bisulphide. Any dinitronaphthalene is by this treatment left undissolved. Pure α-nitronaphthalene is obtained from the filtrate by distilling off the carbon bisulphide and crystallising the residue from alcohol. Less time is required if a stronger acid or a higher temperature is employed—for example, five to six days only are required with the same weight of nitric acid (sp.gr. = 1·4) at a temperature of 50–60°—but in consequence of the readiness with which α-nitronaphthalene undergoes further nitration, a very considerable increase in the percentage of dinitronaphthalene is always experienced under such conditions.

(2) On the large scale, where quantities of nitric acid not greatly exceeding the theoretical are employed, special precautions have to be taken to ensure complete nitration with a minimum production of dinitronaphthalene, otherwise the result would be a technically worthless mixture of α-nitronaphthalene with dinitronaphthalene and unattacked hydrocarbon. The nitration vessel is a wide, shallow, cast-iron cylinder surrounded by a water-jacket for cooling purposes, and fitted with a stirrer having four to six vanes set at an angle of 45°. A hinged cover is so arranged that one-half can be raised like a lid to admit of the introduction of the naphthalene, whilst the other is clamped to the cylinder, and carries an exit pipe for the escaping gases, the lower portion of the pipe being steam-jacketed so that the sublimed naphthalene collecting in it may be fused down from time to time. A charge of 200 kilos. of nitric acid of 40°Bé., 200 kilos. of sulphuric acid of 66°Bé., and 600 kilos. of spent acid from a previous operation is placed in the cylinder, the stirrer set in motion, and 250 kilos. of finely-powdered naphthalene added gradually through a sieve. Reaction at once ensues, and by regulating the flow of water through the cooler, and the rate at which the hydrocarbon is added, the temperature is maintained at 45–50° throughout the operation. Under these conditions, nitration proceeds smoothly, and is completed, with the quantities given, at the end of a day. The contents of the cylinder are then run into lead-lined troughs to cool, the spent acid run off from the solid cake of nitronaphthalene, and the latter freed from acid by washing with hot water and granulated by allowing it to flow in a thin stream into cold water kept constantly stirred. The product forms citron-yellow granules, which should be destitute of odour, and yield no trace of naphthalene when boiled with water. It needs no further treatment if required for the preparation of α-naphthylamine, but if for sale, it may be crystallised. For this purpose it is fused on a water-bath and mixed with one-tenth its weight of cumene or solvent naphtha. The solution remains liquid for a considerable time, during which it may be freed from mechanical impurities by filtration, and dried by warming with fused calcium chloride; when left to itself it slowly crystallises. The crystalline cake of nitronaphthalene is freed from solvent by hydraulic pressure, and the impure substance remaining in solution is recovered by removing the solvent by steam distillation (Witt, Chem. Ind. 10, 216; D. P. J. 265, 227).

Properties.—α-Nitronaphthalene crystallises in long, slender, lustrous needles, melts at 58·5° (Beilstein and Kuhlberg, A. 169, 82), at 61° (Aguiar, B. 5, 371), boils at 304° (Koninck and Marquart, B. 5, 12), and is practically non-volatile with steam. It dissolves in 35·6 parts of 87·5 p.c. alcohol at 15°, and is readily soluble in benzene, carbon bisulphide, ether and hot alcohol.

Reactions.—(1) On distillation with phosphorus pentachloride it yields *α-chloronaphthalene* (Koninck and Marquart, B. 5, 11).

(2) Nitration converts it into 1:1′- and 1:4′-*dinitro-*, [α-] or [γ-]*trinitro-*, or [α-]*tetranitronaphthalene*, according to the conditions employed (*v. infra*).

(3) Chromic acid in acetic acid solution oxidises it to *α-nitrophthalic acid* and *ortho-nitrophthalid* (Beilstein and Kurbatow, A. 202, 217).

(4) Reduction with powerful reducing agents such as tin and hydrochloric acid (Roussin, C. R. 52, 797) converts α-nitronaphthalene into *α-naphthylamine*. In alcoholic solution with sodium amalgam *azoxynaphthalene* is formed (Jaworsky, J. pr. 94, 285). Distillation with zinc-dust converts it into *αβ-naphthazine* (Laurent's naphthase) (Doer, B. 3, 291; Klobukowsky, B. 10, 573; Witt, B. 19, 2794).

(5) On sulphonation with anhydrosulphuric acid it yields a mixture of 1:4′-, 1:3′, and 1:2′-*α-nitronaphthalenesulphonic acids*, the first named being the chief product (Palmaer, B. 21, 3260).

(6) When finely divided sulphur is carefully added to about 4 times its weight of α-nitronaphthalene heated at 200–220°, considerable quantities of sulphur dioxide are evolved, and an impure green dye-stuff, 'naphthylthiazin' of unknown constitution obtained (Bennert, Germ. pat. 48802 of Oct. 23, 1888).

SULPHONIC ACIDS.

α-Nitronaphthalenesulphonic acids are obtained either by the sulphonation of α-nitronaphthalene, or by the nitration of naphthalenesulphonic acids.

α-NITRONAPHTHALENESULPHONIC ACIDS.

(i.) 1:4′-**α-Nitronaphthalenesulphonic acid**[1] (Cleve's [α-]nitronaphthalenesulphonic acid).

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[1] In every case where the constitution of an α-nitronaphthalenesulphonic acid is given, the nitro- group is supposed in the position '1.'

Preparation.—(1) On the large scale this acid is prepared by gradually adding 20 kilos. of finely divided dry α-nitronaphthalene to a mixture of 35 kilos. of sulphuric acid of 66°Bé. and 25 kilos. of 24 p.c. anhydrosulphuric acid at such a rate that the temperature does not rise beyond 90°. When all is added the temperature is maintained at 90° for 8 hours or until sulphonation is completed. The acid is then poured on to an equal weight of ice, and separates as a sparingly soluble crystalline mass, which, without further purification, is employed in the preparation of the corresponding amido-acid.

The crystallised acid so obtained is pure, but the acid mother-liquor in all probability contains impurities in the form of isomeric acids. Palmaer (B. 21, 3260) finds that in addition to the 1:4′-acid a certain proportion of the 1:3′- or [β-] and 1:2′- or [θ-] acids is also formed when α-nitronaphthalene is heated with a mixture of 2 parts of ordinary and 1 part of 'fuming' sulphuric acid at 100° for 10 hours or until sulphonation is completed. The greater part of the 1:4′-acid crystallises from the solution obtained by pouring the product into water. The filtrate, after neutralisation with chalk and concentration, yields a mixed crystallisation of the 1:4′- and 1:3′- calcium salts, whilst the mother-liquor contains a further quantity of the 1:3′-salt mixed with 1:2′-salt. The separation of these mixed salts is effected by fractional crystallisation of the sulphochlorides (*v. infra*).

(2) The 1:4′-acid is formed together with a large, perhaps equal, proportion of the 1:1′-acid (Schöllkopf Co., Germ. pat. 40571) and some 1:4-acid (Cleve, B. 23, 958) by nitrating sodium naphthalene-α-sulphonate. According to Cleve, 1 kilo. of sodium α-naphthalenesulphonate is gradually added to a mixture of 750 grams of nitric acid (sp.gr. = 1·4) and 500 grams of nitric acid (sp.gr. = 1·5), and the product subsequently diluted with water, neutralised with chalk, and filtered hot. The filtrate on cooling gives a considerable separation of pure 1:4′-salt. To separate the remainder from the salts of the isomeric acids the mother-liquor is concentrated and a further separation of calcium salt obtained. This is decomposed with sulphuric acid, and the solution evaporated to the crystallising-point in order to separate a further quantity of the 1:4′-acid; the mother-liquor is then neutralised with potassium carbonate, the solution concentrated, and the successive fractions of the potassium salt treated with phosphorus pentachloride. The first fractions give almost pure 1:4′-nitronaphthalenesulphonic chloride, the later fractions yield mixtures from which the chloride of the 1:4-acid can be obtained by crystallisation from benzene and petroleum spirit. The mother-liquor of the calcium salt contains the 1:1′-acid.

(3) The 1:4′-acid is said to be the only acid formed when α-nitronaphthalene is sulphonated with chlorosulphonic acid (Armstrong and Williamson, C. J. Proc. 1886, 233); 10 parts of α-nitronaphthalene are added to 26 parts of 20 p.c. anhydrosulphuric acid, which has been previously treated with a quantity of fused salt sufficient to convert the dissolved anhydride into chlorosulphonic acid, and the mixture heated on a water-bath for 12 hours or until sulphonation is completed (Erdmann, A. 247, 311).

Salts. — The *acid*, $NO_2.C_{10}H_6.SO_3H + 4H_2O$, crystallises in flat, pale-yellow needles, and dissolves readily in hot and cold water, but is very sparingly soluble in tolerably dilute sulphuric acid. The *barium*, $BaA_2 + 3H_2O$, and *calcium* salt, $CaA_2 + 2H_2O$, crystallise in slender needles, sparingly soluble in cold water; the *potassium* salt, $KA + H_2O$, forms brown hexagonal tables soluble in 47 parts of water at 15°; the *sodium* salt, $NaA + \frac{1}{2}H_2O$, crystallises in very soluble tables.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:4′-*nitronaphthalenesulphonic chloride*, which crystallises from ether in brilliant needles, melts at 113°, and on distillation with phosphorus pentachloride yields 1:4′-dichloronaphthalene (Cleve, Bl. 24, 510; Öfvers. af Kongl. Vetensk.-Akad. Förh. 1875, N:o 9, 13; 1876, N:o 9, 71).

(2) On reduction with ammonium sulphide, zinc or iron and sulphuric acid, &c., it is converted into 1:4′-α-*naphthylaminesulphonic acid*, (Cleve, *l.c.*, Erdmann, A. 247, 316). Reduction with sodium amalgam results in the formation of α-naphthylamine and sulphuric acid (Claus, B. 10, 1303).

(ii) **1:1′-α-Nitronaphthalenesulphonic acid.**

Preparation. — Formed together with the 1:4′- and 1:4-acids by the nitration of sodium naphthalene-α-sulphonate (*v. supra*). Neither the acid nor its salts have been described.

Reactions.—(1) Phosphorus pentachloride reacts energetically with the potassium salt causing carbonisation. If the potassium salt is suspended in carbon bisulphide and treated with the chloride, 1:1′-*chloronaphthalenesulphonic chloride* is formed, which crystallises from acetic acid in colourless thin scales, and melts at 101° (Cleve, B. 23, 962).

(2) On reduction, it yields 1:1′-α-*naphthylaminesulphonic acid*, the S.-acid of the Schöllkopf Co.'s Germ. pat. 40571 (Erdmann, A. 247, 318).

(iii) **1:4-α-Nitronaphthalenesulphonic acid.**

Preparation.—Formed together with the 1:4′- and 1:1′-acids by the nitration of sodium naphthalene-α-sulphonate (*v. supra*), and obtained as barium salt from its chloride by boiling with baryta water (Cleve, B. 23, 959).

Salts.—The *acid* is a soluble yellow crystalline substance. The *barium* salt, $BaA_2 + H_2O$, crystallises in needles and dissolves in 66 parts of cold and 33 parts of boiling water; the *calcium* salt, $CaA_2 + 2H_2O$, crystallises in silvery scales and dissolves in 37 parts of water at 17° and 16 parts at 100°; the *potassium* salt, KA, crystallises in silvery anhydrous needles and is sparingly soluble in cold water; the *sodium* salt, $NaA + H_2O$, forms extremely soluble thin needles.

Reactions.—(1) On treatment with phosphorus pentachloride it yields 1:4-*nitronaphthalenesulphonic chloride*, which crystallises from benzene in large, yellowish prisms melting at 99°.

(2) Reduction with ammonium sulphide converts it into 1:4-α-*naphthylaminesulphonic acid* (Cleve, B. 23, 960).

(iv.) **1:3′-α-Nitronaphthalenesulphonic acid** (Cleve's [β-]nitronaphthalenesulphonic acid).

Preparation.—(1) This acid is formed together with a considerable proportion of 1:2′

and some 1:3-α-nitronaphthalenesulphonic acids, by nitrating sodium naphthalene-β-sulphonate (strength of acid and conditions not stated, but presumably identical with those employed in the nitration of sodium naphthalene-α-sulphonate, for which *v.* 1:4′-acid). The product is neutralised with baryta and the mixed barium salt repeatedly extracted with boiling water. The residue consists of the sparingly soluble 1:3′-salt. The first extractions contain chiefly the readily soluble 1:2′-salt, the later extractions the moderately soluble 1:3-salt together with some 1:3′-salt. By conversion of the mixed barium salts into potassium salts and treatment with phosphorus pentachloride, the corresponding chlorides are obtained, and are separated by fractional crystallisation. The chloride of the 1:2′-acid is sparingly soluble in carbon bisulphide, and is purified by repeated extraction with this solvent until it has a constant melting-point of 169°. The chlorides of the 1:3′- and 1:3-acids crystallise from acetic acid in large yellow prisms and slender pale-yellow needles, and are separated mechanically (Cleve, Bl. 26, 444; 29, 414; B. 19, 2179).

(2) The 1:3′-acid occurs in the product obtained by sulphonating α-nitronaphthalene with anhydrosulphuric acid (*v.* 1:4′-acid *supra*).

Salts.—The *acid* crystallises in readily soluble, radiate, brown needles, and yields brownish-yellow salts. The *barium* salt, $BaA_2 + H_2O$, forms slender needles soluble in 782 parts of water at 22°, and sparingly soluble in boiling water; the *calcium* salt, $CaA_2 + H_2O$, forms tolerably soluble scales; the *potassium* salt, KA, crystallises in brilliant, slender, anhydrous tables sparingly soluble in cold water; the *sodium* salt, $NaA + 3H_2O$, crystallises in crusts consisting of scales, and is tolerably soluble in water.

Reactions.—(1) On treatment with phosphorus pentachloride, it yields 1:3′-*α-nitronaphthalenesulphonic chloride*, which crystallises from benzene in brilliant monoclinic prisms, (*cf.* Palmaer, B. 21, 3263), melts at 125·5°, and on distillation with phosphorus pentachloride gives 1:3′-dichloronaphthalene (Cleve, Bl. 26, 446).

(2) On reduction with ammonium sulphide it is converted into the corresponding 1:3′- or [β-]*α-naphthylaminesulphonic acid* (*ibid.*).

(3) On nitration with a mixture of fuming nitric and concentrated sulphuric acid the chloride is converted into a *dinitronaphthalenesulphonic chloride* (probably $NO_2 : NO_2 : SO_2Cl =$ 1:1′:3′] melting at 145° (Hellström, Öfvers. af Kongl. Vetensk-Akad. Förh. 1888, 613).

(v) **1:2′-α-Nitronaphthalenesulphonic acid** (Cleve's [θ-]nitronaphthalenesulphonic acid).[1]

Preparation.—This acid is formed together with the 1:3′-acid when sodium naphthalene-β-sulphonate is nitrated, and with the 1:4′-acid when α-nitronaphthalene is sulphonated with anhydrosulphuric acid (*q. v.*). It is obtained from its chloride by heating with water at 130°.

Salts.—The *acid* forms very soluble brown needles. The *barium* salt, $BaA_2 + 3\frac{1}{2}H_2O$, forms granular aggregates consisting of needles, and when anhydrous dissolves in 377 parts of water at 17°, and in 9·1 parts of boiling water; the *calcium* salt forms very soluble needles; the *potassium* salt, $KA + \frac{1}{2}H_2O$, crystallises in yellow needles readily soluble in hot and cold water; the *sodium* salt forms extremely soluble, spherical aggregates of needles (Palmaer, B. 21, 3261).

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:2′-*α-nitronaphthalenesulphonic chloride*, which crystallises in well-formed prisms, dissolves sparingly in carbon bisulphide and acetic acid, melts at 169°, and on distillation with phosphorus pentachloride gives 1:2′-dichloronaphthalene (Cleve, Bl. 29, 414; Armstrong and Wynne, C. J. Proc. 1889, 19).

(2) On reduction, it yields 1:2′- or [θ-] *α-naphthylaminesulphonic acid* (Cleve, B. 21, 3264).

(vi) **1:3-α-Nitronaphthalenesulphonic acid** (Cleve's [γ-]nitronaphthalenesulphonic acid).

Preparation.—This acid is formed together with the 1:3′-acid (*q. v.*) when sodium naphthalene-β-sulphonate is nitrated, and is obtained from its chloride by boiling with water (Cleve, B. 19, 2179; *cf.* Armstrong and Wynne, C. J. Proc. 1889, 19).

Salts.—The *barium* salt, $BaA_2 + 3H_2O$, forms small, pale-yellow needles; the *potassium* salt, KA, forms sparingly soluble slender needles; the *sodium* salt crystallises in tolerably soluble, slender needles.

Reactions.—(1) Treatment with phosphorus pentachloride converts the dry potassium salt into 1:3-*α-nitronaphthalenesulphonic chloride*, which crystallises in small, pale-yellow needles, is very sparingly soluble in acetic acid when pure, melts at 140°, and on distillation yields a dichloronaphthalene melting at 61° (Cleve), which by exclusion must be the 1:3-isomeride.

(2) On reduction, it yields the 1:3- or [γ-] *α-naphthylaminesulphonic acid* (Cleve, B. 21, 3271).

α-NITRONAPHTHALENEDISULPHONIC ACIDS.

(i) **1:1′:3-α-Nitronaphthalenedisulphonic acid.**

Preparation.—(1) This acid is formed as chief product, together with some β-nitronaphthalene-1:3′-disulphonic acid (Schultz, B. 23, 77), by nitrating 1:3′-naphthalenedisulphonic acid or its salts. On the large scale, the product obtained by sulphonating 50 kilos. of sodium naphthalene-β-sulphonate with 2½–3 times its weight of 20 p.c. anhydrosulphuric acid at 100° is cooled to 10–15°, and nitrated by adding 22½ kilos. of nitric acid (sp.gr. = 1·4) at such a rate that the temperature does not rise above 20–25°. The nitration is complete in about two hours, and the product, after dilution with 5–10 vols. of water, partial neutralisation with milk of lime and filtration, is ready for reduction with iron borings or zinc-dust (Ewer & Pick, Germ. pat. 52724 of Sept. 16, 1888).

(2) It is also obtained, together with 1:1′:4-α-nitronaphthalenedisulphonic acid, when the mixture of 1:3′- and 1:4′-disulphonic acids formed by sulphonating 20 kilos. of naphthalene with 100 kilos. of 23 p.c. anhydrosulphuric acid is cooled with ice and nitrated by the careful addition of

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[1] This acid was originally termed [δ-] by Cleve, and is so described in his communication to the Paris Chemical Society (Bl 29, 414). In the Swedish paper (Öfvers. af Kongl. Vetensk.-Akad. Förh., 1878 N:o 2, 32), which is practically identical with the French, the term [θ-] is employed, since 'the acid yields a new dichloronaphthalene which being the eighth known is distinguished as θ.'

14 kilos. of nitric acid of 45°Bé. In this case the product is poured into 1,000 litres of water, rendered slightly alkaline with milk of lime, and filtered; it is then ready for reduction with iron and sulphuric acid. A separation of the nitro-acids is not attempted, that of the amido- acids being very readily accomplished (Actieng. f. A., Germ. pat. 45776 of March 16, 1887; Eng. pat. 4625 of 1888).

Salts.—The *potassium* salt crystallises in slender, yellow needles, somewhat sparingly soluble in water, and insoluble in dilute aqueous potash; the *sodium* salt crystallises similarly, and is more soluble (Ewer & Pick, *l.c.*).

Reaction.—On reduction, the acid is converted into *α-naphthylamine*-[ε-]*disulphonic acid.*

(ii) 1:1′:4 - α - **Nitronaphthalenedisulphonic acid** is formed by nitrating 1:4′-naphthalenedisulphonic acid (*v. supra*), and on reduction is converted into the *α-naphthylaminedisulphonic acid* of the Schöllkopf Co.'s Germ. pat. 40571 (Actieng. f. A., Germ. pat. 45776 of Mar. 16, 1888; Bernthsen, B. 22, 3327).

(iii) 1:3:3′ - α - **Nitronaphthalenedisulphonic acid** (Alén's nitronaphthalene-[α-]disulphonic acid).

Preparation.—The *chloride* of this acid is formed, together with dinitronaphthalene-2:2′-disulphonic chloride (m.p. = 218·5–219·5°), by nitrating 2:2′-naphthalenedisulphonic chloride with nitrosulphuric acid at the ordinary temperature, and may be obtained pure by fractional crystallisation from benzene, in which it is the more soluble, and from which it crystallises in small needles melting at 140-141° (Alén, Bl. 39, 63). The chloride is converted into the acid by heating with water at 150°. The salts, like the acid, crystallise in very small needles; the *barium* salt, $BaA + 5H_2O$, is sparingly soluble; the *potassium* salt, $K_2A + 3H_2O$, and *sodium* salt, $Na_2A + 6H_2O$, are readily soluble in water.

Reactions.—(1) Reduction with ammonium sulphide converts it into 1:3:3′-*α-naphthylaminedisulphonic acid*, and with sodium amalgam into *α-naphthylamine* (Alén, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1883, N:o 8, 3).

(2) On distillation of the barium salt with phosphorus pentachloride at 225°, so-called [θ-] *trichloronaphthalene* (m.p. = 76°) is obtained (Alén, *ibid.* 1884, N:o 2, 95), which by exclusion must be the 1:3:3′-derivative.[1]

(iv) 1:3:2′ - α - **Nitronaphthalenedisulphonic acid** (Alén's nitronaphthalene-[β-]disulphonic acid).

Preparation. — 2:3′-Naphthalenedisulphonic chloride, on nitration with nitrosulphuric acid, yields an *α-nitronaphthalene*-2:3′-*disulphonic chloride*, which crystallises from benzene with 1 mol. prop. of benzene in radiate prismatic groups, melts at 190–192°, and yields the acid on heating with water at 130-150°. The *barium* salt, $BaA + 2H_2O$, crystallises in small tables sparingly soluble in hot water; the *potassium* salt, K_2A, crystallises in anhydrous needles sparingly soluble in cold, tolerably soluble in hot water.

Reactions.—(1) Reduction with ammonium sulphide converts it into 1:3:2′-*α-naphthylaminedisulphonic acid*, and with sodium amalgam into *α-naphthylamine* (Alén, *ibid.* 1883, N:o 8, 21).

(2) On distillation of the chloride with phosphorus pentachloride at 200°, so-called [η-]*trichloronaphthalene* (Alén, *l.c.*; *ibid.* 1884, N:o 2, 95), identified as the 1:3:2′- derivative (Armstrong and Wynne, C. J. Proc. 1890, 15), is obtained.

β-Nitronaphthalene.

Preparation.—(1) β-Nitronaphthalene is probably formed in small quantity together with α-nitronaphthalene in the nitration of naphthalene with nitrosulphuric acid, since technical α-naphthylamine contains β-naphthylamine in small quantity (Reverdin and Nölting, Sur la constitution de la naphtaline et de ses dérivés, ed. 1888, 33; *cf.*, however, Witt, Chem. Ind. 10, 220).

(2) It is also formed by the diazo- reaction from 1:2-β-nitro-α-naphthylamine (Lellmann and Remy, B. 19, 236; Lellmann, B. 20, 891), and from β-naphthylamine by conversion into β-diazonaphthalene nitrite and subsequent treatment with cuprous oxide (Sandmeyer, B. 20, 1496), the yield in the latter case being about 8 p.c.

Properties.—It crystallises from dilute alcohol in small yellow needles, melts at 79°, has an odour of cinnamon, is volatile with steam, and dissolves readily in alcohol, acetic acid, ether, &c. On reduction with stannous chloride and hydrochloric acid it yields *β-naphthylamine* (Lellmann and Remy, *l.c.*).

DINITRONAPHTHALENES.

(i) 1:4′-**Dinitronaphthalene** ([α-]dinitronaphthalene).

Preparation. — 100 grams of naphthalene are added to 310 c.c. of nitric acid, and the mixture allowed to stand for twenty-four hours; 160 c.c. of sulphuric acid are then added, and the whole heated on a water-bath for a day. The acid mother-liquor, which is practically free from dinitronaphthalene, is poured off and the product powdered, washed with water, dried, and freed from any contained mononitronaphthalene by extraction with carbon bisulphide. The residue, after again drying, is extracted with small quantities of cold acetone, which dissolves practically nothing but [β-]dinitronaphthalene; then repeatedly boiled with acetone until its melting-point rises to 210-212°. The residue consisting of almost pure 1:4′-dinitronaphthalene is finally crystallised from hot xylene. The purification of the [β-]dinitronaphthalene contained in the acetone extracts is extremely troublesome, and is best effected by repeated crystallisation from benzene (Beilstein and Kurbatow, A. 202, 219). As substitutes for acetone, chloroform (Darmstaedter and Wichelhaus, A. 152, 301), benzene (Aguiar, B. 3, 29; Beilstein and Kuhlberg, A. 169, 85), and acetic acid (Aguiar, B. 5, 372), may be employed.

Properties.—1:4′-Dinitronaphthalene crystallises from acetic acid in six-sided yellow needles, and melts at 216° (Aguiar, B. 5, 372); from nitric acid in lustrous, broad needles, and melts

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[1] Pure 1:3:3′-trichloronaphthalene melts at 80–81° (Armstrong and Wynne, C. J. Proc. 1890, 129). The discrepancy is most probably accounted for by the conditions employed by Alén, which would inevitably lead to the production of an impure substance difficult to purify by any method of simple crystallisation. The 1:3:2′-trichloronaphthalene, the alternative compound, melts at 86° and is consequently excluded.

at 211° (Beilstein and Kuhlberg, A. 169, 86). The best solvents are hot xylene, benzene, acetic acid, and turpentine, but it is sparingly soluble in these and all ordinary solvents, and practically insoluble in carbon bisulphide and cold nitric acid.

Reactions.—(1) Distillation with phosphorus pentachloride converts it into 1:4′-*dichloronaphthalene* (Atterberg, B. 9, 1188, 1730).

(2) On nitration, [α-]*tri-*, [γ-]*tri-*, or [α-]*tetranitronaphthalene* result, according to the conditions employed (*cf.* Aguiar, B. 5, 373, 898; Beilstein and Kuhlberg, A. 169, 98). Prolonged heating with dilute nitric acid (sp.gr. = 1·15) at 150° converts it into *α-nitrophthalic acid* and other nitrated benzene derivatives (Beilstein and Kurbatow, A. 202, 221).

(3) Reduction with alcoholic ammonium sulphide converts it first into 1:4′-*amidonitronaphthalene*, and finally into 1:4′-*diamidonaphthalene* (Beilstein and Kuhlberg, A. 169, 87); reduction in alcoholic solution with tin and hydrochloric acid converts it readily into the latter (Erdmann, A. 247, 360).

(4) When heated with concentrated sulphuric acid at 200°, particularly if some zinc is also present, it yields *naphthazarin* ([β-]dihydroxy-[α]-naphthaquinone) and a small quantity of trihydroxy-[α-]naphthaquinone (Liebermann, B. 3, 905; Aguiar and Bayer, B. 4, 251).

(ii) **1:1′-Dinitronaphthalene** ([β-]dinitronaphthalene).

Preparation.—*v.* 1:4′-Dinitronaphthalene.

Properties.—1:1′-Dinitronaphthalene crystallises in large, yellow rhombic tables, and melts at 170° (Aguiar, B. 5, 372). In hot carbon bisulphide, ether, and petroleum spirit it is almost insoluble, and is sparingly soluble in cold, but readily soluble in hot acetic acid, chloroform, alcohol and benzene. According to Beilstein and Kuhlberg (A. 169, 86), one part dissolves in 91·4 parts of chloroform, in 530 parts of 88 p.c. alcohol, and in 139 parts of benzene at 19°.

Reactions.—(1) On distillation with phosphorus pentachloride, it yields 1:1′-*dichloronaphthalene* in small quantity, the chief product being 1:1′:4-*trichloronaphthalene* (Atterberg, B. 9, 1188, 1732).

(2) On nitration, [β-]*tri-* and [β-]*tetra-nitronaphthalene* result, according to the conditions employed (*cf.* Lautemann and Aguiar, Bl. 3, 261; Beilstein and Kuhlberg, A. 169, 99). Prolonged heating with dilute nitric acid (sp.gr. = 1·15) at 150° converts it into a mixture of nitrated benzene derivatives (Beilstein and Kurbatow, A. 202, 225).

(3) Reduction to 1:1′-*diamidonaphthalene* is effected readily by heating with phosphorus iodide and water (Aguiar, B. 3, 29), and in alcoholic solution by tin and hydrochloric acid (Erdmann, A. 247, 363), but with difficulty by means of ammonium sulphide (Beilstein and Kuhlberg, A. 169, 90). No intermediate reduction product is known.

(iii) **1:3-Dinitronaphthalene** ([γ-]dinitronaphthalene) is obtained from dinitro-α-naphthylamine (m.p. = 235°) by diazotising and boiling with alcohol. It crystallises from dilute alcohol in bright-yellow needles, and melts at 144° (Liebermann and Hammerschlag, A. 183, 274).

(iv) [δ-]**Dinitronaphthalene** [(?)1:3′] is obtained from dinitro-β-naphthylamine (m.p. = 238°) by diazotising and boiling with alcohol. It crystallises from alcohol in bright-yellow needles, and melts at 161·5° (Graebe and Drews, B. 17, 1170).

IV. AMIDO- DERIVATIVES.

Introductory.—α-Naphthylamine and several α-naphthylaminesulphonic acids are obtained by reduction of the corresponding nitro- derivatives with iron and hydrochloric acid or zinc and sulphuric acid. β-Naphthylamine and the β-naphthylaminesulphonic acids, with the one exception of Andresen's β-naphthylamine-1:3′-disulphonic acid (*cf.* Schultz, B. 23, 77), cannot, however, be prepared by this method, and are obtained by heating β-naphthol and the corresponding β-naphtholsulphonic acids with ammonia under pressure. As α-naphthylamine can also be prepared from α-naphthol by heating with ammonia, although the yield is less satisfactory than in the case of the β- compound, it is evident that the hydroxynaphthalenes in this respect present a marked contrast to the hydroxybenzenes, since phenol for example remains unaltered when heated with ammonia at 360°, and yields only traces of aniline when heated either with ammonium chloride at 310°, or with ammonia-zinc chloride at 280-300°.

Secondary amidonaphthalenes are formed when the corresponding hydroxynaphthalenes are heated with primary amines under pressure, and a general method for their production is given in the Badische Anilin- und Sodafabrik's Germ. pat. 14612 (of Feb. 22, 1880).

Diamidonaphthalenes are obtained from corresponding dinitro- or dihydroxy-naphthalenes by similar methods, and no fewer than eight of the ten theoretically possible isomerides have been described. With the exception of the 1:2- (ortho) and 1:1′- (peri) derivatives, these diamines yield tetrazo- compounds which by interaction with phenols form disazo- dyes, and it is especially noteworthy that whilst the colours formed from the homonucleal diamines can only be used for wool and are technically worthless, those from the heteronucleal diamines have the property of dyeing unmordanted cotton.

Amidonaphthols and amidonaphtholsulphonic acids are described in connection with the corresponding naphthols (*q. v.*).

AMIDONAPHTHALENES.

α-Naphthylamine $C_{10}H_7.NH_2$ (Zinin's naphthalidam; Piria's naphthalidine).

Formation.—α-Naphthylamine is formed by the reduction of α-nitronaphthalene in alcoholic solution by ammonium sulphide (Zinin, J. pr. 27, 141), iron filings, and acetic acid (Béchamp, A. Ch. [3] 42, 195; Balló, B. 3, 288, 673), tin and hydrochloric acid (Roussin, C.R. 52, 797), zinc and hydrochloric acid (Böttger, D. P. J. 197, 458), and alcoholic potash (Klobukowsky, B. 10, 571). It is also formed, mixed with azoxynaphthalene, when a mixture of zinc-dust and aqueous calcium chloride (b.p. = 103-115°) is added to α-nitronaphthalene heated at 130° (Dechend, Germ. pat. 43230 of Feb. 9, 1887).

It is also obtained when α-naphthol is heated either with strong aqueous ammonia or with the requisite quantity of ammonium chloride and caustic alkali under pressure at 150-160° for 60-70 hours (B. A. S. F., Germ. pat. 14612 of Feb. 22, 1880). The use of dehydrating agents lessens the duration of the reaction, but brings about the formation of dinaphthylamine in quantities varying with the conditions employed. According to Benz (B. 16, 14), α-naphthol yields 55-60 p.c. of α-naphthylamine when heated for eight hours at 270° with twice its weight of anhydrous or hydrated ammonia-calcium chloride,[1] and as much as 74 p.c. when heated under similar conditions with four times its weight of hydrated ammonia-calcium chloride, small quantities of dinaphthylamine being produced, but is converted almost wholly into dinaphthylamine (60-65 p.c.) when heated with four times its weight of ammonia-zinc chloride[2] at 260°. The substitution of acetamide for ammonia by heating α-naphthol with about twice the theoretical quantity of a mixture of anhydrous sodium acetate and ammonium chloride at 270° for eight hours, results in the formation of acet-α-naphthalid corresponding with about 50 p.c. of α-naphthylamine, together with about 15 p.c. of dinaphthylamine (Calm, B. 15, 615).

Synthetically, α-naphthylamine has been prepared by the interaction of furfuran and aniline (Canzoneri and Oliveri, Gazz. Chim. 16, 492).

Preparation.—On the large scale α-naphthylamine is prepared by reducing α-nitronaphthalene with iron borings and hydrochloric acid in an apparatus similar to that used in the manufacture of aniline, but simpler inasmuch as neither cohobator nor condenser is required; a wide exit-pipe for the escaping gases taking the place of the latter. 800 kilos. of iron borings ('swarf,' *v.* art. ANILINE), 40 kilos. of hydrochloric acid and some water are charged into the apparatus, the stirrer set in motion, and 600 kilos. of air-dried nitronaphthalene added gradually at such a rate that the temperature of the exterior of the cylinder does not rise beyond that bearable by the hand (*circa* 50°). After the whole of the nitronaphthalene has been added the stirrer is kept rotating for 6-8 hours, and the temperature carefully maintained at 70° by blowing in steam through the hollow shaft of the agitator, since cooling would result in a sudden solidification of the mixture with consequent fracture of the stirring apparatus. The end of the reduction is ascertained by submitting test specimens taken from the cylinder to dry distillation in a small retort, and examining the distillate, which ought to dissolve completely in hydrochloric acid, forming a bright-brown solution free from any yellow colour. When the operation is completed, milk of lime made from 50 kilos. of caustic lime is run into the cylinder, and the contents, after vigorous stirring, are then run off. As carried on under these conditions, ferrous chloride in the presence of water is in all probability the reducing agent, the reaction being represented by the following equations:

$$(1)\ 24FeCl_2 + 4C_{10}H_7.NO_2 + 4H_2O = 12Fe_2Cl_4O + 4C_{10}H_7.NH_2;$$

$$(2)\ 12Fe_2Cl_4O + 9Fe = 3Fe_3O_4 + 24FeCl_2.$$

The next stage of the process consists in the recovery of the naphthylamine from the material emptied out of the reduction apparatus, and much loss occurs at this point. Distillation is the only method available, and although every precaution is used to remove the vapours from the retort as rapidly as possible, a certain percentage of naphthylamine is always lost by decomposition at the temperature of the retort, whilst a further portion is oxidised by the magnetic oxide of iron present in the reduction-product. The retorts are frequently about 3 m. long, 1 m. broad, and 0·8 m. high, and are fitted in the interior with shelves, on which cast-iron trays are placed containing the reduction-product spread out in thin layers. The retorts are heated by direct firing, and the distillation requires about 20 hours for its completion. Steam, superheated by passing through an iron coil placed in the furnace gases, may be blown through to drive the naphthylamine vapour as rapidly as possible into the condenser, the cooling water of which is kept at 60° to prevent choking of the worm. The crude naphthylamine distils over as a blackish oil, which solidifies in the receiver to a greyish-black mass; the yield amounts to about 70 p.c. of the theoretical.

For conversion into the commercial product, the crude naphthylamine has to be once rectified. It is separated as far as possible from adhering water, then fused in a suitable vessel by means of a steam coil, and completely dried by prolonged heating under these conditions. It is then run into a wrought-iron retort, heated by a direct fire, and provided with a hood through which a portion of the furnace gases can be led with the object of preventing a portion of the naphthylamine vapours condensing in the upper part and running back. The cooling water in the condenser is kept at 60° as before, and the naphthylamine distils as a water-white oil, which is run into moulds, where it solidifies in bright grey, often almost white, sonorous, crystalline cakes. This product is not quite pure, since it always contains appreciable quantities of naphthalene, one of the results of the decomposition occurring during the first distillation. It not infrequently contains in addition a small proportion of what seems to be the 1:1′-naphthylenediamine, to the presence of which the gradual change in colour from grey to violet shown by most samples of commercial naphthylamine on exposure to the air is to be referred (Witt, Chem. Ind. 10, 218; D. P. J. 265, 228).

Properties.—α-Naphthylamine crystallises from most solvents in slender, flat needles or scales but from aniline in colourless prisms

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[1] Anhydrous ammonia-calcium chloride, $CaCl_2.8NH_3$, is prepared by passing a current of dry ammonia over anhydrous calcium chloride in small lumps. Much heat is evolved, the lumps break down into powder, and about 47 p.c. of ammonia is absorbed.

Hydrated ammonia-calcium chloride is obtained by passing a current of dry ammonia for about 12 hours over granulated calcium chloride containing 16-19 p.c. of water, whereby about 90 p.c. of its weight of ammonia is absorbed (Benz, B. 16, 8, 11).

[2] Ammonia-zinc chloride, $ZnCl_2.NH_3$, is prepared by passing a current of dry ammonia over powdered zinc chloride. The temperature rises to about 300°, and a fused mass is obtained which solidifies on cooling, and contains one part of ammonia to four parts of zinc chloride (Merz and Weith, B. 12, 1300 (*footnote*)).

(Balló, B. 3, 288), melts at 50°, boils at 300° (Zinin, *l.c.*), and is but little volatile with steam. Its odour is characteristic and unpleasant. It is very soluble in alcohol, ether, and aniline, and almost insoluble in water, 100 c.c. of which dissolve about 0·167 gram at the ordinary temperature (Balló, B. 3, 675).

Salts.—The salts are for the most part sparingly soluble in water and crystallise well. The *hydrochloride*, B.HCl, crystallises in long, slender needles or lustrous scales, dissolves in water, alcohol, and ether, and is precipitated from a not too dilute aqueous solution by concentrated hydrochloric acid; the *sulphate*, $B_2.H_2SO_4+2H_2O$, forms white silvery scales, and is sparingly soluble in cold water or alcohol.

Reactions.—(1) On treatment with nitrous acid, α-naphthylamine (as hydrochloride or sulphate) is converted into the *diazo-* compound, which yields *α-naphthol* by boiling with 2–3 p.c. sulphuric acid (Griess, Pr. 12, 419).

(2) Oxidation with potassium bichromate and dilute sulphuric acid converts it into a mixture of 1:4-[α-]*naphthaquinone*, *phthalic acid*, and a brown insoluble substance of unknown composition (Monnet, Reverdin, and Nölting, B. 12, 2306).

(3) When heated with zinc chloride or calcium chloride at 280° it undergoes partial decomposition into *αα-dinaphthylamine* and ammonia, but to a less degree than β-naphthylamine under like conditions (Benz, B. 16, 15).

(4) Treatment with nitric acid (sp.gr. = 1·35) converts it into *dinitro-α-naphthol* (Balló, B. 3, 289).

(5) The action of sulphuric acid on α-naphthylamine is separately discussed (*v. infra*).

(6) Azo- colours are formed both by interaction of the diazotised base with phenols or amines and of the base with diazotised bases. The azo- dyes obtained by interaction of diazonaphthalene with β-naphthol or α- or β-naphtholsulphonic acids give various shades of red, and the azo- or disazo- dyes obtained by interaction with diazo- or tetrazo- compounds give respectively brown or violet shades (*v.* AZO-COLOURING MATTERS).

Tests.—(1) An alcoholic or acetic acid solution of α-naphthylamine is coloured yellow on treatment with a small quantity of an alcoholic solution of nitrous acid, and on addition of hydrochloric acid the colour changes either to red with small quantities or to violet- or magenta-red with larger quantities of the base, owing to the formation of amidoazonaphthalene hydrochloride (Liebermann, A. 183, 265).

(2) When oxidising agents such as ferric chloride, stannic chloride, silver nitrate, gold chloride, zinc chloride, or chromic acid are added to an aqueous solution of an α-naphthylamine salt an azure-blue precipitate of so-called *naphthameïn* is formed which rapidly becomes purple, and does not change colour on treatment with sulphurous acid (Piria, A. 78, 64; Schiff, A. 101, 92; 129, 255).

Commercial tests.—Commercial α-naphthylamine ought to have the right melting-point and dissolve almost completely in dilute acids. Complete solubility is never attained in practice, owing to the presence of small quantities of naphthalene, the proportion of which can readily be determined by distilling a weighed quantity of the naphthylamine with excess of hydrochloric acid in a current of steam, extracting the distillate with ether, and, after drying the ethereal solution evaporating and weighing the residue.

Acet-α-naphthalid, $C_{10}H_7.NH.CO.CH_3$, is formed by heating α-naphthol with ammonium acetate at 270–280° (Calm, B. 15, 615; *v. supra*).

Preparation.—α-Naphthylamine is boiled with 1·25 times its weight of glacial acetic acid for 4–5 days in an apparatus provided with a reflux condenser. The product is granulated by pouring into cold water and crystallised either from boiling water or dilute alcohol, preferably the former (Liebermann and Dittler, A. 183, 229).

Properties.—It crystallises from water in needles, melts at 159°, is easily soluble in alcohol and acetic acid, tolerably soluble in hot but almost insoluble in cold water, and undergoes hydrolysis readily on boiling with acids or alkalis (Liebermann and Dittler, *l.c.*; Tommasi, Bl. 20, 20).

Reactions.—(1) On nitration in acetic acid solution it yields in the first instance a mixture of 1:2-*β-nitroacet-α-naphthalid* and 1:4-*α-nitroacet-α-naphthalid*, and by further nitration 1:2:4-*dinitroacet-α-naphthalid* (Liebermann and Dittler, A. 183, 229, 273; Andreoni and Biedermann, B. 6, 342; Lellmann and Remy, B. 19, 797).

(2) When warmed with 3–4 times its weight of 20–25 p.c. anhydrosulphuric acid at temperatures below 100° it is converted chiefly into the *acetyl-* derivative of 1:4′-α-naphthylaminesulphonic acid, some 1:4- acid also being formed (Ewer and Pick, Germ. pat. 42874; Schultz, B. 20, 3161).

Methyl-α-naphthylamine, $C_{10}H_7.NHCH_3$, is prepared by passing methyl chloride for some hours into α-naphthylamine heated at 150–180° in an apparatus provided with a reflux condenser heated by means of steam to prevent the sublimed naphthylamine choking the tube. The product is extracted with ether, and the filtered solution shaken with dilute sulphuric acid, whereby the unattacked α-naphthylamine separates as sulphate, methyl-α-naphthylamine dissolves in the acid, and dinaphthylamine, which is formed in large quantities in the reaction, remains dissolved in the ether. The methyl-α-naphthylamine is separated by precipitating the acid solution with alkali, and purified by distillation; the yield amounts to about 25 p.c. of the theoretical (Landshoff, B. 11, 638).

Properties.—It is a dark-red oil, which boils at 293°, dissolves readily in dilute acids, alcohol, ether, &c., and in alcoholic solution gives a violet colour with ferric chloride.

Dimethyl-α-naphthylamine is obtained by heating a methylic alcohol solution of α-naphthylamine with methyl iodide (2 mol. prop.) at 100° for a day (Landshoff, B. 11, 643), or by heating dry α-naphthylamine hydrochloride and methyl alcohol at 180° (Hantzsch, B. 13, 1348).

Properties.—It is a pale-yellow oil, which boils at 272–274° (Friedländer and Welmans, B. 21, 3124), at 274·5° under a pressure of 711 mm.

(Bamberger and Helwig, B. 22, 1315), shows a violet fluorescence and dissolves readily in alcohol, ether, and dilute acids. It yields an unstable *nitroso-* derivative which decomposes in aqueous solution forming 1:4-nitroso-*a*-naphthol, and is converted into a *monosulphonic acid* by warming with anhydrosulphuric acid or by heating with 4 parts of concentrated sulphuric acid at 150° (Friedländer and Welmans). The sulphonic acid on fusion with caustic soda is converted into *dimethyl-a-amidonaphthol* (Gesellsch. f. Chem. Ind., Germ. pat. 50142).

Ethyl-*a*-naphthylamine is prepared by heating *a*-naphthylamine with ethyl bromide, extracting the product with very dilute hydrochloric acid, adding ammonia and extracting with ether (Limpricht, A. 99, 117; Friedländer and Welmans, B. 21, 3129). It is an almost colourless oil boiling at 303° under a pressure of 722·5 mm. (Bamberger and Helwig, B. 22, 1312).

Diethyl-*a*-naphthylamine is obtained by heating *a*-naphthylamine with concentrated aqueous sodium carbonate (2 mol. prop.) and the calculated quantity of ethyl bromide or iodide at 100–120°. It is a colourless oil boiling at 283–285° (Friedländer and Welmans, B. 21, 3130). The compound obtained by B. Smith's method (C. J. 41, 180) consists essentially of ethyl-*a*-naphthylamine.

Phenyl-*a*-naphthylamine is formed when *a*-naphthylamine is heated with aniline hydrochloride at 240° for 30–36 hours (Girard and Vogt, C. R. 73, 627; Bl. 18, 68; Streiff, A. 209, 152), and when a mixture of *a*-naphthol (1 mol. prop.) aniline (2 mol. prop.) and calcium chloride (1 mol. prop.) is heated at 280° for 9 hours (Friedländer, B. 16, 2077); the yield in the latter case being about 26·3 p.c. of the theoretical.

Properties.—It crystallises from alcohol in prisms, melts at 62°, boils at 335° under 258 mm. and at 226° under 15 mm. pressure, and is readily soluble in alcohol, ether, benzene, &c., insoluble in dilute acids. By interaction with diazotised *a*-amidonaphthaleneazobenzenedisulphonic acid, it gives a black disazo- dye (Bayer & Co., Germ. pat. 48924 of Oct. 6, 1888).

Orthotolyl-*a*-naphthylamine is prepared by heating *a*-naphthol (1 mol. prop.) with orthotoluidine (2 mol. prop.) and calcium chloride (1 mol. prop.) at 280° for 9 hours; the yield amounts to about 37 p.c. of the theoretical (Friedländer, B. 16, 2084). It crystallises in long flat needles, melts at 94–95°, and is very soluble in alcohol, ether, and benzene, but sparingly in petroleum spirit.

Paratolyl-*a*-naphthylamine is obtained by heating *a*-naphthylamine with paratoluidine hydrochloride (Girard and Vogt, Bl. 18, 68), and by heating *a*-naphthol (1 mol. prop.) with paratoluidine (2 mol. prop.) and calcium chloride (1 mol. prop.) at 280° for 9 hours (Friedländer, B. 16, 2082), the yield in the latter case being about 49·4 p.c. of the theoretical. It crystallises in small prisms, melts at 78·5–79°, boils at 360° under 528 mm. and at 236° under 15 mm. pressure, and is sparingly soluble in petroleum spirit and cold alcohol.

***aa*-Dinaphthylamine** (Girard and Vogt, *l.c.*; Landshoff, *l.c.*; Benz, B. 16, 16) crystallises from alcohol in large quadratic scales, melts at 113°, and is very sparingly soluble in dilute acids, fairly soluble in alcohol, readily soluble in benzene, ether, &c.

SULPHONIC ACIDS.

Introductory. — *a*-Naphthylaminesulphonic acids are prepared by two methods.

(1) By nitration and subsequent reduction of naphthalene-mono- and-di-sulphonic acids.

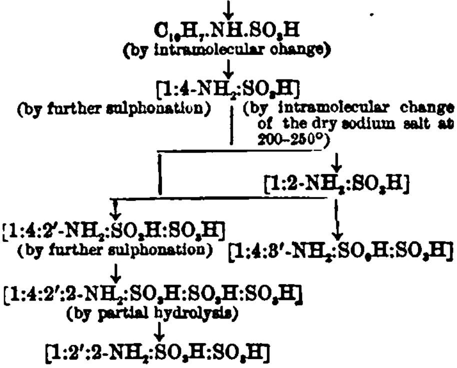
(2) By the action of sulphuric acid on *a*-naphthylamine.

Two mono-, three di-, and one tri-sulphonic acids are known to be formed by the action of sulphuric acid on *a*-naphthylamine. Of the two *a*-naphthylaminemonosulphonic acids, one—the 1:4- or naphthionic acid—is obtained by intramolecular change when the acid sulphate of *a*-naphthylamine is baked at 180–200°, and forms the chief, if not the sole product, when *a*-naphthylamine is sulphonated with 3–5 times its weight of concentrated sulphuric acid at 100–130°. Its production in the latter case is no doubt due to intramolecular change of the initially-formed acid sulphate, which not improbably takes place through naphthalene-*a*-sulphamic acid as intermediary, thus:

$$C_{10}H_7.NH_2,H_2SO_4 \rightarrow C_{10}H_7NH.SO_3H(+H_2O)$$
$$\rightarrow NH_2.C_{10}H_6.SO_3H.$$

The second, or 1:4′-naphthylaminesulphonic acid, is seemingly formed when sulphonation is effected by means of anhydrosulphuric acid under conditions which either prevent the ready formation of the sulphamic acid or do not favour the occurrence of the intramolecular change; thus it constitutes the chief product when the theoretical quantity of anhydrosulphuric acid in the form of 20–25 p.c. anhydrosulphuric acid acts upon acet-*a*-naphthalid at temperatures below 100°, and on *a*-naphthylamine hydrochloride in the cold. The action of anhydrosulphuric acid on derivatives of *a*-naphthylamine containing acid radicles corresponds, therefore, with that on naphthalene-*a*-sulphonic acid and on *a*-nitronaphthalene.

The series of changes which probably occur when *a*-naphthylamine is sulphonated under the conditions described in connection with the respective acids is given in the table, and is also briefly discussed in the section 'Substitution in the Naphthalene Series' (*v. supra*).



Naphthylaminedisulphonic acids differ from naphthalene- and naphthol-disulphonic acids in forming acid salts with great readiness; the acid salt, and not the acid, being liberated when the alkali salts are treated with an excess of an acid such as hydrochloric acid.

α-NAPHTHYLAMINESULPHONIC ACIDS.

(i) **1:4[1]-α-Naphthylaminesulphonic acid** (naphthionic acid).

Formation.—Naphthionic acid was first prepared, mixed with about an equal proportion of thionaphthamic (naphthalene-α-sulphamic) acid, by the action of aqueous ammonium sulphite on α-nitronaphthalene in alcoholic solution (Piria, A. 78, 31). It is also formed with a small proportion of a more soluble acid, when α-naphthylamine is sulphonated with fuming sulphuric acid (proportions and percentage of dissolved anhydride not stated) (Schmidt and Schaal, B. 7, 1367), and constitutes the sole product when it is heated with five times the weight of ordinary sulphuric acid until sulphonation is completed (Witt, B. 19, 57). Pure naphthionic acid is also obtained by baking acid α-naphthylamine sulphate at 180-200° (Nevile and Winther, C. J. 37, 632; B. 13, 1948). The identity of the acids produced by these different methods was established by Witt (B. 19, 55). Naphthionic acid is formed as a subsidiary product when acet-α-naphthalid is sulphonated with 3-4 parts of 20-25 p.c. anhydrosulphuric acid at temperatures below 100° (Lange, B. 20, 2940; Ewer & Pick, Germ. pat. 42874; Schultz, B. 20, 3161), and in relatively small quantity by heating α-naphthylamine with 3 times its weight of potassium bisulphate at 200° for 3 hours (Bischoff and Brodsky, B. 23, 1914).

Preparation.—Naphthionic acid is prepared by two methods:

(1) Acid α-naphthylamine sulphate, or an intimate mixture of α-naphthylamine and 100 p.c. sulphuric acid in the proportion (143 lbs. of amine to 98 lbs. of acid) requisite to form this compound, is baked at 180-200° until the product is completely soluble in dilute alkali (*cf.* Ver. Chem. Fab., Eng. pat. 2237 of 1883).

(2) α-Naphthylamine is heated with 4-5 times its weight of ordinary sulphuric acid at 100-120°, or with 3 times its weight of acid at 130° until the product is soluble in alkali. The melt is poured into water, and the precipitated acid pumped off, washed, and converted into sodium salt by neutralisation with aqueous caustic soda (*cf.* Ver. Chem. Fab., *l.c.*; Witt, B. 19, 578 (footnote)).

Salts.—The *acid*, $NH_2.C_{10}H_6.SO_3H + \frac{1}{2}H_2O$, crystallises from water in small lustrous needles, dissolves sparingly in hot, and is soluble in about 4000 parts of cold water. The salts crystallise well, dissolve readily in water, and, like the acid, show a marked blue fluorescence in dilute solution. The *barium* salt, $BaA_2 + 8H_2O$, crystallises in scales, the *calcium* salt, $CaA_2 + 8H_2O$, in pale rose-coloured monoclinic tables, the *potassium* salt, KA, in scales, and the characteristic *sodium* salt, $NaA + 4H_2O$, in large monoclinic prisms, which, although readily soluble in water, dissolve very sparingly in the presence of alkali.

Reactions.—(1) The *diazo*-compound obtained from 1:4-naphthylaminesulphonic acid by treatment with nitrous acid is a sparingly soluble yellow, microcrystalline powder, and is converted into 1:4-*α-naphtholsulphonic acid* (Nevile and Winther, C. J. 37, 632; Dahl & Co., Monit. Sci. [3] 14, 39), into *dinitro-α-naphthol* (Cleve, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1876, N:o 7, 40; Nevile and Winther, *l.c.*), and into 1:4-*dichloronaphthalene*[1] by the known reactions (Cleve, *l.c.*; B. 20, 73).

(2) When heated with a 50 p.c. solution of caustic soda at 240-260° it is converted into 1:4-*α-naphtholsulphonic acid* with the elimination of ammonia (Actieng. f. A., Germ. pat. 46307).

(3) The acetyl derivative, obtained by heating the sodium salt with acetic anhydride, yields, on nitration, the acetyl derivative of a *nitro-naphthylaminesulphonic acid* [$NH_2:SO_3H:NO_2 = 1:4:4'$], which undergoes hydrolysis on heating with dilute sulphuric acid forming 1:4′-*nitronaphthylamine* (Nietzki and Zübelen, B. 22, 451).

(4) Azo- colours are formed both by interaction of the diazotised acid with phenols or amines, and of the acid with diazotised bases. The azo- dyes formed by interaction with β-naphthol or α- or β-naphtholsulphonic acids, and the disazo- dyes formed by interaction with tetrazo- compounds, give various shades of red and have considerable commercial value (*v.* AZO-COLOURING MATTERS).

(ii) **1:4′-α-Naphthylaminesulphonic acid** (naphthalidinesulphonic acid; Cleve's [α-]naphthylaminesulphonic acid; Laurent's acid).

Formation.—This acid was first prepared by Laurent by reduction of 1:4′- or [α-]nitronaphthalenesulphonic acid, and more particularly examined by Cleve (Öfvers. af Kongl. Vetensk.-Akad. Förh. 1875, N:o 9, 13; Bl. 24, 511); it occurs, therefore, in the product obtained when naphthalene-α-sulphonic acid is nitrated and reduced (Schöllkopf Co., Germ. pat. 40571 of Dec. 23, 1885; Eng. pat. 15775 of 1885). It constitutes the chief product when α-naphthylamine is sulphonated with anhydrosulphuric acid—naphthionic acid being the subsidiary product under these conditions—and is obtained, therefore, when α-naphthylamine is warmed with twice its weight of 'fuming' sulphuric acid (Cleve, Öfvers. 1876, N:o 7, 39; *cf.* Schmidt and Schaal, B. 7, 1367), when α-naphthylamine hydrochloride is sulphonated in the cold by means of 20-25 p.c. anhydrosulphuric acid (Witt, B. 19, 578; Schultz, B. 20, 3161), and when acet-α-naphthalid is warmed with 3-4 times its weight of 20-25 p.c. anhydrosulphuric acid at temperatures below 100° (Lange, B. 20, 2940; Ewer & Pick, Germ. pat. 42874; Schultz, *l.c.*).

Preparation.—(1) The product obtained by sulphonating α-nitronaphthalene with anhydrosulphuric acid (*v.* 1:4′-nitronaphthalenesulphonic acid) is poured on to ice, diluted with water, reduced by adding the requisite quantity of iron borings or zinc-dust, and converted into calcium

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[1] In every case where the constitution of an α-naphthylaminesulphonic acid is given, the NH_2- group is supposed in the position '1.'

[1] Witt (B. 19, 1719) has proved the constitution of naphthionic acid, independently of the phosphorus pentachloride reaction, by showing that orthodiamidonaphthalenesulphonic acid is obtained by reduction of Congo-red—a dye prepared by the interaction of tetrazodiphenyl chloride and naphthionic acid.

and thence into sodium salt in the usual way. On the laboratory scale the nitro- acid is best reduced by dissolving it in ammonia, saturating the solution with sulphuretted hydrogen, and warming until all odour of the gas has disappeared.

(2) Acet-α-naphthalid is dissolved in 3–4 times its weight of 20–25 p.c. anhydrosulphuric acid in the cold, and the product mixed with 3–4 times its bulk of water and boiled for some hours in order to eliminate the acetyl group. On cooling, the greater part of the acid crystallises out in slender needles, and may be filtered off, the portion remaining dissolved in the mother-liquors being recovered by neutralising these with lime and converting into sodium salt in the usual way (Ewer and Pick, Germ. pat. 42874 of June 30, 1887; *cf.* Lange, *l.c.*). The product contains some 1:4-α-naphthylaminesulphonic acid (Schultz, *l.c.*).

(3) Carefully dried α-naphthylamine hydrochloride in fine powder (prepared by mixing α-naphthylamine with 36·5 p.c. hydrochloric acid in the proportion of 143 lbs. of amine to 100 lbs. acid, and drying until all water has been expelled) is stirred into 20–25 p.c. anhydrosulphuric acid cooled by means of ice, the proportions being such that sulphonation is effected by means of the dissolved anhydride. When sulphonation is completed the product is poured on to broken ice, filtered, washed with water, and converted into calcium, and thence into sodium salt in the usual way (Ver. Chem. Fab. Eng. pat. 2237 of 1883; Witt, B. 19, 578). Naphthionic acid is also formed under these conditions (Schultz, *l.c.*), and the 1:4′-acid may be freed from this by fractional crystallisation of the calcium salt, the 1:4′-salt being the less soluble; or on the small scale by extraction of the sodium salt with alcohol in which sodium naphthionate is insoluble (*cf.* Erdmann, A. 247, 315).

Salts.—The *acid* crystallises from water in flocks of anhydrous slender needles, is tolerably soluble in hot water, and dissolves in about 940 parts of cold water. The salts crystallise well, and dissolve readily in water; the calcium and sodium salts are also soluble in alcohol. Both acid and salts show a greenish fluorescence in dilute aqueous solution. The *barium* salt, $BaA_2 + 6H_2O$, crystallises in stellate aggregates of small scales, the *calcium* salt, $CaA_2 + 9H_2O$, in large nacreous tables, the *potassium* salt, $KA + H_2O$, in needles or small prisms, and the *sodium* salt, $NaA + H_2O$, in spherical aggregates of needles which do not effloresce in a desiccator over sulphuric acid (Cleve, Bl. 24, 511; Mauzelius, B. 20, 3401). The presence of impurity in small amount exercises a considerable influence on the amount of water of crystallisation, the sodium salt prepared by Witt's method frequently crystallising in efflorescent scales with 5 mols. H_2O (Witt, B. 19, 579; Mauzelius, *l.c.*).

Reactions.—(1) The *diazo-* compound obtained from 1:4′-naphthylaminesulphonic acid by treatment with nitrous acid forms sparingly soluble, small, yellowish needles, and is converted into 1:4′-*α-naphtholsulphonic acid* (Cleve, *l.c.*; Erdmann, A. 247, 343), and into 1:4′-*dichloronaphthalene* by the known reactions (Cleve, Öfvers. 1876, N:o 9, 71; Mauzelius, *l.c.*); also into 1:2:4:4′-*dinitro-α-naphtholsulphonic acid* by warming with dilute nitric acid, or into *dinitro-α-naphthol*, with loss of its sulphonic radicle, by boiling with nitric acid (Witt, B. 19, 580).

(2) When heated with concentrated aqueous caustic soda at 240–250°, the sodium salt is converted into 1:4′-*amidonaphthol* (Actieng. f. A., Germ. pat. 49448).

(3) Azo- colours are formed both by interaction of the diazotised acid with phenols or amines and of the acid with diazotised bases. The azo- dyes formed by interaction with the naphtholsulphonic acids present no advantage over those obtained from the cheaper naphthionic acid, whilst those formed by interaction with diazotised bases (*e.g.*, benzopurpurin 6B) are not fast to acids, and have little commercial value.

⁂ Identical in all probability with the 1:4′-acid are the α-naphthylaminesulphonic acids described respectively by Nölting and Hirsch. Nölting's acid (Ch. Z., 12, 1212; Monit. Sci. [4] 2, 1256) is formed with naphthionic acid on sulphonating α-naphthylamine ((?) with concentrated sulphuric acid), and forms the more soluble constituent of the product.

Hirsch's so-called 'α-naphthylamine-[δ-]sulphonic acid' is obtained, mixed with some naphthionic acid and α-naphthylamine-di- and -trisulphonic acids, by heating α-naphthylamine with 5 times its weight of concentrated (not fuming) sulphuric acid at 125–130° for 8–9 hours (B. 21, 2370). It crystallises in rhombic tables, dissolves in about 150 parts of boiling and 450 parts of cold water, and forms readily soluble potassium and sodium salts and a calcium salt, $CaA_2 + 10H_2O$, which crystallises in calc-spar-like efflorescent forms sparingly soluble in cold water. The sparingly soluble diazo-compound is converted by boiling with dilute nitric acid into a dinitro-α-naphtholsulphonic acid, characterised by forming a readily soluble potassium salt. The general characters of the [δ-]acid, as described by Hirsch, agree with those of impure 1:4′-acid, with which, indeed, it must be identical, since the other six isomerides are excluded: the 1:2- and 1:4-acids, on account of the formation of a dinitro-α-naphtholsulphonic acid; the 1:3-, 1:2′-, and 1:3′-acids, as proved by Cleve (B. 21, 2373), and the 1:1′-acid, on account of the solubility of the sodium salt.

(iii) **1:1′-α-Naphthylaminesulphonic acid** (naphthylaminesulphonic acid-S.).

Preparation.—This acid is formed with about an equal quantity of 1:4′-acid when naphthalene-α-sulphonic acid is nitrated and subsequently reduced by means of iron borings and sulphuric acid (Schöllkopf Co., Germ. pat. 40571 of Dec. 23, 1885; Eng. pat. 15775 of 1885), and as its sodium salt is very sparingly soluble, whilst that of the 1:4′-acid is easily soluble in water a separation can readily be effected.

Salts.—The *acid* crystallises from water in small, anhydrous, white needles, and is soluble in 238 parts of boiling water and 4800 parts of water at 21°; the solubility in cold water being much increased by the presence of 1:4′-acid as an impurity. The *potassium* salt, KA, crystallises in large, lustrous, anhydrous scales soluble in a litre of water to the extent of 35·6 grams at 19° and 149 grams at 100°; the *sodium* salt, NaA, in anhydrous scales or tables soluble in a litre of water to the extent of 11·3 grams at 24°, and 26·7 grams at 100° (Erdmann, A. 247, 320).

Reactions.—(1) The *diazo*-compound obtained from 1:1′-naphthylaminesulphonic acid by treatment with nitrous acid, forms sparingly soluble, small, yellowish prisms, and is converted into *naphthasultone* (the anhydride of 1:1′-naphtholsulphonic acid) by boiling with dilute sulphuric acid (Erdmann, A. 247, 344).

(2) When sulphonated with three times its weight of 10 p.c. anhydrosulphuric acid in the cold, it is converted into the corresponding *naphthylaminedisulphonic acid-S.* (Schöllkopf Co., *l.c.*).

(iv) 1:3′-α-**Naphthylaminesulphonic acid** (Cleve's [β-]naphthylaminesulphonic acid) is obtained by the reduction of 1:3′- or [β-]α-nitronaphthalenesulphonic acid with ammonium sulphide or ferrous sulphate (Cleve, B. 20, 74).

Salts.—The *acid* crystallises either in anhydrous rhombic tables or with 2 mols. H_2O in slender needles and is sparingly soluble in cold, more soluble in hot water. The *barium* salt, BaA_2+H_2O, forms sparingly soluble brown needles, the *calcium* salt, CaA_2+7H_2O, brilliant efflorescent rhombohedra, the *potassium* salt, $KA+H_2O$, very soluble efflorescent brown needles, and the sodium salt, $NaA+4H_2O$, very soluble thin rhombic tables (Cleve, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1876, N:o 7, 54; Bl. 26, 447).

(v) 1:2′-α-**Naphthylaminesulphonic acid** (Cleve's [θ-] (or [δ-]) naphthylaminesulphonic acid) is prepared by the reduction of 1:2′- or [θ-]α-nitronaphthalenesulphonic acid with ammonium sulphide.

Salts.—The *acid* crystallises with 1 mol. H_2O in silvery scales. The *barium* salt, BaA_2, forms somewhat sparingly soluble flat needles; the *calcium* salt, CaA_2+2H_2O, is usually obtained as a very soluble indistinctly crystalline powder; the *potassium* salt crystallises in very soluble scales, the *sodium* salt, $NaA+\frac{1}{2}H_2O$, in very soluble thin needles (Cleve, Bl. 29, 415; B. 21, 3264).

(vi) 1:3-α-**Naphthylaminesulphonic acid** (Cleve's [γ-] naphthylaminesulphonic acid) is obtained by the reduction of 1:3- or [γ-]α-nitronaphthalenesulphonic acid with ferrous sulphate.

Salts.—The *acid* crystallises in small sparingly soluble needles (Cleve, B. 19, 2181). The *barium* salt, BaA_2+H_2O, crystallises in very soluble scales; the *sodium* salt, NaA, in very soluble anhydrous scales; the *calcium* and *potassium* salts are extremely soluble in water (Cleve, B. 21, 3271).

(vii) 1:2-α-**Naphthylaminesulphonic acid.** The preparation of an α-naphthylaminesulphonic acid, described as new, has been announced by the Chemische Fabrik Grünau, Landshoff and Meyer (Germ. pat. Anm. C 3171 of Jan. 20, 1890; Tobias, B. 23, 1629). This acid, there is reason to believe, is obtained by heating sodium naphthionate at 200–250°, and differs from its isomerides by being readily soluble in water and by forming sparingly soluble potassium and sodium salts. As its diazo-compound yields 1:2-*α-naphtholsulphonic acid* and 1:2-*dichloronaphthalene* by the usual methods, it must be the seventh theoretically possible α-naphthylaminesulphonic acid.

α-NAPHTHYLAMINEDISULPHONIC ACIDS.

(i) [1:2:2′(?)]-α-**Naphthylaminedisulphonic acid** (acid No. I. of Dahl & Co.'s Germ. pat. 41957 of Sept. 4, 1886).

Preparation. — α-Naphthylamine is heated with 4–5 parts of 25 p.c. anhydrosulphuric acid at 120° until a test is completely soluble in water. The product is converted into calcium salt in the usual way, and the filtrate evaporated to dryness. The dry calcium salt is then boiled with 10 parts of 96 p.c. alcohol, which extracts the salt of the No. I. acid; the yield being about 50 p.c. The residue contains the calcium salts of acids II. and III. of the patent in about equal proportions, and is separated into its constituents by boiling with 85 p.c. alcohol which extracts the No. II. salt.

Properties.—The *acid* is extremely soluble in, and cannot be crystallised from, water. The *diazo-* compound does not give a naphthol-yellow when boiled with nitric acid, and yields worthless azo- colours in combination with naphthols.

(ii) 1:4:3′-α-**Naphthylaminedisulphonic acid** (acid No. II. of Dahl & Co.'s patent).

Preparation.—This acid constitutes about 25 p.c. of the product obtained by sulphonating α-naphthylamine with 25 p.c. anhydrosulphuric acid at 120° (*v. supra*), and about 30 p.c. of that obtained by sulphonating naphthionic acid with anhydrosulphuric acid in the cold (*v. infra*). The calcium salt soluble in 85 p.c., but insoluble in 96 p.c. alcohol is converted into potassium or sodium salt in the usual way. According to Armstrong and Wynne (C. J. Proc. 1890, 125), the technical product contains about 20 p.c. of an α-naphthylaminetrisulphonic acid.

Salts.—The *calcium* salt crystallises in long needles very soluble in water and soluble in 85 p.c. but insoluble in 96 p.c. alcohol; the *potassium* and *sodium* salts are extremely soluble in water; the *acid sodium* salt is precipitated in slender needles on the addition of an acid to the aqueous solution of the sodium salt, and is soluble to the extent of about 17 p.c. in water at 20°, very soluble in hot water and in boiling 85 p.c. alcohol. The dilute solutions of the acid and salts show a splendid blue fluorescence.

Reactions.—The *diazo-* compound obtained from 1:4:3′-α-naphthylaminedisulphonic acid by treatment with nitrous acid forms readily soluble, yellow, silky needles, and is converted into the corresponding *α-naphtholdisulphonic acid*, into a *naphthol-yellow* (dinitro-α-naphtholsulphonic acid) precipitable by aqueous caustic potash (Dahl & Co.), into 1:2′-*naphthalenedisulphonic acid*, and into 1:4:3′-*trichloronaphthalene* by the ordinary reactions (Armstrong and Wynne, C. J. Proc. 1890, 126).

(iii) 1:4:2′-α-**Naphthylaminedisulphonic acid** (acid No. III. of Dahl & Co.'s patent).

Preparation.—(1) This acid constitutes about 25 p.c. of the product formed when α-naphthylamine is sulphonated with 25 p.c. anhydrosulphuric acid at 120° (*v. supra*).

(2) It is obtained mixed with about 30 p.c. of acid No. II. by adding 100 kilos. of finely sieved naphthionic acid to 350 kilos. of 25 p.c. anhydrosulphuric acid at such a rate that the

temperature never exceeds 30°, otherwise an appreciable amount of *a*-naphthylaminetrisulphonic acid is formed. The whole is allowed to remain in the cold for 2–3 days, sulphonation being completed when a solution of 6 drops of the acid mixture in 10 c.c. of water remains clear after standing for 5–6 hours. The product is worked up in the usual way by conversion into calcium salt, and as this mixed salt is very soluble in water it is readily washed out of the precipitated gypsum without any very considerable dilution of its solution being brought about. The filtrate is evaporated to dryness, and the dry calcium salt finely sieved and extracted with ten times its weight of 85 p.c. alcohol to remove No. II. salt. The residue amounting to about 70 p.c. of the product is converted into potassium or sodium salt in the usual way (Dahl & Co., *l.c.*).

Salts.—The *acid*, $NH_2.C_{10}H_5(SO_3H)_2 + 2H_2O$, crystallises in colourless, long needles, and is sparingly soluble in cold water. The *barium* salt, BaA, crystallises in small, flat needles, sparingly soluble in water; the *calcium* salt, $CaA + H_2O$, separates in a pulverulent form, and is very sparingly soluble in hot and cold water; the *potassium* salt, $K_2A + 3H_2O$, crystallises in large efflorescent, augite-like tables; the *sodium* salt, $Na_2A + 3H_2O$, forms efflorescent rhombic crystals or sheaves of efflorescent needles readily soluble in water; the *acid sodium* salt, obtained by adding an acid to the aqueous solution of the sodium salt, crystallises in small rosettes of needles, and is soluble in 20 parts of boiling water, but only to the extent of 0·7 p.c. in water at 20°, and insoluble in 85 p.c. alcohol (Dahl & Co., *l.c.*; Haeseler, Inaug. Dissert. Freiburg, i. B. 1889). The solutions of the acid and salts show a marked blue fluorescence.

Reactions.—(1) The *diazo*-compound obtained from 1:4:2′-*a*-naphthylaminedisulphonic acid by treatment with nitrous acid, forms sparingly soluble, yellow needles, and is converted into 1:4:2′-*a-naphtholdisulphonic acid*, into *a-naphthol-yellow-S.* (Dahl & Co.), into 1:3′-*naphthalenedisulphonic acid*, and into 1:4:2′-*trichloronaphthalene* by the known methods (Armstrong and Wynne, C. J. Proc. 1890, 17).

(2) Azo- colours are formed both by interaction of the diazotised acid with phenols or amines, and of the acid with diazotised bases. The azo- dyes obtained by interaction with *β*-naphtholsulphonic acids give bluish-red, and those with *a*- or *β*-naphthylamine give brown shades (Dahl & Co. Germ. pat. 42440 of Oct. 5, 1886).

(iv) **1:1′:4-*a*-Naphthylaminedisulphonic acid** (*a*-naphthylamine-[δ-]disulphonic acid; naphthylaminedisulphonic acid-S. of the Schöllkopf Co.'s Germ. pat. 40571 of Dec. 23, 1885).

Preparation.—(1) 100 kilos. of 1:1′-*a*-naphthylaminesulphonic acid (S.-acid) are gradually added to 300 kilos. of 10 p.c. anhydrosulphuric acid at such a rate that heating is avoided, and the mixture subsequently warmed on a water-bath until a test is completely soluble in water, and the solution shows a green fluorescence on the addition of alkali. The product is poured into water, neutralised with lime, and converted into sodium salt (Schöllkopf Co., *l.c.*).

(2) It is obtained mixed with the 1:1′:3-*a*-naphthylaminedisulphonic acid by the reduction of the nitro- acids formed when the mixture of 1:4′- and 1:3′-naphthalenedisulphonic acids, produced by sulphonating naphthalene with 23 p.c. anhydrosulphuric acid in the cold, is nitrated (Actieng. f. A., Germ. pat. 45776; Bernthsen, B. 22, 3327). For separation *v.* 1:1′:3-acid.

Salts.—The *normal sodium* salt, $Na_2A + 2H_2O$, crystallises from hot aqueous solution in long needles, from a somewhat dilute solution in compact bright-yellow crystals readily soluble in water (Bernthsen, B. 23, 3090 (footnote)); the *acid sodium* salt crystallises in scales sparingly soluble in cold water.

Reactions.—(1) The *diazo*-compound obtained from the acid sodium salt by treatment with nitrous acid forms tolerably soluble yellow scales, and is converted into 1:1′:4-*a-naphtholdisulphonic acid* (Schöllkopf Co., *l.c.*), into 1:4′-*naphthalenedisulphonic acid*, and into 1:4:1′-*trichloronaphthalene* by the usual reactions (Armstrong and Wynne, C. J. Proc. 1890, 126).

(2) Azo- colours are formed by interaction of the acid with diazotised bases (*cf.* Schöllkopf Co., Germ pat. 42304 of Jan. 28, 1886; Eng. pat. 15781 of 1885). Those obtained by the interaction of tetrazodiphenyl or tetrazoditolyl chloride first with 1 mol. prop. of the acid, and then with 1 mol. prop. of *β*-naphthylamine give bluish-red shades (Actieng. f. A., Germ. pat. 43125 of July 28, 1887).

(v) **1:1′:3-*a*-Naphthylaminedisulphonic acid** (*a*-naphthylamine-[ε-]disulphonic acid).

Preparation.—(1) This acid is obtained mixed with about an equal quantity of the 1:1′:4-acid and some *β*-naphthylaminedisulphonic acid (Schultz, B. 23, 77) by the following method. 20 kilos. of naphthalene are sulphonated with 100 kilos. of 23 p.c. anhydrosulphuric acid in the cold, and to the product, carefully cooled with ice, 14 kilos. of nitric acid of 45° Bé. are gradually added with continual stirring. When nitration is completed, the product is mixed with 1000 litres of water, neutralised with milk of lime, filtered from the separated gypsum, reduced by means of iron and sulphuric acid, again neutralised with milk of lime, and the resulting calcium salt converted into sodium salt in the usual way. The filtrate is concentrated to crystallising-point, and on cooling the normal sodium salt of the 1:1′:4-acid separates out. This is pumped off, and the 1:1′:3-acid separated from the mother-liquor as acid sodium salt by adding an excess of hydrochloric acid; the acid salt being purified by recrystallisation from water (Actieng. f. A., Germ. pat. 45776 of Mar. 16, 1888; Eng. pat. 4625 of 1888).

(2) The product obtained by sulphonating 50 kilos. of naphthalene with 2½–3 times its weight of 20 p.c. anhydrosulphuric acid at 100°, is nitrated at a temperature not exceeding 20–25° by carefully adding 22·5 kilos. of nitric acid (sp. gr. = 1·4) and allowing the resulting mixture to stand for 2 hours. The nitration product is mixed with 5–10 times its bulk of water, partly neutralised with milk of lime to get rid of the great excess of sulphuric acid, filtered from gypsum and treated with the necessary amount of iron borings or zinc-dust. The reduction product is neutralised with milk of lime, converted into sodium salt in the usual way, and the latter separated as acid salt by treating the concen-

trated solution with excess of hydrochloric acid (Ewer & Pick, Germ. pat. 52724 of Sept. 16, 1888). Another method, which differs from this only in the mode of preparation of the 1:3′-naphthalenedisulphonic acid, is described by Bernthsen (B. 22, 3328). Andresen's β-naphthylaminedisulphonic acid occurs in both products (Schultz, *l.c.*).

Salts.—The *acid* crystallises in very soluble colourless scales, which, when dried over sulphuric acid retain 3 mol. prop. H_2O. The *normal barium* salt crystallises either with 3 mol. prop. H_2O in yellow aggregates of needles or with 4 mol. prop. H_2O in colourless, lustrous, flat needles, and is readily soluble in hot, sparingly soluble in cold water; the *acid barium* salt, $BaH_2A_2 + 5H_2O$, forms white, microscopic needles almost insoluble in cold water; the *normal sodium* salt, $Na_2A + 6H_2O$, crystallises in long needles or thin prisms very soluble in water; the *acid sodium* salt, $NaHA + 2H_2O$, crystallises in long needles or thin prisms, soluble in about 30 parts of cold water. The normal sodium salt is precipitated from its solution by excess of aqueous caustic soda, and the acid salt by brine or better ((?) as potassium salt) by aqueous potassium chloride (Bernthsen, *l.c.*).

Reactions. — (1) The *diazo-* compound obtained from the acid sodium salt by treatment with nitrous acid forms sparingly soluble white needles and is converted into 1:1′:3-*naphthasultonsulphonic acid* by boiling with dilute sulphuric acid (Ewer & Pick, *l.c.*; Bernthsen, *l.c.*), also into 1:3′-*naphthalenedisulphonic acid*, and into 1:3:1′-*trichloronaphthalene* by the ordinary methods (Armstrong and Wynne, C. J. Proc. 1890, 16).

(2) Azo- colours are formed by interaction of the acid with diazotised bases. Those obtained by the interaction of tetrazoditolyl chloride with 1 mol prop. of the acid and subsequently with 1 mol. prop. of β-naphthylamine or 1 mol. prop. of 2:3′-β-naphthylaminesulphonic acid give respectively bluish-red and yellowish-red shades (Actieng. f. A., Germ. pat. 46953 of April 8, 1888).

(vi) 1:3:3′-α-**Naphthylaminedisulphonic acid** (Alén's [α-]acid) is obtained by reducing 1:3:3′-α-nitronaphthalenedisulphonic acid with ammonium sulphide.

Salts.—The *acid* is very soluble in water and alcohol, and yields α-naphthylamine on reduction with sodium amalgam. The *barium* salt, $BaA + 4H_2O$, forms tolerably soluble tablets, the *calcium* salt, $CaA + 5H_2O$, readily soluble scales or tablets, the *normal potassium* salt very soluble microscopic crystals, the *acid potassium* salt, $KHA + 3H_2O$, tufts of tolerably soluble slender needles (Alén, Öfvers af Kongl. Vetensk.-Akad. Förh. 1883, N:o 8, 8).

(vii) 1:3:2′-α-**Naphthylaminedisulphonic acid** (Alén's [β-]acid) is prepared by reducing 1:3:2′-α-nitronaphthalenedisulphonic acid with ammonium sulphide.

Salts.—The *acid* is sparingly soluble in alcohol, and yields α-naphthylamine on reduction with sodium amalgam. The solutions of the acid and salts show a blue fluorescence. The *barium* salt, $BaA + H_2O$, crystallises in sparingly soluble microscopic needles, the *calcium* salt, $CaA + 2H_2O$, in tufts of needles equally soluble in hot and cold water, the *normal potassium* salt in readily soluble radiate groups of needles, the *acid potassium* salt, KHA, in microscopic prismatic needles tolerably soluble in hot water (Alén, *ibid.* 26).

Reactions.—On treatment with nitrous acid a *diazo-* compound is obtained, which crystallises in yellow needles, does not form a naphthol-yellow precipitable by aqueous caustic potash when boiled with nitric acid, and interacts with β-naphtholdisulphonic acid-R., giving a scarlet azo- dye (Dahl & Co. Germ. pat. 41957 of Sept. 4, 1886).

⁂ The naphthylaminedisulphonic acids obtained by the nitration of 2:2′- and 2:3′-naphthalenedisulphonic acids (either singly or mixed) in sulphuric acid solution and subsequent reduction with iron borings (Freund, Germ. pat. 27346 of Feb. 24, 1883; Eng. pat. 1069 of 1883) must be regarded as identical with the 1:3:3′- and 1:3:2′-α-acids respectively. Freund, on very insufficient grounds, considers them to be derivatives of β-naphthylamine, and gives no data by which the individual acids can be identified.

(viii) 1:2:4′-α-**Naphthylaminedisulphonic acid.** The preparation of an α-naphthylaminedisulphonic acid, described as new, has been announced by the Chemische Fabrik Grünau, Landshoff and Meyer (Germ. pat. Anm. C 3171 of Jan. 20, 1890). This acid is obtained by sulphonation of 1:2-α-naphthylaminesulphonic acid, and as it yields 1:3′-*naphthalenedisulphonic acid* by elimination of the NH_2-radicle (Tobias, B. 23, 1631), and 1:4′-α-*naphthylaminesulphonic acid* by partial hydrolysis, it must have the constitution here assigned.

α-Naphthylaminetrisulphonic Acid.

1:2:4:2′-α-**Naphthylaminetrisulphonic acid** is formed when naphthionic acid is heated with 3–4 parts of 40 p.c. anhydrosulphuric acid at 120° for 6–16 hours. Small quantities only are formed when α-naphthylamine is substituted for naphthionic acid. It is converted into α-*naphthol-yellow-S.* by diazotising and then heating with nitric acid (M. L. B., Germ. pat. 22545 of Sept. 2, 1882, expired Jan. 1885; Eng. pat. 2178 of 1882).

An α-naphthylaminetrisulphonic acid occurs to the extent of 20 p.c. in the technical potassium 1:4:3′-α-naphthylaminedisulphonate. From its origin, it is almost certainly identical with the 1:2:4:2′-acid, and moreover its diazo- compound is converted by Baeyer's hydrazine reaction into an acid apparently identical with the 2:4:2′-naphthalenetrisulphonic acid (Armstrong and Wynne, C. J. Proc. 1890, 125).

Nitro Derivatives.

(i) 1:2-**Nitro-α-naphthylamine** $NO_2.C_{10}H_6.NH_2$.

Preparation.—100 grams of acet-α-naphthalid are dissolved in 600 grams of acetic acid and nitrated by carefully adding a solution of 45 parts of nitric acid (sp.gr. = 1·54) in 40 grams of acetic acid with continual shaking. After standing for two days the mixed crystallisation of crusts of a molecular compound of the 1:2- and 1:4-nitro-derivative (m.p. = 171°) and needles of the 1:4- derivative (m.p. = 190°) is mechanically separated as far as possible and the two products purified by recrystallisation from alcohol. The hot alcoholic solution of the molecular compound is mixed with the calculated quantity of aqueous caustic potash, heated on a water-bath for a short time and allowed to stand for a day. The 1:4-compound alone undergoes hydrolysis by this treatment and separates first in orange needles, the 1:2-nitroacet-α-naphthalid crystallising from the filtrate in slender yellow needles (m.p. = 199°) on further standing. The acetyl compound is finally hydrolysed by heating with the theoretical quantity of alcoholic potash at 110° for 6 hours (Lellmann and Remy, B. 19, 797).

Properties.—It crystallises from alcohol in reddish-yellow, monoclinic prisms, melts at 144° (Lellmann, B. 17, 112) yields 1:2-*nitro-α-naphthol* by boiling with excess of caustic potash, and is converted into *β-nitronaphthalene* by the diazo- reaction (Lellmann and Remy, B. 19, 236).

1:4-**Nitro-α-naphthylamine** is prepared from 1:4-nitroacet-α-naphthalid (*v. supra*) by hydrolysis with alcoholic potash (Liebermann, A. 183, 232). It crystallises from alcohol in orange needles, melts at 191°, and when boiled with aqueous caustic potash is converted into 1:4-*nitro-α-naphthol* (Andreoni and Biedermann, B. 6, 342).

1:4′-**Nitro-α-naphthylamine** (Beilstein and Kuhlberg, A. 169, 87; Nietzki and Zübelen, B. 22, 452) melts at 118–119°.

1:2:4-**Dinitro-α-naphthylamine** is obtained by nitrating acet-α-naphthalid in warm acetic acid solution with the theoretical quantity of nitric acid (sp.gr. = 1·5) dissolved in acetic acid, and hydrolysing the resulting dinitroacet-α-naphthalid (m.p. = 247°) by heating with alcoholic ammonia under pressure at 160° (Witt, B. 19, 2033, *cf.* Meldola, B. 19, 2683). It crystallises in citron needles, melts at 235°, yields 1:3-*dinitronaphthalene* by the diazo-reaction and like its acetyl- derivative is converted into *dinitro-α-naphthol* by boiling with aqueous caustic soda (Liebermann and Hammerschlag, A. 183, 272).

(ii) **β-Naphthylamine.**

Formation.—β-Naphthylamine is obtained, mixed with varying proportions of ββ-dinaphthylamine, when β-naphthol is heated under pressure with ammonia at 160° for 60–70 hours (B. A. S. F., Germ. pat. 14612, of Feb. 22, 1880), with twice its weight of ammonia-zinc chloride at 200–210° for 2 hours (Merz and Weith, B. 13, 1300), and with four times its weight of anhydrous or hydrated ammonia-calcium chloride at 270–280° for 8 hours [1] (Benz, B. 16, 19). It is also formed with an equal amount of β-naphthol when ββ-dinaphthylamine is digested with concentrated hydrochloric acid at 240° (Ris, B. 19, 2017). It was first prepared by reduction of 1:2-bromo-β-nitronaphthalene with tin and hydrochloric acid (Liebermann and Scheiding, A. 183, 264), and has been obtained by reduction of β-nitronaphthalene (Lellmann and Remy, B. 19, 237).

Preparation.—(1) β-Naphthol is mixed with four times its weight of hydrated ammonia-calcium chloride,[1] and heated under pressure for 2 hours at 230–250° and then for 6 hours at 270–280°. Unattacked β-naphthol is removed from the product by treatment with aqueous caustic soda, and the β-naphthylamine subsequently extracted with dilute hydrochloric acid; the residue consists of ββ-dinaphthylamine. The yield of β-naphthylamine under these conditions amounts to about 80 p.c. and that of ββ-dinaphthylamine to 13–14 p.c. of the β-naphthol employed (Benz, B. 16, 11).

(2) 10 kilos. of β-naphthol are intimately mixed with 4 kilos. of caustic soda and 4 kilos. of ammonium chloride and heated under pressure for 60–70 hours at 150–160° (B. A. S. F., *l.c.*), or 10 kilos. of dry sodium β-naphtholate are mixed with 4 kilos. of ammonium chloride and heated at about 200° for 24 hours (Oehler, Eng. pat. 2516, prov. spec. of June 21, 1880). The crude product is extracted two or three times with boiling weak caustic soda solution, dried and distilled.

Properties.—It crystallises from alcohol in odourless, lustrous rhombic scales, melts at 112°, boils at 294° (Liebermann and Jacobson, A. 211, 41), is slightly volatile with steam, dissolves readily in alcohol and ether, and is also soluble in water. The aqueous solution exhibits a marked blue fluorescence. Unlike α-naphthylamine it gives no colour reactions with ferric chloride, chromic acid, bleaching powder, or an alcoholic solution of nitrous acid.

Salts.—The *hydrochloride*, B.HCl, crystallises in colourless scales extremely soluble in water and alcohol, sparingly soluble in dilute hydrochloric acid; the *nitrate*, $B.HNO_3$, and *sulphate*, $B_2.H_2SO_4$, in colourless scales sparingly soluble in water. The solutions are destitute of fluorescence.

Reactions.—(1) β-Naphthylamine in acid solution is readily diazotised on treatment with nitrous acid forming a yellow, crystalline *diazo-*compound which is converted into *β-naphthol* by boiling with acidified water, and into *β-chloro-*, *β-bromo-*, *β-iodo-*, and *β-cyano-naphthalene*, &c. by the known methods (*cf.* Liebermann and Palm, A. 183, 267; Jacobson, B. 14, 804; Sandmeyer, B. 17, 1633, 2650; 20, 1496; 23, 1880).

(2) Azo- colours are formed both by interaction of the diazotised base with amines or phenols and of the base with diazotised bases. The azo- dyes obtained by interaction with α- or β-naphtholsulphonic acids exhibit bluer or more yellow shades than the corresponding colouring matters from α-naphthylamine.

Tests.—β-Naphthylamine ought to be free from β-naphthol and ββ-dinaphthylamine, and should therefore be completely soluble in dilute hydrochloric acid, and have the right melting-point.

Acet-β-naphthalid $C_{10}H_7.NH.CO.CH_3$ is formed together with about 14 p.c. of ββ-dinaphthylamine by heating β-naphthol with ammo-

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[1] A tabular statement of the yield of β-naphthylamine and ββ-dinaphthylamine obtained when the temperature and duration of the reaction are varied is given by Benz.

[1] The preparation of this substance has been described in connection with α-naphthylamine (*q. v.*).

nium acetate at 270–280° for 8 hours (Merz and Weith, B. 14, 2343; Calm, B. 15, 610).

Preparation. — β-Naphthylamine is boiled with 1·25–1·5 times its weight of glacial acetic acid for 12 hours in a reflux apparatus. About 10 p.c. of ββ-dinaphthylamine is formed in the reaction, and can readily be separated by crystallisation from alcohol in which it is sparingly soluble. The yield of acet-β-naphthalid amounts to about 80–85 p.c. of the theoretical (Liebermann and Jacobson, A. 211, 42).

Properties.—It crystallises from water or alcohol in lustrous scales, melts at 132°, and is readily soluble in alcohol, sparingly in water. It is more easily hydrolysed by boiling with dilute acids than alkalis (Calm, B. 15, 612). On nitration it yields 1:2-*nitroacet-β-naphthalid* (Jacobson, B. 14, 805, 1794), and on sulphonation with sulphuric acid of 66°Bé. at 20–30° it forms the 2:4′-, and at 150–160° the 2:2′-*acet-β-naphthalidsulphonic acid* (Kinzelberger & Co., Monit. Sci. [4] 2, 50).

Dimethyl-β-naphthylamine is prepared by heating β-naphthol with trimethylamine at 200° for 20 hours, and is purified by conversion into trimethyl-β-naphthylammonium hydroxide which is subsequently decomposed by distillation (Hantzsch, B. 13, 2054). A better method consists in heating β-naphthylamine with a mixture of methyl iodide, caustic soda, and water at 120° for some hours, and decomposing the resulting trimethyl-β-naphthylammonium iodide by distillation with caustic potash (Bamberger and Müller, B. 22, 1306). It melts at 46° and boils at 305°.

Ethyl-β-naphthylamine (Henriques, B. 17, 2668), is a colourless, viscid liquid boiling at 191° under 25 mm., and at 305° under 716 mm. pressure (Bamberger and Müller, B. 22, 1297).

Diethyl-β-naphthylamine is a colourless, viscid oil boiling at 316° under 717 mm. pressure (Bamberger and Williamson, B. 22, 1760). Its hydrochloride on distillation with lime is converted into β-naphthylamine and butylene.

Phenyl-β-naphthylamine.

Preparation.—(1) Phenyl-β-naphthylamine can be prepared by heating either 6 kilos. of β-naphthol and 5 kilos. of aniline hydrochloride for 7–9 hours at 170–190°, or 7 kilos. of β-naphthol and 5 kilos. of aniline under pressure for 10 hours at 200–210° (B. A. S. F., Germ. pat. 14612, of Feb. 22, 1880). Also by heating 11 parts of β-naphthol with 10 parts of aniline hydrochloride in an open vessel for 12 hours at 180° (Oehler, Eng. pat. 2516 of 1880, prov. spec.). The unattacked aniline and β-naphthol are respectively extracted by water or dilute acid and by aqueous caustic soda, and the phenyl-β-naphthylamine purified by distillation.

(2) According to Friedländer the yield of β-naphthylamine is about 37·5 p.c. of the theoretical when β-naphthol is heated with 2 mol. prop. of aniline at 280–290° for 9 hours, and about 52·6 p.c. when heated with 2 mol. prop. of aniline hydrochloride at 220–230° for 9 hours (B. 16, 2085, 2087). A yield of 90–98 p.c. can, however, be obtained by heating 1 mol. prop. of β-naphthol (15 parts), 2 mol. props. of aniline (19·4 parts) and 1 mol. prop. of calcium chloride (11·6 parts) under pressure at 280° for 9 hours (*ibid.* 2076). Zinc chloride has also been employed as a dehydrating agent by Merz and Weith (B. 13, 1299).

Properties.—It crystallises from alcohol in needles, melts at 108°, boils at 395–395.5° (Crafts, A. 202, 5), and is soluble in the ordinary organic solvents forming solutions having a blue fluorescence. When heated with concentrated hydrochloric acid at 240° it is converted into β-naphthol and aniline (Friedländer, B. 16, 2090). The *acetyl* derivative (m.p. = 93°) and two *nitro-* derivatives have been described by Streiff (A. 209, 159).

Reaction.—By interaction with nitrosodimethylaniline hydrochloride in acetic acid solution, it is converted into a violet-coloured *azine*-derivative (Witt, Germ. pat. 19224 of Feb. 18, 1882; B. 21, 723; *v.* Azines).

Derivatives. — **Phenyl-β-naphthylaminesulphonic acids** have been prepared by two methods:

(1) The sodium salt of 2:3′-β-naphtholsulphonic acid is heated with an equal weight of aniline hydrochloride and twice its weight of aniline at 190–200° for 1½–2 hours in an open vessel provided with a reflux condenser; the yield consists of about 70 p.c. of sodium phenyl-β-naphthylaminesulphonate and about 8 p.c. of phenyl-β-naphthylamine, the latter becoming the chief product when the heating is prolonged (Actieng. f. A., Germ. pat. 38424 of March 31, 1886).

(2) The action of sulphuric acid on the amine. According to Streiff (A. 209, 160) phenyl-β-naphthylamine forms a trisulphonic acid when heated with 6 times its weight of concentrated sulphuric acid on a water-bath; Zimmer (Germ. pat. 45940 of May 17, 1888, taken over by Actieng. f. A., April 1890), however, states that the action of sulphuric acid at 75–125° always results in the production of a mixture of sulphonic acids, but that a 90–95 p.c. yield of a uniform *monosulphonic acid* can be obtained by heating the amine with 3–4 parts of 100 p.c. sulphuric acid at 25–45°. According to the Clayton Aniline Co. (Germ. pat. 53649 of Nov. 12, 1889; Eng. pat. 10934 of 1889) two isomeric *monosulphonic acids* are formed in Zimmer's process, and are best obtained by dissolving phenyl-β-naphthylamine in 4 parts of 100 p.c. sulphuric acid at temperatures below 50°, allowing the whole to stand for 2 days at 15–20°, pouring into water, converting the separated acid into ammonium salt and separating the mixed salt by fractional crystallisation. The proportions of the acids [A] and [B] vary with the temperature employed during sulphonation; at 15–20° the yield of [A] amounts to about 40 p.c., but becomes smaller at higher temperatures.

Salts.—(i) [A]-acid.—The *barium* and *calcium* salts are very sparingly soluble amorphous precipitates; the *potassium* salt crystallises in soluble needles, the *sodium* salt in needles soluble in 4·25 parts of boiling water, also in alcohol forming a non-fluorescent solution, the *ammonium* salt in plates soluble in about 240 parts of water at 20°.

(ii) [B]-acid.—The *calcium* salt crystallises in soluble needles or prisms, the *potassium* salt in soluble plates, the *sodium* salt, $NaA + 8H_2O$, in plates soluble in an equal weight of water, also in alcohol forming a solution showing a blue fluorescence, the *ammonium* salt in long needles soluble in less than an equal weight of water at 20°.

(iii) Zimmer's acid.—The *sodium* salt, $NaA + 2H_2O$, crystallises in silvery scales soluble in 5–6 parts of boiling and in about 33 parts of cold water, also in alcohol of 85–90 p.c. Tr. forming a solution showing a blue fluorescence. The acid not improbably is impure [B]-acid.

Orthotolyl-β-naphthylamine is obtained by heating β-naphthol (1 mol. prop.) orthotoluidine (2 mol. prop.) and calcium chloride (1 mol. prop.) at 280° for 9 hours; the yield amounts to about 80·3 p.c. of the theoretical (Friedländer, B. 16, 2082).

Properties.—It crystallises from petroleum spirit in lustrous scales, melts at 95–96°, and is readily soluble in alcohol, ether, and benzene. When treated with 5 parts of 100 p.c. sulphuric acid at 10–50°, it yields a mixture of two isomeric *monosulphonic acids*, which can be separated by conversion into calcium salts, one of which is soluble, the other almost insoluble in water (Clayton Aniline Co., Eng. pat. 10934 of 1889).

Paratolyl-β-naphthylamine is formed by heating β-naphthol (1 mol. prop.) with paratoluidine (2 mol. prop.) and calcium chloride (1 mol. prop.) at 280° for 9 hours; the yield amounts to about 92·7 p.c. of the theoretical (Friedländer, B. 16, 2078). Also by heating β-naphthol with paratoluidine hydrochloride at 200° (Witt, B. 20, 578); the yield after 9 hours' heating at 220–230° amounting to 55·6 p.c. of the theoretical (Friedländer, B. 16, 2087).

Properties.—It crystallises in scales, melts at 104° (Witt), and is readily soluble in alcohol, acetic acid, benzene, and ether, forming solutions which show a violet-blue fluorescence. A *sulphonic* acid has been prepared by heating the sodium salt of 2:3′-β-naphtholsulphonic acid with paratoluidine hydrochloride and paratoluidine at 200° for 6 hours (Actieng. f. A., Germ. pat. 38424, *v. supra*).

ββ-Dinaphthylamine, formed as a secondary product in the manufacture of β-naphthylamine, is obtained as chief product (60–80 p.c.) when β-naphthol is heated with four times its weight of ammonia-zinc chloride at 280° (Merz and Weith, B. 13, 1300; 14, 2344; Calm, B. 15, 614; Benz, B. 16, 14) and with zinc acetate and ammonium chloride at 270° for 8 hours (Calm). It is also obtained by heating β-naphthol with β-naphthylamine (B. A. S. F., Germ. pat. 14612 of Feb. 22, 1880), or better with β-naphthylamine and calcium chloride at 270–280° (Benz, B. 16, 17). From β-naphthylamine it is formed to the extent of 3·5 p.c. by heating at 280–300° (Benz, B. 16, 14), of 10 p.c. by boiling with 1·5 times its weight of glacial acetic acid for 12 hours (Liebermann and Jacobson, A. 211, 43), and in considerable quantity by heating with calcium chloride at 260–280 (Merz and Weith, B. 14, 2343). It is freed from β-naphthylamine and β-naphthol respectively by extraction with dilute acids and alkalis, and purified by distillation and subsequent crystallisation from boiling benzene (Ris, B. 20, 2618).

Properties.—It crystallises in silvery scales, melts at 171°, boils at 471° (Ris, *l.c.*), and is readily soluble in hot alcohol and benzene forming solutions which show an intense blue fluorescence. On digestion with concentrated hydrochloric acid at 240°, it decomposes quantitatively into β-naphthylamine and β-naphthol (Ris, B. 19, 2017). When heated with sulphur at 250° for 10 hours (Ris, B. 19, 2241), or treated with sulphur dichloride in benzene solution (Kym, B. 21, 2811), it is converted into *thiodinaphthylamine*, which on distillation with finely divided copper yields *dinaphthylcarbazole*.

α-β-Dinaphthylamine is obtained by heating α-naphthylamine with β-naphthol (but not β-naphthylamine with α-naphthol) and calcium chloride at 270–280°. It crystallises in long, thick prisms, melts at 110–111°, and is very soluble in warm benzene, ether, and alcohol, sparingly soluble in petroleum spirit (Benz, B. 16, 17).

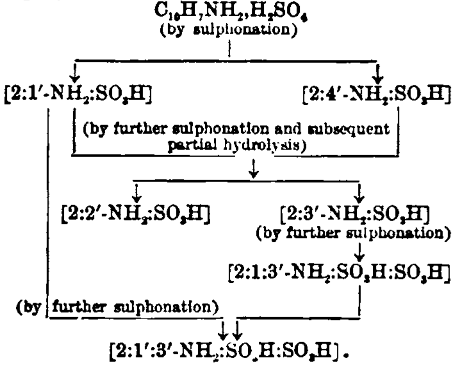
Sulphonic Acids.

Introductory.—As already pointed out (*v. Nitro- derivatives*), the 1:3′-disulphonic acid is the only naphthalenesulphonic acid known to give a β-nitro- derivative on nitration; consequently β-naphthylaminesulphonic acids, with the one exception of Andresen's compound, cannot be prepared by nitration and subsequent reduction of naphthalenesulphonic acids. In practice β-naphthylaminesulphonic acids are obtained by two methods :—

1. Digestion of the sodium salts of the corresponding β-naphtholsulphonic acids with ammonia under pressure.

2. Sulphonation of β-naphthylamine.

The product formed by heating β-naphthylamine sulphate with three times its weight of sulphuric acid of 66°Bé. at 100° contains the four theoretically possible heteronucleal monosulphonic acids, but at 25–30° consists almost entirely of the two αβ-acids, and at 160–170° of the two ββ-acids in about equal proportions: each αβ-acid being converted into a mixture of the two ββ-acids containing more than 50 p.c. of the 2:2′-acid when heated with 3 times its weight of sulphuric acid of 66°Bé. at 160–170° (Weinberg, B. 20, 3354). Five β-naphthylaminedisulphonic acids have been obtained by the action of anhydrosulphuric acid in the cold on the β-naphthylaminemonosulphonic acids, and of these the 2:1′:3′-acid and at least one other are present in the β-naphthylamine-[γ-]disulphonic acid prepared by the methods given in Germ. pat. 35019 of Gans & Co. (*v. infra*). The series of changes which probably occur when β-naphthylamine is sulphonated under conditions described in connection with the respective acids is given in the table, reference having already been made to the part played by polysulphonic acids in the conversion of the β-naphthylamine-α- into the β-naphthylamine-β-sulphonic acids (*v.* Substitution in the naphthalene series, *supra*).



The β-naphthylaminedisulphonic acids resemble the α- compounds in the readiness with which they form acid salts; the acid salt and not the acid being precipitated on the addition of an acid to a solution of either the normal potassium or normal sodium salt.

β-Naphthylaminemonosulphonic Acids.

(i) 2:1′-[1] **β-Naphthylaminesulphonic acid** (β-naphthylamine-[α-]sulphonic acid; Badische acid).

Formation.—When β-naphthylamine is heated with three times its weight of concentrated sulphuric acid of 66°Bé. at 100–105° for about six hours until sulphonation is completed, it is converted into a product consisting chiefly of a sulphonic acid sparingly soluble in water. This acid was at one time regarded as practically uniform (B. A. S. F., Germ. pat. 20760 of Nov. 17, 1881) but is now known to contain the four heteronucleal β-naphthylaminesulphonic acids in the approximate proportion of 50 p.c. of the 2:1′- or [α-], 40 p.c. of the 2:4′- or [γ-], and 5 p.c. each of the 2:2′- or [δ-] and the 2:3′- or [β-] acids (Dahl & Co., Germ. pat. 29084 of March 2, 1884; Eng. pat. 7712 of 1884; Green, C. J. 55, 35). These conditions seemingly afford the best method of preparing the 2:1′-acid, since the proportion is not greater (about 45 p.c.) when β-naphthylamine sulphate is sulphonated in the cold (*v.* 2:4′-acid) and also diminishes at higher temperatures until at 160–170° the product contains only the two ββ-acids. Forsling's statement that the sulphonation product at 140° consists almost entirely of a mixture of the 2:1′- and 2:4′-acids (B. 20, 2100) must be regarded as incorrect in view of the fact that the product at 120° compared with that at 100° contains a smaller proportion of the 2:1′-acid and a considerably increased yield of the ββ-acids (*cf.* Dahl & Co., *l.c.*).

Preparation.—(1) The product obtained by sulphonating β-naphthylamine with three times its weight of concentrated sulphuric acid at 100–105° is poured into water, and the precipitated acid washed, pressed, and converted into sodium salt. This is dried, powdered, boiled for about an hour with six times its weight of 90–95 p.c. alcohol, again extracted with a further quantity of alcohol, and the residue, consisting of the pure sodium salt of the 2:1′-acid, dissolved in hot water and precipitated by the addition of hydrochloric acid (Dahl & Co., *l.c.*; Green, *l.c.*).

(2) The pure acid may be readily obtained by heating a salt of 2:1′-β-naphtholsulphonic acid with ammonia under pressure (Bayer and Duisberg, B. 20, 1427; Pfitzinger and Duisberg, B. 22, 397).

Salts.—The *acid*, $NH_2.C_{10}H_6.SO_3H$, is precipitated from solutions of its salts in slender matted needles, but crystallises from hot water in prismatic tables, dissolves in about 200 parts of boiling or 1000–1700 parts of cold water, and is almost insoluble in alcohol. The salts, except those of silver and copper, crystallise well, dissolve readily for the most part in water, and like the acid show a blue fluorescence in solution. The *barium* salt, $BaA_2 + 4H_2O$, crystallises in aggregates of broad long prisms soluble in about 23 parts of cold and very soluble in hot water; the *calcium* salt, $CaA_2 + 6H_2O$, crystallises in large broad tables soluble in about 11 parts of cold water; the *magnesium* salt, $MgA_2 + 3\frac{1}{2}H_2O$, forms small granular aggregates extremely soluble in water; the *potassium* salt, $KA + \frac{1}{2}H_2O$, crystallises in six-sided tables; the *sodium* salt is anhydrous and crystallises in large prisms or in large, thin, four-sided scales soluble in about 120 parts of boiling 96 p.c. alcohol; the *ammonium* salt forms very soluble, large, solid prisms.

Reactions.—(1) The *diazo-* compound obtained from 2:1′-β-naphthylaminesulphonic acid by treatment with nitrous acid is a sparingly soluble, greenish-yellow powder, and is converted into 2:1′-β-*naphtholsulphonic acid* (Dahl & Co., *l.c.*), into *naphthalene-α-sulphonic acid* (Pfitzinger and Duisberg, B. 22, 397), and into 2:1′-*dichloronaphthalene* by the known reactions (Armstrong and Wynne, B. A. Report 1888, 96; C. J. Proc. 1888, 105; 1889, 53; *cf.* Forsling, *l.c.*; B. 21, 2802; 22, 619).

(2) On interaction with diazotised bases—*e.g.* tetrazodiphenyl chloride—it does not form azo- dyes but is converted into soluble yellow *diazoamido-* compounds (Bayer and Duisberg, B. 20, 1428; Witt, B. 21, 3483).

(3) When sulphonated in the cold with four times its weight of 20 p.c. anhydrosulphuric acid, it gives an almost uniform product consisting of 2:1′:3′-β-*naphthylaminedisulphonic acid* (amido-G. or [γ-] acid) (Armstrong and Wynne, C. J. Proc. 1890, 128).

(ii) 2:4′-β-**Naphthylaminesulphonic acid** (β-naphthylamine-[γ-]sulphonic acid; Dahl acid).

Formation.—2:4′-β-Naphthylaminesulphonic acid occurs to the extent of 40 p.c. in the product obtained by heating β-naphthylamine with three times its weight of concentrated sulphuric acid at 100–105° (*v.* 2:1′-acid, *supra*). A yield of about 55 p.c. is obtained when β-naphthylamine sulphate is sulphonated at 15–20° with three times its weight of sulphuric acid of 66°Bé. (Dahl & Co., Germ. pat. 32276 of Nov. 14, 1884), and of about 68–70 p.c. when β-naphthylamine is heated with three times its weight of 20 p.c. anhydrosulphuric acid at 70–80° until sulphonation is completed (Dahl & Co., Germ. pat. 29084). It also forms the chief product when

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[1] In every case where the constitution of a β-naphthylaminesulphonic acid is given, the NH_2-group is supposed in the position '2.'

acet-β-naphthalid is sulphonated at 20–30° with five times its weight of sulphuric acid of 66°Bé. and the product boiled with water to eliminate the acetyl-radicle (Kinzelberger & Co., Monit. Sci. [4] 2, 50).

Preparation.—85 kilos. of β-naphthylamine sulphate are gradually mixed with 270 kilos. of sulphuric acid of 66°Bé. at a temperature not exceeding 20°, and the mass stirred during 48–70 hours in a closed iron vessel until a test gives a clear solution in dilute ammonia. The product is poured on to broken ice and the precipitated acid washed, pressed, and converted into sodium salt, which after drying is freed from 2:1′-salt by extraction with six times its weight of boiling 90–95 p.c. alcohol. The alcoholic filtrate containing the 2:4′- and any 2:2′- and 2:3′-salt is evaporated, the residue dissolved in water, treated with hydrochloric acid, and the precipitated sulphonic acids suspended in water and converted into barium salts by boiling with barium carbonate. On cooling, the filtrate deposits the sparingly soluble barium salts of the 2:2′-and 2:3′-acids, whilst the mother-liquor contains the easily soluble salt of the 2:4′-acid, and on addition of hydrochloric acid gives a crystalline precipitate of the pure acid (Dahl & Co.). A partial separation can be effected previous to the extraction with alcohol by converting the sulphonation product into calcium salt, concentrating the solution to crystallising-point, and allowing it to stand for two days; the crystalline separation contains the greater part of the 2:1′-salt, almost the whole of the 2:2′- and 2:3′-salts and some 2:4′-salt, and the mother-liquor chiefly 2:4′-salt (Dahl & Co., Germ. pat. 32271 of May 28, 1884).

Salts.—(Forsling, B. 20, 2103.) The *acid* crystallises in long, slender, anhydrous needles or nacreous scales, dissolves in about 260 parts of boiling and in 590 parts (Dahl & Co.) or 1300 parts (Forsling) of cold water, and is almost insoluble in alcohol. The salts, apart from the unstable silver and copper salts, crystallise well, dissolve easily in water, and like the acid show a reddish-blue fluorescence in solution. The *barium* salt, $BaA_2 + 2\frac{1}{2}H_2O$, crystallises in extremely soluble, granular aggregates; the *calcium* salt, $CaA_2 + 11H_2O$, crystallises from a 'cold' aqueous solution in broad needles soluble in about 11 parts of 'cold' water, and from an aqueous solution at 10° in efflorescent forms; the *magnesium* salt, $MgA_2 + 8H_2O$, crystallises in small forms, the *potassium* salt, $KA + H_2O$, in extremely soluble small rhombohedra, the *sodium* salt, $NaA + 5H_2O$, in thick, broad tables extremely soluble in water and soluble in about 10 parts of boiling or cold 95 p.c. alcohol, the *ammonium* salt in extremely soluble tables.

Reactions.—(1) The *diazo-* compound obtained from 2:4′-β-naphthylaminesulphonic acid by treatment with nitrous acid is a sparingly soluble greenish-yellow microcrystalline powder, and is converted into 2:4′-*β-naphtholsulphonic acid* (Dahl & Co.), and into 2:4′-*dichloronaphthalene* by the known reactions (Armstrong and Wynne, B. A. Report, 1888, 96; C. J. Proc. 1889, 49; *cf.* Forsling, *l.c.*).

(2) When sulphonated with four times its weight of 20 p.c. anhydrosulphuric acid in the cold, it forms a product containing the 2:4′:1- and 2:4′:2′-*β-naphthylaminedisulphonic acids* (Armstrong and Wynne, C. J. Proc. 1890, 128).

(3) The azo- dyes formed by interaction of the diazotised acid with α-naphtholsulphonic acids give bluish-red and with β-naphtholsulphonic acids give yellowish-red shades and are more soluble than the corresponding colours from the 2:1′- and 2:3′-acids (Dahl & Co., Germ. pat. 30640 of May 20, 1884). The disazo- dyes obtained by interaction of the acid with tetrazodiphenyl and tetrazoditolyl chloride are respectively red and orange, and have no commercial value.

(iii) 2:2′-β-**Naphthylaminesulphonic acid** (β-naphthylamine-[δ-]sulphonic acid; naphthylaminesulphonic acid-F.).

Formation.—2:2′-β-Naphthylaminesulphonic acid is formed when β-naphthylamine is heated with six times its weight of sulphuric acid of 66°Bé. at 180–190°, when β-naphthylamine sulphate is heated with three times its weight of sulphuric acid of 66°Bé. at 160–170° for an hour, and when either 2:1′- or 2:4′-β-naphthylaminesulphonic acid is heated with three times its weight of sulphuric acid of 66°Bé. at 160–170° for about two hours (Bayer & Co., Germ. pat. 39925 of April 15, 1886; 41505 of Dec. 17, 1886; 42272 of Jan. 1, 1887; 42273 of Jan. 23, 1887; Eng. pat. 5846 of 1886, Bayer and Duisberg, B. 20, 1426). In addition, the product contains 2:3′-β-naphthylaminesulphonic acid (Bayer & Co., Germ. pat. 39925), and the proportion of this [β-]acid, which is seemingly greatest in the product obtained by the first method, amounts to about 50 p.c. by the second, and to less than 50 p.c. by the last two methods (Weinberg, B. 20, 2909, 3354; Schultz, B. 20, 3159). It is also obtained by heating acet-β-naphthalid with 6 times its weight of sulphuric acid of 66°Bé. at 150–160° for 1–1½ hours, and eliminating the acetyl radicle from the product by pouring the hot melt into water (Kinzelberger & Co., Monit. Sci. [4] 2, 50; *cf.* Friedländer, Fortschritte der Theerfarbenfabrikation, 431). Pure 2:2′-acid is produced when the sodium salt of 2:2′-β-naphtholsulphonic acid is heated with twice its weight of 20 p.c. ammonia under pressure at 250° (Cassella & Co., Germ. pat. 43740 of Sept. 22, 1886; 45221 of June 4, 1887; Eng. pat. 12908 of 1886; Bayer and Duisberg, B. 20, 1432; Weinberg, B. 20, 2908; Schultz, B. 20 3159; Erdmann, B. 21, 637), and the mixed 2:2′- and 2:3′-acids are obtained when the mixture of 2:2′- and 2:3′-β-naphtholsulphonic acids, formed by heating β-naphthol with an equimolecular proportion of 100 p.c. sulphuric acid at 100–130°, is heated in the form of sodium salt with ammonia either by Landshoff's method (*v. infra*) or under pressure (Green, Eng. pat. 15849 of 1888; C. J. 55, 37; B. 21, 724).

Preparation.—(1) 50 kilos. of sodium 2:2′-β-naphtholsulphonate and 100 kilos. of 20 p.c. ammonia are heated under pressure for 6 hours at 250°, or a mixture of 33 kilos. of sodium 2:2′-naphthalenedisulphonate and 25 kilos. of 40 p.c. aqueous caustic soda is heated under pressure for 10 hours at 200–250°, a solution of 7 kilos. of ammonium chloride in 20 kilos. of water added, and the whole heated for another

10 hours at 200-250°. The product is dissolved in boiling water and the pure 2:2′-acid precipitated by acidifying the solution (Cassella & Co., *l.c.*; Weinberg, *l.c.*).

(2) A mixture of 100 kilos. of dry β-naphthylamine sulphate and 300 kilos. of sulphuric acid of 66°Bé. is heated at 160–170° for an hour, the product poured on to broken ice, and the precipitated acid filtered off and washed. Both the 2:2′- and 2:3′-acids are formed under these conditions, and the complete separation of the two substances is attended with difficulty, for although pure 2:3′-acid can be got from the product with little trouble it is by no means easy to obtain the 2:2′-acid free from its isomeride. According to Schultz (Chemie des Steinkohlentheers, 2nd ed. 2, 313) the best method is one based on the very different solubility of the copper salt of the two acids in water, for whilst the copper salt of the 2:3′-acid forms golden crystals scarcely soluble in cold and only slightly soluble in warm water, the copper salt of the 2:2′-acid is readily soluble even in cold water. A solution of 20 kilos. of the sodium salt of the mixed acids in 300 litres of boiling water is treated with a solution of 10 kilos. of copper sulphate in 30 litres of water, and, after cooling slightly, is filtered from the precipitated copper salt of the 2:3′-acid. The filtrate, on addition of hydrochloric or sulphuric acid gives a precipitate of the nearly pure 2:2′-acid, and this can, it is said, be obtained 'chemically pure' by fractional crystallisation of its barium salt (Actieng. f. A., Germ. pat. 44248 of Jan. 7, 1888; Eng. pat. 687 of 1888). The method can be modified, and the 2:3′-acid alone converted into copper salt by adding copper sulphate solution only so long as a precipitate forms and then filtering, or an alternative process based on the slight solubility of the 2:3′- and ready solubility of the 2:2′- lead salt and conducted on similar lines may be employed (Actieng. f. A., Germ. pat. 44249 of Jan. 12, 1888).

This method has not, in the writer's experience, come up to expectation, and a better method of separation is the one based on the difference in solubility of the two acids in hot water. A boiling dilute solution of the mixed sodium salts, after acidification with hydrochloric or sulphuric acid, is allowed to cool to about 80°, and the crystalline separation (thin scales) of the 2:3′-acid at once filtered off and washed with hot water. The filtrate crystallises in poorly defined needles having a 'mixed' appearance, and consisting of 2:2′- mixed with some 2:3′-acid; this is filtered off and repeatedly submitted to the same treatment until no further separation of the characteristic thin plates of the 2:3′-acid occurs, and the 2:2′-acid crystallises from the solution below 80° in uniform, slender, voluminous needles.

Salts.—The *acid*, $NH_2.C_{10}H_6.SO_3H+H_2O$, crystallises from water in long, lustrous, slender, voluminous needles soluble in 350 parts of boiling and sparingly soluble in cold water. When boiled with a quantity of water insufficient for its dissolution, the crystalline acid breaks down into a very sparingly soluble, anhydrous, sandy powder. The *barium* salt, BaA_2+5H_2O, crystallises in tufts of slender scales soluble in about 400 parts of cold and readily soluble in hot water the *calcium* salt, CaA_2+6H_2O, in scales showing a blue fluorescence and soluble in about 270 parts of cold water, the *potassium* salt in slender tufts of needles soluble in 40 parts of cold water, the *ammonium* salt in tolerably soluble small plates, the *sodium* salt, $NaA+4H_2O$, in small white needles soluble in 70 parts of cold and very soluble in hot water, soluble also in hot 90 p.c. alcohol from which it crystallises in small lustrous scales showing a reddish-blue fluorescence. The solutions of the salts show a reddish-violet fluorescence.

Reactions.—(1) The *diazo-* compound obtained from 2:2′-β-naphthylaminesulphonic acid by treatment with nitrous acid is a tolerably soluble, coarsely crystalline, glittering, orange-red powder (Erdmann, B. 21, 638), and is converted into 2:2′-*β-naphtholsulphonic acid* (Bayer and Duisberg, B. 20, 1431; Schultz, B. 20, 3161), into *naphthalene-β-sulphonic acid* (Weinberg, B. 20, 2910), and into 2:2′-*dichloronaphthalene* by the known reactions (Erdmann, B. 21, 638; Armstrong and Wynne, B. A. Report, 1888, 96; C. J. Proc. 1889, 49).

(2) When sulphonated with four times its weight of 20 p.c. anhydrosulphuric acid at 20°, it yields at least two *β-naphthylaminedisulphonic acids*, one of which is probably the 2:2′:4′-acid (Armstrong and Wynne, C. J. Proc. 1890, 130).

(3) On fusion as sodium salt with twice its weight of 50 p.c. aqueous caustic soda at 260–300° for 2–3 hours, it is converted into 2:2′-*β-amidonaphthol* (Gesell. f. Chem. Ind., Germ. pat. 47816 of Dec. 15, 1888).

(4) By interaction with tetrazo- compounds it forms bluish-red disazo- dyes (Bayer & Co., Germ. pat. 42021, 46623, 48074; Cassella & Co., Germ. pat. 46134; *v.* Azo- COLOURING MATTERS).

Alkyl derivatives.—2:2′-Methyl- or ethyl-β-naphthylaminesulphonic acid is obtained when a 12·5 p.c. aqueous solution of the 2:2′-sodium salt is heated with the requisite quantity of methyl or ethyl chloride, bromide, or iodide under pressure in a lead-lined vessel at 100–110° for some hours. Both acids are readily soluble in hot, sparingly soluble in cold water, and by interaction with tetrazoditolyl or tetrazodianisoïl form bluish-red disazo- dyes of much bluer shade than the corresponding colours from the 2:2′-acid (Bayer & Co., Germ. pat. 41506, 41761, 43024, 43196; *v.* Azo- COLOURING MATTERS).

(iv) **2:3′-β-Naphthylaminesulphonic acid** (β-naphthylamine-[β-]sulphonic acid; Brönner acid).

Formation.—2:3′-β-Naphthylaminesulphonic acid occurs to the extent of about 5 p.c. in the product obtained when β-naphthylamine is heated with 3 times its weight of sulphuric acid of 66°Bé. at 100–105° for 6 hours (Green, C. J. 55, 35; B. 21, 722), and of about 50 p.c. in that formed when β-naphthylamine sulphate or 2:1′- or 2:4′-β-naphthylaminesulphonic acid is heated with 3 times its weight of sulphuric acid of 66°Bé. at 160–170° for 2 hours (Weinberg, B. 20, 2909, 3354; Schultz, B. 20, 3159; *v.* 2:2′-acid). It is also produced, mixed with a small proportion of 2:2′-acid, when an intimate mixture of 14·3 kilos. of β-naphthylamine and 10 kilos. of concentrated sulphuric acid—the proportions necessary to form acid β-naphthylamine sulphate—is baked at 200–210° for 2–3 hours (Liebmann, Monit. Sci. [3] 15, 1043; quoted by Bayer and Duisberg, B. 23, 1914); and a 60 p.c. yield of a similar product is obtained when β-naphthylamine is heated with 3 times its weight of potassium bisulphate at about 230° (Bischoff and Brodsky, B. 23, 1914). Pure 2:3′-acid is obtained by heating the sodium salt of pure 2:3′-β-naphtholsulphonic acid with ammonia, either at 180° under pressure (Farbfab. v. Brönner, Germ. pat. 22547 of July 5, 1882; Eng. pat. 3724 of 1882), or at 200–250° under the ordinary pressure (Landshoff, Germ. pat. 27378 of Jan. 23, 1883; B. 16, 1931).

Preparation.—(1) 60 kilos. of the ammonium salt of 2:3′-β-naphtholsulphonic acid (Schaeffer acid) is heated with 12 kilos. of slaked lime and 60 kilos. of water for 24 hours under pressure at 180°, and the product dissolved in 50 litres of hot water, filtered, and acidified (Farbfab. v. Brönner, *l.c.*). The sparingly soluble 2:3′-acid is precipitated in small scales, and does not require purification if pure 2:3′-β-naphtholsulphonic acid is employed; if, however, an impure acid containing either the 2:1′- or 2:2′-acid is used, the corresponding 2:1′- or 2:2′- β-naphthylaminesulphonic acid will occur in the product and necessitate its purification by one of the methods described in connection with these acids.[1]

(2) The dry sodium salt of 2:3′-β-naphtholsulphonic acid is heated at 200–250° under the ordinary pressure in a current of moist or dry ammonia for about 12 hours. The process is conducted in an iron cylinder provided with a horizontal stirrer, and surrounded with an iron jacket which serves for an air or oil bath (Landshoff, *l.c.*).

The acid obtained by either method, or from the product of the action of concentrated sulphuric acid on β-naphthylamine at 160–170°, can be separated from 2:2′-acid (*q.v.*) by precipitation from a dilute aqueous solution of its sodium salt at temperatures above 80°, and further purified by conversion into its ammonium salt, which is fractionally crystallised until a uniform separation in the characteristic large, thin, fluorescent plates is obtained (Green, C. J. 55, 36).

Salts.—(Limpricht, *cf.* Schultz, Chemie des Steinkohlentheers, 2nd ed. 2, 525; Forsling, B. 20, 77). The *acid*, $NH_2.C_{10}H_6.SO_3H + H_2O$ (F.) crystallises from water in lustrous silvery scales[2] soluble in about 630 parts[3] of boiling (Weinberg, B. 20, 2909), and very sparingly soluble in cold water. The salts crystallise for the most part in needles or scales, dissolve sparingly in water, and, like the acid, show a blue fluorescence in solution. The *lead* salt, $PbA_2 + 2H_2O$ (F.), $+4H_2O$ (L.), crystallises in small silvery scales soluble in about 670 parts of water at 1°; the *copper* salt, $CuA_2 + 4H_2O$, forms very sparingly soluble microscopic golden needles (F.); the *barium* salt, $BaA_2 + 6H_2O$, crystallises in long silvery needles soluble in about 450 parts of cold water (F.) and in about 550 parts of water at 0° (L.); the *calcium* salt, $CaA_2 + 5H_2O$ (L.), $+6H_2O$ (F.), crystallises in colourless silvery scales soluble in about 225 parts of 'cold' water, and of water at 5°; the *potassium* salt, $KA + H_2O$, crystallises in long white silky needles readily soluble in hot water, soluble in 40–45 parts of 'cold' water (F.), in about 62 parts of water at 4°, and in about 72 parts of 90 p.c. alcohol at 5° (L.); the *sodium* salt, $NaA + 3H_2O$ (L.), $+2H_2O$ (F.; Green, *l.c.*) crystallises in silky flat needles, dissolves in water to about the same extent as the potassium salt (F.), and is easily soluble in hot 90 p.c. alcohol and in about 50 parts at 0° (L.); the *ammonium* salt, $NH_4A + H_2O$ (F.), crystallises in large thin plates often 1 or 2 inches long, shows a violet fluorescence, and of the ammonium salts of the isomeric β-acids is the least soluble in cold water (Green, *l.c.*).

Reactions.—(1) The *diazo*-compound obtained from 2:3′-β-naphthylaminesulphonic acid by treatment with nitrous acid is a tolerably soluble, microcrystalline yellow powder, convertible into 2:3′-*dichloronaphthalene* by the ordinary reactions (Forsling, *l.c.*; Armstrong and Wynne, B. A. Report, 1888, 96; C. J. Proc. 1889, 52).

(2) On sulphonation with 4 times its weight of 20 p.c. anhydrosulphuric acid at 20°, it forms a mixture of 2:1:3′- with about 20 p.c. of 2:1′:3′- or [γ-] *β-naphthylaminedisulphonic acids* (Armstrong and Wynne, C. J. Proc. 1890, 130). The former acid is seemingly obtained as chief product when the 2:3′-acid is heated with 3–4 parts of 'fuming' sulphuric acid at 110° until the product is soluble in water (Forsling, B. 21, 3495; *cf.* Armstrong and Wynne, *l.c.*).

(3) Azo- colours are formed both by interaction of the diazotised acid with phenols or amines, and of the acid with diazotised bases. The azo- dyes obtained by interaction with β-naphthol or β-naphtholsulphonic acids give various shades of orange, and with diazotised bases give shades varying from brownish-yellow to brownish-red. The disazo- dyes formed by interaction with tetrazo- compounds give red or bluish-red shades (*v.* AZO- COLOURING MATTERS).

Alkyl derivatives.— 2:3′-Methyl-β-naphthylaminesulphonic acid is obtained when a mixture of 100 kilos. of 2:3′ sodium salt, 500 litres of water, and 55 kilos. of sodium methylsulphate is heated under pressure at 180–200° for about 10 hours. The ethyl derivative is formed if 65 kilos. of sodium sulphovinate are substituted for the methylsulphate. By interaction with tetrazo- compounds both acids give disazo- dyes of much bluer shade than the corresponding colours from the 2:3′-acid (Bayer & Co., Germ. pat. 41506, 41761, 43204; *v.* AZO- COLOURING MATTERS).

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[1] A second naphthylaminesulphonic acid—characterised by its solubility in water, the solubility of its sodium salt in alcohol, and the fact that the derived azo- dyes exhibit a redder shade than the corresponding dyes from the 2:3′-acid—is stated by the Farbfabrik vorm. Brönner (*l.c.*) to occur in the Brönner product. The occurrence of this second acid is to be attributed to the presence of 2:1′-β-naphtholsulphonic acid, and possibly 2:1′:3′-β-naphtholdisulphonic acid in the Schaeffer acid employed, which at the date of the patent (1882) was generally regarded as a uniform substance.

[2] Green's statement that the acid from pure ammonium salt crystallises in compact needles refers to crystallisation from an ammonium acetate solution obtained by dissolving the acid in *excess* of ammonia and adding acetic acid to the hot solution. The presence of ammonium acetate retards the precipitation, and the acid slowly crystallises out in needles on cooling (*priv. comm.*).

[3] In Germ. pat. 22547 of the Farbfabrik vorm. Brönner it is stated that the acid is soluble in 260 parts of boiling water. The discrepancy is accounted for by the fact that 2:3′-acid mixed with its isomerides has a greater solubility in water than when pure (Weinberg, *l.c.*).

β-NAPHTHYLAMINEDISULPHONIC ACIDS.

(i) 2:1′:3′-β-**Naphthylaminedisulphonic acid** (β-naphthylamine- [γ-]disulphonic acid, amido-G.-acid.

Formation.—This acid is present as chief product in the mixture of acids obtained when β-naphthylamine sulphate is heated with three times its weight of 20–30 p.c. anhydrosulphuric acid at 110–140°, or when the 'β-naphthylaminesulphonic acid sparingly soluble in water'[1] is heated with three times its weight of 10 p.c. anhydrosulphuric acid at 100° until the product is soluble in water (Gans & Co., Germ. pat. 35019 of Jan. 15, 1884, expired May 1887; Gans & Hoffmann, Eng. pat. 816 of 1884); also when 2:1′-β-naphthylaminesulphonic acid is stirred into four times its weight of 20 p.c. anhydrosulphuric acid at 15–20°, and allowed to stand for about three months until the product is soluble in water (Armstrong and Wynne, C. J. Proc. 1890, 128), and to the extent of about 20 p.c. when 2:3′-β-naphthylaminesulphonic acid is stirred into four times its weight of 20 p.c. anhydrosulphuric acid at 15–20°, and allowed to remain for 16-20 hours until sulphonation is completed (*ibid.* 130). The pure acid is obtained by heating the sodium salt of the β-naphthol-[γ-]disulphonic acid of Germ. pat. 36491 with ammonia under pressure (*cf.* also Landshoff, Germ. pat. 27378).

Reactions.—(1) The acid sodium or potassium salt on treatment with nitrous acid forms a sparingly soluble, bright-yellow crystalline *diazo-* compound, convertible into *β-naphthol-disulphonic acid-G.* (Gans & Co., *l.c.*); into 1:3-*naphthalenedisulphonic acid*, and into 2:1′:3′-*trichloronaphthalene* by the ordinary reactions (Armstrong and Wynne, C. J. Proc. 1890, 12).

(2) When fused with concentrated aqueous caustic soda at 200–230°, it is converted into the diazotisable *β-amidonaphtholsulphonic acid-G.* (M. L. B., Germ. pat. 53076 of Sept. 8, 1889; Eng. pat. 15176 of 1889; Cassella & Co., Eng. pat. 16699 of 1889).

(3) Amido-G.-acid does not interact with diazotised bases under any conditions (Schultz, quoted B. 21, 3487). The azo- compound obtained from the diazotised acid by interaction with α-naphthylamine finds employment in the production of naphthol-blacks (Cassella & Co., Germ. pat. 39029).

(ii) 2:3:3′-β-**Naphthylaminedisulphonic acid** (β-naphthylamine- [α-]disulphonic acid; amido-R.-acid.

Formation.—Pure amido-R.-acid is obtained by heating the sodium salt of the corresponding β-naphtholdisulphonic acid (the R.-salt of Germ. pat. 3229) with ammonia under pressure (Pfitzinger and Duisberg, B. 22, 398).

Reactions.—(1) The acid sodium salt on treatment with nitrous acid forms a sparingly soluble, bright-yellow crystalline *diazo-* compound, convertible into 2:2′-*naphthalenedisulphonic acid* (Pfitzinger and Duisberg, *l.c.*), and into 2:3:3′-*trichloronaphthalene* by the ordinary reactions (Armstrong and Wynne, C. J. Proc. 1890, 12).

(2) When amido-R.-acid is fused with concentrated aqueous caustic soda at 230–250°, it yields the diazotisable *β-amidonaphtholsulphonic acid-R.* (M. L. B., Germ. pat. 53076 of Sept. 8, 1889; Eng. pat. 15176 of 1889).

(3) Amido-R.-acid interacts with diazotised bases, and the 'intermediate' azo- compounds formed from 1 mol. prop. of the acid with 1 mol. prop. of tetrazo- compounds are employed in the production of 'mixed' disazo- dyes by interaction with 1 mol. prop. of 2:3′-β-naphthylaminesulphonic acid, &c. (Actieng. f. A., Germ. pat. 41095, 47026).

(iii) 2:3:2′-β-**Naphthylaminedisulphonic acid** (β-naphthylamine-[δ-]disulphonic acid).

Formation.—This acid is formed by heating the sodium salt of the corresponding β-naphtholdisulphonic acid (the [δ-]acid of Germ. pat. 44079, and Weinberg, B. 20, 2911) with an equal weight of 25 p.c. ammonia under pressure at about 200° for twelve hours (Cassella & Co., Germ. pat. 46711 of March 23, 1888).

Salts.—The *acid potassium* salt crystallises in sparingly soluble scales; the *acid sodium* salt is readily soluble in hot water.

Reactions.—(1) The acid potassium salt on treatment with nitrous acid forms a sparingly soluble, bright-yellow *diazo-* compound, convertible into 2:3′-*naphthalenedisulphonic acid* and into 2:3:2′-*trichloronaphthalene* by the known reactions (Armstrong and Wynne, C. J. Proc. 1890, 127).

(2) The disazo- dye obtained from the acid by interaction with tetrazodiphenyl gives a red shade remarkably fast to light and acids, and thus differs from the technically worthless disazo-dyes obtained from other β-naphthylaminesulphonic acids under similar conditions (Cassella & Co., *l.c.*). The azo- compound formed by interaction of the diazotised acid with α-naphthylamine is employed in the production of naphthol-blacks (Cassella & Co., Germ. pat. 50907 of Dec. 13, 1888; Eng. pat. 18425 of 1888).

(iv) 2:1:3′-β-**Naphthylaminedisulphonic acid.**

Formation.—This acid is obtained as chief product mixed with about 20 p.c. of 2:1′:3′-acid, when 2:3′-β-naphthylaminesulphonic acid is stirred into four times its weight of 20 p.c. anhydrosulphuric acid at a temperature not exceeding 20°, and allowed to stand for 16–20 hours until the product is soluble in water (Armstrong and Wynne, C. J. Proc. 1890, 130). An acid seemingly identical with it is formed as chief product by heating 2:3′-β-naphthylaminesulphonic acid with 3–4 parts of fuming sulphuric acid (percentage of dissolved SO_3 not stated) at 110° until soluble in water (Forsling, B. 21, 3495).

Salts.—The *acid* crystallises in small white needles extremely soluble in water, sparingly soluble in alcohol. The normal salts are very soluble, the acid salts sparingly soluble in water, and in dilute solution show, like the acid, a blue fluorescence. Of the normal salts, the *potassium* salt, $K_2A + 2H_2O$, crystallises in large, yellow forms, the *sodium* salt in very soluble, long, white needles; the *ammonium* salt, $(NH_4)_2A + H_2O$, in large triclinic forms; and of the acid salts the *potassium* salt, $KHA + H_2O$,

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[1] The sparingly soluble acid of the B.A.S.F.'s Germ. pat. 20760 (*v.* 2:1′-acid, *supra*), which at the date of Gans & Co.'s patent (1884) was generally regarded as a uniform substance.

and *sodium* salt, NaHA + $2H_2O$, crystallise in long, slender, white needles (Forsling, *l.c.*).

Reactions.—The acid potassium salt on treatment with nitrous acid forms a sparingly soluble, yellow, crystalline *diazo-* compound, convertible into 1:3′-*naphthalenedisulphonic acid*, and into 1:2:3′-*trichloronaphthalene* by the known reactions (Armstrong and Wynne, C. J. Proc. 1890, 130).

(v) 2:1:4′-β-**Naphthylaminedisulphonic acid.**

Formation.—A mixture of this acid (as minor product) with the 2:2′:4′ acid is obtained when 2:4′-β-naphthylaminedisulphonic acid is stirred into 4 times its weight of 20 p.c. anhydrosulphuric acid at a temperature not exceeding 20°, and allowed to stand for about 5 days until the product is soluble in water. It is separated from its isomeride by fractional crystallisation of its normal potassium salt, which crystallises in tolerably soluble rectangular tablets, whilst that of the 2:2′:4′-acid is very soluble.

Reactions.—The acid potassium salt on treatment with nitrous acid yields a crystalline, yellow *diazo-* compound, convertible into 1:2:4′-*trichloronaphthalene* by the ordinary method (Armstrong and Wynne, C. J. Proc. 1890, 129).

(vi) 2:2′:4′-β-**Naphthylaminedisulphonic acid.**

Formation.—*v.* 2:1:4′-acid.

Salts.—The *normal potassium* salt is extremely soluble in water; the *acid potassium* salt crystallises in very soluble, thistledown-like aggregates.

Reactions.—The acid potassium salt on treatment with nitrous acid forms an orange, easily decomposable *diazo-* compound, convertible into 1:3-*naphthalenedisulphonic acid*, and into 2:2′:4′-*trichloronaphthalene* by the known reactions (Armstrong and Wynne, C. J. Proc. 1890, 129).

(vii) [(?) 2:3:1′-] β-Naphthylaminedisulphonic acid (Andresen's acid) occurs in the product obtained when 1:3′-naphthalenedisulphonic acid is nitrated and reduced (Schultz, B. 23, 77).

⁂ Freund's so-called β-naphthylaminedisulphonic acids (Germ. pat. 27346 of Feb. 24, 1883; Eng. pat. 1069 of 1883), are described as α- compounds (*v.* 1:3:2′-α-naphthylaminedisulphonic acid.

β-Naphthylaminetrisulphonic Acid.

[(?) 2:3:1′:3′-] β-**Naphthylaminetrisulphonic acid** is obtained by heating the β-naphtholtrisulphonic acid of Germ. pat. 22038 with ammonia by Landshoff's method (Germ. pat. 27378; *v.* 2:3′-β-naphthylaminesulphonic acid).

Reactions.—When mixed with twice its weight of caustic soda and half its weight of water, and fused at 240–260° for 15–30 minutes it is converted into a β-*amidohydroxynaphthalenedisulphonic acid*, and when further heated at 260–270° for about 2 hours it is converted into a β-*amidodihydroxynaphthalenesulphonic acid* (M. L. B., Germ. pat. 53023 of Sept. 7, 1889; Eng. pat. 15175 of 1889).

Nitro-Derivatives.

2:1-Nitro-β-naphthylamine is obtained when acet-β-naphthalid in acetic acid solution is nitrated with half its weight of fuming nitric acid free from nitrous acid, and the resulting nitroacet-β-naphthalid (m.p. 123·5°) boiled in alcoholic solution with one-fourth its weight of caustic potash. It crystallises in lustrous orange-yellow needles, melts at 126–127°, and is tolerably soluble in hot water, readily soluble in alcohol (Jacobson, B. 14, 1792; Liebermann and Jacobson, A. 211, 64). The acetyl derivative is converted into β-*amidonaphthol* by boiling with aqueous caustic soda (Jacobson, B. 14, 806; Liebermann and Jacobson, A. 211, 45).

[(?) 2:1:3′-] Dinitro-β-naphthylamine, prepared by heating the ethyl derivative of dinitro-β-naphthol with concentrated aqueous ammonia at 140°, melts at 238°, is very sparingly soluble in water, alcohol and benzene, and yields a *dinitronaphthalene* (m.p. = 161·5°) by the diazo-reaction (Graebe and Drews, B. 17, 1172).

Diamidonaphthalenes.

(i) 1:2-**Naphthylenediamine** $C_{10}H_6(NH_2)_2$.

Preparation.—Orthonaphthylenediamine is obtained by reduction of the azo- derivatives of β-naphthylamine, such as phenylazo-β-naphthylamine, parasulphophenylazo-β-naphthylamine, &c. (Griess, B. 15, 2193; Witt, B. 19, 2795; 21, 3482), of hydrazimido- derivatives of β-naphthylamine (Lawson, B. 18, 800, 2423; Sachs, B. 18, 3128; *cf.* Zincke and Lawson, B. 19, 1452; 20, 1176), of [β-]naphthaquinonedioxime (Koreff, B. 19, 179), of 1:2-nitro-β-naphthylamine (Lawson, B. 18, 2427; Lellmann and Remy, B. 19, 805), and of 1:2-nitro-α-naphthylamine (Lellmann and Remy, B. 19, 803), with a solution of stannous chloride in hydrochloric acid. On the laboratory scale, an almost quantitative yield can readily be obtained by dissolving 10 grams of phenylazo-β-naphthylamine[1] in 300 grams of boiling acetic acid (1:5), adding zinc-dust in successive small quantities until the colour changes to bright yellow, filtering the boiling solution into dilute sulphuric acid, and decomposing the resulting crystalline sulphate by boiling with aqueous sodium carbonate until completely dissolved (Bamberger & Schieffelin, B. 22, 1376).

Properties.—It crystallises from hot water in silvery, rhombic scales, melts at 95–96°, at 98°·5 (Lellmann & Remy), and is readily soluble in benzene, ether, &c., less so in hot water. It is readily oxidised, becoming coloured on exposure to the air. Ferric chloride added to a neutral aqueous solution of the hydrochloride gives an olive-green colour, changing rapidly to brown and orange, and, on warming, to golden yellow. The *hydrochloride*, B.2HCl, crystallises in short prisms or slender needles readily soluble in water, sparingly soluble in hydrochloric acid, the *sulphate* in scales, the *diacetyl* derivative in needles melting at 234° (Lawson).

Reactions.—(1) It reacts like an orthodiamine with benzil, [β-]naphthaquinone, and phenanthraquinone forming *azines* (Lawson, *l.c.*; Witt, B. 19, 2795, *v.* Azines).

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[1] Phenylazo-β-naphthylamine can be quantitatively prepared by diazotising 93 grams of aniline, dissolved in 245 grams of 40 p.c. hydrochloric acid diluted with 245 grams of water, with 71 grams of sodium nitrite dissolved in a little water, stirring the solution of the diazo-salt into a lukewarm solution of 143 grams of β-naphthylamine in a litre of 90 p.c. alcohol, adding 45 grams of crystallised sodium acetate, and filtering off the crystalline separation.

Derivatives.—1:2-Naphthylenediaminesulphonic acids have been obtained by the reduction of azo- derivatives of (*a*) 1:4-α-naphthylaminesulphonic acid (Griess, B. 15, 2195; Witt, B. 19, 1720), of (*b*) 2:2′- or [δ-], (*c*) 2:3′- or [β-], and (*d*) 2:4′- or [γ-] β-naphthylaminesulphonic acids (Witt, B. 21, 3484), and of (*e*) 2:3:3′-β-naphthylamine-[α-]disulphonic acid (Witt, B. 21, 3487). By interaction with phenanthraquinone these compounds are converted into the corresponding *naphthaphenanthrazinesulphonic acids* (Witt).

Phenyl-1:2-naphthylenediamine (*cf.* Zincke and Lawson, B. 20, 1170; Witt, B. 20, 1184).

(ii) 1:3-**Naphthylenediamine**, obtained by reducing 1:3-dinitronaphthalene with tin and hydrochloric acid, reacts like a metadiamine with nitrous acid and diazo- compounds. The *acetyl* derivative crystallises in prisms melting at 154–156° (Urban, B. 20, 973).

(iii) 1:4-**Naphthylenediamine.**

Preparation. — Paranaphthylenediamine is formed by reduction of the azo- derivatives of α-naphthylamine, such as amidoazonaphthalene (Perkin, A. 137, 359), and parasulphophenylazo-α-naphthylamine (Griess, B. 15, 2192), with a solution of stannous chloride in hydrochloric acid, and of 1:4-nitro-α-naphthylamine with tin and hydrochloric acid (Liebermann and Dittler, A. 183, 238, 241). It can readily be prepared on the laboratory scale by boiling phenylazo-α-naphthylamine with zinc-dust and water, filtering the colourless solution into dilute sulphuric acid, and decomposing the resulting crystalline sulphate by warming with aqueous sodium carbonate for about five minutes until the crystalline mass becomes a uniform greenish-yellow colour, then cooling rapidly and filtering (Bamberger and Schieffelin, B. 22, 1381).

Properties.—It crystallises from water in white needles or small prisms, melts at 120°, and is readily soluble in alcohol, ether, and chloroform, somewhat sparingly soluble in hot water. The moist crystals rapidly become coloured green, and the aqueous solution decomposes rapidly with the separation of violet flocks on exposure to the air. Ferric chloride added to a neutral solution of the hydrochloride gives a green colour changing to yellow, and finally a brown precipitate of impure [α-]naphthaquinone (Griess, *l.c.*). The *hydrochloride*, B.2HCl, crystallises in lustrous four-sided scales, readily soluble in water, but insoluble in hydrochloric acid. The *diacetyl* derivative crystallises in needles melting at 305° (Kleemann, B. 19, 334; Bamberger and Schieffelin, *l.c.*). The disazo- compounds, obtained by combining its tetrazo- derivative with amines or phenols, are not direct cotton dyes (*cf.* Ewer & Pick, Germ. pat. 45549).

Reactions.—(1) On oxidation with a 1–2 p.c. chromic acid solution, with ferric chloride, or with even the weakest oxidising agents, it is converted into [α-] *naphthaquinone.*

(2) When heated in the form of hydrochloride with α-naphthylamine and α-amidoazonaphthalene at 130–140°, it gives a considerable yield of *Magdala red* (Witt, Germ. pat. 40868 of Dec. 30, 1886, *v.* Azines).

(3) On reduction in boiling amyl alcohol solution with sodium it yields, as sole product, *ar.-tetrahydro*-1:4-*naphthylenediamine* (Bamberger and Schieffelin, B. 22, 1382), which differs from the parent amine, and closely resembles paraphenylenediamine in forming colouring matters of the indamine, saffranine, and thionine series (Bamberger, A. 257, 5).

Derivatives. — Ethyl-, phenyl-, and α-naphthyl-1:4-naphthylenediamines (Wacker, A. 243, 302; Kock, A. 243, 312).

1:4-Amidodimethylnaphthylamine, obtained by the reduction of sulphophenylazodimethyl-α-naphthylamine or nitrosodimethyl-α-naphthylamine with stannous chloride, is a readily oxidisable oil (Friedländer and Welmans, B. 21, 3124).

(iv) 1:1′-**Naphthylenediamine** ([β-] or peri-diamidonaphthalene).

Preparation. — 1:1′-Naphthylenediamine is obtained by the reduction of 1:1′-dinitronaphthalene with phosphorus iodide and water (Aguiar, B. 3, 29), or with tin and hydrochloric acid (Ladenburg, B. 11, 1651; Erdmann, A. 247, 363), and of 1:1′:4-dinitro-α-naphthoic acid (m.p. = 265°) with tin and hydrochloric acid (Ekstrand, B. 20, 1353). Also by heating 1:1′-dihydroxynaphthalene with concentrated aqueous ammonia for 8–10 hours under pressure, first at 150–180° and later at 250–300° (Erdmann, *l.c.*). The methods are similar to those employed in the preparation of 1:4′-naphthylenediamine (*q. v.*).

Properties.—It crystallises in long white brittle needles from a solution in aqueous alcohol evaporated in a vacuum over sulphuric acid, melts at 67°, dissolves sparingly in cold water, readily in alcohol, ether, and chloroform, and tends to separate from most solvents in oily drops which subsequently solidify. Ferric chloride colours the aqueous solution dark chestnut-brown. The *hydrochloride*, B.2HCl, crystallises in very soluble scales which melt at 280° (Ekstrand), the *oxalate* in white glistening crystals resembling those of potassium iodide. The oxalate seems to undergo change readily, and is said by Aguiar to furnish a substance resembling gold in appearance and lustre and of great stability, but no description has been given of the nature or mode of preparation of this compound (B. 7, 313).

Reactions.—1:1′-Naphthylenediamine forms two remarkable condensation-compounds by interaction with ethylic oxalate and with nitrous acid; it also yields an *ethenyl* derivative by condensation with benzaldehyde (Ladenburg, B. 11, 1650), and, like many 1:1′-or peri- derivatives of naphthalene, simulates the character of an orthodi- derivative.[1] It does not, however, form an azine on treatment with phenanthraquinone and thus differs from orthonaphthylenediamine (Hinsberg, B. 22, 861).

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[1] This pseudortho- character of [β-]naphthylenediamine and other peri- compounds is of great theoretical importance, since it is an argument of very great weight in the determination of the constitution of the two heteronucleal αα-di- derivatives of naphthalene, and is generally accepted as practically conclusive evidence that the radicles occupy the positions 1:1′. No absolute method, free from reproach, has yet been devised of determining the constitution of *any* heteronucleal di- derivative of naphthalene, and the constitutional formulæ now assigned to the heteronucleal di-derivatives are based on the assumption that the peri- compounds are 1:1′- derivatives (*cf.* Erdmann and Kirchhoff, A. 247, 366; Erdmann, B. 21, 3446; Armstrong and Wynne, C. J. Proc. 1889, 5, 34, 48).

(1) When heated with 10 parts of ethylic oxalate in sealed tubes at 100° for a day, a compound of the formula $C_{14}H_{12}N_2O_2$ and unknown constitution is produced, which crystallises from chloroform in magnificent red needles like chromic anhydride (Aguiar, B. 7, 313).

(2) On addition of aqueous potassium nitrite to a cold aqueous solution of an equimolecular proportion of 1:1′-naphthylenediamine sulphate a compound, $C_{10}H_7N_3$, of unknown constitution[1] is obtained as a red precipitate, which crystallises from benzene in lustrous slender red needles, can be partially sublimed, and has none of the properties of a diazo- compound (Aguiar, B. 7, 315; Erdmann, A. 247, 365).

(3) It is diazotised with considerable difficulty forming an extremely unstable *tetrazo*-compound which, by interaction with boiling cuprous chloride solution, is converted into 1:1′-*dichloronaphthalene* (Erdmann, A. 247, 365).

(v) 1:3′-**Naphthylenediamine**, prepared by heating 1:3′-dihydroxynaphthalene with ammonia under pressure at 150–300°, is an oil at ordinary temperatures. Its *tetrazo-* compound, on combination with phenols or amines, forms direct cotton disazo- dyes, which give peculiar brown shades (Ewer & Pick, Germ. pat. 45788 of Nov. 18, 1887, expired Feb. 1889; *cf.* Loewe, B. 23, 2546).

(vi) 1:4′-**Naphthylenediamine** ([α-]diamidonaphthalene; Zinin's semi-naphthalidam).

Preparation.—1:4′-Naphthylenediamine is obtained by the reduction of 1:4′-dinitronaphthalene with ammonium sulphide (Zinin, A. 52, 361; 85, 329), with tin and hydrochloric acid (Hollemann, Z. [2] 1, 556; Ladenburg, B. 11, 1651; Erdmann, A. 247, 360), and with phosphorus iodide and water (Aguiar, B. 3, 32; 7, 306). Also by heating 1:4′-dihydroxynaphthalene under pressure for eight to ten hours with 5 parts of ammonia solution saturated at −10°, or with 10 parts of commercial aqueous ammonia, first at 150–180°, and finally at 250–300° (Ewer & Pick, Germ. pat. 45549 of Nov. 4, 1887; exp. Feb. 1889). On the laboratory scale, 30 grams of 1:4′-dinitronaphthalene are boiled with 100 c.c. of alcohol and 100 grams of granulated tin in a reflux apparatus so arranged that the alcohol gradually evaporates, concentrated hydrochloric acid is added from time to time, and the operation continued for about four hours until a brown solution, which solidifies on cooling, is obtained. This is diluted with 3–4 litres of boiling water, freed from tin by sulphuretted hydrogen, concentrated to crystallising-point, and the separated hydrochloride decomposed by ammonia (Erdmann, *l.c.*).

Properties.—It crystallises in needles, melts at 189·5°, sublimes without decomposition, and is readily soluble in chloroform and ether, tolerably soluble in hot, and almost insoluble in cold water. Ferric chloride added to the base suspended in water gives an intense bluish-violet colour, and after some time a like coloured precipitate. The *hydrochloride*, B.2HCl, crystallises in needles readily and almost equally soluble in hot and cold water, insoluble in hydrochloric acid; the *sulphate*, $B.H_2SO_4$, in slender needles insoluble in dilute sulphuric acid and alcohol.

Reactions.—(1) It can be diazotised in an ice-cold, strongly acid solution, and forms a very unstable soluble *tetrazo-* compound which, in combination with naphthylaminesulphonic acids, gives red, and with naphtholsulphonic acids, red- to blue-violet direct cotton disazo-dyes (B. A. S. F., Germ. pat. 39954, of Nov. 9, 1886; Eng. pat. 14625 of 1886).

(2) The tetrazo- compound by interaction with boiling cuprous chloride solution is converted into 1:4′-*dichloronaphthalene* (Erdmann, A. 247, 362).

(vii) 2:2′-**Naphthylenediamine** is obtained by heating 2:2′-dihydroxynaphthalene with ammonia under pressure at 150–300° (Ewer & Pick, Germ. pat. 45788 of Nov. 18, 1887), with ammonia and ammonium chloride at 200–250° (Lange, Ch. Z. 12, 856), and with four times its weight of ammonia-calcium chloride at 260–270° for eight hours (Bamberger and Schieffelin, B. 22, 1384).

Properties.—It crystallises from water in silvery scales, melts at 161°, is readily soluble in alcohol, ether, benzene and boiling water, and forms very soluble salts. The *tetrazo-* compound, in combination with phenols or amines, is converted into direct cotton disazo- dyes which respectively give more violet and more yellow shades than the corresponding colours from the 2:3′- or 1:4′-diamine (Lange, *l.c.*; Ewer & Pick, *l.c.*).

Diphenyl-2:2′-naphthylenediamine, $C_{10}H_6(NH.C_6H_5)_2$, is formed when 16 kilos. of 2:2′-dihydroxynaphthalene are heated with 37 kilos. of aniline and 13 kilos. of aniline hydrochloride at 140–180° in an open or closed vessel until water is no longer given off. The excess of aniline is removed by extraction with dilute hydrochloric acid, and the product pressed, dried, and purified by crystallisation (Durand & Huguenin, Germ. pat. 40886 of Sept. 23, 1886; Annaheim, Eng. pat. 14283 of 1886; B. 20, 1372).

Properties.—It crystallises in slender, lustrous scales, melts at 163–164°, and is insoluble in water and petroleum spirit, sparingly soluble in cold alcohol, readily in ether, acetic acid, benzene, toluene, &c. When warmed with solid zinc chloride it gives a beautiful magenta colour, which disappears slowly in the air and at once on addition of water. By interaction in methyl alcohol solution with an equal weight of nitrosodimethylaniline hydrochloride at 100°, it is converted into *Basle blue* (Durand & Huguenin, *l.c.*; *v.* AZINES).

(viii) 2:3′-**Naphthylenediamine** is obtained by heating 2:3′-dihydroxynaphthalene with ammonia under pressure at 150–300° (Ewer & Pick, Germ. pat. 45788 of Nov. 18, 1887; expired Feb. 1889), and with ammonia and ammonium chloride at 200–250° (Lange, Ch. Z. 12, 856).

Properties.—It melts at 216–218°, and forms less soluble salts than the 2:2′-diamine. The *tetrazo-* compound, on combination with phenols or amines, is converted into direct cotton disazo- dyes, giving shades which are respectively bluer and redder than those produced by the corresponding dyes from the isomeric naphthylenediamines (Ewer & Pick, *l.c.*).

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[1] The formula $C_{10}H_6\left\langle\begin{matrix}NH\\N{:}N\end{matrix}\right\rangle$ has been suggested for the compound, but seems in no way to account for the colour.

Diphenyl-2:3′-naphthylenediamine, obtained by heating 30 kilos. of 2:3′-naphthylenediamine with 70 kilos. of aniline and 25 kilos of aniline hydrochloride at 170° for many hours, is converted by digestion with nitrosodimethylaniline hydrochloride and alcohol at 100° into a green *azine*, giving very fast colours (Leonhardt & Co., Germ. pat. 54087 of Dec. 24, 1889).

V. DIAZO- AND AZO- DERIVATIVES.

The diazo- compounds obtained from the naphthylamines and naphthylaminesulphonic acids are generally more stable than those from aniline, sulphanilic acid, and their homologues, and in many instances suffer no appreciable decomposition at temperatures below 25°, whilst some remain unchanged when boiled with alcohol (*cf.* Forsling, B. 21, 3497). In most cases, therefore, it is not imperative to cool with ice during the addition of the nitrite, although there is little doubt that the diazo- compounds formed at temperatures below 5° frequently give azo- dyes of cleaner and purer shade than those obtained when cooling is dispensed with. Technically, diazonaphthalenesulphonic acids are employed in the production of azo- dyes and naphtholsulphonic acids.

The naphthalene azo- dyes of commercial importance have already been described at length (*v.* AZO- COLOURING MATTERS), and a summary of what is known of the connection between their constitution and properties has been drawn up by Meldola (P. M. 1888, 403; *cf.* also Jacobson and Schenke, B. 22, 3232; Goldschmidt and Rosell, B. 23, 487; Armstrong, C. J. Proc. 1888, 29; Nietzki, Chemie der organischen Farbstoffe, ed. 1889, 27). Many other azo- colours have, however, been obtained from naphthalene derivatives, and a brief reference in general terms is therefore made under each naphthylamine- and naphthol-sulphonic acid to the shades given by the derived azo- and disazo- dyes, irrespective of their commercial value. One azo- derivative remains to be described here.

α-Amidoazonaphthalene (azodinaphthyldiamine, nitrosonaphthyline) $C_{10}H_7.N_2.C_{10}H_6.NH_2$, is obtained by adding an aqueous solution of 2 parts of caustic potash and 3 parts of potassium nitrite to a warm solution of 13 parts of α-naphthylamine hydrochloride (Perkin and Church, C. J. 16, 210; Nietzki and Goll, B. 18, 298), or by leading nitrous gas into a warm alcoholic solution of α-naphthylamine (Martius, Z. [2] 2, 138).

Properties. — It crystallises in long, red needles, melts at 180°, is tolerably soluble in hot alcohol, benzene, and ether, insoluble in water, and forms salts which dissolve in alcohol with a violet colour. When heated with α-naphthylamine hydrochloride or acetate, it yields *Magdala red*, and the *induline* of the naphthalene series (Hofmann, B. 2, 374, 412; Julius, B. 19, 1366, *v.* AZINES), and an *induline* is also obtained when it is heated with paraphenylenediamine and some benzoic acid at 185° for 2-3 hours (Dahl & Co., Germ. pat. 45803 of May 23, 1888).

VI. HYDROXY- DERIVATIVES.

Introductory.—α- and β-Naphthol and several of the α- and β-naphtholsulphonic acids are obtained on the large scale by fusing the sodium salts of naphthalenesulphonic acids with caustic potash or soda, and the method is very generally employed in the preparation of dihydroxynaphthalenes. Given the proportion of alkali and the temperature found to work best in practice, the success of a fusion depends on the extent to which unequal heating of the melt is avoided, consequently the fusion vessels, whether closed or open, are provided with mechanical stirrers.

The two naphthols, and β-naphthol in a more marked degree than α-naphthol, exhibit several noteworthy differences when compared with phenol and its homologues; thus both are converted into amidonaphthalenes by digestion with ammonia under pressure (B. A. S. F., Germ. pat. 14612 of Feb. 22, 1880), into naphthyl sulphates by treatment with concentrated sulphuric acid in the cold (Armstrong, B. 15, 202; Nietzki, B. 15, 305), into alkyl derivatives by heating with alcohol and hydrochloric acid at 150° (Liebermann and Hagen, B. 15, 1427), and into naphthyl ethers by boiling with dilute (1:1) sulphuric acid (Graebe, B. 13, 1850), whilst phenol under similar conditions is either unaffected or yields mere traces of the corresponding products. Similar differences can be traced when the dihydroxynaphthalenes are compared with the dihydroxybenzenes. These specific properties of the hydroxynaphthalenes disappear when the influence of the second 'ring' is removed by reduction; thus the 'aromatic' tetrahydronaphthols behave like phenol and its homologues under the above conditions, and in particular resemble the orthoxylenols in properties (*cf.* Bamberger, A. 257, 1).

The nitro- and amido-naphthols are described in this section, the nitrosonaphthols as quinonoximes under *Naphthaquinones* (*v. infra*).

HYDROXYNAPHTHALENES.

(i) **α-Naphthol**, $C_{10}H_7.OH$.

Formation.—α-Naphthol occurs in the high-boiling fractions of coal tar (Schulze, A. 227, 150). It was obtained first from α-naphthylamine by the diazo-reaction (Griess, Pr. 12, 419), and has been prepared synthetically by boiling phenylisocrotonic acid (Fittig and Erdmann, A. 227, 242). On the large scale it is prepared by fusing sodium naphthalene-α-sulphonate with caustic soda or potash (*cf.* Schaeffer, A. 152, 281; Levinstein, Eng. pat. 2300 of 1883).

Preparation.—The process adopted in the manufacture of α-naphthol from sodium naphthalene-α-sulphonate is identical with that described under β-naphthol (*q. v.*), except that the press-cakes prior to distillation are dried at a lower temperature (O. N. Witt, *priv. comm.*).

Properties.—α-Naphthol crystallises in lustrous monoclinic needles (*cf.* Groth, A. 152, 284), melts at 94°, boils at 278-280° (Schaeffer, A. 152, 281), has a sp.gr. = 1·224 at 4° (Schröder, B. 12, 1613), dissolves readily in alcohol, ether, chloroform, and benzene, and is very sparingly soluble in hot water. It has a phenolic odour, and volatilises readily with steam. The naphtholates, formed by dissolution of α-naphthol in alkalis, are decomposed with the separation of α-naphthol on treatment with carbon dioxide or ammonium chloride.

Reactions.—(1) Nitrous acid reacts with it forming 1:2-*β-nitroso-α-naphthol* and 1:4-*α-nitroso-α-naphthol* (*v. Naphthaquinonoximes*), the former as chief product (Fuchs, B. 8, 626).

(2) It is converted into *α-dinaphthylene oxide*, $\left<\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right>O$, by boiling in the air, by distilling with 3 times its weight of litharge, and together with naphthalene and other products by heating in a tube at 350-400° (Graebe, Knecht, and Unzeitig, A. 209, 134; Merz and Weith, B. 14, 195).

(3) On treatment with nitric acid it yields *dinitro-α-naphthol* (Martius, J. pr. 102, 442), and subsequently *phthalic acid*. Potassium permanganate oxidises it to *phthalic acid* in acid, and to *orthocarboxyphenylglyoxylic acid* $COOH.C_6H_4.CO.COOH$ in alkaline solution (Henriques, B. 21, 1608).

(4) The action of ammonia, acetamide, aniline, &c. (*v. α-Naphthylamine*), and of sulphuric acid (*v. α-Naphtholsulphonic acids*), are separately discussed.

Colour reactions.—Bleaching-powder added to an aqueous solution of α-naphthol gives first a deep dark-violet colouration and then a dark-violet flocculent precipitate, which becomes brown on warming and colourless on the addition of ammonia. Ferric chloride added to an aqueous solution produces a milky opalescence, which changes through red into violet, violet flocks of *α-dinaphthol* (m.p. = 300°) separating at the same time (Schaeffer, *l.c.*; Dianin, B. 6, 1252; 7, 487). With chloroform and aqueous caustic potash α-naphthol gives colours similar to those obtained with β-naphthol (*q. v.*). On treatment with sodium nitrite and concentrated sulphuric acid it is coloured a deep green (Bamberger and Bordt, B. 23, 216).

Tests.—Commercial α-naphthol should be colourless, have a melting-point very nearly that of the pure compound, and leave only a small residue on dissolution in alkali.

α-Naphthyl methyl ether (α-methoxynaphthalene, α-naphthanisoïl) is formed by heating α-naphthol, caustic potash and methyl iodide in methyl alcohol solution in a reflux apparatus (Schertel, A. 217, 42), by heating sodium α-naphtholate with methyl chloride and methyl alcohol under pressure at 100° for five hours (Bayer & Co., Eng. pat. 1168 of 1879), by passing methyl chloride through sodium α-naphtholate at 280° (Vincent, Bl. [2] 40, 107), and by heating α-naphthylamine with methyl alcohol and zinc chloride at 180-200° (Hantzsch, B. 13, 1347). It is best prepared by heating 25 parts of α-naphthol with 25 parts of absolute methyl alcohol and 10 parts of concentrated sulphuric acid in a reflux apparatus for four hours at 125°, or better at 140° with the aid of a small mercury column (Gattermann, A. 244, 72).

Properties.—It is an oil with an orange-like odour, boils at 269° (cor.), is volatile with steam, has a sp.gr. = 1·09636 at 13·9° (comp. with water at 4°), and is readily soluble in the ordinary organic solvents, sparingly in methyl alcohol, and almost insoluble in water.

α-Naphthyl ethyl ether, obtained by methods similar to those employed in the preparation of the methyl ether (Schaeffer, A. 152, 286; Liebermann and Hagen, B. 15, 1428; Gattermann, *l.c.*), is an oil of peculiar odour, boils at 280·7° (cor.), and is volatile with steam.

α-Naphthyl acetate, $C_{10}H_7.O.CO.CH_3$, prepared by boiling α-naphthol with acetic chloride (Schaeffer, A. 152, 289), or by heating with acetic acid at 200° (Graebe, A. 209, 151), crystallises in broad needles or tables, melts at 49°, at 46° (Miller, A. 208, 248), dissolves readily in alcohol and ether, and is decomposed by boiling with water.

α-Naphthyl sulphate, $C_{10}H_7O.SO_3H$, (Nietzki, B. 15, 306).

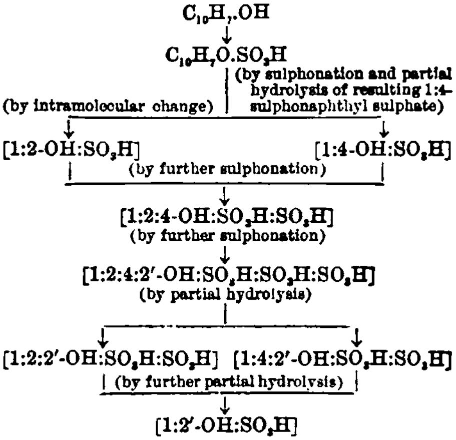
SULPHONIC ACIDS.

Introductory.—Two general methods are employed in the preparation of α-naphtholsulphonic acids:—

(1) Decomposition of the diazo- compound of the corresponding α-naphthylaminesulphonic acid by boiling with weak sulphuric acid.

(2) Action of sulphuric acid on α-naphthol.

The action of sulphuric acid on α-naphthol has given rise to much discussion owing to the fact that no satisfactory means of isolating and purifying the individual acids has as yet been described. Everything goes, however, to support the view that three mono-, *three* di-, and one tri-sulphonic acid are obtained by the sulphonation of α-naphthol, and that several of these owe their production to the partial hydrolysis of polysulphonic acids. The series of changes which occur when α-naphthol is sulphonated under conditions described in connection with the respective acids is given in the table (*cf.* also *Action of sulphuric acid*, under the heading *Substitution in the Naphthalene Series*):—



The readiness with which certain of the sulphonic acids undergo partial hydrolysis in the presence of the hot and relatively dilute sulphuric acid formed in the process of sulphonation seems first to have been remarked by Bender (B. 22, 993; C. J. 56, 717), who considers that Leonhardt & Co.'s supposed uniform α-naphtholdisulphonic acid (Eng. pat. 11318 of 1887) is derived from the 1:2- and 1:4-α-naphtholsulphonic acids in the manner indicated in the table. As pointed out in connection with this acid (*v. infra*), there can be little doubt that Leonhardt & Co.'s product is not uniform but a mixture of the 1:2:2′- and 1:4:2′-α-naphtholdisulphonic acids with varying proportions of the trisulphonic acid.

α-Naphtholsulphonic Acids.

(i) **1:2[1]-α-Naphtholsulphonic acid** (Schaeffer acid; probably the α-naphthol-β-sulphonic acid of Claus and Knyrim [2] (B. 18, 2924)).

Formation.—This acid is obtained as chief product mixed with some 1:4-mono- and 1:2:4-di-sulphonic acid (*cf.* Bender, B. 22, 999) when α-naphthol is heated with twice its weight of concentrated sulphuric acid on a water-bath until sulphonation is completed (Schaeffer, A. 152, 293; J. pr. 106, 466; Darmstaedter and Wichelhaus, Eng. pat. 89 of 1869, *cf.* A. 152, 299). It is also formed together with the 1:4-acid, when 144 kilos. of α-naphthol, dissolved in 1–2 times its weight of acetic acid, is treated at 60° with 100 kilos. of 80 p.c. anhydrosulphuric acid or 116·5 kilos. of chlorosulphonic acid, and heated at 50–60° during 5–6 hours, the two acids being separated by converting the product into barium salt and concentrating to crystallising-point; the separation consists of the 1:2- salt, and the mother-liquors contain chiefly the 1:4- salt (Baum, Eng. pat. 3498 of 1883, prov. spec.).

Salts.—The *acid* and the *lead* and *calcium* salts obtained by Schaeffer's method (*l.c.*) and the *acid*, and the *lead*, *barium*, *potassium* and *sodium* salts obtained by Baum's process (Claus and Knyrim, *l.c.*) have been described, but the statements with regard to the acids and lead salts are discrepant and there is no guarantee of the purity of the acids used. The *sodium* salt crystallises in small scales, is sparingly soluble in strong alcohol (Ver. Chem. Fab., Germ. pat. 26012), and gives with ferric chloride a violet-red colouration which quickly changes to brown (Baum, *l.c.*).

Reactions.—(1) On warming with dilute (65 p.c.) sulphuric acid it regenerates α-naphthol. By the further action of concentrated sulphuric acid it is converted successively into 1:2:4-*α-naphtholdisulphonic* and 1:2:4:2′-*α-naphtholtrisulphonic acid* (*cf.* Bender, *l.c.*).

(2) Nitrous acid reacts with it in the cold forming 1:2:4-*α-nitroso-α-naphtholsulphonic acid*, which gives a *potassium* salt crystallising in yellow scales, does not form a naphthol-green with iron salts, and like 1:2-α-naphtholsulphonic acid[1] yields 1:2:4-*dinitro-α-naphthol* on warming with dilute nitric acid (*cf.* Bender, *l.c.*).

(3) By interaction with diazotised bases it forms orange-red and brown azo-dyes (Ver. Chem. Fab., *l.c.*), which are sensitive to acids and technically worthless.

(ii) **1:4-α-Naphtholsulphonic acid** (Nevile and Winther's acid).

Formation.—This acid is present, seemingly in considerable quantity, in the product obtained by sulphonating α-naphthol under the conditions of Baum's prov. spec. (*v. supra*), and occurs as minor product in that prepared by Schaeffer's method. A modification of the latter process, in which α-naphthol is sulphonated in the cold with concentrated or weakly fuming sulphuric acid, results in an increased yield of the 1:4-acid, and a separation from its isomerides can be effected by converting the product into sodium salt and extracting the readily soluble 1:4-salt by boiling with strong (at least 90 p.c.) alcohol (Ver. Chem. Fab., Germ. pat. 26012 of Feb. 27, 1883; Eng. pat. 2237 of 1883). The pure acid is obtained from 1:4-α-naphthylaminesulphonic acid by the diazo- reaction or by heating with aqueous caustic soda under pressure.

Preparation.—(1) Naphthionic acid is diazotised in the usual way and the sparingly soluble diazo- compound, after filter-pressing, is boiled with about 10 p.c. sulphuric acid until nitrogen is no longer evolved; the product is then converted into sodium salt (Nevile and Winther, C. J. 37, 632; B. 13, 1949; Dahl & Co., Eng. pat. 2296 of 1883, Monit. Sci. [3] 14, 39; Ver. Chem. Fab. *l.c.*; Erdmann, A. 247, 341).

(2) Sodium naphthionate is heated with an equal weight of 50 p.c. aqueous caustic soda under pressure at 240–260° for 8–10 hours, the product dissolved in water, boiled to expel ammonia, neutralised with hydrochloric acid, and either employed for the preparation of azo- dyes without further purification or saturated with salt to precipitate the normal (acid) sodium

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[1] In every case where the constitution of an α-naphtholsulphonic acid is given, the OH-radicle is supposed in the position '1.'

[2] The α-naphtholsulphonic acids have been investigated by Claus and his pupils, but it is not easy to deal with the recorded results, for no account is given in the various papers of special precautions taken to isolate and characterise the individual acids before submitting them to treatment with phosphorus pentachloride, whilst the constitution of the chloro- derivatives resulting from the phosphorus pentachloride reaction is deduced in three instances from the oxidation products obtained by treatment with chromic acid—a method which cannot now be regarded as trustworthy.

Claus and Oehler (B. 15, 312) obtain a 'uniform' monosulphonic acid by warming α-naphthol with 2 parts of ordinary sulphuric acid on a water-bath for *two hours*, describe neither mode of purification nor salts, and get a 'dichloronaphthalene' which they assume to be the 1:4-derivative, although it melts at 94° instead of 67–68°. This 'dichloronaphthalene' is beyond doubt the 1:2:4-trichloronaphthalene derived from 1:2:4-α-naphtholdisulphonic acid in the 'uniform' product (Armstrong and Wynne, C. J. Proc. 1890, 80).

Claus and Knyrim (B. 18, 2924) describe salts of the monosulphonic acid of Baum's Patent-Anmeldung B 4197 of June 30, 1883, characterised by forming a sparingly soluble barium salt, and find that the sodium salt interacts with phosphorus pentachloride at 50° yielding a *di*chloronaphthol, convertible into a trichloronaphthalene melting at 90° and forming 1:2:3:4-dichloro-[α-]naphthaquinone on oxidation with chromic acid. Such a reaction with phosphorus pentachloride is without precedent in the naphthalene series, and the most probable explanation of the discrepancy seems to be that the material actually employed for the pentachloride experiment contained a quantity of the 1:2:4-disulphonic acid, and differed from that used in the preparation of the salts.

Claus and Mielcke (B. 19, 1182) obtain a di- and a trisulphonic acid by heating α-naphthol with 5 times its weight of 20 p.c. anhydrosulphuric acid for 2 hours on a water-bath and separate them by the difference in solubility of the potassium salts. The disulphonic acid gives a trichloronaphthalene melting at 82°, the trisulphonic acid a tetrachloronaphthalene which melts at 140°, yields 1:2:3:4-dichloro-[α-]naphthaquinone on oxidation with chromic acid, and is consequently but erroneously regarded as a homonucleal derivative. The trichloronaphthalene may have been an impure form of the 1:2:2′-derivative (m.p. =86°) indicating the presence of the corresponding disulphonic acid in the melt, whilst the heteronucleal character of the trisulphonic acid has been placed beyond question by the fact that the derived dinitro-α-naphtholsulphonic acid yields β-sulphophthalic acid on oxidation (Graebe, B. 18, 1126; Rée, C. J. 49, 511).

[1] Resinous substances are also formed when the acid is nitrated without previous conversion into the nitroso- compound.

salt, which is sparingly soluble in brine (Actieng. f. A., Germ. pat. 46307 of Aug. 16, 1888).

Salts.—The *barium*, *potassium*, and *sodium* salts are readily soluble in water, soluble also in hot alcohol, and give with ferric chloride a blue or bluish-green colouration which on warming becomes red (Dahl & Co., *l.c.*, Erdmann, *l.c.*).

Reactions.—(1) On boiling with dilute (65 p.c.) sulphuric acid it regenerates α-naphthol. By the further action of concentrated sulphuric acid it yields successively *sulpho-α-naphthyl sulphate* and 1:2:4-*α-naphtholdisulphonic acid* (Armstrong, *priv. comm.*), and eventually, it is to be expected, the 1:2:4:2′-α-naphtholtrisulphonic acid.

(2) Nitrous acid reacts with it in the cold forming 1:2:4-*β-nitroso-α-naphtholsulphonic acid*, which gives a *potassium* salt crystallising in small orange prisms, forms a *naphthol green* with iron salts (Gans & Co., Germ. pat. 28065 of Jan. 19, 1884; Hoffmann, B. 18, 46), and like 1:4-α-naphtholsulphonic acid[1] yields 1:2:4-*dinitro-α-naphthol* on warming with dilute nitric acid (*cf.* Bender, B. 22, 997).

(3) By interaction with diazotised bases it forms azo- dyes which in general give bluer shades than the corresponding colours from β-naphtholdisulphonic acid-R., are little affected by acid and alkali, and have considerable commercial importance. The azo- dyes vary in shade from orange with aniline to bluish-red with naphthionic acid; the disazo- dyes with amidoazobenzenesulphonic acid and its homologues give dark-red to bluish-red (*cf.* Ver. Chem. Fab., *l.c.*) and with tetrazo- compounds give pure blue or violet-blue shades (*cf.* Bayer & Co., Germ. pat. 35341, 38802, *v.* Azo- COLOURING MATTERS).

(iii) 1:2′-α-**Naphtholsulphonic acid** (Liebmann and Studer's acid).

Formation.—This acid is formed when 1:2:4:2′-α-naphtholtrisulphonic and the heteronucleal α-naphtholdisulphonic acids obtained by the sulphonation of α-naphthol are partially hydrolysed by boiling with dilute (say, 65 p.c.) sulphuric acid (Liebmann and Studer, Eng. pat. 7812 of 1887).

Preparation.—α-Naphthol is heated with four times its weight of concentrated sulphuric acid at 130° for an hour, and the resulting mixture of sulphonic acids converted into barium salt. This is suspended in about 10 parts of water, gaseous hydrogen chloride passed in to saturation, and the mixture boiled for about 2 hours in a reflux apparatus, evaporated to remove excess of hydrochloric acid, filtered from the separated barium sulphate and neutralised with barium carbonate; the barium salt can be purified by crystallisation from alcohol (*ibid.*).

Reactions.—(1) Nitrous acid reacts with it forming a *nitroso*-1:2′-*α-naphtholsulphonic acid*[2] which crystallises well and readily yields *naphthol-yellow-S.* on warming with dilute nitric acid (Bender, B. 22, 996). The acid gives only a poor yield of the yellow on nitration.

(2) By interaction with diazotised bases it yields both azo- and disazo- dyes (Bender, *l.c.*).

(iv) 1:4′-α-**Naphtholsulphonic acid** (Cleve's acid).

Preparation.—(1) 1:4′-α-Naphthylaminesulphonic acid is diazotised at 5°, the diazo- compound boiled with dilute (10 p.c.) sulphuric acid, and the product converted into sodium salt in the usual way (Ver. Chem. Fab., Germ. pat. 26012 of Feb. 27, 1883; Eng. pat. 2237 of 1883; *cf.* Witt, B. 19, 578; Gaess, Monit. Sci. [3] 14, 336; Schöllkopf Co., Eng. pat. 15781 of 1885).

(2) Sodium 1:4′-naphthalenedisulphonate is fused with 3–4 times its weight of caustic soda at 160–190°, and the melt dissolved in water, acidified with hydrochloric acid, filtered and left to crystallise. The sparingly soluble sodium 1:4′-α-naphtholsulphonate separates on cooling and can be obtained in transparent spear-like forms by recrystallisation (Ewer & Pick, Germ. pat. 41934 of Jan. 25, 1887).

Salts.—The *acid* forms a semi-crystalline deliquescent mass (Erdmann, A. 247, 343); the *sodium* salt is readily soluble in warm alcohol, and gives with ferric chloride a violet-red colouration which becomes reddish-brown on boiling (Gaess, *l.c.*).

Reactions.—(1) 1:4′-α-Naphtholsulphonic acid regenerates α-naphthol when heated with dilute (65 p.c.) sulphuric acid.

(2) Nitrous acid reacts with it in the cold forming a *nitroso*-1:4′-*α-naphtholsulphonic acid*,[1] which crystallises well and on nitration is converted into a *naphthol yellow* precipitable by caustic potash but not identical with naphthol yellow S.

(3) The azo- dyes obtained by interaction with diazotised bases vary in shade from yellowish-scarlet with aniline to bluish-red with naphthionic acid (Schöllkopf Co., *l.c.*), and, unlike phenolic para-azo- compounds, are stated to be fast to acids (Friedländer, Theerfarbenfabrikation, p. 393; Erdmann, *l.c.*). The disazo- dyes with amidoazobenzene and its homologues are bluer in shade than the corresponding colours from 1:4-α-naphtholsulphonic acid.

(v) 1:1′-α-**Naphtholsulphonic acid** (Perinaphtholsulphonic acid).

Formation.—Unlike its isomerides 1:1′-α-naphthylaminesulphonic acid when diazotised and boiled with dilute (10–15 p.c.) sulphuric acid yields not 1:1′-α-naphtholsulphonic acid but its anhydride, the so-called naphthasultone (*v. infra*) which can be converted into a salt of the peri- acid by heating either with alcoholic ammonia at 130° or with concentrated aqueous caustic potash or soda (Erdmann, A. 247, 345).

Salts.—The very soluble crystalline *acid*, $OH.C_{10}H_6.SO_3H+H_2O$, has a strongly acid reaction, shows little tendency to pass into its anhydride even in the presence of dehydrating agents, and like the ammonium salt gives with a single drop of ferric chloride a dark-green colouration which immediately changes to dark-corinth. The *potassium* salt, KA, crystallises in lustrous scales very soluble in water, sparingly soluble in aqueous potassium chloride; the *basic sodium* salt, $Na_2A+1\frac{1}{2}H_2O$, in very soluble aggregates of small needles; the *ammonium* salt, NH_4A, in very soluble lustrous scales (*ibid.*).

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[1] Resinous substances are also formed when the acid is nitrated without previous conversion into the nitroso- compound.

[2] Two nitroso- compounds are theoretically possible, but it is not known whether one or both are formed in this reaction.

[1] This may be a mixed product, as two nitroso- derivatives of 1:4′-α-naphtholsulphonic acid are theoretically possible.

Reactions.—(1) Nitrous acid reacts with the sodium salt in cold aqueous solution forming a sparingly soluble *nitroso-* compound, which yields *brilliant-yellow* on heating with nitric acid (Schöllkopf Co., Germ. pat. 42304 of Jan. 28, 1886).

(2) The azo- dye formed by interaction with diazotised naphthionic acid is yellow in acid, but an intense bluish-violet in alkaline solution (Erdmann, *l.c.*).

Naphthasultone,[1] $C_{10}H_6\left\langle\begin{matrix}SO_2\\O\end{matrix}\right\rangle$, (naphtholsulphonic acid-S. of the Schöllkopf Co.'s Germ. pat. 40571 of Dec. 23, 1885; Eng. pat. 15775 of 1885, *cf.* Erdmann, A. 247, 343 (footnote)), is obtained almost quantitatively by boiling diazotised 1:1′-α-naphthylaminesulphonic acid with alcohol, water, or dilute (10-15 p.c.) sulphuric acid.

Properties.—It crystallises from alcohol or benzene in large colourless prisms, melts at 154°, distils above 360° but considerably below 448° under the ordinary pressure with slight decomposition, is tolerably soluble in alcohol, readily in chloroform and hot benzene, and is not affected by cold aqueous alkalis or boiling aqueous ammonia (Schultz, B. 20, 3162; Erdmann, *l.c.*). Digestion with hot concentrated aqueous caustic potash or alcoholic ammonia converts it into 1:1′-α-naphtholsulphonic acid (*v. supra*).

Reactions.—(1) On fusion with caustic potash at 200-230° it is converted into 1:1′-*dihydroxynaphthalene* (Erdmann, A. 247, 357).

(2) When heated with twice its weight of sulphuric acid of 66°Bé. at 80-90° until the product is completely soluble in water,[2] it yields the Schöllkopf or 1:1′:4-α-*naphtholdisulphonic acid* (Schöllkopf Co., *l.c.*).

(vi) 1:3-α-**Naphtholsulphonic acid.** The preparation of this acid from 1:3-naphthalenedisulphonic acid by careful fusion with aqueous caustic soda and from 1:2′:3-β-amido-α-naphtholsulphonic acid by the diazo-reaction, and its use in the production of blue azo- dyes has been announced (B. A. S. F., Germ. pat. Anm. B 10485).

α-NAPHTHOLDISULPHONIC ACIDS.

(i) 1:2:4-α-**Naphtholdisulphonic acid.**

Formation.—This acid is formed by the further sulphonation of both the 1:2- and the 1:4-α-naphtholsulphonic acids. As the product obtained by heating α-naphthol with 2½ times its weight of concentrated sulphuric acid at 100-105° for about three hours contains in addition about 45 p.c. of heteronucleal disulphonic and some trisulphonic acid (Bender, B. 22, 998) it is evident that the best conditions for preparing the acid will be found in sulphonating at 100° for a much shorter time, or at lower temperatures (say, below 50-60°) with possibly a larger quantity of acid. The separation of the acid from its isomerides has not been described, but could, no doubt, be accomplished by avoiding the formation of trisulphonic acid in the first instance and removing the monosulphonic acids by fractionally treating with a diazotised base and subsequently salting out the azo- dyes.

Reactions.—(1) On boiling with dilute (65 p.c.) sulphuric acid it regenerates α-naphthol. By the further action of concentrated or weakly fuming sulphuric acid it is converted into 1:2:4:2′-α- *naphtholtrisulphonic acid.*

(2) It forms neither azo- dyes nor nitroso-compounds, but readily yields 1:2:4-*dinitro-α-naphthol* (free from resinous substances) on warming with nitric acid (Bender, *l.c.*).

(ii) 1:4:2′-α-**Naphtholdisulphonic acid** has been prepared by the diazo- reaction from 1:4:2′-α-naphthylaminedisulphonic acid (Acid No. III. of Dahl & Co.'s Germ. pat. 41957 of Sept. 4, 1886).

Reactions.—(1) When warmed with dilute (65 p.c.) sulphuric acid it does not regenerate α-naphthol, being probably partially hydrolysed with the formation of 1:2′-α-*naphtholsulphonic acid.*

(2) Nitrous acid reacts with it forming a very soluble *nitroso-* compound which like the acid yields *naphthol yellow S.* on warming with nitric acid.

(3) The azo-dyes formed by interaction with diazotised bases give red shades but little affected by acids and alkalis (*cf.* Dahl & Co., *l.c.*).

(ii and iii) Heteronucleal α-**naphtholdisulphonic acid** of Leonhardt & Co.'s Eng. pat. 11318 of Aug. 18, 1887, and other patents; beyond doubt a mixture of (ii) the 1:4:2′- with (iii) the 1:2:2′-α-naphtholdisulphonic acid.[1]

Formation.—This 'uniform' acid has been prepared (1) by dissolving α-naphthol in twice its weight of a mixture composed of three parts of 45 p.c. anhydrosulphuric acid and two parts of sulphuric acid of 66°Bé. at a temperature not exceeding 50°, and then adding an equal weight of 45 p.c. anhydrosulphuric acid (Seltzer, Germ. pat. 20716 of Jan. 20, 1882); (2) by dissolving α-naphthol in four times its weight of sulphuric acid of 170°Tw. at 100°, and then heating at 130° for an hour (Levinstein, Eng. pat. 5692 of 1882); by heating α-naphthol (3) with a mixture of five parts of 100 p.c. sulphuric acid and two parts of glacial phosphoric acid at 100° for five hours (Durand & Huguenin, Eng. pat. 2591 of 1883, prov. spec.), (4) with three parts of 100 p.c. sulphuric acid at 100-110° for 8-10 hours

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[1] Contracted from naphthalenesulphone-lactone or naphthalenesulpholactone.

[2] The fact that this test is given in the Schöllkopf Co.'s patents as a means of determining when sulphonation is completed, affords additional confirmation of Erdmann's contention that the 'naphtholsulphonic acid-S.' of the patents is the practically insoluble sultone and not the very soluble sulphonic acid.

[1] In view of the readiness with which the 1:2- and 1:4-α-naphtholsulphonic acids are hydrolysed, it is extremely probable that 1:2:4:2′-α-naphtholtrisulphonic acid on partial hydrolysis yields a mixture of the 1:4:2′- and the 1:2:2′-α-naphtholdisulphonic acids, the latter doubtless being the chief product since the SO_3H radicle is in general more easily eliminated from α- than from β- positions. This point was seemingly overlooked by Bender (B. 22, 998), otherwise there can be little doubt that by fractional treatment with diazoxylene he would have obtained in the first fractions azo- dyes chiefly derived from the 1:2:2′- acid, and in the last fractions those from the 1:4:2′- acid, the former judging from those of the 1:2-α-naphtholsulphonic acid being yellowish-brown in shade and sensitive to acids and alkalis, the latter by analogy with those of the 1:4-α-naphtholsulphonic acid being red and little affected by acids and alkalis (*v.* 1:4:2′- acid, *supra*). It should be noted that the azo- dyes derived from the disulphonic acid of L. Vignon & Co.'s. Germ. pat. 32291 are known to be sensitive to acids (*cf.* Actieng. f. A., Germ. pat. 45776) indicating their origin from a product containing so far as heteronucleal disulphonic acids are concerned, chiefly the 1:2:2′- acid.

(L. Vignon & Co., Germ. pat. 32291 of Feb. 27, 1884, exp. July 1887; Eng. pat. 6872 of 1884), (5) with six times its weight of sulphuric acid of 66°Bé. at 80–100° for 8–10 hours (L. Vignon & Co., Eng. pat. 9808 of 1884, prov. spec.), or (6) with 2–3 times its weight of ordinary sulphuric acid of 65–66°Bé. (containing about 93 p.c. H_2SO_4) at 125–130° for about two hours (Leonhardt & Co., Eng. pat. 11318 of 1887).

It is recorded in the case of each of these products, except those prepared by L. Vignon & Co.'s patents, that a nitroso-*a*-naphtholdisulphonic acid is obtained by interaction with nitrous acid, consequently each must have contained a certain proportion of heteronucleal *a*-naphtholdisulphonic acid. An acid prepared by Bender (B. 22, 998) by heating *a*-naphthol with 2½ times its weight of concentrated sulphuric acid at 100–105° for three hours, gave on analysis[1] numbers indicating the presence of considerable quantities of 1:2:4-*a*-naphtholdisulphonic and 1:2:4:2′-*a*-naphtholtrisulphonic acids mixed with an amount of heteronucleal disulphonic acid corresponding with 45 p.c. of the *a*-naphthol employed. There can, therefore, be very little doubt that the products obtained by the above methods are mixtures, and it is probable that the acids of Levinstein's, L. Vignon & Co.'s[2] (Germ. pat. 32291) and particularly Leonhardt & Co.'s patents contain considerable quantities of the supposed uniform heteronucleal *a*-naphtholdisulphonic acid, whilst those of the other patents, in which the use of lower temperatures and of larger proportions of sulphuric acid are directed, consist chiefly of the trisulphonic and 1:2:4-*a*-naphtholdisulphonic acids. A method for separating the mixed acids has not yet been described, and in practice one is not required, since the azo- dyes and nitroso- compounds derived from the disulphonic acids are technically worthless, and naphthol yellow S., obtainable from both the trisulphonic and the heteronucleal disulphonic acids in the mixture, is prepared more cheaply from other sources.

(iv) **1:4:3′-*a*-Naphtholdisulphonic acid**, obtained by boiling diazotised 1:4:3′-*a*-naphthylaminedisulphonic acid (Acid No. II.) with water, gives red azo- dyes with diazotised bases (Dahl & Co., Germ. pat. 41957 of Sept. 4, 1886).

(v) **1:1′:4-*a*-Naphtholdisulphonic acid** (naphtholdisulphonic acid-S. of the Schöllkopf Co.'s Germ. pat. 40571 of Dec. 23, 1885; Eng. pat. 15775 of 1885; *a*-naphthol-[δ-]disulphonic acid of Bernthsen, B. 22, 3335).

Preparation.—(1) Naphthasultone (so-called naphtholsulphonic acid-S.) is heated with 2–3 times its weight of sulphuric acid of 66°Bé. on a water-bath (at 80–90°) until a test dissolves completely in water; the product is poured into water and subsequently converted into sodium salt in the usual way (Schöllkopf Co., *l.c.*), or:

(2) 1:1′:4-*a*-Naphthylaminedisulphonic acid is diazotised at 5°, the diazo- compound boiled with dilute sulphuric acid, and the product converted into sodium salt (Schöllkopf Co., Germ. pat. 40571).

Salt.—The *sodium* salt, $Na_2A + H_2O$, crystallises in scales (Actieng. f. A., Germ. pat. 45776), is very soluble in water, and in aqueous solution gives a deep-blue colouration with ferric chloride (Bernthsen, B. 23, 3091).

Reactions.—(1) On nitration it is converted into a sparingly soluble *dinitro-a-naphtholsulphonic acid* (brilliant-yellow).

(2) When fused with caustic potash it yields *dihydroxynaphthalenesulphonic acid-S.* (Bayer & Co., Eng. pat. 13655 of 1889).

(3) The azo- and disazo- dyes obtained respectively by interaction with diazotised xylidine and amidoazobenzene or their homologues give red to bluish-red shades, and are fairly fast to acids (Schöllkopf Co., Eng. pat. 15775). The disazo- dyes formed with tetrazo- compounds give violet shades.

1:1′:4-Naphthasultonsulphonic acid (naphthasultonsulphonic acid-δ) is obtained as sodium salt when 1 part of naphthasultone is mixed with 8 parts of 5 p.c. anhydrosulphuric acid in the cold, left for an hour or until a test is completely soluble in water, and then stirred into an externally-cooled mixture of 12 parts of ice and 16 parts of saturated brine; the sodium salt crystallises out after some time (B. A. S. F., Germ. pat. Anm. B 9553; Bernthsen, B. 23, 3091).

Salt.—The *sodium* salt, $C_{10}H_5S_2O_6Na + 3H_2O$, crystallises in thin scales or tables, is much more soluble than the 1:1′:3-salt (*infra*), and is readily converted into a salt of 1:1′:4-*a*-naphtholdisulphonic acid by alkaline carbonates, alkalis, boiling dilute (5 p.c.) sulphuric acid or prolonged boiling with water. It gives no colouration with ferric chloride. The solution in concentrated ammonia gives on addition of hydrochloric acid a precipitate of 1:1′:4-*a*-naphtholsulphonamidsulphonic acid (δ-acid) as sodium salt $OH.C_{10}H_5(SO_2NH_2).SO_3Na + 2H_2O$, which crystallises in rhomb-like scales or tables, and yields azo- dyes having properties similar to those of the azo- colours obtained from the ε-acid (*v. infra*; Bernthsen, *l.c.*).

(vi) **1:1′:3-*a*-Naphtholdisulphonic acid** (*a*-naphthol-[ε-]disulphonic acid).

Preparation.—The sparingly soluble diazo-compound from sodium 1:1′:3-*a*-naphthylaminedisulphonate is boiled with water acidified with sulphuric acid, and the product converted into sodium salt in the usual way (Actieng. f. A., Germ. pat. 45776 of Mar. 16, 1888; Eng. pat. 4625 of 1888; Bernthsen, B. 22, 3330).

Salts.—The *sodium* salt, $Na_2A + 6H_2O$, crystallises in long, colourless prisms soluble in about 5·5 parts of water at the ordinary tempera-

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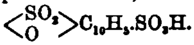
[1] The method of analysis adopted was as follows:—A sample of the product corresponding with 100 grams of *a*-naphthol was mixed in the cold with a litre of water, and the solution divided into two equal quantities. The first half was nitrated with 125 grams of nitric acid of sp.gr. = 1·38, and then mixed with twice its volume of brine, allowed to stand for twelve hours, filtered, pressed, and the resulting nitro- compound extracted with boiling water; the soluble dinitro-*a*-naphtholsulphonic acid (derived from the heterodi- and the tri-sulphonic acids) and the insoluble dinitro-*a*-naphthol (derived from the 1:2:4-disulphonic acid) being weighed in the form of potassium salts. The second half was diluted to 3 litres, rendered alkaline with soda and titrated with a diazoxylene solution of known strength in order to estimate the quantity of heterodisulphonic acids; the solution was then acidified with sulphuric acid and the filtrate, after concentration, treated with nitric acid as just described to determine the amount of soluble dinitro-*a*-naphtholsulphonic acid (derived from the trisulphonic acid).

[2] According to the Actieng. für Anilinfab. (Germ. pat. 45776), the acid of Germ. pat. 32291 gives azo- dyes, and on nitration a mixture of dinitro-*a*-naphthol and dinitro-*a*-naphtholsulphonic acid.

ture, and is precipitated from concentrated solutions by salt. Ferric chloride colours the aqueous solution deep blue.

Reactions.—The acid does not form a naphthol-yellow on treatment with nitric acid. The azo- colours obtained by interaction with diazotised aniline, xylidine, *α*-naphthylamine, and benzidine give respectively orange, scarlet, red, and violet shades fairly fast to acids (Bernthsen, *l.c.*).

1:1′:3-Naphthasultonsulphonic acid (naphthasultonsulphonic acid-ε; zetanaphtholdisulphonic acid),  $<\substack{SO_2\\O}>C_{10}H_5.SO_3H$.

Preparation.—20 kilos. of strong sulphuric acid are stirred into a solution of 36 kilos. of sodium 1:1′:3-*α*-naphthylaminedisulphonate in 500 litres of cold 1 p.c. aqueous caustic soda, the cooled mixture diazotised with a solution of 7 kilos. of sodium nitrite in 75 kilos. of water, and the product boiled just long enough to expel all nitrogen and then at once rapidly cooled; the sparingly soluble sodium salt crystallises out in considerable quantity on cooling (Ewer & Pick, Germ. pat. 52724 of Sept. 16, 1888; Bernthsen, B. 22, 3331).

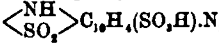
Salts.—The *acid* crystallises in silky white needles readily soluble in water, and the *barium* salt in long colourless needles very sparingly soluble in cold water. The *sodium* salt, $C_{10}H_5SO_3.SO_3Na + 3H_2O$, forms long slender needles, dissolves in about 93 parts of cold water, is precipitated from a 1 p.c. solution by brine, gives no colouration with ferric chloride, and is rapidly converted even in the cold into a salt of 1:1′:3-*α*-naphtholdisulphonic acid by alkaline carbonates and fixed alkalis. Ammonia reacts with it forming

1:1′:3-*α*-Naphtholsulphonamidsulphonic acid ([ε-] or zeta-naphtholsulphamidsulphonic acid), $OH.C_{10}H_5(SO_2NH_2).SO_3H$.

Preparation.—Sodium 1:1′:3-naphthasultonsulphonate dissolves rapidly when stirred into twice its weight of strong ammonia, and after a few hours' standing the resulting solution of the sodium ammonium naphtholsulphonamidsulphonate can be employed for the production of azo- dyes. The salt may be separated either by careful evaporation, or better by the addition of alcohol and ether to the solution (B. A. S. F., Germ. pat. 53934 of Mar. 31, 1889; Bernthsen, B. 22, 3334).

Salts.—The *acid* crystallises in needles tolerably soluble in cold water, the *sodium* salt, $C_{10}H_8NS_2O_6Na + H_2O$, in needles tolerably soluble in cold water, the *sodium ammonium* salt, $C_{10}H_8NS_2O_6Na,NH_3 + H_2O$ ($3H_2O$ in Germ. pat. 53934), in small prisms or needles very soluble in water, sparingly in alcohol. The salts can be boiled with alkalis for a short time without decomposition, but yield naphthasultonsulphonic, and eventually 1:1′:3-*α*-naphtholdisulphonic acid on boiling with dilute acids (*ibid.*).

Reactions.—The azo- dyes obtained by interaction with diazotised aniline, xylidine, *α*-naphthylamine, and benzidine, give respectively 'bluish' orange, bluish-scarlet, wine-red, and bluish-violet shades, and therefore afford redder or bluer shades than the corresponding 1:1′:3-*α*-naphtholdisulphonic acid colours, into which they are converted with elimination of ammonia by dissolution in concentrated sulphuric acid.

A remarkable reaction ensues on boiling the four above-named naphtholsulphonamidsulphonic acid dyes with alkalis or alkaline carbonates for a short time, since new azo- dyes are formed which give respectively bluish-scarlet, cochineal, reddish-violet, and steel-blue shades on wool in an acid bath. These colouring matters are azo- derivatives of a *peri*-anhydride of 1:2-orthonaphthylenediamine-1′:3-disulphonic acid,  $<\substack{NH\\SO_2}>C_{10}H_4(SO_3H).N_2.R$ (Bernthsen, B. 23, 3094).

(vii) **A Naphtholdisulphonic acid** (possibly the 1:3:3′- derivative) is obtained by fusing the sodium salt of Gürke and Rudolph's naphthalenetrisulphonic acid (*q.v.*) at 170–180° for many hours with half its weight of caustic soda and an equal weight of water. A mixed product is formed containing as chief constituent this acid, which is characterised by yielding an *acid sodium* salt, $SO_3H.C_{10}H_5(OH)SO_3Na$, readily soluble in alcohol of 80° Tralles (Gürke and Rudolph, Germ. pat. 38281 of Sept. 2, 1885, Eng. pat. 15716 of 1885, Germ. pat. Anm. G 3636 of 1886), and has been employed in the preparation of azo- dyes (*v.* Azo- COLOURING MATTERS).

α-NAPHTHOLTRISULPHONIC ACIDS.

(i) **1:2:4:2′-*α*-Naphtholtrisulphonic acid.**

Formation.—This acid is obtained when *α*-naphthol is heated with 3 times its weight of 25 p.c. anhydrosulphuric acid at 100–110° for six hours, or with about 4 times its weight of about 45 p.c. anhydrosulphuric acid at 40–50°[1] (B. A. S. F., Germ. pat. 10785 of Dec. 28, 1879; Caro, Eng. pat. 5305 of 1879). It is also formed by the diazo- reaction from 1:2:4:2′-*α*-naphthylaminetrisulphonic acid.

Preparation.—10 kilos. of *α*-naphthol are stirred into 20 kilos. of 25 p.c. anhydrosulphuric acid and heated at 40–50° until a test no longer gives a separation of *α*-naphthol on dilution with water; 18 kilos. of 70 p.c. anhydrosulphuric acid are then gradually added during four hours at 40–50°, and the reaction continued until a test dissolved in about twice its volume of water and boiled with nitric acid (sp.gr. = 1·38) remains clear, or nearly so, on the addition of water, but gives a copious yellow precipitate with aqueous caustic potash (*ibid.*). A certain amount of evidence tends to show that an *α*-naphtholtetrasulphonic acid occurs to some extent in the product.

Reactions.—(1) When heated with dilute (65 p.c.) sulphuric acid, it is converted into 1:2′-*α-naphtholsulphonic acid* (*cf.* Liebmann and Studer, Eng. pat. 7812 of 1887).

(2) It gives neither azo- dyes nor nitroso-compounds, but is very readily converted, even at 50°, into *naphthol yellow S.* when heated

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[1] The acid formed by heating *α*-naphthol with *three* parts of sulphuric acid (sp.gr. = 1·84) at 110–115° for twelve to fifteen hours (*l.c.*) would serve as a source of naphthol yellow S., but so far from containing *α*-naphtholtrisulphonic acid 'in überwiegender Menge' would probably consist largely of the mixed heteronucleal disulphonic acids of Leonhardt & Co.'s Eng. pat. 11318 of 1887. It should be noted that the conditions named are practically those of L. Vignon & Co.'s Germ. pat. 32291 for the preparation of these disulphonic acids.

with dilute nitric acid (B. A. S. F., Caro, *l.c.*; Lauterbach, B. 14, 2029).

(ii) 1:3:1′:3′-*a*-**Naphtholtrisulphonic acid.** This acid is prepared by the diazo- reaction from the naphthylaminetrisulphonic acid obtained when Gürke and Rudolph's naphthalenetrisulphonic acid is nitrated and reduced (Koch, Germ. pat. Anm. K 7567). As it yields azo-dyes of bluish shade, and can be converted into a *naphthasultondisulphonic acid*, it must have the constitution just given.

(iii) A [(?)*a*-]**Naphtholtrisulphonic acid** is obtained when sodium naphthalenetetrasulphonate dissolved in a minimum of water is fused with about six-tenths its weight of caustic soda at 180° for six hours. By interaction with diazo- and tetrazo- compounds it gives yellowish-red to bluish-violet azo- dyes extremely soluble in water (Bayer & Co., Germ. pat. 40893 of Dec. 7, 1886).

NITROSO- DERIVATIVES.

v. Naphthaquinonoximes (*infra*).

NITRO- DERIVATIVES.

(i) 1:2 **Nitro-*a*-naphthol**, $NO_2.C_{10}H_6.OH$.

Formation.—It is obtained by boiling 1:2-nitroacet-*a*-naphthalid (Liebermann and Dittler, A. 183, 246; Lellmann and Remy, B. 19, 802) with aqueous caustic soda; by oxidising 1:2-nitroso-*a*-naphthol with potassium ferricyanide in alkaline solution (Fuchs, B. 8, 629) and, together with dinitro-*a*-naphthol as chief product, by boiling *a*-diazonaphthalene sulphate with an equimolecular proportion of nitric acid (Nölting and Wild, B. 18, 1339).

Properties.—It crystallises in greenish-yellow scales, melts at 128°, is sparingly soluble in dilute alcohol, and resembles orthonitrophenol in being volatile with steam and forming dark red salts.

(ii) **Campobello yellow** (French yellow, chryseinic acid) is the sodium salt of—

1:4-**Nitro-*a*-naphthol.**

Formation.—1:4-Nitro-*a*-naphthol is prepared by boiling 1:4-nitroacet-*a*-naphthalid with aqueous caustic soda (Andreoni and Biedermann, B. 6, 343, *cf.* Lellmann and Remy, B. 19, 796). It is also formed in small quantity when a mixture of *a*-nitronaphthalene and potash-lime (not soda-lime) is heated at 150° in a current of air for ten to twelve hours (Darmstaedter and Nathan, B. 3, 943).

Properties.—It crystallises in yellow needles, melts at 164°, is readily soluble in alcohol and acetic acid, soluble to some extent in warm water, and, like paranitrophenol, does not volatilise with steam. On nitration it yields *dinitro-a-naphthol*. The salts (Biedermann, B. 6, 1118) are orange-red to dark-red in colour, and dissolve readily in water; the *sodium* salt, $NO_2.C_{10}H_6.ONa + 2H_2O$, crystallises in very soluble carmine-red needles, and was formerly used as a yellow dye for silk and wool.

(iii) **Naphthalene yellow** (*Martius yellow, naphthol yellow, Manchester yellow, golden yellow*) is the ammonium or sodium, or more rarely the calcium salt of—

1:2:4-**Dinitro-*a*-naphthol.**

Formation.—Dinitro-*a*-naphthol is obtained by the action of nitric acid on *a*-naphthol (Dale, Caro and Martius, Eng. pat. 2785 of Nov. 9, 1864; Martius, J. pr. 102, 442), 1:4-*a*-nitroso-*a*-naphthol, 1:2-*β*-nitroso-*a*-naphthol (Fuchs, B. 8, 629), 1:4-nitro-*a*-naphthol, 1:2-nitro-*β*-naphthol (Liebermann and Dittler, A. 183, 249), 1:2-*a*-naphtholsulphonic acid (Darmstaedter and Wichelhaus, Eng. pat. 89 of Jan. 12, 1869; A. 152, 299), 1:4-*a*-naphtholsulphonic acid (Cleve, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1876, N:o 7, 40), 1:2:4-*a*-naphtholdisulphonic acid (Bender, B. 22, 996), tolueneazo-*β*-naphthol, &c. (Zincke and Rathgen, B. 19, 2486), or *a*-naphthylamine (Balló, B. 3, 288). It is also formed when dinitroacet-*a*-naphthalid is boiled with aqueous caustic soda (Liebermann and Hammerschlag, A. 183, 273).

Preparation.—Direct nitration of any of the preceding substances, except the 1:2:4-*a*-naphtholdisulphonic acid, results in the production of much resinous matter and a poor yield of dinitro-*a*-naphthol. In practice a very good yield of clean dinitro-*a*-naphthol is obtained, either from 1:2:4-*a*-naphtholdisulphonic acid by direct nitration, or from the two *a*-naphtholmonosulphonic acids present in the mixed product formed when *a*-naphthol is sulphonated under Schaeffer's conditions (*v.* 1:2-*a*-naphtholsulphonic acid) by treatment with the requisite quantities of sodium nitrite and sulphuric acid in the cold, and then warming the resulting nitroso- derivatives with nitric acid (*cf.* Bender, B. 22, 996 (footnote)).

Properties.—It crystallises from alcohol in slender citron-yellow needles, melts at 138°, and is insoluble in water, sparingly soluble in alcohol, ether and benzene. It has strongly acid properties, expels carbon dioxide from carbonates, and forms a series of soluble, orange-coloured salts. The *sodium* salt, $C_{10}H_5(NO_2)_2ONa + H_2O$, and *ammonium* salt, $NH_4A + H_2O$, crystallise in very soluble, small orange needles, the *calcium* salt, $CaA_2 + 6H_2O$, in tolerably soluble, orange-yellow needles (Martius, *l.c.*). Dinitro-*a*-naphthol possesses considerable tinctorial power, and is used either singly or in combination with other dyestuffs as a golden-yellow dye for wool, but has the disadvantage of gradually volatilising from the fibre.

Reactions.—(1) Concentrated nitric acid at temperatures below 40–50° converts it into *trinitro-a-naphthol* (Ekstrand, B. 11, 162; Diehl and Merz, B. 11, 1661), but on continued boiling oxidises it to *oxalic* and *phthalic acids* (Martius, *l.c.*). Phthalic acid is now largely manufactured from this source.

(2) When heated with alcoholic ammonia at 190–200° for six to seven hours it yields *dinitro-a-naphthylamine* (Witt, B. 19, 2032).

Sulphonic Acids.

(*a*) **Naphthol yellow S.** (*acid yellow S., citronine*) is the calcium, sodium, or ammonium salt of—

1:2:4:2′-Dinitro-*a*-naphtholsulphonic acid.

Formation. — Dinitro-*a*-naphtholsulphonic acid is formed by nitration of 1:2′-*a*-naphtholsulphonic acid (Liebmann and Studer, Eng. pat. 7812 of 1887; *cf.* Bender, B. 22, 996), 1:4:2′-*a*-naphtholdisulphonic acid (Dahl & Co., Germ. pat. 41957 of Sept. 4, 1886), the mixed 1:4:2′-

and 1:2:2′-α-naphtholdisulphonic acids (Seltzer, Germ. pat. 20716 of Jan. 20, 1882; Levinstein, Eng. pat. 5692 of 1882; Durand and Huguenin, Eng. pat. 2591 of 1883, prov. spec.; L. Vignon & Co., Eng. pat. 9808 of 1884; Leonhardt & Co., Eng. pat. 11318 of 1887), 1:2:4:2′-α-naphtholtrisulphonic acid (B. A. S. F., Germ. pat. 10785 of Dec. 28, 1879,[1] Eng. pat. 5305 of 1879; M. L. B., Germ. pat. 22545 of Sept. 2, 1882, exp. Jan. 1885, Eng. pat. 2178 of 1882), or α-methoxynaphthalenedisulphonic acid (Dahl & Co., Eng. pat. 1964 of 1883).

Preparation.—(1) The melt obtained by sulphonating 10 kilos. of α-naphthol as described under 1:2:4:2′-α-naphtholtrisulphonic acid (*q.v.*) is diluted to 100 litres with water, and nitrated at a temperature not exceeding 50° by gradually adding 25 kilos. of nitric acid (sp.gr. = 1·38) or the corresponding quantity of a nitrate, the reaction being completed either at 50° or by allowing the mixture to stand in the cold for twelve hours. Dinitro-α-naphtholsulphonic acid separates from the solution in needles, and, after one crystallisation from water, is converted into the sodium or ammonium salt. The mother-liquors contain 'nitronaphtholsulphonic acids' and a 'dinitronaphtholdisulphonic acid,' which can be recovered in the form of potassium or sodium salts in the usual way (B. A. S. F., *l.c.*); the former may possibly owe their origin to incomplete nitration, the latter to the presence of α-naphtholtetrasulphonic acid in the sulphonation product.

(2) The mixed α-naphtholdisulphonic acid of Leonhardt & Co.'s Eng. pat. 11318 is treated in acid solution in the cold with the quantity of sodium nitrite requisite to form the nitroso-compound, and the product nitrated at 50° with commercial nitric acid in the proportion of 100 kilos. to every 40 kilos. of α-naphthol sulphonated (Leonhardt & Co., *l.c.*).

(3) A hot mixture of 8 kilos. of sulphuric acid of 66°Bé. and 8 litres of water is added to a boiling solution of 10 kilos. of calcium 1:2:4:2′-α-naphthylaminetrisulphonate, 3–4 kilos. of sodium nitrite, and 6 kilos. of sodium nitrate in 30 litres of water, and the product worked up as just described (M. L. B., *l.c.*).

Salts.—The *acid*, $OH.C_{10}H_4(NO_2)_2.SO_3H$, crystallises in long, yellow needles, and yields a characteristic reddish-yellow and somewhat gelatinous precipitate of the very sparingly soluble *basic potassium* salt on addition of aqueous caustic potash, or potassium chloride or sulphate to its solution (Lauterbach, B. 14, 2029). The *basic sodium* salt, Na_2A, is a readily soluble, orange-yellow crystalline powder. Naphthol-yellow-S. has considerable tinctorial power, is largely used as a yellow dye for wool, and, unlike naphthalene-yellow, does not volatilise from the fibre.

Reaction.—(1) On oxidation with nitric acid (sp.gr. = 1·33) it is quantitatively converted into *β-sulphophthalic acid* (Graebe, B. 18, 510; Rée, C. J., 49, 511).

(*b*) **Brilliant yellow** is the sodium salt of—

1:2:4:1′-Dinitro-α-naphtholsulphonic acid.

Preparation.—(1) 65 kilos. of nitric acid of 40°Bé. are gradually added to a solution of 100 kilos. of sodium 1:1′:4-α-naphtholdisulphonate in 200 litres of water; the mixture is then heated at 60–70°, and after some time the yellow sodium salt separates from the solution (Schöllkopf Co., Germ. pat. 40571 of Dec. 23, 1885; Eng. pat. 15775 of 1885).

(2) 300 kilos. of sulphuric acid of 66°Bé. are slowly mixed with a solution of 100 kilos. of sodium 1:1′-α-naphtholsulphonate and 28·5 kilos. of sodium nitrite in 1000 litres of water, 70 kilos. of nitre are subsequently added, and the product, after some hours' standing, heated on a water-bath (Schöllkopf Co., Germ. pat. 42034 of Jan. 28, 1886).

Properties.—Brilliant yellow is a yellow powder, and forms a yellow aqueous solution which gives, with aqueous caustic soda in the cold, an orange-yellow precipitate soluble on boiling. In an acid bath it dyes silk and wool yellow.

(*c*) 1:2:4:4′-Dinitro-α-naphtholsulphonic acid is obtained when the nitroso-compound from 1:4′-α-naphtholsulphonic acid is warmed with nitric acid. The *potassium* salt crystallises in lustrous, golden-yellow scales, and is precipitated by aqueous caustic potash from an aqueous solution of the acid.

(iv) **Heliochrysin** (sun-gold), the sodium salt of—

Tetranitro-α-naphthol, is obtained by digesting tetranitro-α-bromonaphthalene (m.p. = 170·5°) with warm, concentrated aqueous sodium carbonate (M. L. B., Germ. pat. 14954 of Dec. 17, 1880, expired Aug. 1883, Eng. pat. 5327 of 1880; Merz and Weith, B. 15, 2714; *cf.* S. C. I. 2, 85). Tetranitro-α-naphthol crystallises in lustrous yellowish scales, melts at 180°, is sparingly soluble in benzene and cold acetic acid, and forms reddish-yellow salts, which dissolve sparingly in water, but readily for the most part in alcohol. The *sodium* salt $(NO_2)_4C_{10}H_3.ONa + 2H_2O$ forms reddish-yellow scales soluble in about 94 parts of water at 19°, and was at one time used as a golden-yellow dye for silk and wool.

Amido- Derivatives.

(i) 1:2-**Amido-α-naphthol**, $NH_2.C_{10}H_6.OH$, obtained by reduction of 1:2-nitro-α-naphthol or 1:2-nitroso-α-naphthol with tin and hydrochloric acid (Liebermann and Dittler, A. 183, 248; Liebermann and Jacobson, A. 211, 55), does not form dyes with diazotised bases.

(ii) 1:4-**Amido-α-naphthol**, prepared by reduction of 1:4-nitro-α-naphthol (Liebermann and Dittler, A. 183, 247), and of azo- dyes derived from α-naphthol such as α-naphthol-orange (Liebermann and Jacobson, A. 211, 61) with tin and hydrochloric acid, yields [α-]*naphthaquinone* on treatment with nitrous acid, ferric chloride, &c., and does not form azo- dyes.

(iii) 1:4′-**Amido-α-naphthol** is obtained by heating 6 kilos. of sodium 1:4′-α-naphthylamine sulphonate with 6 kilos. of caustic soda and 4 litres of water under pressure at 240–250° for 8–10 hours. The hydrochloride gives an intense orange-yellow solution with nitrous acid, and a

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[1] In a judgment concerning the validity of Germ. pat. 10785 it is stated, on the authority of Dr. Caro (C), that dinitronaphtholsulphonic acid is always produced in larger or smaller quantity in the preparation of Martius yellow from α-naphtholsulphonic acid; this must be due to the presence of tri- or heterodi-sulphonic acid in the acid nitrated (Patentblatt 1890, 369).

cornflower-blue dye with diazonaphthalenesulphonic acid (Actieng. f. A., Germ. pat., 49448 of Feb. 13, 1889).

[(?) 1:4′-] **Dimethyl-α-amidonaphthol** is formed when sodium dimethyl-α-naphthylaminesulphonate, obtained by sulphonating dimethyl-α-naphthylamine with weakly fuming sulphuric acid, is heated with an equal weight of water and twice its weight of caustic soda at 280–290° for about half an hour. It crystallises in six-sided tablets, melts at 112°, and is very sparingly soluble in boiling water, readily in alcohol, ether, and benzene (Gesell. f. Chem. Ind., Germ. pat. 50142 of June 1, 1889).

(iv) 1:1′-**Amido-α-naphthol.** The preparation of this compound has been announced (B. A. S. F., Germ. pat. Anm. B 10147), and there is reason to believe that it is obtained by fusing sodium 1:1′-α-naphthylaminesulphonate with caustic alkalis and that on the treatment with nitrous acid it is converted into a *diazo-* compound which interacts with amines or phenols forming azo- dyes.

(v) 1:2′:3-β-**Amido-α-naphtholsulphonic acid** (amidonaphtholsulphonic acid-G.; amidonaphthol-[γ-]sulphonic acid) [$OH:NH_2:SO_3H = 1:2':3$].

Preparation.—2:1′:3′-β-Naphthylaminedisulphonic acid (Amido-G.-acid) is fused with concentrated aqueous soda under conditions similar to those adopted in the preparation of β-amido-β-naphtholsulphonic acid (*q.v.*) from amido-R.-acid (M. L. B., Germ. pat. 53076 of Sept. 8, 1889; Eng. pat. 15176 of 1889), or 30 kilos. of the acid (?-acid sodium salt) are heated under pressure with 50 kilos. of aqueous caustic soda of 40°Bé. at 190–195° for 16 hours (Cassella & Co., Eng. pat. 16699 of 1889); the melt is then dissolved in water and the acid separated by acidifying with hydrochloric acid. According to Cassella & Co., the temperature ought not to exceed 200°, 'as decomposition[1] sets in a few degrees above 200° and is completed at 230°.'

Properties.—The *acid* crystallises in sparingly soluble small scales, the *sodium* salt in readily soluble needles. In neutral solution the salts show a blue fluorescence, and give with ferric chloride a dirty claret colouration. The acid yields a canary-yellow *diazo-* compound which when boiled with alcohol is converted into 1:3-*α-naphtholsulphonic acid* (B. A. S. F., Germ. pat. Anm. B 10485). The azo- dyes formed by interaction with diazotised bases give reddish-violet to bluish-black shades and are said to be fast to milling and scouring (Cassella & Co., Germ. pat. 55024; *l.c.*).

(vi) [(?)1:2′:3:3′-] β-**Amidonaphtholdisulphonic acid** [$(?)OH:NH_2:(SO_3H)_2 = 1:2':3:3'$].

Preparation.—100 kilos. of 2:3:1′:3′-β-naphthylaminetrisulphonic acid, probably as acid sodium salt, are heated with 200 kilos. of caustic soda and 50 kilos. of water at 240–260° for 15–30 minutes until the frothing ceases and the melt becomes thick.[2] On addition of excess of hydrochloric acid to the aqueous solution of the product, the *acid sodium* salt separates as a microcrystalline precipitate.

Properties.—The acid salts dissolve very readily in water giving solutions which show a violet-blue fluorescence changing into blue-green on addition of alkali. In neutral solution ferric chloride gives a dark-brown colouration. On treatment with nitrous acid a tolerably sparingly soluble, bright-yellow *diazo-* compound is obtained from which azo- dyes can be prepared in the ordinary way (M. L. B., Germ. pat. 53023 of Sept. 7, 1889; Eng. pat. 15175 of 1889).

THIO- DERIVATIVES.

Thio-α-naphthol, $C_{10}H_7.SH$, is prepared by warming naphthalene-α-sulphonic chloride with zinc-dust and dilute (1:3) sulphuric acid, and purified by distillation in a vacuum (Maikopar, Z. [2] 5, 711; Krafft & Schönherr, B. 22, 822). It is a colourless, heavy, strongly-refractive oil with a slight mercaptan-like odour, boils at 152·5–153·5° under 15 mm., at 286° under the ordinary pressure, and dissolves readily in alcohol and ether, sparingly in aqueous alkalis.

'**Thionaphtholsulphonic acid-C**' is obtained when a solution of 5·5 kilos. of sodium 1:4-α-naphtholsulphonate in 50 litres of water is boiled with 4·8 kilos. of aqueous soda of 40°Bé. and 2·5 kilos. of powdered sulphur until dissolved. The *sodium* salt seems to contain 1 at. prop. of sulphur to 2 mol. prop. of α-naphtholsulphonic acid, and yields *thio-α-naphthol* when boiled with excess of alkali (Actieng. f. A., Germ. pat. 50613 of Feb. 13, 1889).

(ii) β-**Naphthol.**

Formation.—β-Naphthol occurs in the high-boiling fractions of coal-tar (Schulze, A. 227, 150). On the large scale it is formed by fusing sodium naphthalene-β-sulphonate with caustic soda or potash (*cf.* Wallach and Wichelhaus, B. 3, 846 (footnote); Levinstein, Eng. pat. 2300 of 1883).

Preparation.—The melt obtained by heating 250 kilos. of naphthalene with 230–240 kilos. of sulphuric acid of 66°Bé. for 8 hours at 170° (*v.* naphthalene-β-sulphonic acid) is stirred into 6–8 times its bulk of water and directly neutralised with caustic soda. The sodium salt which separates on standing is collected and dried in a centrifugal machine, mixed with 500 kilos. of 40 p.c. caustic soda solution and the resulting paste boiled down with constant stirring until quite thick. It is then removed to the cast-iron hemispherical melting-pots which are immersed in a bath of paraffin, or better, Russian machine oil (oleonaphthe) and heated at 300° for 12 hours. Sodium β-naphtholate is formed gradually and rises to the top as a chocolate-coloured oil which is skimmed off as it forms, and run into wooden vats with mechanical stirrers where it is dissolved in water and subsequently decomposed by dilute (50 p.c.) sulphuric acid. After cooling, the separated β-naphthol, which filters badly, is filtered off either in a filter-press with thin chambers or on a suction-filter similar to those used in the manufacture of caustic soda, and the press-cakes submitted to powerful hydraulic pressure until quite hard and brittle, then thoroughly dried on iron trays in chambers heated at 60°, and finally distilled from iron

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[1] The nature of this 'decomposition' is not stated in the patent; possibly it refers to the production of amidodihydroxynaphthalene. It is noteworthy that no mention is made of decomposition in the Farbw. vorm. Meister, Lucius and Brüning's patents.

[2] A diazotisable *β-amidodihydroxynaphthalenesulphonic acid* is obtained if the fusion is continued for a further 2 hours at 260–270° (M. L. B., *l.c.*).

stills identical in shape with those used for rectifying the naphthylamines (O. N. Witt, *priv. comm.*).

Properties.—β-Naphthol crystallises in odourless scales or rhombic tables (*cf.* Groth, A. 152, 285), melts at 122° (Schaeffer, A. 152, 282), boils at 285–286° (Ebert and Merz, B. 9, 611), has a sp.gr. = 1·217 at 4° (Schröder, B. 12, 1613), and is readily soluble in alcohol, ether, chloroform, benzene, and alkalis, sparingly in hot water. It is only slightly volatile with steam at 100°, but can readily be distilled with superheated steam. It has marked antiseptic properties (*v.* Disinfectants).

Reactions.—(1) Nitrous acid reacts with it, forming *nitroso-β-naphthol* (Fuchs, B. 8, 1026; *v.* Naphthaquinonoximes, *infra*).

(2) On oxidation with potassium permanganate it yields either *orthocarboxycinnamic acid* (Ehrlich and Benedikt, M. 9, 527), or *a-carboxyphenylglyoxylic acid* (Henriques, B. 21, 1618).

(3) It is converted by prolonged boiling in the air, more readily by distillation with phosphoric oxide or by heating with three times its weight of litharge into *β-dinaphthylene oxide* (Dianin, B. 8, 166; Graebe, Knecht, and Unzeitig, A. 209, 138).

(4) When treated in acetic acid solution with nitrosodimethylaniline hydrochloride it yields bronze-coloured needles of a bluish-violet colouring-matter—the hydrochloride of *β-naphthol-violet* (Meldola, B. 12, 2066; C. J. 39, 38).

(5) Iodine solution added to a solution of β-naphthol in aqueous caustic soda gives a yellowish-green precipitate of so-called *β-naphthol iodide* (Messinger and Vortmann, B. 22, 2322; Bayer & Co., Germ. pat. 49739 of March 9, 1889).

(6) The action of ammonia, acetamide, &c. (*v.* β-Naphthylamine) and of sulphuric acid (*v.* β-Naphtholsulphonic acids) on β-naphthol are separately discussed.

Colour reactions.—Bleaching-powder solution gives to the aqueous solution a pale-yellow colouration which disappears on addition of an excess. Ferric chloride oxidises it to *β-dinaphthol* (Dianin, B. 6, 1252; 7, 125; *cf.* Walder, B. 15, 2166) producing a pale-green colouration and afterwards white flocks which become brown on boiling. When dissolved in strong aqueous potash and heated with chloroform at 50°, it gives like α-naphthol a Berlin-blue colour which gradually changes through green into brown (Lustgarten, M. 3, 720; *cf.* Rousseau, A. Ch. [5] 28, 148).

Tests.—Commercial β-naphthol should be almost colourless, and have approximately the right melting-point. It ought not to become brown on exposure to air and should dissolve almost completely in alkalis forming an almost colourless solution. No ready method of determining the presence of α- in β-naphthol or *vice versâ* has been described.

Estimation.—3–4 grams of β-naphthol are dissolved in aqueous caustic soda in such proportions that at least 4 mols. NaHO are present to each mol. of naphthol, and the solution diluted to 250 or 500 c.c. Of this 5–10 c.c. are warmed at 60°, titrated with excess of decinormal iodine, cooled, acidified with dilute sulphuric acid, made up to 250 or 500 c.c. and an aliquot proportion filtered off and titrated back with decinormal sodium thiosulphate. The quantity of iodine employed multiplied by the factor 0·37843106 (1 mol. naphthol/3 at. iodine = 143·66/379·62 = 0·37843106) gives the amount of pure naphthol present (Messinger and Vortmann, B. 23, 2754).

β-Naphthyl methyl ether is prepared by the methods described under the α- compound (*q. v.*). It crystallises in lustrous scales, melts at 72° (Städel, A. 217, 43), at 70° and boils at 274° (Marchetti, J. 1879, 543), is sparingly soluble in alcohol, readily in ether and benzene, and has an odour of pineapple.

β-Naphthyl ethyl ether, prepared like the α- compound (*q. v.*), melts at 33° (Schaeffer, A. 152, 287), boils at 274–275° (Liebermann and Hagen, B. 15, 1428), has an odour of pineapple, and is readily soluble in alcohol and ether, insoluble in water.

β-Dinaphthyl ether $(C_{10}H_7)_2O$, is obtained by boiling β-naphthol with 50 p.c. sulphuric acid for some hours (Graebe, B. 13, 1850), by passing hydrogen chloride through β-naphthol heated at 200–240° (*ibid.*), by heating β-naphthol with twice its weight of zinc chloride at 180–200° (Merz and Weith, B. 14, 199), and readily by heating sodium β-naphthyl sulphate with β-naphthol at 180–200° (Nietzki, B. 15, 305). It crystallises in scales, melts at 105°, boils above 360° without decomposition, and is readily soluble in benzene, ether, and hot alcohol.

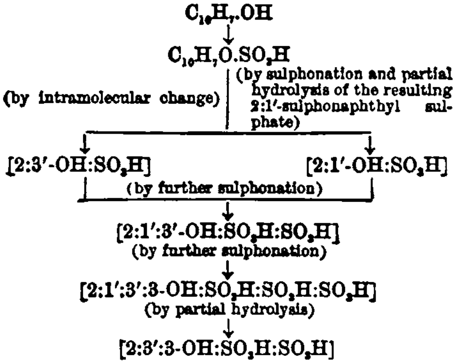
β-Naphthyl acetate, obtained by heating β-naphthol with acetic chloride (Schaeffer, A. 152, 288), or with acetic acid at 240° (Graebe, A. 209, 150), crystallises in needles, melts at 70° (Miller, B. 14, 1602 (footnote)), dissolves sparingly in water, readily in alcohol and ether, and is hydrolysed by distillation with steam.

β-Naphthyl sulphate is formed when β-naphthol is mixed with 1½–2 parts of ordinary sulphuric acid in the cold, and the resulting solution allowed to stand for some time until a crystalline mass is obtained, or when β-naphthol dissolved in carbon bisulphide is shaken with an equimolecular proportion of chlorosulphonic acid in the cold (Armstrong, B. 15, 202; Nietzki, B. 15, 305). The acid has not been isolated. The *potassium* and *sodium* salts crystallise in very soluble scales, are not affected by acids in the cold, but regenerate β-naphthol when boiled in acid solution, yield *dinitro-β-naphthol* on warming with dilute nitric acid, and do not form azo- compounds on treatment with diazotised bases.

Sulphonic Acids.

Introductory.—The majority of the β-naphtholsulphonic acids are prepared by the action of sulphuric acid on β-naphthol, as other methods, such as fusion of naphthalenesulphonic acids with caustic alkalis, or decomposition of diazotised β-naphthylaminesulphonic acids with boiling weak sulphuric acid are applicable only in a few cases.

On sulphonation, β-naphthol is known to form three mono-, three di-, and one tri- sulphonic acids, and the series of changes which probably occur in the production of five of these under conditions described in connection with the respective acids is given in the table (*cf.* also, *Action of sulphuric acid*, under the heading *Substitution in the naphthalene series*):



The β-naphtholsulphonic acids are largely used in the manufacture of azo- dyes, and it is noteworthy that each of the acids containing the radicles OH and SO_3H in the positions [OH:SO_3H = 2:1′]—viz. the 2:1′-mono-, 2:1′:3′-di-, and 2:1′:3′:3-tri-sulphonic acids—interact only slowly with diazotised bases, and yield azo- dyes of much yellower shade than those obtained from their isomerides.

β-NAPHTHOLMONOSULPHONIC ACIDS.

(i) 2:1′[1]-β-**Naphtholsulphonic acid** (β-naphthol-[α-]sulphonic acid of the Farbenfabriken vorm. F. Bayer & Co.'s patents; β-naphthol-[β-]sulphonic acid of Schultz; β-naphthol-*o*-sulphonic acid of Claus and Volz;[2] croceïnic or crocic acid; Bayer's or Rumpff's acid).

Formation.—2:1′-β-Naphtholsulphonic acid is formed together with the 2:3′- and a third, possibly the 2:2′- acid, when β-naphthol is rapidly sulphonated with twice its weight of concentrated or weakly fuming sulphuric acid at temperatures below 60° (Bayer & Co., Germ. pat. 18027 of March 18, 1881; Eng. pat. 1225 of 1881; Germ. pat. 20397 of Jan. 18, 1882; 26231 of May 10, 1883; and Eng. pat. 2411 of 1883). The maximum yield under these conditions amounts to about 80 p.c., but cannot be realised unless excess of sulphuric acid beyond that indicated is avoided, the temperature kept below 50–60°, and the β-naphthol added as rapidly as possible with the object of reducing to a minimum the time during which sulphuric acid can act on the 2:1′- acid. In a modification of the method, sulphonation is conducted at a temperature not exceeding 20° and continued during seven days, or until the initially formed β-naphthyl sulphate has undergone complete conversion into the isomeric sulphonic acids (Leonhardt & Co. and R. Schulz, Germ. pat. 33857 of July 4, 1884; exp. Nov. 1886). It occurs, moreover, to the extent of 15–20 p.c. in the product formed when β-naphthol is sulphonated by Schaeffer's method (A. 152, 296), that is, by heating with twice its weight of concentrated sulphuric acid on a water-bath until dissolved, and is also present in the so-called Armstrong acid produced when β-naphthol is heated with an equimolecular proportion of 100 p.c. sulphuric acid at 100° (Beyer and Kegel, Germ. pat. 32964 of April 19, 1884; expired Sept. 1890). The acid has been obtained, mixed doubtless with its isomerides, from the mixture of β-naphthylaminesulphonic acids of the Badische Anilin- und Sodafabrik's Germ. pat. 20760, and in the pure form from 2:1′-β-naphthylaminesulphonic acid (Dahl & Co., Germ. pat. 29084) by boiling the diazo- compound with 2 p.c. sulphuric acid.

Preparation.—2:1′-β-Naphtholsulphonic acid is obtained, mixed with at least 20 p.c. of impurities in the form of the 2:3′- and a 'third acid,' by stirring dry and finely powdered β-naphthol as rapidly as possible into twice its weight of warm sulphuric acid of 66°Bé. The temperature tends to rise rapidly during the reaction, but is kept constant at 50–60° by cooling, if necessary. The β-naphthol dissolves rapidly in the acid, and as soon as sulphonation is completed, that is in about 10–15 minutes, when a sample of the melt after addition of a slight excess of ammonia gives a clear coloured solution on treatment with diazobenzene chloride, the product is poured into water to prevent any further action of the sulphuric acid. With the object of separating from $\frac{4}{5}-\frac{5}{6}$ of the 2:3′-acid present, the sulphonation product is either (*a*) stirred into twice its weight of water, neutralised in the cold with solid potassium or sodium carbonate, and filtered from the white crystalline precipitate of the 2:3′- salt, or (*b*) poured into three times its weight of water, treated with two-thirds the quantity of caustic alkali required for complete neutralisation, and, after cooling, filtered from the separated acid sodium or potassium salt of the 2:3′- acid (Bayer & Co., Germ. pat. 26678 of June 22, 1883; Eng. pat. 8390 of 1884). The mother-liquor is then freed from the 'third acid'[1] and remainder of the 2:3′-acid by fractional treatment with a diazotised base, advantage being taken of the fact that the 2:1′- acid interacts less readily than its isomerides with diazo- compounds, and not at all with diazoxylene in dilute solution under the ordinary conditions (Pfaff, quoted by Liebermann, B. 16, 2864; Schultz, B. 17, 461). A preliminary experiment is made by adding tetrazodiphenyl chloride,[2] or any diazotised base, to a sample of the mother-liquor rendered alkaline with soda, until on salting out the resulting dyes a solution is obtained which gives pure crocein-scarlet on treat-

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[1] In every case where the constitution of a β-naphtholsulphonic acid is given the OH-radicle is supposed in the position '2.'

[2] Claus and Vols assign the constitution [2:3] to this acid because the derived dichloronaphthalene (m.p. = 61°) yields the homonucleal dichloro-[α-]naphthaquinone on oxidation with chromic acid (B. 18, 3160). The method is, however, untrustworthy (*cf.* Armstrong, B. A. Report, 1887; C. J. Proc. 1889, 9), and in this instance is recognised as leading to erroneous conclusions as shown by Pfitzinger and Duisberg (B. 22, 397), and by Nietzki and Zübelen (B. 22, 454).

[1] According to the Farbenfabriken vorm. F. Bayer & Co. (Germ. pat. 26231, 30077) this 'third acid' interacts more readily than the 2:3′- acid with diazo- compounds, and the resulting azo- dyes separate as sparingly soluble precipitates. The dyes derived from diazotised aniline, toluidine, &c., give blue shades, and dissolve readily in hot water.

[2] The azo- colour obtained by interaction of tetrazodiphenyl chloride with the 2:3′- acid is insoluble in water, but that with the mixed 2:3′- and 'third' acid is readily soluble, and gives claret shades.

ment with diazoazobenzenesu'phonic acid. The calculated quantity of diazotised base is then added to the mother-liquor, the dyes salted out, and the solution of technically pure sodium 2:1′-β-naphtholsulphonate either concentrated to crystallising point, or at once used for the production of crocein-scarlet, &c. (Bayer & Co., Germ. pat. 26231 of May 10, 1883; 30077 of March 1, 1884; Eng. pat. 2411 of 1883; 8495 of 1884; *cf.* also Dahl & Co., Germ. pat. 26308 of May 6, 1883; exp. Sept. 1886).

To purify the acid on the laboratory scale, the sulphonation product is stirred into about ten times its weight of water, converted into barium or calcium salt, boiled, filtered hot, and the filtrate concentrated until the 2:3′- salt separates out as a precipitate. About four-fifths of the 2:3′- acid is in this way removed, and the remaining impurities can be separated by converting the soluble calcium salt into neutral (basic) sodium salt, drying, boiling with three to four times the weight of 90 p.c. alcohol, and filtering hot from the practically insoluble 2:3′-salt. The filtrate, on cooling, gives a pure crystallisation of the 2:1′-sodium salt in large aggregates of needles.

Salts.—The *acid* is only known in solution and decomposes into β-naphthol and sulphuric acid when this is evaporated; it forms both normal (acid) and basic (neutral) salts. The *normal lead* salt, $PbA_2 + 2\frac{1}{2}H_2O$, crystallises in lustrous rhombohedra soluble in water and aqueous alcohol; the normal and basic *barium* and *calcium* salts are very soluble in water, insoluble in absolute alcohol; the *normal sodium* salt, NaA, crystallises in lustrous, six-sided scales readily soluble in water, sparingly in hot alcohol; the *basic sodium* salt, $ONa.C_{10}H_6.SO_3Na$, crystallises from alcohol with 2 mol. props. of alcohol in large aggregates of radially-grouped deliquescent needles, and on drying at 100° forms an amorphous powder extremely soluble in water, very soluble in hot alcohol, and soluble in about 100 parts of 95 p.c. alcohol at 15° (B. A. S. F., Germ. pat. 20760; Claus and Volz, B. 18, 3155).

Reactions.—(1) On digestion with about three times its weight of phosphorus pentachloride at 165–170°, the sodium salt yields, among other products, a *dichloronaphthalene*, melting at 61·5° (Claus and Volz, *l.c.*), which must be regarded as the 2:1′- derivative.

(2) Unlike its isomerides, it does not give a nitroso- compound (*cf.* Gans & Co., Germ. pat. 28065), but is readily nitrated, forming a *dinitro-β-naphtholsulphonic acid* (crocein-yellow) on warming with dilute nitric acid (Bayer & Co., Germ. pat. 18027; Nietzki and Zübelen, B. 22, 454).

(3) On sulphonation with three times its weight of sulphuric acid of 66°Bé. at temperatures below 50°, it is converted into 2:1′:3′-β-*naphtholdisulphonic acid* (Gans and Hoffmann, Eng. pat. 816 of 1884).

(4) As already mentioned, this acid interacts slowly with diazotised bases. The azo- dyes vary in shade from orange with aniline to scarlet with naphthionic acid; the disazo- dyes with amidoazobenzenesulphonic acid and its homologues give respectively scarlet and bluish-scarlet, and with tetrazo- compounds violet-red shades. The dyes are more soluble in water, and the shades are purer and much more yellow than those from the 2:3′-acid.

(ii) **2:4′-β-Naphtholsulphonic acid** has been prepared by the diazo- reaction from 2:4′-β-naphthylaminesulphonic acid (Dahl & Co., Germ. pat. 29084 of March 2, 1884; Claus, J. pr. [2] 39, 315).

(iii) **2:2′-β-Naphtholsulphonic acid** (β-naphthol-[δ-]sulphonic acid of Bayer and Duisberg; naphtholsulphonic acid-F. of Cassella & Co.).

Formation.—Pure 2:2′-β-naphtholsulphonic acid is obtained when sodium 2:2′-naphthalenedisulphonate is heated under pressure with 10–50 p.c. aqueous caustic soda at 250° (Weinberg, B. 20, 2907; Cassella & Co., Germ. pat. 42112 of Sept. 22, 1886; Eng. pat. 12908 of 1886), and when 2:2′-β-naphthylaminesulphonic acid is diazotised and boiled with dilute sulphuric acid (Bayer and Duisberg, B. 20, 1431). It is also formed together with the 2:3′-acid when β-naphthol is heated with an equimolecular proportion of 100 p.c. sulphuric acid at 100–130° until sulphonation is completed, but does not seem to have been isolated from the product (Green, Eng. pat. 15849 of 1888; C. J. 55, 37).

Preparation.—(1) 100 kilos. of sodium 2:2′-naphthalenedisulphonate are stirred into about 400 kilos. of 50 p.c. aqueous caustic soda and heated at 200–250° until an acidified test on extraction with ether gives traces of dihydroxynaphthalene, or until a test freed from sulphur dioxide gives with diazoxylene an amount of dye equivalent to the quantity of disulphonate employed. The formation of the naphtholsulphonic acid is not conditioned by pressure, so that an autoclave is not necessary, but depends on the temperature, which must not exceed 300°. The melt is mixed with about 1000 litres of water, acidified with hydrochloric acid, boiled to expel sulphur dioxide, and left to crystallise, the greater part of the sodium salt crystallising out on cooling (Cassella & Co., *l.c.*).

(2) 130 kilos. of the crude mixture of ββ-disulphonic acids obtained by the sulphonation of naphthalene (*v.* 2:2′-naphthalenedisulphonic acid) are heated with 35 kilos. of caustic soda, 40 kilos. of salt, and 180 litres of water under pressure for sixteen hours at 240–270°. After cooling, the mixed crystallisation of sodium sulphite and the basic sodium salt of the 2:3′-acid is separated from the alkaline mother-liquor containing principally the basic salt of the 2:2′- acid, which can be obtained from the solution as normal salt by acidifying and salting out. Or, the melt is dissolved in 500 litres of water, acidified with hydrochloric acid to expel sulphur dioxide, saturated with salt at the boiling-point, and after a short time filtered boiling hot. The sodium salt of the 2:3′- acid is practically insoluble in the brine and remains almost completely behind, whilst the sodium 2:2′-β-naphtholsulphonate crystallises from the filtrate on cooling (Cassella & Co., Germ. pat. 45221 of June 4, 1887).

Salts.—The *acid* crystallises from concentrated hydrochloric acid in hydrated needles, which, after drying over potash, melt at 89°, carbonise at 150°, and are readily soluble in water and alcohol. When heated above 200° with dilute acids, it decomposes into β-naphthol and sulphuric acid. The *barium* salt crystallises in poorly-defined prisms sparingly soluble in water, but more so than the 2:3′- salt, the *magnesium* salt, $MgA_2 + 5\frac{1}{2}H_2O$, in scales, the *potassium* salt, $KA + H_2O$, in large rhombic forms readily soluble in water, the *sodium* salt, $NaA + 2\frac{1}{2}H_2O$, in large scales soluble in 12·5 parts of water at 15° (Weinberg, *l.c.*). The alkaline solutions of the salts show a pure blue fluorescence; the neutral solutions give a dark-blue colouration with ferric chloride (Cassella & Co., *l.c.*).

Reactions.—(1) When the sodium salt is heated with 3 parts of phosphorus pentachloride at 165° for some hours, 2:2′-*dichloronaphthalene* is obtained (Weinberg, *l.c.*; Bayer and Duisberg, B. 20, 1432).

(2) On treatment with nitrous acid it yields a *nitroso-* compound, the sodium salt of which crystallises with $2H_2O$ in golden needles, and gives a green colouring matter on treatment with ferric chloride (Weinberg, *l.c.*).

(3) It is converted into 2:3:2′-β-*naphthol-disulphonic acid* ([δ-]acid) when the sodium salt is heated with twice its weight of sulphuric acid of 66°Bé. at 120° for about twelve hours (Cassella & Co., Germ. pat. 44079 of Mar. 15, 1887).

(4) The azo- dyes formed by interaction with diazotised bases are said to be redder or bluer than those from the 2:3′- acid.

(iv) 2:3′-β-**Naphtholsulphonic acid** (β-naphthol-[α-]sulphonic acid of Armstrong and Graham and of Schultz; Schaeffer or Armstrong acid).

Formation.—2:3′-β-Naphtholsulphonic acid, obtained from β-naphthyl sulphate by intramolecular change at the temperature of a water-bath (Armstrong, B. 15, 204), is formed as chief product, mixed with about 15–20 p.c. of the 2:1′-acid when β-naphthol is heated with twice its weight of concentrated sulphuric acid on a water-bath until it is completely dissolved and a test gives no separation of β-naphthol when stirred into water (Schaeffer, A. 152, 296), and mixed with 2:2′-acid, some disulphonic acid and unattacked β-naphthol when equimolecular proportions of β-naphthol and 100 p.c. sulphuric acid are heated together at 100–105° for 2-3 hours until sulphonation is completed[1] (Armstrong, B. 16, 201; *cf.* Green, C. J. 55, 37; B. 22, 724). It is also obtained when β-dinaphthyl ether is heated with 2–3 parts of sulphuric acid of 66° Bé. at 90–100° until a test dissolves completely in water (Farbfab. vorm. Brönner, Germ. pat. 26938 of July 21, 1883, exp. May 1887; Eng. pat. 3606 of 1883), and when potassium 2:3′-naphthalenedisulphonate is fused with 2–3 times its weight of caustic potash (Ebert and Merz, B. 9, 610; Armstrong and Graham, C. J. 39, 136).

Preparation.—*v.* 2:1′- and 2:2′-β-Naphthol-sulphonic acids. The product obtained by Schaeffer's method is stirred into water, neutralised with lead or preferably (Armstrong and Graham, *l.c.*) with calcium carbonate, and the filtrate concentrated to crystallising-point. The crystalline separation is purified by recrystallisation and converted into alkali salt in the usual way.

Salts.—The *acid* crystallises in small non-deliquescent laminæ, melts at 125°, and is readily soluble in alcohol and water. The *lead* salt, $PbA_2 + 6H_2O$, crystallises in small, silvery scales readily soluble in water, less so in alcohol, the *barium* salt, $BaA_2 + 6H_2O$, in long, narrow prisms, the *calcium* salt, $CaA_2 + 5H_2O$, in silky scales, or by spontaneous evaporation of a saturated solution in large, irregular prismatic forms readily soluble in alcohol and soluble in 30 parts of water at 18°. Both the barium and calcium salts part with water of crystallisation when introduced into hot water forming anhydrous salts which dissolve only with extreme difficulty. The *potassium* salt, KA, crystallises with 1–3 p.c. of water in prismatic forms soluble in about 50 parts of water at 15°, the *sodium* salt, $NaA + 2H_2O$, in silky scales, soluble in about 3·3 parts of water at 80°, in 57·8 parts at 14° and in 69 parts at 11·5° (Schaeffer, *l.c.*; Armstrong and Graham, *l.c.*), the *ammonium* salt, NH_4A, in long flat prisms or plates soluble in about 34 parts of water at 24° (Meldola, C. J. 39, 41). The aqueous solutions of the salts show a pale-blue fluorescence and give a pale-green colour with ferric chloride. The potassium salt is hydrolysed with the regeneration of β-naphthol by heating with hydrochloric acid at 200–210° (Ebert and Merz, B. 9, 611).

Reactions.—(1) On digestion with about three times its weight of phosphorus pentachloride at 165° for 5 hours, it yields, among other products, 2:3′-*dichloronaphthalene* (Claus and Zimmermann, B. 14, 1483).

(2) Nitrous acid reacts with its salts forming *nitroso*-2:3′-β-*naphtholsulphonic acid* (Meldola, *l.c.*) which by treatment with ferric chloride is converted into *naphthol green B.* (Gans & Co., Germ. pat. 28065).

(3) Nitric acid added to a warm solution of the salt gives a characteristic deep, and somewhat bluish-red colouration which disappears on boiling without any separation of a nitro- derivative taking place (Schaeffer, *l.c.*; Armstrong and Graham, *l.c.*).

(4) Sulphonation with a mixture of equal weights of potassium pyrosulphate and sulphuric acid at 150–160° converts it into the 2:3:3′-β-*naphtholdisulphonic acid* (*q.v.*).

(5) The azo- dyes formed by interaction with diazotised bases give shades varying from orange with aniline to carmine-red with naphthionic acid and are throughout redder than those from the 2:1′-acid. The disazo- dyes with diazotised amidoazobenzene and its derivatives and with tetrazo- compounds exhibit bluer shades than those from the 2:1′- acid, and seem to have little commercial value.

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[1] According to Beyer and Kegel (Germ. pat. 32964 of April 19, 1884, exp. Sept. 1890; Eng. pat. 7098 of 1884), the product obtained by Armstrong's method can be decomposed into two isomeric acids by adding 38 kilos. of ammonia-soda to the melt formed from 100 kilos. of β-naphthol, filtering from unattacked naphthol and saturating the hot solution with salt. A sodium salt separates as the liquid cools and is stated to give yellower dyes with diazo-hydrocarbons and redder dyes with diazo-sulphonic acids than Schaeffer's acid. The salt remaining in the mother-liquor gives dyes similar to but somewhat more yellow than those from Schaeffer's acid. The precipitated salt would seem to be regarded as chiefly that of the 2:1′-acid, but this seems very improbable (apart from the fact that the reaction is continued long enough to ensure an almost entire absence of 2:1′-acid from the product) in view of the comparative solubilities of the 2:1′- and 2:3′-sodium salts in brine. Possibly the separated salt consists chiefly of 2:3′-, the more soluble of a mixture of 2:2′- and 2:3′- sodium salts.

β-Naphtholdisulphonic Acids.

(i) [(?)2:1:3′]β-**Naphtholdisulphonic acid**, obtained with other products by the action of 2 mol. props. of chlorosulphonic acid on β-naphthol in carbon bisulphide solution, is characterised by its *barium* salt, which crystallises in large prisms, is very sparingly soluble in water when once separated from solution and yields a very sparingly soluble *nitro-β-naphtholsulphonate* on warming with nitric acid (Armstrong, B. 15, 204 and *priv. comm.*).

(ii) 2:1′:3′-β-**Naphtholdisulphonic acid**[1] (β-naphthol-[γ-]disulphonic acid; β-naphthol-disulphonic acid-G.; G.-acid (Y.-acid of Eng. pats.): also known as β-naphthol-[β-]disulphonic acid when mixed with some R.-acid).

Formation.—When β-naphthol is heated with three times its weight of concentrated sulphuric acid at 100–110° for 12 hours (M. L. B., Germ. pat. 3229 of April 24, 1878; Eng. pat. 1715 of 1878; Griess, B. 13, 1956, *cf.* B. 14, 2325), or with four times its weight of acid at 125–150° for 5–6 hours (Beyer and Kegel, Germ. pat. 33916 of April 19, 1884; Eng. pat. 7097 of 1884) a mixture of G.- with a large proportion of R.-acid is obtained. At lower temperatures, as when β-naphthol is mixed with 5 parts of sulphuric acid of 66°Bé. at 0° and gradually heated to 60° in the course of 36 hours (Gans and Hoffmann, Eng. pat. 816 of 1884; M. L. B., Germ. pat. 36491 of March 1, 1884), G.-acid constitutes the chief product,[2] and is also obtained in relatively pure condition when 2:1′-β-naphtholsulphonic acid (or its generators) is mixed with three times its weight of sulphuric acid of 66°Bé. and either heated at 40–50° during 5–6 hours or allowed to stand at 25° during 8-10 days (Gans and Hoffmann, *l.c.*). G.-acid, probably in an impure form, has been prepared by the diazo- reaction from the β-naphthylaminedisulphonic acid of Gans & Co.'s Germ. pat. 35019 (*v.* 2:1′:3′-β-naphthylamine-disulphonic acid).

Preparation.—Finely powdered β-naphthol is stirred into five times its weight of sulphuric acid of 66°Bé. at 0° and the temperature raised to 60° in the course of 36 hours, or mixed with 4 parts of 66°Bé. acid, and the temperature, which rises to 50–60°, maintained at 60° during 48 hours or at 20° during 8–10 days. The product is converted into sodium salt in the usual way and freed from impurities by fractional treatment with a diazotised base, advantage being taken of the fact that G.-acid like the 2:1′- or Bayer acid interacts less readily than the admixed β-naphtholsulphonic acids with diazo- compounds. For this purpose the calculated quantity of diazo- compound ascertained from a preliminary experiment with, *e.g.*, diazotised α-naphthylamine is added to the sodium salt in alkaline solution, and the resulting azo- dye salted out; the filtrate containing the sodium salt of technically pure G.-acid can be at once used for the production of azo- dyes (M. L. B., *l.c.*).

Fractional crystallisation of the barium or sodium salt of the mixed product has been proposed as a means of purification, the salts of G.-acid being more soluble than those of the impurities (Gans and Hoffmann, *l.c.*). The [β-] acid separated from the mixed R.- and G.-acids by this method (Griess, B. 13, 1956)—like the old G.-acid of the Farbw. vorm. Meister, Lucius, and Brüning's Germ. pat. 3229 obtained by extracting the mixed sodium salt of the two acids with 3-4 parts of alcohol of 80-90°Tr. and evaporating the filtrate to dryness—consists, however, of G.-acid mixed with varying proportions of sulphonic acids which interact with diazotised bases in dilute solution and requires to be purified by the method just indicated.

Salts.—The salts of pure G.-acid do not appear to have been described with the exception of the *potassium* salt which is said to dissolve in 2·5 parts of boiling water. The *barium* and *sodium* salts of Griess' [β-]acid crystallised in prismatic forms very soluble in water forming solutions which showed a marked bluish-green fluorescence.

Reactions.—Like the 2:1′-acid, G.-acid interacts slowly with diazotised bases. The azo- dyes generally, and the disazo- dyes obtained with diazotised amidoazo- compounds exhibit somewhat more yellow shades of orange and scarlet than those of the corresponding colours from the 2:1′-acid, and on account of their clearness, beauty, and relative cheapness, have considerable commercial importance. The disazo- dyes formed with tetrazo- compounds give redder shades than the corresponding colours from the 2:1′- acid.

(iii) 2:3:3′-β-**Naphtholdisulphonic acid** (β-naphthol-[α-]disulphonic acid; β-naphtholdisulphonic acid-R.; R.-acid).

Formation.—As already stated (*v.* 2:1′:3′- or G.-acid, *supra*), R.-acid is formed as chief product when β-naphthol is heated with 3-4 times its weight of sulphuric acid of 66°Bé. at temperatures above 100°. It is said to be obtained as an almost uniform product when dry potassium 2:3′-β-naphtholsulphonate is intimately mixed with an equal weight of potassium pyrosulphate, stirred into its own weight of concentrated sulphuric acid at 130°, and heated for 5–6 hours at 160°[1] (Baum, Eng. pat. 3523 of 1883, prov. spec.).

Preparation.—β-Naphthol is rapidly stirred into 4 times its weight of sulphuric acid of

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[1] Claus and Schmidt (B. 19, 3174) obtained from the [β-]acid, by digestion with phosphorus pentachloride at 210°, a trichloronaphthalene (m.p. 90°) which they regard as the 2:3:3′- derivative from a study of the trichloro-[α-]naphthaquinone formed by oxidising it with chromic acid. The constitution given above to G.-acid has been arrived at by examination of amido-G.-acid (*v.* 2:1′:3′-β-naphthylamine-disulphonic acid), and the corresponding trichloronaphthalene is known to melt at 113° (Armstrong and Wynne, C. J. Proc. 1890, 13). The fact that a dichloronaphthalene was also present in Claus and Schmidt's product shows that no special precautions were taken to purify the technical product employed by them, and there can be little doubt that their trichloronaphthalene was derived from admixed R.-acid which like amido-R.-acid (*q.v.*) would yield a trichloronaphthalene melting at 90–91°.

[2] The minor product in this case consists almost exclusively of 2:3′-β-naphtholsulphonic acid.

[1] The acid obtained according to Krügener (Monit. Sci. [3] 14, 819) by dissolving β-naphthol in 1½ parts of 100 p.c. sulphuric acid, raising the temperature in the course of an hour to 100°, cooling to 50°, adding 2 parts of 40 p.c. anhydrosulphuric acid, and heating at 50–60° until the greater part of mono- is converted into di-sulphonic acid, must almost unquestionably be a mixture containing chiefly R.-acid mixed probably with some G.-acid and Cassella's 2:3:2′- or [δ-]disulphonic acid derived respectively from the 2:1′- and 2:2′-acids which would be present in the mono-sulphonic acid first formed.

66°Bé. heated at 125°, and the temperature maintained at 125-150° for 5–6 hours (Beyer and Kegel, Germ. pat. 33916 of April 19, 1884; Eng. pat. 7097 of 1884), or into 3 times its weight of acid and heated at 100–110° for 12 hours (M. L. B., Germ. pat. 3229 of April 24, 1878; Eng. pat. 1715 of 1878; Griess, B. 13, 1956). The product is then mixed with sufficient water, and either immediately, or, according to Beyer and Kegel, after neutralisation with soda, saturated with salt, and left to cool. The crystalline separation is filtered off, and after washing with brine, forms technically pure R.- salt, the mother-liquors containing a mixture of G.- with some R.- salt. The technical product can be further purified by extracting with alcohol of 80–90° Tralles; the residue consists of pure sodium 2:3:3′-β-naphtholdisulphonate.

Salts.—The *acid* crystallises in white, silky, deliquescent needles very soluble in water and alcohol, the *barium* salt, $BaA + 6H_2O$, in needles soluble in 12 parts of boiling water, sparingly soluble in cold water and insoluble in alcohol, the *sodium* salt in granular aggregates of minute needles readily soluble in cold water and sparingly soluble in dilute or strong alcohol and in brine. The aqueous solutions show a marked bluish-green fluorescence (Griess, *l.c.*).

Reactions.—The azo- dyes formed by interaction with diazotised bases give shades varying from orange with aniline to scarlet with xylidine and claret with naphthionic acid. These shades are in every case redder than the corresponding colours from 2:3′-β-naphtholsulphonic acid (*v.* Azo- COLOURING MATTERS), and the same is true also of the disazo- dyes obtained by interaction with tetrazo- compounds derived from diamines other than paradiamines such as benzidine, dianisidine, diamidodiphenic acid, &c. The disazo- dyes from the paradiamines named give blue or bluish-violet shades, and thus differ in a marked manner from the corresponding dyes from other β-naphtholsulphonic acids which give red or reddish- to greyish-violet shades (*cf.* Schultz, B. 17, 461).

(iv) 2:3:2′-β-**Naphtholdisulphonic acid** (β-naphthol-[δ-]disulphonic acid).

Preparation.—Sodium 2:2′-β-naphtholsulphonate is mixed with twice its weight of sulphuric acid of 66°Bé. heated at 120-140°, and the temperature maintained at about 120° during 12 hours or until a test in alkaline solution gives with diazotised α-naphthylamine a claret which is bluer in shade than 'Bordeaux B.' obtained in like manner from R.- acid. The product is converted into sodium salt in the usual way (Cassella & Co., Germ. pat. 44079 of March 15, 1887; Eng. pat. 8265 of 1887). The technical product can be purified by means of the sparingly soluble barium salt.

Salts.—The *barium* salt, $BaA + 2\frac{1}{2}H_2O$, crystallises in small prisms soluble in 185 parts of boiling water; the *sodium* salt, NaA_2, is soluble in 100 parts of 80 p.c. alcohol and very soluble in water forming a solution which shows a green fluorescence (Cassella & Co., *l.c.*; Weinberg, B. 20, 2911).

Reactions.—The azo- dyes obtained by interaction with diazotised bases give bluer and purer shades than the corresponding colours from R.- acid (Cassella & Co., *l.c.*).

β-Naphtholtrisulphonic Acid.

[(?) 2:3:1′:3′-] β-**Naphtholtrisulphonic acid.**[1]

Preparation.—β-Naphthol is stirred into 4–5 parts of 20 p.c. anhydrosulphuric acid at such a rate that the temperature rises to 140–160°, and the reaction is continued at this temperature until a test gives a pure green fluorescence in ammoniacal solution, and does not immediately interact with diazotised xylidine but only forms a dye after standing some time. The product is then converted into sodium salt in the usual way (M. L. B., Germ. pat. 22038 of May 26, 1882; Eng. pat. 2544 of 1882; Limpach, S. C. I. 2, 38). Instead of β-naphthol, the 2:1′- or 2:3′-β-naphtholsulphonic acids, or G.- or R.-acid may be employed with suitable alteration in the quantity of sulphuric acid used, and a method involving first the production of the mixed mono-, then the mixed di-, and finally the trisulphonic acid has been described by Levinstein (Eng. pat. 706 of 1883; B. 16, 462, *cf.* Limpach, B. 16, 726).

Reactions.—The azo- dyes formed by interaction with diazotised bases give shades intermediate between those afforded by the corresponding colours from G.- and R.-acids, and have little technical importance.

Nitroso- Derivatives.

v. Naphthaquinonoximes (*infra*).

Nitro- Derivatives.

1:2-**Nitro-β-naphthol** is obtained by oxidising 1:2-nitroso-β-naphthol with dilute nitric acid (Stenhouse and Groves, C. J. 32, 51), and by boiling 1:2-nitroacet-β-naphthalid with 6 p.c. aqueous caustic soda (Jacobson, B. 14, 806; Liebermann and Jacobson, A. 211, 46). It crystallises in yellow needles or scales, melts at 103°, and dissolves readily in alcohol. The *sodium* salt forms red needles insoluble in aqueous caustic soda.

Dinitro-β-naphthol [(?) $OH:NO_2:NO_2 = 2:1:3'$] is formed by nitration of β-naphthol (Wallach and Wichelhaus, B. 3, 846; Graebe and Drews, B. 17, 1170), and by the action of nitric acid on β-naphthyl sulphate and 1:2-nitroso-β-naphthol (Armstrong, B. 15, 202). It crystallises in bright-yellow needles, melts at 195°, and is readily soluble in ether and chloroform, less so in alcohol, and very sparingly in hot water. On oxidation with nitric acid or potassium permanganate it yields β-nitrophthalic acid. When heated with concentrated aqueous ammonia at 140° it is converted into *dinitro-β-naphthylamine.* The *sodium* and *potassium* salts crystallise in sparingly soluble yellow needles.

Crocein yellow, $OK.C_{10}H_4(NO_2)_2.SO_3K$, the potassium salt of a *dinitro-β-naphtholsulphonic acid*, is prepared by dissolving 10 kilos. of basic sodium 2:1′-β-naphtholsulphonate in 20 kilos. of water, boiling to expel the alcohol of crystallisation, cooling to 40–50°, adding 15 kilos. of 50 p.c. nitric acid, and allowing the mixture to re-

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[1] The constitution here provisionally assigned to this acid seems highly probable since the acid appears to be formed by the sulphonation of G.- and R.- acids, and, moreover, interacts only slowly with diazotised xylidine, thus resembling the 2:1′- and the 2:1′:3′- (or G.-) sulphonic acids. As pointed out in the introduction, this acid is not improbably an intermediate product in the formation of R.- from G.- acid.

main for several days at 30-40° until nitration is completed. The product is treated with excess of potassium carbonate, and the potassium salt of the dye, which separates as a crystalline meal, purified by recrystallisation. It forms soluble golden-yellow scales, and in an acid bath dyes wool a pure yellow, but has little tinctorial power and is not met with in commerce (Bayer & Co., Germ. pat. 18027 of Mar. 18, 1881; Eng. pat. 1225 of 1881; Nietzki and Zübelen, B. 22, 454).

AMIDO- DERIVATIVES.

(i) 1:2-Amido-β-naphthol.

Formation.—Amido-β-naphthol may be obtained by reducing nitroso-β-naphthol with ammonium sulphide (Groves, C. J. 45, 296) and 1:2-nitro-β-naphthol with tin and hydrochloric acid (Jacobson, B. 14, 806), but is usually prepared from β-naphthol-azo- dyes, *e.g.* β-naphthol-orange,[1] by reduction with stannous chloride in hydrochloric acid solution (Liebermann, B. 14, 1310; Liebermann and Jacobson, A. 211, 53, 59; Witt, B. 21, 3472.

Properties.—It crystallises in colourless, lustrous scales (on addition of sodium acetate to the aqueous solution of its hydrochloride), is very sparingly soluble in hot water, and dissolves in alkalis and ammonia forming solutions which very rapidly become brown on exposure to the air. On oxidation with ferric chloride or dilute chromic acid mixture, it is converted into [β-]*naphthaquinone.* The *hydrochloride*, B.HCl, crystallises in lustrous, white needles readily soluble in water, sparingly in dilute hydrochloric acid.

Sulphonic Acids.

Amido-β-naphtholsulphonic acids are obtained by reducing the azo- dyes[1] formed by interaction of diazotised bases, preferably aniline, with the isomeric mono- and di-sulphonic acids of β-naphthol. The general method of preparation is as follows:—A warm solution of 45 kilos. of stannous chloride in 50 kilos. of hydrochloric acid (sp.gr. = 1·19) or 60 kilos. of the ordinary acid (sp.gr. = 1·16) is stirred into a warm solution of 32 kilos. of the sodium salt of a phenylazo-β-naphtholsulphonic acid, *e.g.* 'Ponceau 4 G. B.,' or 40 kilos. of the sodium salt of a phenylazo-β-naphtholsulphonic acid, *e.g.* 'Orange G.,' in the minimum of water (200–500 litres). The mixture rapidly becomes colourless, and on cooling the amido-β-naphtholsulphonic acids crystallise out; the disulphonic acids, however, being present in solution as acid sodium salts, require the addition of 60 kilos. of salt to bring about crystallisation. The products, if monosulphonic acids, can when necessary be readily purified by dissolution in aqueous sodium acetate or, preferably, sulphite and subsequent precipitation with hydrochloric acid, but the method is not applicable to the disulphonic acids owing to the readiness with which they undergo intramolecular change into dihydroxynaphthalenedisulphonic acids (Witt, B. 21, 3474; C. J. 56, 271; Germ. pat. 49857 of Jan. 13, 1889). The acids are readily oxidised in alkaline solution, and their use as photographic developers has been patented by Andresen (Germ. pat. 50265 of Feb. 10, 1889).

(*a*) **1:2:1′-Amido-β-naphtholsulphonic acid** crystallises in small, striated, pale rose-coloured scales, and is very sparingly soluble in water and sodium acetate solution. It does not react with diazo- compounds, but unlike its isomerides interacts with nitrosodimethylaniline hydrochloride forming a characteristic violet colouring-matter.

(*b*) **1:2:2′-Amido-β-naphtholsulphonic acid**, which crystallises in sparingly soluble rose-red needles, resembles the 1:2:3′-acid in properties, but is less readily oxidised, and is characterised by reacting only with some diazo-compounds, *e.g.* tetrazostilbenedisulphonic acid, and then but slowly.

(*c*) **1:2:3′-Amido-β-naphtholsulphonic acid** is obtained either from 'Ponceau 4 G. B.' as described above (Witt, B. 21, 3475, *cf.* Griess, B. 14, 2042) or from nitroso-2:3′-β-naphtholsulphonic acid by reduction with tin and hydrochloric acid (Meldola, C. J. 39, 47; S. C. I. 8, 958), and forms long, snow-white needles, which though soluble in hot water cannot be crystallised from it, except in small quantities, owing to decomposition. It readily interacts with diazotised bases free from nitrous acid forming beautiful reddish-violet colouring matters, which, however, do not dye wool. In alkaline solution it very rapidly undergoes a colour change like that of alkaline pyrogallol solution, and on account of its easily oxidisable nature has been introduced in the form of its well-crystallised, soluble *sodium* salt, $NH_2.C_{10}H_5(OH)SO_3Na + 2\frac{1}{2}H_2O$, as a photographic developer under the name *eikonogen* (Andresen, Germ. pat. 50265 of Feb. 10, 1889; Farbenindustrie, 1889, 187, *v.* PHOTOGRAPHY).

(*d*) **1:2:4′-Amido-β-naphtholsulphonic acid** crystallises in small, rose-red aggregates, is the least soluble as well as the most stable of the isomeric acids, and does not form colouring matters with diazotised bases.

(*e*) **1:2:1′:3′-Amido-β-naphtholdisulphonic acid**, obtained from 'Orange G.' as described above, is separated from its solution as *acid sodium* salt, $NH_2.C_{10}H_4(OH)(SO_3H)SO_3Na$, on addition of brine, in snow-white prisms or small aggregates of prisms. This is less readily oxidised and more stable than the 1:2:3:3′-salt, but otherwise resembles it in properties and on boiling in aqueous solution undergoes intramolecular change into the *sodium ammonium* salt of 1:2:1′:3′-*dihydroxynaphthalenedisulphonic acid* (Witt, B. 21, 3482, Germ. pat. 49857 of Jan. 13, 1889).

(*f*) **1:2:3:3′-Amido-β-naphtholdisulphonic acid**, prepared from 'Ponceau 2 G.' as described above, is separated from its solution on the addition of brine as *acid sodium* salt. $NH_2.C_{10}H_4(OH)(SO_3H)SO_3Na$, in slender silky needles. In the dry state the salt is stable, but in aqueous solution it decomposes at once into the *sodium ammonium* salt of 1:2:3:3′-*dihydroxynaphthalenedisulphonic acid* (the so-called amido-β-naphthol-[α-]disulphonic acid of Griess, B. 14, 2042; *cf.* Witt, B. 21, 3481). The amido- acid is rapidly oxidised in alkaline

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[1] In these reactions two amines are formed, one being the base from which the diazo- compound was obtained and the second the amido- derivative of β-naphthol or the β-naphtholsulphonic acid employed.

solution, and does not react with diazotised bases or nitrosodimethylaniline (Witt, *l.c.*).

(ii) 2:2′-**Amido-β-naphthol** (β-amido-[β-]naphthol).

Preparation.—1 kilo. of sodium 2:2′-β-naphthylaminesulphonate is stirred into a mixture of 2 kilos. of caustic soda with an equal weight of water heated at 260°, and the heating continued for two to three hours at 260–300°; the product is then treated with acid in the usual way, and the amidonaphthol separated from the concentrated filtrate by addition of aqueous sodium carbonate (Gesell. f. Chem. Ind., Germ. pat. 47816 of Dec. 15, 1888).

Properties.—It crystallises in small, white, concentrically-grouped needles, and dissolves readily in dilute acids and alkalis, also in alcohol and ether, but sparingly in water.

Amido-β-naphtholsulphonic acid (amidonaphtholsulphonic acid-R.) [OH:NH_2:SO_3H = 2:3:2′ or less probably 2:3′:2′].

Preparation.—30 kilos. of 2:3:3′-β-naphthylaminedisulphonic acid (amido-R.-acid), probably as acid sodium salt, are mixed with 60 kilos. of caustic soda and 20 litres of water and gradually heated to 230–250°, at which temperature it is kept for an hour and then heated at 260–280° for ten minutes. The melt is dissolved in water and the acid separated by saturating the solution with hydrochloric acid.

Properties.—The salts, in neutral solution, show a violet fluorescence and give with ferric chloride a dark-blue colouration. Unlike the 1:2-amido-β-naphtholsulphonic acids, the acid reacts with nitrous acid forming an orange-red *diazo-* compound which gives a claret-red azo-dye on interaction with 2:3:3′-β-naphtholdisulphonic acid (R.-acid) in alkaline solution (M. L. B., Germ. pat. 53076 of Sept. 8, 1889; Eng. pat. 15176 of 1889).

α-Amido-2:2′-β-ethoxynaphthalenesulphonic acid.

Preparation.—24·6 kilos. of sodium 2:2′-β-naphtholsulphonate and 4 kilos. of caustic soda are dissolved in 200 litres of 50 p.c. alcohol, 11 kilos. of ethyl bromide added, and the whole heated at 60–80° for several hours; on cooling sodium 2:2′-ethoxynaphthalenesulphonate separates in large silvery crystals. After drying, this is stirred into cooled nitric acid of 40°Bé., and the resulting α-nitro-2:2′-ethoxynaphthalenesulphonic acid salted out from the solution in shining yellow crystals and reduced with 'zinc' (? tin), and hydrochloric acid. The method is capable of general application (Cassella & Co., Eng. pat. 7067 of 1889).

Properties.—It crystallises in very sparingly soluble, colourless needles, and yields azo- dyes characterised by giving dark greenish-blue shades.

THIO- DERIVATIVES.

Thio-β-naphthol, $C_{10}H_7.SH$, is prepared by reducing naphthalene-β-sulphonic chloride with zinc-dust and dilute (1:3) sulphuric acid (Maikopar, Z. [2] 5, 711; Krafft and Schönherr, B. 22, 824), or tin and hydrochloric acid (Billeter, B. 8, 463), and purified by distillation in a vacuum. It crystallises in small lustrous scales, has a slight mercaptan-like odour, melts at 81°, boils at 153·5° under 15 mm., and at 286° under the ordinary pressure, is volatile with steam (6 grams passing over with 400 grams of water), and dissolves readily in alcohol and ether, very sparingly in water.

Thio-β-naphtholsulphonic acids. Two 'thio-β-naphtholsulphonic acids,' A and B, are obtained, (A) when 9 kilos. of sulphur are boiled with 7 kilos. of caustic soda and 40 kilos. of water until dissolved, and the solution mixed with 36 kilos. of sodium 2:3′-β-naphtholsulphonate, and heated for 12 hours at about 200° under pressure; (B) when 5·5 kilos. of sodium 2:3′-β-naphtholsulphonate and 4·8 kilos. of aqueous caustic soda of 40°Bé., dissolved in 15 kilos. of hot water, are boiled with 3·4 kilos. of powdered sulphur until dissolved. The azo- dyes, obtained by interaction of diazotised bases with the A-acid are much bluer and browner, and with the B-acid are more yellow than the corresponding colours from the 2:3′-β-naphtholsulphonic acid (Actieng. f. A., Germ. pat. 50077 of Feb. 5, 1889).

DIHYDROXYNAPHTHALENES.

(i) 1:2-**Dihydroxynaphthalene** ([β-]naphthaquinol, [β-]naphthahydroquinone).

Preparation.—It is obtained by reducing [β-] naphthaquinone with concentrated sulphurous acid in the cold (Liebermann and Jacobson, A. 211, 58).

Properties.—It crystallises in silvery scales, melts at about 60°, dissolves in alkalis forming yellow solutions which become green on exposure to the air, and in aqueous solution exerts a powerful caustic action on the skin (Liebermann and Jacobson, *l.c.*). The *diacetyl* derivative forms scales melting at 104–106° (Korn, B. 17, 3025).

Unlike pyrocatechol, it reacts normally with diazotised bases forming orange-red or brown colouring matters, which differ from all hitherto known azo- dyes in giving red to bluish-violet lakes with aluminium and particularly chromium salts. The azo- dye obtained by interaction with diazotised aniline gives, for example, reddish-violet and deep-violet shades on cotton mordanted with alumina and chromium salts respectively, and that with diazotised sulphanilic acid, which dyes unmordanted wool orange, gives garnet-red and deep red-violet shades on wool mordanted with alumina and chromium salts respectively (Witt, Germ. pat. 49979 of Feb. 3, 1889; Eng. pat. 2499 of 1889).

1:2:3′-Dihydroxynaphthalenesulphonic acid ([β-]naphthahydroquinonesulphonic acid) is formed when 1:2:3′-amido-β-naphtholsulphonic acid[1] is gradually added, with continual stirring, to an equal weight of cooled nitric acid (sp.gr. = 1·2), or when 11 parts of the amido- acid, ground to a cream with ice-cold water, are carefully treated in the cold with 9 parts of bromine, or with 6 parts of sulphuric acid and 12 parts of finely ground lead peroxide, and the resulting golden-yellow ammonium [β-] naphthaquinonesulphonate is reduced with the requisite quantity of sulphurous acid. On evaporation of the solution, ammonium dihydroxynaphthalenesulphonate is obtained in readily soluble white, nacreous scales (Witt, Germ. pat. 50506 of April 5, 1889).

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[1] The method is equally applicable to the isomeric amido-β-naphtholsulphonic acids.

Properties.—Like 1:2-dihydroxynaphthalene, it reacts normally with diazotised bases, *e.g.* the isomeric α- and β-diazonaphthalenesulphonic acids, forming carmine-red azo- colouring matters, which dye wool mordanted with chromic salts in very fast shades of violet and blue (Witt, Germ. pat. 49872 of May 30, 1889).

1:2:1′:3′- and 1:2:3:3′-**Dihydroxynaphthalenedisulphonic acids** (naphthatannins) are respectively obtained as *sodium ammonium* salts, $(OH)_2C_{10}H_4(SO_3Na)SO_3NH_4$, by boiling 1:2:1′:3′- and warming 1:2:3:3′-amido-β-naphtholdisulphonic acid in the form of acid sodium salts with water (Witt, B. 21, 3480).

Properties.—The salts of both acids are very soluble in water, tolerably soluble in alcohol, and in alkaline solution become brown on exposure to the air. The aqueous solutions have most of the properties of a tannin solution, precipitating gelatine and all basic aniline dyes from solution; they can, therefore, be employed in tanning, and as substitutes for tannin in dyeing and calico-printing (Witt, Germ. pat. 49857 of Jan. 13, 1889).

(ii) 1:4-**Dihydroxynaphthalene** ([α-]naphthaquinol, [α-]naphthahydroquinone).

Formation.—It is formed when [α-]naphthaquinone is reduced with hydriodic acid and phosphorus (Groves, C. J. 26, 210), with tin and hydrochloric acid, and with sulphurous acid at 140–150° (Plimpton, C. J. 37, 635), but cannot be obtained from 1:4-α-naphtholsulphonic acid by fusion with caustic potash owing to decomposition at the minimum temperature (200–230°) required (Erdmann, A. 247, 355). It is best prepared by adding powdered [α-]naphthaquinone to a boiling mixture of tin and hydrochloric acid.

Properties. — It crystallises in colourless needles, melts at 176°, is readily soluble in alcohol, ether, acetic acid and boiling water, sparingly in benzene, and on oxidation with chromic acid is converted into [α-]*naphthaquinone*. The *diacetyl* derivative forms lustrous tables melting at 128–130° (Korn, B. 17, 3025).

(iii) 1:4′-**Dihydroxynaphthalene.**

Preparation.—(1) Potassium 1:4′-α-naphtholsulphonate is fused with caustic potash (Cleve, Öfvers. af Kongl. Vetensk.-Akad. Förh. 1875, N:o 9, 28; Bl. 24, 513), at 200–250° for about 15 minutes, or until a test in aqueous solution gives a pure blue instead of a red colouration with diazotised naphthionic acid (Erdmann, A. 247, 356; *cf.* Ewer & Pick, Germ. pat. 41934 of Jan. 25, 1887).

(2) 100 kilos. of sodium 1:4′-naphthalenedisulphonate are fused with 300–400 kilos. of caustic soda at 220–260° until a test dissolved in water gives with tetrazodiphenyl chloride a blue dye, which separates in flocks leaving the mother-liquor free from violet colour (Ewer & Pick, *l.c.*; Armstrong and Wynne, C. J. Proc. 1887, 43; Bernthsen and Semper, B. 20, 938).

Properties.—It crystallises from water in slender scales, sublimes in long needles, melts at about 258–260°, and is readily soluble in alcohol, ether, and acetic acid, sparingly in water, and almost insoluble in benzene and petroleum spirit. The crystalline *diacetyl* derivative melts at 159–160°.

Reactions.—(1) On oxidation with chromic acid mixture it is converted into *juglone* (α-hydroxy-[α-]naphthaquinone) (Bernthsen and Semper, *l.c.*).

(2) When heated with two to five times its weight of sulphuric acid of 66°Bé. it yields both a *mono-* and a *di- sulphonic acid*. These acids give worthless blue azo- dyes, and, moreover, are very unstable, both acids and salts decomposing very readily[1] (Ewer & Pick, *l.c.*; *cf.* Majert, Eng. pat. 4243 of 1887).

(3) It interacts with diazotised bases forming blue dyes, which are sensitive to acids and technically worthless. The azo- dye, formed with diazotised naphthionic acid closely resembles litmus in the colours given with acids, alkalis and carbon dioxide (Erdmann, *l.c.*).

(iv) 1:1′-**Dihydroxynaphthalene.**

Preparation.—30 parts of caustic potash, 10 parts of water, and 7 parts of 1:1′-naphthasultone are fused at 200–230° during fifteen to twenty minutes; the product is then treated with acid in the ordinary way, and the resulting solution filtered hot and left to crystallise. Oxidation takes place rapidly during the fusion, and the melt becomes black, but experiments undertaken to prevent this by using a closed vessel led only to the production of potassium 1:1′-α-naphtholsulphonate even when a smaller proportion of water was employed (Erdmann, A. 247, 356).

Properties.—It crystallises in long white needles, or in a hydrated form, $C_{10}H_6(OH)_2 + H_2O$, in scales, melts at 140° when anhydrous, and is readily soluble in ether and benzene, tolerably sparingly soluble in water and petroleum spirit. In aqueous solution it gives with ferric chloride a white flocculent precipitate and a green liquid: the precipitate rapidly becomes green and the liquid colourless. The *diacetyl* derivative crystallises in silvery scales melting at 147–148°.

Reactions.—(1) On oxidation with chromic acid mixture it seems to give *juglone* (Erdmann, *l.c.*).

(2) The azo- dyes obtained by interaction with diazotised α- and β-naphthylaminesulphonic acids give archil-red shades on unmordanted wool, but violet to black shades on wool mordanted with chromium salts (B. A. S. F., Germ. pat. 51559 of April 30, 1889; 52958 of June 8, 1889). The disazo- dyes, with diazotised benzidine, &c., give violet or bluish-violet shades on cotton, are fast to acids, and possess great affinity for the fibre (B. A. S. F., Germ. pat. 52140 of April 30, 1889; 53499 of June 9, 1889).

(v) 1:2′-**Dihydroxynaphthalene.**

Formation.—It is obtained by fusing the dry basic sodium salt of 2:1′-β-naphtholsulphonic acid with caustic potash (Schultz, Steinkohlenth. 2nd ed. 1, 639; Emmert, A. 241, 371; *cf.* Bayer & Co., Germ. pat. 53915 of Sept. 15, 1889).

Properties.—It crystallises in white needles, melts at 178°, is very soluble in alcohol, ether, and benzene, tolerably in water, and in alkaline solution rapidly becomes black on exposure to the air. On addition of ferric chloride to its solution a dark-blue precipitate is obtained. The *diacetyl* derivative crystallises in rhombic tables melting at 108° (Emmert, *l.c.*).

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[1] The instability of these acids accords with expectation, since they would almost certainly bear the same relation to 1:4′-dihydroxynaphthalene that the Schaeffer or 1:2-α-naphtholsulphonic acid bears to α-naphthol.

Reactions.—Of the known dihydroxynaphthalenes, the 1:2′- compound is the only one which resembles resorcinol in forming dyes of the fluorescein type by condensation with phthalic anhydride, and this is noteworthy as a further illustration of the ortho- function of the peri- or 1:1′-position.

(vi) 1:3′-**Dihydroxynaphthalene.**

Preparation.—Sodium 1:3′-naphthalenedisulphonate is fused with four to five times its weight of caustic soda in an open, or, with the addition of water, in a closed vessel at 230–350° (Ewer and Pick, Germ. pat. 45229 of Oct. 23, 1887), or potassium 2:4′-β-naphtholsulphonate is fused with four times its weight of caustic potash and a little water at 260–270° (Claus, J. pr. [2] 39, 316). The dihydroxynaphthalene crystallises in white needles from a concentrated acid solution of the melt.

Properties.—It crystallises from benzene in short prisms or serrated scales, melts at 135°, is readily soluble in ether, benzene, and hot alcohol, and tolerably soluble in water. On addition of ferric chloride to a dilute aqueous solution a transient blue colouration is obtained. The *diacetyl* derivative forms colourless prisms melting at 73° (Claus). The disazo- dye obtained by interaction with tetrazodiphenyl chloride gives a bluish-violet shade on cotton.

(vii) 2:3-**Dihydroxynaphthalene.** The preparation of this compound has been announced (B. A. S. F., Germ. pat. Anm. B 10958). It is possibly obtained by hydrolysis of the 2:3:3′-dihydroxynaphthalenesulphonic acid.

(viii) 2:2′-**Dihydroxynaphthalene.**

Preparation.—Sodium 2:2′-naphthalenedisulphonate is dissolved in a minimum of water, and fused with two and a half times its weight of caustic soda at 290–300° (Ebert and Merz, B. 9, 609; Weber, B. 14, 2206).

Properties.—It crystallises in slender, white needles, melts at 184–185°, and dissolves readily in alcohol, ether, and hot water, sparingly in benzene and petroleum spirit. In alkaline solution it rapidly blackens, but ferric chloride imparts no colour to its aqueous solution. The *diacetyl* derivative forms scales melting at 129°.

Reactions.—When heated with concentrated sulphuric acid at 120° it is converted into a *sulphonic acid*; at 160–180°, however, sulphur dioxide is evolved, and a black melt obtained which dissolves in alkalis with a cherry-red colour, is precipitated by acids in red flocks, dyes wool and silk red, and seems to be identical with the colouring matter formed when 2:2′-dihydroxynaphthalene is heated with zinc chloride or with hydrochloric acid at 160–180° (Weber, *l.c.*).

(ix) 2:3′-**Dihydroxynaphthalene.**

Formation.—It is obtained by fusing sodium 2:3′-β-naphtholsulphonate (Armstrong and Graham, C. J. 39, 140; Emmert, A. 241, 369) or sodium 2:3′-naphthalenedisulphonate with caustic potash (*cf.* Dusart, C. R. 64, 859; Darmstaedter and Wichelhaus, A. 152, 306; Armstrong and Graham, *l.c.*).

Properties.—It crystallises in thin, glistening scales, melts at 215–216°, dissolves readily in alcohol and ether, sparingly in cold water, and on addition of ferric chloride gives a yellowish-white precipitate. The *diacetyl* derivative forms lustrous scales, melting at 175°.

Reactions.—When warmed with sulphuric acid at 100°, it yields a *disulphonic acid* characterised by forming a very sparingly soluble *barium* salt $(OH)_2C_{10}H_4(SO_3)_2Ba + 2H_2O$. By interaction with diazotised bases, the acid yields yellow, red, and violet azo- dyes, which are, however, technically worthless (Griess, B. 13, 1959).

DIHYDROXYNAPHTHALENESULPHONIC ACIDS.

(*a*) **Dihydroxynaphthalenesulphonic acid** (S.-acid) [OH:OH:SO_3H = 1:1′:4 or, less probably, 1:4:1′] is obtained when sodium 1:1′:4-α-naphtholdisulphonate is fused with three times its weight of caustic soda in a closed vessel at about 250° until a test no longer gives a fluorescent solution, and when acidified emits a strong odour of sulphur dioxide. The melt is freed from sulphur dioxide in the ordinary way, and the neutral solution employed without further treatment, or the sodium salt is salted out and purified, if necessary, by extraction with alcohol (Bayer & Co., Eng. pat. 13665 of 1889).

Properties.—The crystalline sodium salt is very stable and on fusion with caustic soda yields [(?)1:1′:4-]*trihydroxynaphthalene.* The azo- (?-disazo-) dyes formed by interaction with diazotised toluidine and anisidine give shades very closely resembling those from 'acid-magenta,' and may possibly serve as substitutes on account of their clearness, beauty, and fastness to light (Bayer & Co., Germ. pat. 54116 of Oct. 25, 1889; Eng. pat. 18517 of 1889).

(*b*) **Dihydroxynaphthalenesulphonic acid** [OH:OH:SO_3H = 2:1′:3′ or, less probably, 2:3′:1′] is formed when sodium 2:1′:3′-β-naphtholdisulphonate (G.-salt), dissolved in a small quantity of water, is fused with about half its weight of caustic soda under pressure at 220–230° for 3–7 hours until a test no longer gives a fluorescent solution. The *sodium* salt crystallises from the strongly acidified solution of the melt, dissolves in hot brine, and gives a fugitive green colour with ferric chloride (M. L. B., Eng. pat. 9642 of 1889).

(*c*) **Dihydroxynaphthalenesulphonic acid** [OH:OH:SO_3H = 2:3:3′[1] or, less probably, 2:3′:3] is obtained from sodium 2:3:3′-β-naphtholdisulphonate (R.-salt) by the method described under (*b*). The *sodium* salt crystallises in leaflets, is very sparingly soluble in brine, and in neutral solution gives with ferric chloride an intense violet colour which changes to brown-red on addition of soda (M. L. B., Eng. pat. 9642 of 1889).

Identical in all probability with this acid is the **Dihydroxynaphthalenesulphonic acid** prepared from sodium 2:3:2′-β-naphtholdisulphonate by the method described under (*a*). It yields disazo- dyes and on fusion with caustic soda is converted into 2:3:2′-*trihydroxynaphthalene* (Bayer & Co., Eng. pat. 13665 of 1889).

(*d*) **Dihydroxynaphthalenesulphonic acid** [OH:OH:SO_3H = 1:4:2′ or, less probably, 1:2′:4] is formed when 30 kilos. of sodium 1:4:2′-α-naphthylaminedisulphonate are stirred into a hot (180°) mixture of 110 kilos. of caustic soda

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[1] This constitution seems by far the more probable of the two in view of the fact that neither of the heteronucleal ββ-dihydroxynaphthalenes give colour reactions with ferric chloride.

and 20 kilos. of water, and heated at 200–220° for eight to ten hours. The *acid* crystallises in small plates sparingly soluble in water; the *sodium* salt is very sparingly soluble in brine. The disazo- dyes formed by interaction with tetrazo- compounds give violet or blue shades (Dahl & Co., Eng. pat. 735 of 1890).

(*e*) **A Dihydroxynaphthalenesulphonic acid** is prepared by fusing the sodium salt of Gürke and Rudolph's naphthalenetrisulphonic acid (*q. v.*) with two and a half times its weight of caustic soda and a quarter its weight of water at 250° until a portion of the melt acidified with hydrochloric acid gives with ammonia a reddish-brown solution showing a blue fluorescence (Actieng. f. A., Germ. pat. 42261 of June 30, 1886). The salts are extremely soluble in water and 80 p.c. alcohol. The azo- colours formed by interaction with diazotised aniline and its homologues give yellowish- and reddish-brown shades and have no technical value (Actieng. f. A., Germ. pat. 42270 of Oct. 8, 1886).

(*f*) **A Dihydroxynaphthalenedisulphonic acid** is formed when 9 parts of sodium 2:3:1′:3′-β-naphtholtrisulphonate, dissolved in a small quantity of water, are fused with 3-4 parts of caustic soda under pressure at 220–230° for 3-4 hours until a test no longer shows a green fluorescence on dissolution in water. The *sodium* salt separates in a microcrystalline form from the strongly acid solution of the melt, gives in neutral solution a pure blue changing to a grey-blue with ferric chloride, interacts with diazo-xylene and -cumene forming clear red azo-dyes, and on fusion with caustic soda at 260–270° for 12 hours yields the sodium salt of a *trihydroxynaphthalenesulphonic acid* (M. L. B., Eng. pat. 9642 of 1889).

(*g*) **A Dihydroxynaphthalenedisulphonic acid** is obtained when 100 kilos. of sodium naphthalenetetrasulphonate, dissolved in a minimum of water, are fused with 60 kilos. of caustic soda at 250° for 6 hours. The salts are readily soluble in water and alcohol. The azo- dyes formed by interaction with diazotised aniline and its homologues give yellowish- to reddish-brown shades, and the disazo- dyes with tetrazo-diphenyl and homologues give violet and blue shades (Bayer & Co., Germ. pat. 40893 of Dec. 7, 1886.

VII. QUINONES.

Two naphthaquinones are known with certainty, but derivatives of a third—the so-called [γ-], peri-, or 1:1′-naphthaquinone have been described by Quincke (B. 21, 1460), and a pale-yellow compound (m.p. above 220°) obtained among the products of the action of fuming nitric acid on dibromo-α-naphthol has been described by Meldola and Hughes[1] (C. J. 57, 631) as the [γ-] quinone in question. The naphthaquinones, like quinones generally, are now usually regarded as diketones for reasons which have already been given (*v.* KETONES), and like ketones react with hydroxylamine forming quinonoximes.

Quinonoximes also result from the action of nitrous acid on mono- and dihydroxynaphthalenes, and also on those naphtholsulphonic acids which containing the radicle OH in the position '1' have the positions '2' or '4' or both unoccupied by the SO_3H-radicle, or in the position '2' have the position '1' free with the significant exceptions of the 2:1′-β-naphtholsulphonic acid (Badische-acid) and the 2:1′:3′-β-naphtholdisulphonic acid (Amido G.-acid). These compounds, which being more generally known as nitrosonaphthols and nitrosonaphtholsulphonic acids[1] are in this article frequently referred to under the old names, have in many instances been mentioned in connection with the isomeric naphthols and naphtholsulphonic acids, and only those quinonoximes which have been found in practice to give useful lakes will be described in this section. For the production of a naphthol-green with iron salts or lakes with mordants generally, it is essential that the nitrosonaphthol should be either an orthoquinonoxime or contain the radicles N.OH and OH in the ortho-position (Kostanecki, B. 20, 3147; 21, 1349). Derivatives of nitroso-β-naphthol serve chiefly for the production of lakes, those of the two nitroso-α-naphthols being in many instances employed in the manufacture of naphthol-yellow and naphthol yellow S.

1:4-Naphthaquinone ([α-]naphthaquinone).

Formation.—[α-]Naphthaquinone is obtained by the oxidation of naphthalene (Groves, C. J. 26, 209; Plimpton, C. J. 37, 633; Japp and Miller, C. J. 39, 220) and α-naphthol (Miller, B. 14, 1602) in acetic acid solution with chromic acid, also of 1:4-naphthylenediamine and 1:4-amido-α-naphthol (Liebermann and Dittler, A. 183, 242, 248), and of α-naphthylamine, dimethyl-α-naphthylamine and 1:4-α-naphthylaminesulphonic acid with chromic acid mixture (Monnet, Reverdin, and Nölting, B. 12, 2306).

Preparation.—(1) A solution of 100 grams of naphthalene in 1 kilo. of glacial acetic acid is gradually stirred into an ice-cold solution of 400 grams of chromic acid in 740 grams of 80 p.c. acetic acid, and the mixture allowed to remain for three days at the ordinary temperature with occasional shaking; 8·5 litres of water are then added and the precipitated naphthaquinone filtered, washed, dried, and crystallised from hot petroleum spirit (b.p. = 85–120°). The yield amounts to about 50 p.c. of the naphthalene employed (Miller, B. 17, Ref. 355).

(2) Two parts of 1:4-amido-α-naphthol hydrochloride are oxidised with a solution of 3 parts of potassium bichromate in 6 parts of dilute sulphuric acid (1 vol. of acid to 2 vols. of water), and the separated naphthaquinone purified by distillation with steam. The yield

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[1] The 'dihydroxynaphthalene' obtained from this compound by reduction has no definite melting-point, but blackens and shrinks at about 205° and its diacetyl derivative melts at 226–227°. The discrepancy between these data and those obtained by Erdmann in his examination of the 1:1′-dihydroxynaphthalene (*q. v.*) has been noted by Meldola and Hughes (C. J. 57, 809 (footnote)) with the suggestion that, in the conversion of Erdmann's 1:1′-sultone into dihydroxynaphthalene by fusion with caustic alkali, intramolecular change has ensued. This, however, is extremely improbable in view of what is known of Erdmann's compound, and it remains to be seen whether further investigation will not lead to the adoption of other views as to the constitution of the 'third naphthaquinone.'

[1] The data which have led to the adoption of the quinonoxime formula $O:C_{10}H_6:N.OH$ for compounds which were previously formulated as nitrosonaphthols $HO.C_{10}H_6.NO$ may be found in the papers of Goldschmidt (B. 17, 803). Goldschmidt and Schmid (B. 17, 2069; 18, 571, 2224), and Ilinski (B. 19, 343).

amounts to about 40 p.c. of the theoretical (Liebermann and Jacobson, A. 211, 61).

Properties.—It crystallises in yellow triclinic needles, melts at 125°, begins to sublime below 100°, has an odour similar to that of benzoquinone, is readily volatile with steam, and dissolves easily in alcohol, ether, benzene, chloroform, and acetic acid, sparingly in petroleum spirit and water. When boiled for a short time with dilute sulphuric acid (10 parts by weight of water to 12 of acid) it yields a violet condensation product (Stenhouse and Groves, C. J. 33, 422; Liebermann, B. 18, 966), whilst in alkalis it dissolves to reddish-brown solutions from which acids precipitate a bright-red substance.

Reactions.—(1) When heated with hydriodic acid and phosphorus or with tin and hydrochloric acid it is converted into 1:4-*dihydroxynaphthalene*; it is not, however, reduced by sulphurous acid in the cold, and gives only a poor yield of the naphthaquinol when heated with it at 140-150° (Groves, *l.c.*; Plimpton, C. J. 37, 633). Partial reduction results in the formation of the *naphthaquinhydrone.*

(2) Oxidation with nitric acid converts it and its homonucleal derivatives into *phthalic acid.*

(3) When treated in acetic acid solution with aqueous phenylhydrazine hydrochloride it yields the corresponding *hydrazone*, identical with benzeneazo-α-naphthol (Zincke and Bindewald, B. 17, 3026).

(4) On treatment in acetic acid solution with aniline it is converted into 1:4-*naphthaquinonanilide* [O:NHPh:O = 1:2:4] which crystallises in lustrous red needles melting at 190-191° (Liebermann and Jacobson, A. 211, 82).

Amido-[α-]naphthaquinonimide (diimidonaphthol) [$O:NH_2:NH = 1:2:4$] is prepared by reducing dinitro-α-naphthol with tin and hydrochloric acid, freeing the solution from tin by precipitation on strips of zinc, and treating the decanted liquor with ferric chloride so long as a precipitate of the red hydrochloride is produced. The hydrochloride, after washing with dilute hydrochloric acid, is decomposed with ammonia (Graebe and Ludwig, A. 154, 314). It crystallises in yellow microscopic needles, is practically insoluble in cold water, readily in alcohol, yields *hydroxy-*[α-]*naphthaquinonimide* (oximidonaphthol) [O:OH:NH = 1:2:4, *cf.* Kehrmann, B. 23, 2454] on warming with water (Martius and Griess, A. 134, 377; Graebe and Ludwig, A. 154, 318), and 1:2:4-*hydroxy-*[α-] *naphthaquinone* on heating with alkalis or dilute hydrochloric acid, and is converted into *diamido-α-naphthol* on reduction.

QUINONOXIMES.

1:4-Naphthaquinonoxime (α-nitroso-α-naphthol; Goldschmidt's α-isonitroso-α-naphthon) $O:C_{10}H_6:N.OH$ [O:N.OH = 1:4].

Formation.—1:4-Naphthaquinonoxime is obtained when an alcoholic solution of [α-]naphthaquinone is boiled with hydroxylamine hydrochloride (Goldschmidt and Schmid, B. 17, 2064), and, together with 1:2-naphthaquinonoxime (β-nitroso-α-naphthol), when α-naphthol is treated with nitrous acid (Fuchs, B. 8, 626; Worms, B. 15, 1816). The best yield, 40 p.c. of the white 1:4- and 50 p.c. of the yellow 1:2-naphthaquinonoxime, is obtained when a solution of 1 part of α-naphthol and 1 part of zinc chloride in 6 parts of alcohol is heated to boiling, ½ part of sodium nitrite in aqueous solution added, and the mixture boiled for 2-3 hours (Henriques and Ilinski, B. 18, 706; *cf.* Ilinski, B. 17, 2590).

Properties.—It crystallises in needles, decomposes at 190° without previous fusion, and dissolves readily in alcohol, ether, and aqueous sodium carbonate, sparingly in chloroform, carbon bisulphide, and hot benzene. Concentrated nitric acid in acetic acid solution converts it into *dinitro-α-naphthol*, and potassium ferricyanide in alkaline solution slowly oxidises it to 1:4-*nitro-α-naphthol* (Fuchs, *l.c.*). Like 1:4-*naphthaquinonedioxime* (Nietzki and Guiterman, B. 21, 433), it is destitute of tinctorial powers, giving no colours with mordanted fibres (Kostanecki, B. 20, 3147).

HYDROXY- DERIVATIVES.

(i) **Juglone** (hydroxy-[α-]naphthaquinone [OH:O:O = 1':1:4]; regianin, nucin).

Formation.—Juglone is obtained by oxidation of the 1':1:4-trihydroxynaphthalene ([α-]hydrojuglone) contained in the green shells of the walnut with ferric chloride (Mylius, B. 17, 2411; 18, 463, 2567) or chromic acid mixture (Bernthsen and Semper, B. 18, 204), and of 1:4'-dihydroxynaphthalene with chromic acid mixture (Bernthsen and Semper, B. 20, 939).

Properties. — It crystallises in lustrous yellowish-red or brown needles, melts at 151–154° and is very soluble in chloroform and hot alcohol, sparingly in cold alcohol, ether and benzene, and almost insoluble in water. The aqueous solution colours the skin yellow like walnut juice.

(ii) 1:2:4 - **Hydroxy** - [α-]**naphthaquinone** (naphthalic acid).

Formation.—Hydroxy-[α-]naphthaquinone is obtained by boiling amidonaphthaquinonimide with dilute acids (Martius and Griess, A. 134, 377; Graebe and Ludwig, A. 154, 321) or with concentrated aqueous sodium carbonate and afterwards precipitating with hydrochloric acid (Diehl and Merz, B. 11, 1315); also by heating 1:2-naphthaquinonanilide with hydrochloric acid at 130° or 1:4-naphthaquinonanilide with aqueous caustic soda (Liebermann and Jacobson, A. 211, 80).

Properties. — It crystallises in lustrous, bright-yellow needles, melts at 190–191°, sublimes in reddish-yellow needles resembling sublimed alizarin, and is readily soluble in alcohol and ether, sparingly in boiling water. It expels carbon dioxide from carbonates, and dyes wool and silk yellow.

Reactions.—(1) On reduction with tin and hydrochloric acid it yields 1:2:4-*trihydroxynaphthalene* (Graebe and Ludwig, A. 154, 324).

(2) By interaction with diazobenzene chloride (free from nitrous acid) in the presence of sodium acetate, it is converted into *hydroxy-*[α-]*naphthaquinoneazobenzene* [$O:OH:N_2Ph:O = 1:2:3:4$], which crystallises in garnet-red needles melting at 220°, and, if an azo- dye and not a hydrazone, is remarkable as the only known naphthalene derivative in which the azo- group has taken up the contiguous β- instead of the α- position to the β-hydroxyl (Kehrmann, Ch. Z. 1890, 146).

(3) By condensation with orthophenylenediamine it forms *α-naphtheurhodole* (Kehrmann, B. 28, 2453).

(iii) 1:2:3:4-**Dihydroxy-[α-]naphthaquinone.**

Preparation. — Amidohydroxy-[α-]naphthaquinone is heated with dilute hydrochloric acid at 170–180° for about an hour (Diehl and Merz, B. 11, 1322).

Properties.—It crystallises from alcohol in slender reddish-brown needles, from acetic acid in dark-red scales, is sparingly soluble in boiling water, dissolves in alkalis with a dark-violet colour, and dyes wool mordanted with aluminium salts violet, and with iron salts dark blue, the colours being fast to soap.

(iv) **Naphthazarin** (dihydroxynaphthaquinone).

Preparation.—To a solution of 40 grams of 1:4′-dinitronaphthalene in a mixture of 400 grams of concentrated and 40 grams of 'fuming' sulphuric acid, heated at 200°, 5–10 grams of granulated zinc are gradually added at such a rate that the temperature is maintained at 195–205°. At the end of 15 minutes, or when a test after boiling with water gives a clear red filtrate which on cooling deposits red flocks, the product is diluted with ten times its volume of water, filtered hot, and the separated naphthazarin purified by dissolution in aqueous potash, precipitation with sulphuric acid, extraction with warm acetic acid, and concentration of the filtrate (Liebermann, A. 162, 330; *cf.* Roussin, C. R. 52, 1033, 1177; Aguiar and Bayer, B. 4, 251). The yield is poor.

Properties.—It sublimes between 215–240° in long, slender, dark-red needles, is readily soluble in alcohol, sparingly in ether and boiling water, and dissolves in concentrated sulphuric acid with a magenta, and in alkalis with a cornflower-blue colour. With aluminium salts it gives carmine-red, and with iron salts bluish-grey lakes, which, when printed on cotton, are decolourised by boiling in a soap bath. The lakes with chromium salts are, however, very fast to light, air, acids, and alkalis, and naphthazarin has been introduced in the form of its soluble sodium bisulphite compound,[1] under the names of alizarin black S. and naphthazarin S., for the production in the presence of chromium mordants of black or grey shades on wool and cotton (B. A. S. F., Germ. pat. 41518 of April 3, 1887; Eng. pat. 7833 of 1887).

1:2-**Naphthaquinone** ([β-]naphthaquinone).

Formation.—[β-]Naphthaquinone is obtained by the oxidation of 1:2-amido-β-naphthol with chromic acid mixture (Stenhouse and Groves, C. J. 32, 52; 33, 415; Liebermann and Jacobson, A. 211, 49).

Preparation. — 1 part of amido-β-naphthol hydrochloride is mixed with 2 parts of a saturated solution of sulphur dioxide and 40 parts of boiling water, and agitated until dissolved. The solution, after cooling in a closed vessel, is filtered from any undissolved impurity, poured into 12–14 parts of a solution of ferric chloride (100 c.c. = 10 grams Fe_2O_3), and the separated naphthaquinone filtered off after the lapse of half an hour, washed thoroughly to remove iron salts and acid, and dried at a gentle heat in an atmosphere free from acid fumes (Groves, C. J. 45, 298); or 11 parts of the hydrochloride are dissolved in 700 parts of water with the addition of 30 parts of a saturated solution of sulphur dioxide and 30 parts of dilute sulphuric acid (1 vol. of acid to 2 vols. of water), the cold filtered solution stirred into a solution of 15 parts of potassium bichromate in 150 parts of water, and the separated naphthaquinone filtered off, washed thoroughly, and dried (Stenhouse and Groves, *l.c.*). According to Groves, the first method is to be preferred. The yield by either process amounts to about 70–72 p.c. of the weight of the hydrochloride taken, corresponding with about 73–75 p.c. of the weight of the β-naphthol, or about 25 p.c. of that of the 'β-naphthol-orange' employed in the preparation of the amido-β-naphthol.

Properties.—It crystallises from ether in small red needles, from benzene in bright orange scales, decomposes at 115–120° with blackening (Liebermann and Jacobson, *l.c.*), and resembles [α-]naphthaquinone in solubility, but differs from it by being destitute of odour and non-volatile with steam. Dilute alkalis dissolve it, forming yellow solutions, which rapidly become dark on shaking with air.

Reactions.—(1) Dissolution in cold concentrated aqueous sulphurous acid, or treatment with hydriodic acid, reduces it to 1:2-*dihydroxynaphthalene*, but stannous chloride in hydrochloric acid solution converts it into *β-dinaphthyldihydroquinone* (Stenhouse and Groves, *l.c.*; Liebermann and Jacobson, *l.c.*).

(2) With nitric acid of sp.gr. = 1·2 (Stenhouse and Groves, C. J. 33, 416), preferably of sp.gr. = 1·38 (Zaertling, B. 23, 175), it yields in the first instance the crimson *nitro-[β-]naphthaquinone*, and eventually *phthalic acid*. Potassium permanganate oxidises it to *phthalic acid* (Liebermann and Jacobson, *l.c.*).

(3) When treated in acetic acid solution with aqueous phenylhydrazine hydrochloride it is converted into the corresponding *hydrazone* [O:N_2HPh = 1:2], which crystallises in long, deep-red needles (m.p. = 138°) and is not identical with benzeneazo-β-naphthol (Zincke and Bindewald, B. 17, 3030; Zincke and Rathgen, B. 19, 2483).

(4) On treatment in alcoholic solution with 1½ parts of aniline it is converted into 1:2-*naphthaquinonanilide* (anilido-[β-]naphthaquinone) [O:OH:NPh = 1:2:4] which crystallises in red needles melting above 240° (Liebermann and Jacobson, A. 211, 75; Zincke, B. 14, 1494), and on further treatment with aniline yields *anilido-1:2-naphthaquinonanilide* (naphthaquinonedianilide) [O:NHPh:NPh = 1:2:4] (Zincke, B. 15, 481). This crystallises in long red needles, melts at 187°, and when heated with an equal weight of aniline hydrochloride and 3½ times its weight of aniline at 130–160° for about 6 hours is converted into a red basic dye of the induline class (B. A. S. F., Germ. pat. 45370 of May 6, 1888; Eng. pat. 15259 of 1888).

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[1] Obtained by warming naphthazarin in the form of a 10 p.c. paste with 2–3 times its weight of aqueous sodium bisulphite solution of 30–40° Bé. at 50–70° for several days, and either evaporating the filtrate to dryness or salting out the dye. The aqueous solution is stable towards acids, but is decomposed with the separation of naphthazarin on treatment with caustic alkalis or alkaline carbonates.

QUINONOXIMES.

(i) 1:2-**Naphthaquinonoxime** (β-nitroso-α-naphthol; Goldschmidt's β-isonitroso-α-naphthon) $O{:}C_{10}H_6{:}N.OH$ [$O{:}N.OH = 1{:}2$].

Formation.—1:2-Naphthaquinonoxime is obtained together with the 1:4- derivative by the action of nitrous acid on α-naphthol (Fuchs, B. 8, 626; Worms, B. 15, 1816; Ilinski, B. 17, 2589; Henriques and Ilinski, B. 18, 706), also by boiling [β-]naphthaquinone in alcoholic solution with hydroxylamine hydrochloride (Goldschmidt, B. 17, 215).

Properties.—It crystallises from water in yellow needles, melts at 152° (Goldschmidt), dissolves in alcohol with a yellow, in aqueous alkalis with a dark-yellow, in concentrated sulphuric acid with an intense red colour, and is readily soluble in alcohol and acetic acid, less so in benzene, chloroform, ether and hot water. The *potassium* and *ammonium* salts crystallise respectively in lustrous green scales and needles (Fuchs, *l.c.*).

Reactions.—(1) Concentrated nitric acid in acetic acid solution converts it into *dinitro-α-naphthol*, and potassium ferricyanide in alkaline solution readily oxidises it to 1:2-*nitro-α-naphthol* (Fuchs, *l.c.*).

(2) It closely resembles 2:1-naphthaquinonoxime (*q. v.*) in its behaviour with hydroxylamine (Goldschmidt and Schmid, B. 17, 2066), concentrated hydrochloric acid (*ibid.*), metallic salts (Ilinski, B. 17, 2592) and mordants, and has been introduced as an alizarin substitute under the name 'Gambin Y.' (Erdmann, Chem. Ind. 12, 155).

Nitroso-1:1′-dihydroxynaphthalene is obtained together with a dinitroso- derivative by the action of nitrous acid on 1:1′-dihydroxynaphthalene (Erdmann, A. 247, 358). These compounds dye wool mordanted with metallic salts a deep dark-brown, and when printed with metallic salts on cotton give intense black lakes fast to air, light and washing (Bayer & Co., Germ. pat. 51478 of Sept. 1, 1889).

Nitroso-1:4-α-naphtholsulphonic acid, prepared by the action of nitrous acid on 1:4-α-naphtholsulphonic acid, gives with ferric chloride a sparingly soluble *naphthol-green* of yellowish shade (Gans & Co., Germ. pat. 28065 of Jan. 19, 1884).

(ii) 2:1-**Naphthaquinonoxime** (α-nitroso-β-naphthol, Goldschmidt's α-isonitroso-β-naphthon).

Formation.—2:1-Naphthaquinonoxime is obtained by the action of nitrous acid on β-naphthol (Fuchs, B. 8, 1026; Stenhouse and Groves, C. J. 32, 47; Ilinski, B. 17, 2584; Groves, C. J. 45, 295), and by digesting β-naphthol with an aqueous solution of zinc sulphate and sodium nitrite at 60–70° (Köhler, Germ. pat. 25469 of May 31, 1883; expired Oct. 1884).

Preparation.—A solution of 4 parts of β-naphthol and 3 parts of zinc chloride in 24 parts of alcohol is heated to boiling, and mixed with a concentrated aqueous solution of 2 parts of sodium nitrite. The solution soon becomes red, and after boiling for a short time gives a separation of the reddish-brown zinc salt of the quinonoxime, which after standing overnight is filtered off, washed with a little alcohol, mixed with about 40 parts of water, and digested for a short time with a solution of 4 parts of caustic soda until completely converted into the crystalline green sodium salt. This is filtered off from the cold solution, washed with a little water and decomposed by dilute hydrochloric acid in the cold, the product being purified if necessary by dissolution in aqueous sodium carbonate and precipitation with sulphuric acid. The yield amounts to 110–115 p.c. of the β-naphthol employed (Henriques and Ilinski, B. 18, 705).

Properties.—It crystallises from water in minute bright-yellow needles containing water of crystallisation, from alcohol, ether, benzene, &c., in anhydrous orange-brown thin plates or short thick prisms, which melt at 109°·5, dissolve very sparingly in hot water, sparingly in petroleum spirit, and readily in most other solvents, requiring about 42 parts of alcohol at 13° for dissolution (Stenhouse and Groves, *l.c.*). In the pure form it is readily volatile with steam, but when impure, is for the most part resinified on boiling with water (Ilinski, *l.c.*).

Salts.—The copper salt, CuA_2, is a coffee-brown precipitate insoluble in water, alcohol, and 50 p.c. acetic acid (Knorre, B. 20. 283); the *ferric* salt, FeA_3, a brownish-black precipitate insoluble in water and 50 p.c. acetic acid (Ilinski and Knorre, B. 18, 2728); and the *cobalt* salt, CoA_3, a purple-red precipitate very slightly soluble in boiling 50 p.c. acetic acid (Ilinski and Knorre, B. 18, 699). As Hg, Pb, Cd, Al, Cr, Ni, Zn, Mn, &c., are not precipitated in acetic acid solution, 2:1-naphthaquinonoxime can be employed for the quantitative separation of Cu, or Fe, or Co from any of the metals named. The *potassium* salt, KA, crystallises in soluble green scales having a metallic lustre; the *sodium* salt is a green precipitate insoluble in alcohol and dilute aqueous caustic soda (Ilinski, B. 17, 2885).

Reactions.—(1) When heated in methyl alcohol solution with hydroxylamine hydrochloride it yields 1:2-*naphthaquinonedioxime*, but with hydroxylamine in alkaline solution it gives the anhydride (m.p. = 78°) of this compound (Goldschmidt and Schmid, B. 17, 2067). 1:2-Naphthaquinonedioxime colours iron and cobalt mordants brown (Kostanecki, B. 21, 1349).

(2) On fabrics mordanted with tartar and sodium bichromate, it produces shades resembling those obtained with alizarin paste, and when printed with chromium acetate or with iron salts it gives brown or olive-green shades; the colours are not fast to light or soap. According to Erdmann, it has been introduced under the name 'Gambin R.' as a cheap alizarin substitute (Chem. Ind. 12, 155).

Nitroso-2:3′-β-naphtholsulphonic acid is formed when the requisite quantity of sodium nitrite is added to a well-cooled aqueous solution of a salt of 2:3′-β-naphtholsulphonic acid, and hydrochloric acid is stirred into the cold solution to acid reaction (Meldola, C. J. 39, 40).[1] It crystallises in very soluble orange granules, and can be purified by conversion into

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[1] A decomposition product, obtained by the action of nitrous acid on 2:3′-β-naphtholsulphonic acid at a temperature of 50°, is stated to be a brown dye for silk (Walder, Germ. pat. 40897 of Jan. 5, 1887; Eng. pat. 126 of 1887).

the well-characterised *barium* salt, which crystallises with 2 mols. H_2O in green microscopic needles and with 1 mol. H_2O in long orange needles.

Reactions.—(1) Reduction with tin and hydrochloric acid converts it into 1:2:3′-*amido-β-naphtholsulphonic acid* (Eikonogen) (Meldola, *l.c.*; S. C. I. 8, 581).

(2) Like 2:1-naphthaquinonoxime, it forms coloured metallic salts with Co, Ni, and Fe, from which the metal is not precipitated by alkalis or alkaline carbonates. With cobalt and nickel salts it gives brown and yellow dyes respectively, whilst with ferric chloride it forms

Naphthol green. This dye is prepared by adding a solution of 5 kilos. of ferric chloride in 20 litres of water to a cold solution of 27·5 kilos. of sodium nitroso-β-naphtholsulphonate in 100 litres of water. After some hours' standing the brownish-black solution is freed from excess of iron by addition of alkali, the clear green filtrate evaporated to dryness, and the dye purified either by crystallisation from dilute alcohol or by conversion into the insoluble basic lead salt, which, after washing, is reconverted into sodium salt by treatment with sodium sulphate (Gans & Co., Germ. pat. 28065 of Jan. 19, 1884, Eng. pat. 2269 of 1884; Hoffmann, B. 18, 46). It is a soluble dark-green powder, which in a weak sulphuric acid bath, best in the presence of a little ferrous sulphate (Gans & Co., Germ. pat. 28901 of Mar. 16, 1884), dyes wool in olive- to dark-green shades, which are remarkable for their fastness to light and soap.

Nitroso-2:1′-dihydroxynaphthalene (Bayer & Co., Germ. pat. 53915 of Sept. 15, 1889), nitroso-2:2′-dihydroxynaphthalene (Leonhardt & Co., Eng. pat. 17223 of 1889) and nitroso-2:3′-dihydroxynaphthalene (Bayer & Co., Eng. pat. 14230 of 1889) are obtained by adding the requisite quantity of sodium nitrite to an ice-cold solution of the dihydroxynaphthalene in aqueous alkali, and acidifying with dilute acetic or sulphuric acids. They give deep-brown or black lakes when printed on cotton with iron or chromium salts, and on wool mordanted with these salts dark-brown shades remarkable for their fastness to light, air, and fulling.

Nitrosonaphtharesorcinol (nitroso-1:3-dihydroxynaphthalene), prepared by the action of hydroxylamine in alkaline solution on hydroxy-[α-]naphthaquinone, gives lakes with nickel, cobalt, ferrous, and ferric salts, and dyes mordanted fabrics. It crystallises from acetic acid in yellow needles, is practically insoluble in cold water, and on treatment with nitrous acid is converted into dinitrosonaphtharesorcinol which in its tinctorial properties closely resembles dinitrosoresorcinol (solid-green), but gives somewhat darker shades (Kostanecki, B. 22, 1342).

VIII. CARBOXY- ACIDS.

The naphthoic acids are related to naphthalene in the same way that benzoic acid is related to benzene, and give analogous reactions. The chief mode of preparation of both mono- and di-carboxylic acids consists in hydrolysing the corresponding nitriles with hydrochloric acid or alcoholic potash, the nitriles being obtained by the dry distillation of the sodium salts of the corresponding naphthalenesulphonic acids with potassium ferrocyanide. The nitro-, amido-, and other derivatives of α- and β-naphthoic acid have been described by Ekstrand (*cf. inter alia*, B. 17, 1603; J. pr. 38, 139, 241).

α- and β-Naphthol in the form of dry sodium salts interact with carbon dioxide under pressure, forming orthohydroxynaphthoic acids, thus resembling phenol, and it is noteworthy that the intramolecular change of potassium orthohydroxybenzoate into parahydroxybenzoate is paralleled in the naphthalene series by the change of the unstable sodium orthohydroxy-β-naphthoate into the very stable heteronucleal β-hydroxy-β-naphthoate (*v. infra*). Naphthalic acid is the only naphthalenedicarboxylic acid described in this article.

α-Naphthoic acid, $C_{10}H_7.COOH$.

Preparation.—α-Naphthoic acid is prepared by heating α-naphthanitrile either with an equal volume of concentrated hydrochloric acid at 200° (Boessneck, B. 16, 639), or with alcoholic soda in the proportion of 12 grams of the nitrile, 7·5 grams of caustic soda, and 55 c.c. of 90 p.c. alcohol at 160° (Bamberger and Philip, B. 20, 242).

Properties. — It crystallises in colourless needles, melts at 160°, boils at about 300°, dissolves sparingly in hot water, readily in alcohol and ether, and yields naphthalene on distillation with lime. The *calcium* salt, $CaA_2 + 2H_2O$, crystallises in needles soluble in 93 parts of water at 15° (Merz and Mühlhäuser, Z. [2] 4, 72).

β-Naphthoic acid.

Formation.—β-Naphthoic acid is obtained by the oxidation of β-methylnaphthalene with nitric acid (Ciamician, B. 11, 272), and by boiling β-naphthanitrile with alcoholic potash (Vieth, A. 180, 305).

Properties.—It crystallises in silky needles, melts at 184°, dissolves sparingly in hot water, readily in alcohol and ether, and yields naphthalene on distillation with baryta. The *calcium* salt, $CaA_2 + 3H_2O$, crystallises in needles soluble in 1800 parts of water at 15° (Merz and Mühlhäuser, Z. [2] 4, 72).

HYDROXY- DERIVATIVES.

(i) **1:2-α-Hydroxynaphthoic acid.**

Formation.—1:2-α-Hydroxynaphthoic acid is obtained by heating a mixture of α-naphthol and sodium in a current of dry carbon dioxide (Eller, A. 152, 277; Schaeffer, A. 152, 291), also by acting on dry sodium α-naphtholate with solid, liquid or gaseous carbon dioxide in the cold, and subsequently heating the resulting sodium α-naphthyl carbonate at 120-140° (Schmitt, Germ. pat. 31240 of Sept. 19, 1884; Schmitt and Burkard, B. 20, 2699).

Preparation.—The requisite quantity of dry carbon dioxide is allowed to act under pressure on perfectly dry sodium α-naphtholate heated at 120–145° in a closed vessel provided with a stirrer. The acid, precipitated from an aqueous solution of the product by a mineral acid, is purified by crystallisation (Dr. F. v. Heyden's Nachfolger, Germ. pat. 38052 of June 8, 1886).

Salts.—The *acid*, $OH.C_{10}H_6.COOH$, crystallises from alcohol in stellate groups of needles, melts at 187°, dissolves readily in alcohol, ether, and benzene, very sparingly in water (0·058 gram in 100 c.c. at 17°), and regenerates α-naphthol and carbon dioxide only to a small extent by prolonged boiling with water. Its aqueous solution gives with ferric chloride a blue colouration. The *sodium* salt, NaA, crystallises with 3 mol. H_2O in large, thin, nacreous scales from water, in anhydrous rhombic scales from 90 p.c. alcohol, and dissolves to the extent of 6·37 gram in 100 c.c. of water at 17°; the *ammonium* salt, NH_4A, crystallises in anhydrous, long needles readily soluble in hot water (Schmitt and Burkard, *l.c.*).

Reactions.—(1) Nitrous acid reacts with it, forming *nitroso-α-naphthol* with the elimination of carbon dioxide, and nitric acid converts it into *dinitro-α-naphthol* (Nietzki and Guiterman, B. 20, 1275).

(2) It interacts with diazotised aniline, naphthylamine, &c., best in sodium carbonate solution, forming azo- dyes which give orange-yellow shades on wool and are sensitive to acids and alkalis (Bischoff, B. 23, 1910; *cf.* M. L. B., Germ. pat. 46203, 48357).

1:2:4-α-Hydroxysulphonaphthoic acid [OH:COOH:SO_3H = 1:2:4] is obtained by stirring 1 part of α-hydroxynaphthoic acid into an ice-cold mixture of 2 parts of 20 p.c. anhydrosulphuric acid and 3 parts of concentrated sulphuric acid, and afterwards warming at 60° until the mass becomes solid (König, B. 22, 787), or by heating α-hydroxynaphthoic acid with 5 times its weight of sulphuric acid of 66°Bé. at 60–70° for about an hour until a test mixed with water and freed from excess of acid dissolves readily in water (Dahl & Co., Germ. pat. 51715 of Jan. 5, 1889; *cf.* Bayer & Co., Germ. pat. 38802 of Nov. 19, 1885).

Salts.—The *acid*, $OH.C_{10}H_5(COOH)SO_3H + 5H_2O$, crystallises in small needles, dissolves readily in water and alcohol, and shows a blue fluorescence in alkaline solution. The *acid sodium* salt, NaA, crystallises in thin, silky needles readily soluble in water, less so in brine; the *basic sodium* salt, Na_2A, forms very soluble, long, efflorescent needles (König, *l.c.*).

Reactions.—Nitric acid converts it into 1:2:4-*nitro-α-hydroxynaphthoic acid* and *dinitro-α-naphthol.* Diazotised bases react with it, forming azo- dyes, which, owing to the elimination of carbon dioxide, are derivatives not of the carboxy-acid, but of 1:4-α-naphtholsulphonic acid (König, B. 23, 806).

α-Hydroxydisulphonaphthoic acid is formed by stirring 1 part of 1:2-α-hydroxynaphthoic acid into 4 parts of 'fuming' sulphuric acid and warming the mixture for some time on a water-bath (König, B. 22, 788). The *acid*, $OH.C_{10}H_4(COOH)(SO_3H)_2 + 4H_2O$, crystallises in stellate groups of white needles, is very soluble in water and alcohol, and shows a strong bluish-green fluorescence in alkaline solution.

Reactions.—When heated with water under pressure it yields what is stated to be a new *α-naphtholsulphonic acid*, and on treatment with diazotised bases it loses carbon dioxide forming azo- dyes with the resulting *α-naphtholdisulphonic acid*[1] (König, B. 23, 810).

(ii) 2:1-β-Hydroxynaphthoic acid.

Formation.—2:1-β-Hydroxynaphthoic acid is obtained by acting on dry sodium β-naphtholate with solid, liquid, or gaseous carbon dioxide under pressure in the cold, and subsequently heating the resulting sodium β-naphthyl carbonate at 120–140° (Schmitt, Germ. pat. 31240 of Sept. 19, 1884; Schmitt and Burkard, B. 20, 2701; Dr. F. v. Heyden's Nachfolger, Germ. pat. 38052 of June 8, 1886). To separate the acid from β-naphthol the product is treated with ammonium carbonate in the cold, and the precipitate obtained by adding hydrochloric acid to the solution is crystallised from alcohol at a temperature not exceeding 30–40°.

Salts.—The *acid* crystallises in slender, matted needles, melts at 156–157° when rapidly heated, but begins to decompose at 124–128° when slowly heated, and is quantitatively decomposed into β-naphthol and carbon dioxide by prolonged boiling with water. Ferric chloride colours the aqueous solution a pure blue. The salts are more stable than the acid.

Reaction.—When treated with diazotised bases, carbon dioxide is eliminated and azo-derivatives of β-naphthol formed (Nietzki and Guiterman, B. 20, 1275).

2:1:3′-β-Hydroxysulphonaphthoic acid is formed when dry 2:1-β-hydroxynaphthoic acid is gradually stirred into five times its weight of 20 p.c. anhydrosulphuric acid at a temperature not exceeding 20–25°; the mixture, after dissolution of the acid, being eventually heated to 40° for a short time. The *acid* crystallises in slender needles, and is converted into 2:3′-*β-naphtholsulphonic acid* with elimination of carbon dioxide when warmed in aqueous solution at 60°[1] (Seidler, Germ. pat. 53343 of June 21, 1889; exp. Nov. 1890). The azo- dyes, formed from it by interaction with diazotised bases, must unquestionably be derivatives of 2:3′-β-naphtholsulphonic acid.

(iii) [? 2:3′] β-Hydroxynaphthoic acid.

Preparation.—It is obtained in small quantity by heating a mixture of sodium β-naphtholate and sodium in a rapid stream of carbon dioxide at 280–290° (Schmitt and Burkard, B. 20, 2702), and on the large scale by allowing the requisite quantity of carbon dioxide to act under pressure on perfectly dry sodium β-naphtholate heated at 200–250° in a closed vessel provided with a stirrer (Dr. F. v. Heyden's Nachfolger, Germ. pat. 50341 of June 1, 1889).

Properties. — It crystallises in lustrous, rhombic, yellow scales, melts at 216° without decomposition, is readily soluble in alcohol and ether, tolerably in benzene and chloroform, and very sparingly in hot water, and in aqueous solution gives a blue colouration with ferric chloride. It is characterised by its great stability.

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[1] It is by no means improbable that this acid has the constitution [OH:COOH:SO_3H:SO_3H = 1:2:4:2′], in which case the resulting α-naphtholdisulphonic and α-naphtholsulphonic acids would respectively be the known 1:4:2′- and 1:2′-acids.

[1] The β-hydroxysulphonaphthoic acid obtained by Harmsen (Germ. pat. 22707 of Sept. 9, 1882, exp. July, 1883) by heating β-hydroxynaphthoic acid with 2 parts of sulphuric acid at 160°, and stated to give azo- colours distinguished by their fastness and tinctorial power, must, in the absence of any definite information as to its origin and nature, be regarded as 2:3′-β-naphtholsulphonic acid.

(iv) 1:1′-**Hydroxynaphthoic acid** is prepared by dissolving 1:1′-naphthalactone[1] in warm dilute aqueous caustic potash and precipitating the solution with hydrochloric acid. It crystallises in slender needles, melts at 169°, is very soluble in alcohol and ether, readily in water, and does not exhibit a very marked tendency to revert to the lactone (Ekstrand, B. 19, 1138).

(v–viii) The following hydroxynaphthoic acids have been obtained by fusing sulphonaphthoic acids with caustic potash: *a-a*-acid (m.p. = 234–237°) from [*a*-]sulpho-*a*-naphthoic acid, *a-β*-acid (m.p. = 245–247°) from [*β*-]sulpho-*a*-naphthoic acid, *a-β*-acid (m.p. = 186–187°) from [*γ*-]sulpho-*a* naphthoic acid, and *a-β*-acid (m.p. = 210–211°) from sulpho-*β*-naphthoic acid (Battershall, A. 168, 121; Stumpf, A. 188, 1).

DICARBOXY- ACIDS.

1:1′-**Naphthalenedicarboxylic acid** (naphthalic acid).

Formation.—Naphthalic acid is obtained by the oxidation of acenaphthene with chromic acid mixture (Behr and Van Dorp, A. 172, 266), and of pyreneketone with potassium permanganate (Bamberger and Philip, A. 240, 180; B. 20, 237).

Preparation.—5 parts of acenaphthene are gently warmed with a solution of 30 parts of potassium bichromate, 45 parts of sulphuric acid, and 150 parts of water, and the separated naphthalic acid purified by crystallisation from alcohol, any residue being sublimed. The yield amounts to 12–22 p.c. of the weight of the acenaphthene employed (Behr and Van Dorp, *l.c.*; Terisse, A. 227, 135).

Properties.—It crystallises in long, slender, silky needles, dissolves readily in warm alcohol, is converted by boiling with alcohol or by heating at 140–150° without previous fusion into the *anhydride* (m.p. = 266°), and when heated with resorcinol at 260–270°, or with the addition of zinc chloride at 215°, yields *naphthafluoresceïn* (Terisse, *l.c.*).

For information with regard to naphthalene derivatives not described in this article reference should be made to WATTS' DICTIONARY OF CHEMISTRY. W. P. W.

NAPHTHALENE YELLOW *v.* NAPHTHALENE.

NAPHTHAQUINONE *v.* NAPHTHALENE.

NAPHTHASE *v.* AZINES.

NAPHTHAZARIN *v.* NAPHTHALENE.

NAPHTHAZINES *v.* AZINES.

NAPHTHIONIC RED or **ARCHIL SUBSTITUTE** *v.* AZO- COLOURING MATTERS.

NAPHTHOL BLACK *v.* AZO- COLOURING MATTERS.

NAPHTHOL GREEN *v.* NAPHTHALENE.

NAPHTHOL ORANGE *v.* AZO-COLOURING MATTERS.

NAPHTHOL YELLOW *v.* NAPHTHALENE.

NAPHTHOPHENAZINE *v.* AZINES.

NAPHTHYLAMINE BROWN *v.* AZO-COLOURING MATTERS.

NAPHTHYLAMINE VIOLET. A dyestuff of little commercial value and unknown composition, obtained from *a*-naphthylamine hydrochloride by oxidation with potassium chlorate (*cf.* Blumer-Zweifel, D. P. J. 196, 66; Kielmeyer, D. P. J. 196, 67).

NAPLES YELLOW *v.* ANTIMONY.

NARCEÏNE *v.* AZO- COLOURING MATTERS; also VEGETO-ALKALOIDS.

NARCOTINE *v.* VEGETO-ALKALOIDS.

NARINGIN $C_{21}H_{26}O_{11}$. A glucoside obtained from the blossoms of *Citrus decumana.* It is a white substance which dissolves in alcohol and in warm water, and crystallises with 4 mols. H_2O, sp. rotatory power in aqueous solution $[a]_D = 84°{\cdot}5$; in alcoholic solution $[a]_D = 87°{\cdot}6$. By hydrolysis is resolved into isodulcite and *naringenin* $C_{15}H_{12}O_5$, a white crystalline substance, m.p. 248° with decomposition. Gives a deep-brown-coloured solution with ferric chloride, and is readily soluble in alcohol, ether, and benzene. Naringenin is readily decomposed when boiled with conc. KHO, into phloroglucinol and *naringenic acid* C_9H_8O, a white crystalline powder m.p. 207°, soluble in water, giving a red-brown-coloured solution with ferric chloride. Its aqueous solution treated with sodium amalgam gives hydronaringeninic acid ($C_9H_{10}O_3$), m.p. 126° (W. Will, B. 20, 294).

NATROLITE $Na_2O.Al_2O_3.3SiO_2.2H_2O$. A mineral occurring in cavities in amygdaloïdal trap, basalt, &c., and in seams in gneiss. Crystallises in trimetric prisms with pyramidal summits. Occurs fibrous, radiating, and massive of a vitreous lustre; colourless, grey, yellow, or pale green. Is capable of receiving a high polish, and has been used for rings and other ornaments.

NATRON is the name of the native sesquicarbonate of soda, which occurs as a deposit on the sides of several lakes to the west of the Delta of Egypt; also as thin crusts on the surface of the earth, rarely an inch in thickness, at the bottom of a rocky mountain, in the province of Sukena, near Tripoli, and two days' journey from Fezzan; known also as *Trona.* The walls of Cassar (Tasrr), a fort now in ruins, are said to have been built of it. At the bottom of a lake at Lagunillas near Merida in Venezuela is found a substance called by the Indians *Urao*, which is tolerably pure sesquicarbonate of soda. It is collected every two years by the natives, who, aided by a pole, plunge into the lake, separate the bed of earth which covers the mineral, break the urao, and rise with it to the surface of the water; it is then removed to the magazine, and dried in the sun. Natron is also found near Smyrna, in Tartary, Siberia, Hungary, Hindostan, and Mexico; in the last country there are several natron lakes a little to the north of Zacatecas, as well as in many other provinces (Ure).

NEAPOLITAN YELLOW *v.* ANTIMONY.

NEEDLE-ORE or **ACICULITE.** *Native bismuth sulphide v.* BISMUTH.

NEEDLE-SPAR. A variety of Arragonite.

NEODYMIUM *v.* CERIUM METALS.

NEOGEN. An alloy resembling silver in colour, said to have the following composition (Sauvage, D. P. J. 215, 377).

Cu	Zn	Ni	Sn	Al	Bi
58·0	27·0	12·0	2·0	0·5	0·5

NEOSOTE *v.* DISINFECTANTS.

NEPHRITE *v.* JADE.

NEROLI *v.* OILS, ESSENTIAL.

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[1] Naphthalactone, $C_{10}H_6\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle$ (m.p. = 108°), is formed when 1:1′-amidonaphthoic acid dissolved in dilute aqueous caustic potash is treated with the requisite quantity of potassium nitrite, the mixture slowly poured into very dilute cold sulphuric acid, and the whole subsequently boiled (Ekstrand, *l.c.*).

NEURIDINE *v.* PTOMAÏNES.

NEURINE *v.* PTOMAÏNES.

NEUROSTEARIC ACID *v.* FATTY ACIDS.

NEUTRAL RED. *Toluylene red v.* AZINES.

NEUTRAL VIOLET *v.* AZINES.

NEW BLUE, *Naphthylene blue, Fast blue 2 B or R, Meldola's blue v.* OXAZINE COLOURING MATTERS.

NEW COCCIN *v.* AZO- COLOURING MATTERS.

NEW KIRKITE. *Hydrated manganese dioxide v.* MANGANESE.

NEW RED *v.* AZO- COLOURING MATTERS.

NEW YELLOW, *Diphenylamine yellow, Acid yellow D, Tropæoline OO v.* AZO- COLOURING MATTERS.

NICHOLSON'S BLUE *v.* ANILINE BLUE.

NICKEL. Atomic weight 58·6; symbol Ni.

History.—This metal was discovered by Cronstedt in 1751, who isolated it from an ore containing arsenide of nickel NiAs, a copper coloured mineral called by the German miners kupfer-nickel or false copper, because of its resemblance to the colour of certain copper ores.

Occurrence.—The ores of nickel are widely distributed and have been worked for some time in many countries, especially in Saxony, Norway, and Sweden, Austria, Spain, Russia, the United States, and to some extent in different parts of Great Britain. Nickel exists in these countries usually associated with cobalt, as *kupfer-nickel* NiAs, *nickel-glance* $Ni(AsS)_2$, *nickel-blende* or *millerite* NiS, *cobalt-speiss* $(CoNiFe)As_2$, magnetic pyrites, &c.

The ores that have been found in the above countries are generally very complex in composition, containing, besides nickel and cobalt, copper, antimony, arsenic, iron, manganese, sulphur, &c. This fact renders the extraction of metallic nickel from such ores both expensive and troublesome.

Analysis of nickel ore from Spain—Readman, analyst.

	Per cent.
Copper	14·32
Antimony	2·15
Arsenic	12·21
Iron	11·90
Sulphur, combined with above	17 39
Oxides of iron and alumina .	4·29
Oxide of nickel	6·45
Oxide of cobalt	3·95
Lime	5·34
Magnesia	5·35
Carbonic acid	6·50
Sulphuric acid	·85
Silica	8·25
Moisture, &c.	1·05
	100·00

Nickel is always present in meteoric iron, and has been detected in the atmosphere of the sun.

During the last twenty-five years a remarkable and most important ore of nickel has been discovered in the French island of New Caledonia, South Pacific Ocean, by Garnier, while engaged in an exploring expedition undertaken under the auspices of the French Government. This new ore, although it has a very characteristic green colour, was at first mistaken for carbonate of copper. It has been called *garnierite* after its discoverer. Very large and beautiful specimens of the ore were sent to the Paris International Exhibition of 1878, and there they attracted a great deal of interest.

The New Caledonia nickel deposits are found in veins in the serpentine and other rocks as an emerald-green coloured ore. The nickel is present as a double silicate of magnesia and nickel $2(NiMg)_3Si_4O_{13} + 3H_2O$.

The sp.gr. of garnierite is 2·60. Its colour is light or dark green, and its streak light green. When heated it gives off water, and when mixed with borax and fused the ordinary nickel bead is obtained.

These ores contain no cobalt, and are probably the simplest in composition of all the ores of nickel yet discovered. The following analyses of various typical specimens of the ore obtained by the author during a visit to the island will show their composition:—

—	Per cent.	Per cent.	Per cent	Per cent.
Oxide of nickel .	11·08	12·68	18·04	24·28[1]
Oxide of iron .	7·34	7·14	·88	3·80
Alumina . .	1·56	1·50	1·24	
Lime . . .	1·90	·72	trace	·58
Magnesia . .	22·50	21·83	16·37	15·35
Silica . .	37·96	43·41	45·74	40·24
Water . .	17·30	12·38	17·28	16·21
	99·64	99·66	99·55	100·46

Analyst—Readman.

The New Caledonia nickel mines are now worked on an extensive scale by a wealthy French company, La Société 'Le Nickel,' whose seat of administration is in Paris. This company manufactures pure metallic nickel from these ores, which are imported to their European works reduced to a matte containing from 50 to 60 p.c. of nickel, or as ore, which on an average contains from 8 to 10 p.c. of metallic nickel.

Besides the above nickel ore there is likewise found in many parts of New Caledonia surface deposits of a manganiferous ore containing both cobalt and nickel; but the quantity of the latter metal present in these ores is too small to make them valuable as a source of nickel, though as a source of cobalt they are worked to a considerable extent by the French company; and during the extraction of the latter the nickel is obtained as a by-product. The following is the composition of these ores:—

—	Per cent.	Per cent.	Per cent.
Oxide of cobalt . .	3·48	3·81	5·56
Oxide of nickel . .	1·05	1·24	1·48
Peroxide of manganese .	23·34	24·91	15·94
Protoxide of manganese .	2·22	8·43	3·40
Ferric oxide . . .	15·71	9·45	16·06
Alumina . . .	21·20	25·55	10·30
Lime	2·68	1·64	1·53
Magnesia . . .	2·16	trace	·70
Silica and chrome ore .	9·20	9·52	23·00
Combined water . .	17·84	16·36	9·23
Moisture . . .	1·70		12·86
	100·58	100·91	100·06

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[1] Picked specimen.

The great advantage possessed by the New Caledonia nickel ores (garnierite) over the cuprous or arsenical ores found in other places is in the simplicity of the process of refining. There is no necessity, when these ores are employed, to use a wet method of extraction, for the entire process from beginning to end is a metallurgical one, and is done without the use of any chemical reagents in solution.

So great has been the development of the nickel mines of New Caledonia since they were discovered, about a quarter of a century ago, that during late years the world's supply of nickel has been principally derived from this source.

Within the last year or so, another ore containing nickel has been discovered in Sudbury, Province of Ontario, Canada, which promises to be of importance. The following is the account of the mines, kindly supplied by the manager there: 'These ores are deposits existing in diorite dykes in the Theronian rocks, and consist of tolerably massive pyrrhotite, sprinkled through with chalcopyrite. In the pyrrhotite a portion of the iron (3 to 8 p.c.) is replaced by nickel; no trace of arsenic; about $\frac{1}{8}$ p.c. cobalt in solid pyrrhotite, and an ounce or so of platinum. (The celebrated arsenide of platinum, sperrylite, occurs near here, but evidently has nothing to do with our platinum.) The deposits are lens-shaped, and may average 1 to 300 feet long, and 5 to 100 (average 30 feet) wide. The ore is tolerably massive, though seams and nodules of diorite occur in every shape, size, and position. The ore is roasted and smelted in water-jacket furnaces. The furnace averages 130 tons daily. A matte is shipped to the United States and Europe averaging 30 p.c. copper and 20 p.c. nickel. The future of these mines is important, as every month opens up more ore.'

The results of these operations at Sudbury point to an enormous increase in the world's supply of nickel. The production there already exceeds the world's consumption, which is roughly estimated at about 1,000 tons a year.

Extraction from cuprous and arsenical ores. In order to obtain metallic nickel from those ores which contain—in addition to nickel—arsenic, antimony, copper, cobalt, iron, sulphur, &c., &c., a preliminary roasting is required in order to remove as much of the arsenic as possible. The roasted mineral is next ground and dissolved in hydrochloric acid, and sulphuretted hydrogen is then passed through the diluted solution until all the copper, arsenic, antimony, and lead that may be present are precipitated as sulphides. These are removed by filtration, with subsequent washing, and the iron contained in the filtrate is peroxidised by the cautious addition of bleaching-powder or other suitable oxidising agent. Chalk in fine powder is then added to precipitate the iron as basic carbonate, which is filtered off and washed. The clear filtrate should now contain all the cobalt and nickel present in the roasted ore operated upon. To separate these metals a clear solution of bleaching-powder is carefully added until all the cobalt is precipitated as sesquioxide, care being taken to stop whenever it is found that nickel is precipitating. The clear solution of chloride of nickel is removed from the precipitated cobalt by decantation, and the oxide of nickel is finally precipitated by the addition of milk of lime. The oxide of nickel so obtained is washed, dried, and mixed with wood charcoal, and reduced to the metallic state by heat.

Extraction of nickel from New Caledonia ores.—The New Caledonia ores are treated in an entirely different manner. At first, and for some time after the deposits began to be worked on a large scale, the ores were concentrated on the spot previous to being exported to Europe, and to accomplish this the raw ore was mixed with limestone—which is found in great abundance in the island—to act as a flux, and it was then reduced with coke in a blast-furnace precisely as iron ores are reduced—using a hot blast. The result yielded a 'fonte' of nickel of which the following are two analyses:—

—	Per cent.	Per cent.
Nickel	65·2	70·70
Iron	29·74	22·00
Graphite	1·20	1·78
Silicon	1·26	—
Sulphur	2·24	1·65
Manganese	—	trace
Aluminium	—	1·37
Magnesium	—	·10
Oxygen and combined carbon	—	1·88
	99·64	99·48

This 'fonte' was exported to Europe in pigs resembling cast iron both in appearance and general condition.

(*a*) *Refining the fonte.*—To remove iron and other impurities it is necessary as a preliminary stage to pass the fonte through a cupola furnace along with gypsum, which gives up part of its sulphur to the metal, forming a matte or regulus of nickel which usually contains from 15 to 18 p.c. of sulphur and is brittle enough to be crushed beneath iron rollers in a pan mill. An improvement has since taken place in the treatment of the ore by which the latter is sulphurised in the first operation, thus saving the expense and loss attending a double furnacing.

To carry out this process the ore is first ground and then mixed with about half its weight of alkali waste or of gypsum, and about 5 p.c. of ground coal. These ingredients, all thoroughly incorporated together, are made into blocks or bricks with water, and dried sufficiently to enable them to be handled.

They are then smelted either in a reverberatory furnace or in a cupola of low height, to prevent, as far as possible, the reduction of the iron. Water-jacketed cupolas have been used with much success in this operation; they are 10 feet high × 6 feet in diameter, and work continuously night and day for weeks together, using coke as the fuel. The matte or regulus so obtained has the following composition:

Metallic nickel	67·17	per cent.
„ iron	11·90	„
Silicon	·20	„
Sulphur	17·08	„
Graphite, &c.	3·65	„
	100·00	

The slag which is obtained during the smelting weighs 2 or 3 times as much as the matte for a given weight of mixture operated upon. It contains the following substances:

Silica	53·62	per cent.
† Sesquioxide of iron .	1·28	„
Alumina	2·28	„
* Protoxide of nickel .	·46	„
Lime, magnesia, &c. .	42·36	„
	100·00	

† Equal to metallic iron ·90 per cent.
* „ nickel . . ·36 „

(*b*) *Refining the regulus.*—Regulus of nickel containing only nickel, iron, sulphur, and carbon may be refined by a process similar to the Welsh copper-smelting process. The process depends on the fact that iron has a greater affinity for oxygen than nickel, while nickel has a greater affinity for sulphur than iron has. In this way it is possible to oxidise the iron in a compound containing nickel, iron, and sulphur, so that the oxygen introduced tends towards the iron while the nickel remains as sulphide. It is also obvious that on treating such a mixture as this partially oxidised body is with silica the tendency will be to form silicate of iron, while the sulphide of nickel will in great measure escape decomposition.

It may be premised that, in the description of the process which follows, no definite details can be given, experience being the only sure guide.

The regulus is ground under edge rollers and passed through a sieve of 40 meshes to the linear inch, then it is carefully roasted in a long reverberatory furnace at a gentle heat, the greatest care being taken not to stir the charge. The length of time required for this roasting varies with the amount of iron in the material —the roasting is continued until three-fourths of the iron has been converted into oxide. The heat must never rise above dull redness, otherwise the charge will melt and oxidation be greatly reduced. On the roasting being completed as indicated the charge is withdrawn and mixed with a proper proportion of sharp sand as free from clay and ferruginous matter as possible. The quantity of sand used varies with the amount of oxide of iron present in the calcined regulus. The mixing must be very complete and the mixture must be carefully riddled to remove any lumps. This mixture is now introduced into a reverberatory furnace identical with those used for the first melting of copper in the Welsh process, except that it is smaller, holding generally about 30 cwt. The charge is introduced through a hopper, and is spread over the hearth as rapidly as possible, the door is then closed, and the fire made up.

The charge gradually melts, and the iron oxide is at once attacked by the silica of the sand forming silicate of iron, while the nickel from its greater affinity for sulphur escapes the action of the silica, and remains under the surface of melted slag as a layer of fused sulphide of nickel. The operation lasts from 10 to 24 hours, according to the composition of the charge. The slag is drawn out at the front of the furnace by means of flat-headed rakes, and is received in sand moulds, while the nickel regulus is tapped out into similar moulds at the side. In general this process must be several times repeated before the iron is completely removed, sometimes as many as five alternate roastings and fusions are required to eliminate all the iron. The slags from these fusions all contain nickel, and are resmelted in cupola furnaces with sand and gypsum, when they yield a regulus poor in nickel and a slag which with careful working should not contain more than ·2 p.c. of that metal.

Working up poor reguli.—The poor qualities of regulus thus obtained are treated by themselves until they are rich enough to be worked in the manner previously described. Their preliminary treatment is as follows. The regulus is crushed and intimately mixed with dried and powdered sulphate of lime and sand, and the whole fused in reverberatory furnaces. The sulphate of lime being attacked by the sand yields oxygen which oxidises the iron, and the oxide of iron thus formed combines with the silicate of lime, forming a very fusible slag. Two or three fusions of this sort may be required before the regulus becomes rich enough to be treated by the action of sand as before described.

The sulphide of nickel when freed from iron is oxidised by being exposed in powder to a dull red heat on the hearth of a small reverberatory furnace, and is there roasted till all the sulphur is removed, a minute quantity of Chili saltpetre being sometimes added towards the end of the process. As a rule, however, this addition is not required, as every trace of sulphur can be removed by roasting alone if the operation is carefully conducted.

Reduction of the oxide to metallic nickel.—Oxide of nickel thus produced is mixed with finely powdered wood charcoal and compressed into cakes about the diameter of a penny, but much thicker. The coherent cakes are next packed with charcoal into fireclay cylinders, which are afterwards heated to bright redness, whereby the oxide of nickel is reduced to the metallic state ready for the market.

The following is an analysis of the nickel so prepared:

Metallic nickel . .	98·83	per cent.
Metallic iron . .	·72	„
Carbon, silicon, &c. .	·45	„
	100·00	

Properties of nickel.—Nickel is a lustrous silver-white metal having a slight steel-grey tinge which is very observable when silver is compared along with it.

Next to manganese, nickel is the hardest of the metals, and it is capable of taking a very fine polish.

Nickel is magnetic at ordinary temperatures, but when heated to about 250°C. it temporarily loses this property. It melts at about the same temperature as iron, and is more fusible if combined with carbon. It fuses at a lower temperature than manganese, and slowly absorbs oxygen at a red heat. A wire of nickel previously heated and then plunged into oxygen burns in that gas like iron.

Pure nickel is not a readily oxidisable metal, and its resistance to the action of the atmosphere, and also to the action of both fresh and salt water, admits of its being ranked in these respects with the precious metals. It dissolves slowly in dilute sulphuric and hydrochloric acids, rapidly in nitric acid. In contact with concentrated nitric acid it becomes passive like iron. Acetic, citric, tartaric, and oxalic acids have little or no action on nickel unless they are left in contact with the metal for a long time.

Caustic soda may be fused in nickel vessels without any change taking place.

Nickel may be deposited as a brilliant metallic layer by electrolysing a solution of the double sulphate of nickel and ammonia

$[NiSO_4.(NH_4)_2SO_4 + 6H_2O]$.

When nickel is prepared by the method described, viz., by reducing the oxide along with carbon, the metal is somewhat brittle, and when broken the fracture has a dull-grey colour and crystalline structure. Its sp.gr. is 8·43.

During recent years Fleitmann, of Iserlohn, has worked out a process for making nickel malleable and rendering it suitable for rolling and stamping. His process consists in adding to the fused nickel contained in a fireclay crucible a small quantity (1 oz. to 60 lbs. nickel) of metallic magnesium. The effect of this, according to some authorities, is to deprive the nickel of a minute quantity of oxygen or of occluded carbonic oxide, which forms with the magnesium oxide of magnesia and separates out the carbon as graphite. Nickel so treated can be rolled into very thin sheets, and in this condition has been welded on to sheet iron or steel to be used for the manufacture of culinary and other utensils. This nickel may be drawn into wire. It may also be cast or forged.

Nickel readily alloys with the majority of metals. The alloys known as German silver, China silver, argentan, similor, silveroid, &c., are prepared with the assistance of nickel.

An admixture of nickel increases the hardness of bronze to a considerable extent, but decreases its tenacity – as little as 1 p.c. to 1½ p.c. are required to improve the quality of the bronze.

Nickel may be separated from copper by dissolving the alloy in hydrochloric, sulphuric, or nitric acids, and subjecting the solution to the action of the electric current with a cathode of brass and an anode of carbon. The copper is reduced by the electric current and deposited on the cathode, and the acid which was combined with the copper is liberated at the carbon anode.

Alloys of nickel. The best coloured alloy of nickel and copper is made from four parts of copper to three parts of nickel; it is, however, very difficult to fuse.

German silver having a silver-white appearance is made, containing copper 55·2, zinc 24·1, nickel 20·7.

Some varieties of German silver contain different quantities of iron, manganese, tin, or even lead. All reduce the quality of the alloy and lessen the power to resist the action of dilute acids.

Lead makes German silver more fusible. Tin makes it denser and more sonorous, and causes it to take a better polish. Iron or manganese increases the white colour of the alloy, but it becomes more refractory and more inclined towards brittleness.

German silver is better than brass as regards hardness, strength, and power of resisting chemical action. Arsenic is very injurious to the alloy, making it brittle and giving it ultimately a brownish colour.

Fleitmann has shown that pure nickel and its alloys with copper, cobalt, and iron, can have other metals added without their losing the power of being welded. The metals that can thus be added are zinc, tin, lead, and cadmium. Iron and manganese up to as much as 10 p.c.

Alloys of nickel, copper, and aluminium may be obtained by first melting the nickel and stirring in the copper, adding lastly the aluminium at a somewhat higher temperature.

A new alloy of nickel and steel has quite recently been investigated, which promises to have important applications. It may be prepared in a crucible or in a good open-hearth steel furnace working at a fairly good heat. Riley, who has devoted much attention to this alloy, states that the charge can be made in as short a time as an ordinary 'scrap' charge of steel—say about seven hours—and its working does not demand so much care as is required in working many other kinds of charges, the composition being easily and definitely controlled. If the charge is properly worked nearly all the nickel will be found in the steel, almost none is lost in the slag, in this respect being widely different from charges of chrome steel. The ingots are clean and smooth in appearance on the outside, but those richest in nickel are a little more 'piped' than are ingots of ordinary mild steel. No extraordinary care is required when re-heating the ingots for hammering or rolling. The addition of 4·7 p.c. of nickel raises the elastic limit of the alloy from 16 up to 28 tons, and breaking strain from 30 up to 40 tons per square inch, without impairing the elongation or contraction of area to any noticeable extent. The hardness increases as the nickel is increased until 20 p.c. is reached, when a change takes place and successive additions of nickel tend to make the steel softer and more ductile. As regards corrodibility, the steels rich in nickel are practically non-corrodible, while those poor in nickel are much better than other steels.

Uses of nickel.—The chief use of nickel is in the manufacture of alloys, and in the preparation of sulphate of nickel for use in electroplating.

Nickel is employed in coinage. It was first used for this purpose by Switzerland about the year 1850, and nickel coinage has since been adopted by the United States, Belgium, Germany, and other countries.

Vessels of pure nickel for laboratory purposes are an excellent substitute for those made of iron or copper. Basins may be used for boiling with caustic alkalis or alkaline carbonates, and crucibles may be employed for fusing minerals or salts with caustic alkalis or nitrates of the alkalis. Water-baths, spatulas, and tongs of nickel are very serviceable.

Oxides of nickel. There are two oxides of nickel, the protoxide NiO and the sesquioxide Ni_2O_3.

Protoxide of nickel NiO is found native, and may be prepared by strongly heating the hydroxide NiO,H_2O, carbonate $NiCO_3$, or nitrate $Ni(NO_3)_2$. It is a greyish-green powder, permanent in the air, and reduced to the metallic state by ignition in hydrogen.

Sesquioxide of nickel Ni_2O_3 is a black powder obtained by gently igniting the nitrate or carbonate in air. It is decomposed by heat

Salts of nickel. The most important salt of nickel used in the arts is the ammonium nickel sulphate $(NH_4)_2SO_4,NiSO_4 + 6H_2O$ which is largely employed in the process of nickel-plating. It is obtained by dissolving either metallic nickel or its protoxide in sulphuric acid, and adding sulphate of ammonia to the concentrated acid solution. The crystals first deposited are purified by re-crystallisation. It crystallises in short monoclinic prisms.

Detection.—When salts of nickel are heated in the reducing flame of the blow-pipe along with carbonate of soda and charcoal, the metal is obtained as a grey powder. In the oxidising flame salts of nickel impart to borax a red colour whilst hot, changing to yellow on cooling. In solutions containing hydrochloric or sulphuric acid, nickel sulphide is not precipitated by sulphuretted hydrogen. Alkaline hydrates give a pale apple-green precipitate with soluble nickel salts soluble in carbonate of ammonia, yielding a greenish-blue liquid. Ammonia gives a similar precipitate soluble in excess. Cyanide of potassium produces a green precipitate soluble in excess, forming an amber-coloured liquid. Sulphide of ammonium in neutral solutions gives a black precipitate soluble with difficulty in hydrochloric acid.

Nickel salts when hydrated or in solution have a fine emerald-green colour. When anhydrous they are yellow.

Separation and estimation.—Having dissolved the substance containing the nickel in hydrochloric or nitric acids the solution is filtered and evaporated nearly to dryness to expel the excess of acid, and to render silica insoluble. The residue is dissolved in few additional drops of hydrochloric acid, and sulphuretted hydrogen is passed through the warm solution. This precipitates the metals whose sulphides are insoluble in acid. The solution is now filtered and iron and alumina removed by the addition of acetate of ammonia or soda to the boiling filtrate in the usual way. These substances are removed by filtration and sulphuretted hydrogen again passed through the filtrate for some time, to precipitate the sulphides of cobalt and nickel. These are collected on a filter and washed, and then dissolved in aqua regia.

The solution containing the two metals in the form of chlorides is mixed with an excess of phosphate of ammonia, and for every part of the latter 5 parts of hydrochloric acid are added, and the mixture is boiled for several minutes to convert all the phosphoric acid into ortho-phosphoric acid. The beaker is then removed, and, while still nearly boiling, ammonia is carefully added in small quantities at a time, till the precipitate which is at first produced redissolves.

The solution is then stirred vigorously for about a minute, when the cobalt will separate out as a fine purple crystalline precipitate, consisting of ammonio-phosphate of cobalt. A few drops of ammonia are then added and the beaker placed for a few minutes on the top of the water-bath. After settling, the solution is filtered, washed with cold water, then ignited and weighed as pyrophosphate of cobalt ($Co_2P_2O_7$) containing 40·4 p.c. of cobalt.

The filtrate from the cobalt will be more or less of a clear blue colour, the intensity of which will depend on the quantity of nickel present.

As the filtrate generally contains a small quantity of cobalt, it is advisable to boil the filtrate till a little of the nickel begins to come down. This precipitate will be reddish in colour if it contains any cobalt, is filtered off, dissolved in hydrochloric acid, and the cobalt estimated as before, and the filtrate which contains nickel is added to the other nickel filtrate.

From this solution the nickel may be precipitated by saturating the ammoniacal solution with sulphuretted hydrogen, filtering off the sulphide of nickel, igniting and then dissolving it in a mixture of hydrochloric and nitric acids, precipitating with caustic potash, washing well, drying and igniting to protoxide, in which condition it is weighed.

The ignited and weighed residue is now introduced into a weighed glass tube and reduced at a red heat in a current of hydrogen. The reduced metallic nickel is afterwards weighed.

J. B. R.

NICOTIDINE *v.* BONE OIL; also VEGETO-ALKALOIDS.

NICOTINE *v.* VEGETO-ALKALOIDS.

NICOTINIC ACID *v.* BONE OIL.

NIGELLA SEEDS or **BLACK CUMMIN.** The seeds of *Nigella sativa*, a ranunculaceous plant growing on the Mediterranean coasts, and in Egypt, Trans-Caucasia, and India, were found by Reinsch, in 1841, to yield 35·8 p.c. of fat oil, 0·8 p.c. of volatile oil, and only 0·6 p.c. of ash. He gave the name of *Nigellin* to a bitter extract resembling turpentine, yet soluble in water as well as in alcohol, though not in ether.

By submitting 25 lbs. of fresh seed to distillation, Flückiger (Ph. [2] 2, 161) has obtained a nearly colourless essential oil, but in smaller quantity than Reinsch. It has a slight odour, somewhat resembling that of parsley oil, with a magnificent bluish fluorescence, as already remarked by Reinsch. In a column 50 mm. long this oil deviates the ray of polarised light 9·8° to the left. Its sp.gr. is 0·8909. The chief part of it, when distilled with calcium chloride in a current of dry carbonic acid, comes over at 256°. It contains C 83·3, and H 11·8 p.c. coresponding with the formula $2C_{10}H_{16}.H_2O$.

The residual portion, which was almost entirely devoid of rotatory power, yielded C 87·89, and H 11·72 p.c., after having been rectified by means of sodium. This part of the oil consequently belongs to the terebenes $C_{10}H_{16}$. The fat oil, extracted by means of boiling ether from seed grown in Germany, previously finely powdered (necessarily including some essential oil which imparted to the other its fluorescence), amounted to 25·6 p.c. It is a fluid fat which does not congeal at 15°; it was found to consist chiefly of olein, besides which it yielded a considerable amount of a solid fatty acid, the crystals of which, after repeated purification, melted at 55°. The melting-point did not rise by recrystallisation, the acid being probably a mixture of palmitic and myristic acids.

Nigella seeds, powdered and dried over sulphuric acid, yielded 3·32 p.c. N, answering to about 21⅕ p.c. of albuminous matter.

It is stated in the Pharmacopœia of India that Nigella seeds are carminative, and they were formerly so regarded in Europe. In the East, generally, they are used as a condiment to food, and in Greece, Turkey, and Egypt, they are frequently strewed over the surface of bread and cakes in the same manner as anise or sesame. The fixed oil of the seeds is also expressed for use (Watts' Dict. 2nd edit., vol. vii. 852).

NIGHT BLUE. A colouring matter obtained by the action of *p*-tolyl-*a*-naphthylamine on tetramethyl diamido benzophenone. Resembles Victoria blue *v.* ANILINE BLUE.

NIGROSENE *v.* INDULINES.

NILE BLUE. The sulphate of dimethyl phenyl *p*-ammonium *a*-amido-naphthoxazine *v.* OXAZINE COLOURING MATTERS.

NIOBITE *v.* NIOBIUM.

NIOBIUM. *Columbium.* Symbol Nb. At. w. 93·9 (Krüss and Nilson, Marignac).

Niobium occurs with tantalum in many minerals; in *tantalite*, from Finland and Sweden (76 p.c. Ta_2O_5, 7·5 p.c. Nb_2O_5), and from Alabama and Dakota; in *columbite* from Massachusetts (28·5 p.c. $Ta_2O_5$51·5 p.c. Nb_2O_5); *niobite* from the Isergebirge (16·25 p.c. Ta_2O_5 62 p.c. Nb_2O_5 with a little zirconium, titanium, and tungsten) and *pyrochlore* from Siberia (51 p.c. Nb_2O_5). With cerium and its associated metals it occurs in *polycrase*, *euxenite*, *yttro-tantalite*, and *fergusonite.* It is also found in tinstone, pitchblende, and other minerals.

As obtained by Roscoe, niobium is a steel-grey metal of sp.gr. 7·06 at 15·5°, burning when gently heated in air or chlorine. It dissolves in concentrated sulphuric acid with formation of a colourless solution, but is only slightly attacked by hydrochloric or nitric acids, or by aqua regia. Niobium forms three oxides, Nb_2O_2, Nb_2O_4, and Nb_2O_5, and two chlorides, $NbCl_3$ and $NbCl_5$. The pentabromide, pentafluoride, oxychloride, oxybromide, oxyfluoride, and oxysulphide are known. Niobates and hexniobates produced from the pentoxide, and fluoniobates and fluoxyniobates which are combinations of alkaline-fluoride with niobium-pentafluoride and niobium-oxyfluoride respectively, have also been prepared.

NITRE. *Potassium nitrate v.* POTASSIUM.

NITRE, CUBIC. *Sodium nitrate v.* SODIUM.

NITRIC ACID *v.* NITROGEN.

NITRIFICATION. Nitrates are continually being produced in fertile soil; if they are removed by washing they are speedily replaced by a fresh formation. The production is greatest in the case of well-manured soils.

The occurrence of potassium nitrate as an efflorescence on soils, rocks, and old walls, especially in hot climates, has been long known. East Indian saltpetre is obtained by lixiviating the soil surrounding the house-drains in old villages (C. J. 1868, 318). The enormous deposits of sodium nitrate in the rainless tableland of Peru are of the highest technical importance.

The process of nitrification has in former years been artificially conducted on a large scale, nearly all the nitre employed on the continent of Europe being produced in this manner. This manufacture is now superseded, saltpetre being produced more cheaply at the present time by the reaction of sodium nitrate with potassium chloride. The nitre-yielding 'beds' or 'walls,' formerly constructed, consisted of porous earth, enriched with animal manure and wood ashes, watered at first with urine and afterwards with water. After two years the nitre-beds were sufficiently rich in nitre to be worth extraction; 1,000 lbs. of soil might then yield 5 lbs. of crude nitre. General information regarding this manufacture will be found in Dumas' 'Traité de Chimie.' The French mode of operation is described in detail in Boussingault's 'Agronomie, Chimie Agricole et Physiologie,' 2, 1861, 23.

Numerous theories have been held as to the manner in which nitrates are produced in soil. It has been assumed that nitrogen gas is oxidised in a moist porous soil by ordinary oxygen or by ozone, or that ammonia is oxidised in a similar manner, or by the ferric oxide generally present in soil. Nitrogenous organic matter is supposed to contribute to the production of nitre by acting as a source of ammonia or nitrogen gas. An account of most of the theories of this description will be found in a lecture on nitrification by Clöez (Leçons de Chimie et de Physique professées en 1861, à la Société chimique de Paris). The theories in question were in fact entirely unsatisfactory, as although nitrogen, ammonia, and many nitrogenous organic bodies could be oxidised by powerful means so as to yield nitric acid, chemists were unable to produce this acid under the conditions of a natural soil unless *soil itself was present.*

The first suggestion that nitrification might possibly be due to the action of a living organism came from Pasteur in 1862. A. Müller, in 1873, suggested that the process was due to a ferment. Schloesing & Müntz, in 1877, satisfactorily proved that nitrification was the work of a living agent. They showed in this and subsequent communications that the nitrifying agent could be transplanted from one medium to another, that its action was strictly limited by the conditions necessary for the life and activity of bacteria, and that its function was destroyed by temperatures (55°) and reagents (as chloroform), which are fatal to such organisms. The principal papers of Schloesing and Müntz are C. R. 84, 301; 85, 1018; 86, 892; 89, 891, 1074. The main conclusions were confirmed by Warington (C. J. 33, 44), and afterwards by many other investigators.

The nitrifying organism is one proper to the soil; it occurs also in sewage and in river water; it is not usually present in air or rain. The organism does not occur in soil beyond a certain depth below the surface. In the heavy soil at Rothamsted, Herts, out of 39 samples of soil of about 0·2 gram each, taken at various depths down to 3 feet, only *one* failed to produce nitrification when introduced into a weak urine solution. At 5 feet *one half* the samples failed to produce nitrification. Below 6 feet the soil had apparently no nitrifying power (C. J. 51, 1887, 118).

Schloesing and Müntz attempted to isolate the organism producing nitrification. After making many successive cultures in weak sterilised sewage, they found finally remaining a small round or oval coccus, which they believe to be the organism in question. No satisfactory proof was, however, given that they had obtained a pure culture. Attempts to isolate the organism by cultivation on gelatin have failed.

Lately, P. F. Frankland (Pr. 47, 296), by employing the dilution method of isolation has apparently succeeded in obtaining the organism in a pure state. When cultivated in an ammoniacal solution containing only mineral salts its form is that of a very short bacillus; grown in broth it becomes distinctly a bacillus. It is characteristic of the organism that when grown in ammoniacal mineral solutions it refuses to propagate on gelatin. From broth cultures a tardy growth on gelatin may be obtained. The organism is of very slow growth, and produces little, if any, turbidity in ammoniacal mineral solutions.

Still more recently the organism has been isolated by Winogradsky (A. de l'Institut-Pasteur, 1890, 213, 257). By successive cultivations in mineral solutions he had at last only two organisms present. In these cultures he observed the formation of gelatinous clots at the bottom of the vessel; these clots possessed the power of nitrifying in a high degree. He collected these clots, washed them, and spread them on gelatin. After ten days he seeded fresh ammoniacal solutions from those parts of the gelatin surface on which *no growth had appeared.* He thus obtained the organism pure. When young it is nearly round, but is most often ellipsoid; diameter, $0\cdot9$–$1\cdot0\mu$; length, $1\cdot1$–$1\cdot8\mu$. The longer ones show the strangulation preceding division; the form is occasionally spindle-shaped, with blunt ends. Chains of three or four individuals are rare. There are no spores. The organism is generally immobile, and collected at the bottom of the solution in a mass of zooglœa; but for a short period in the course of nitrification a general mobility sets in, and the liquid becomes turbid; a day after the organism is again in repose. Provisionally, the author designates it a *nitromonas.*

Little is yet known of the action of the organism when alone, nearly all the experiments on nitrification hitherto made having been confessedly performed with a mixture of organisms.

The substances which are nitrifiable by soil, or in solutions seeded with soil, are very numerous; they include ammonia, ethylamine, urea, asparagine, thiocyanates, albuminoids, gelatin, &c. In every case apparently in which an organic substance is nitrified the formation of ammonia precedes the formation of nitrous or nitric acid; ammonia, or rather ammonium carbonate, is thus perhaps the only nitrifiable substance. Whether the nitrifying organism is itself capable of attacking organic matter and producing ammonia, or whether the action of other organisms is necessary to effect the preliminary formation of ammonia, is yet undetermined.

The products of nitrification may be nitrites or nitrates. When nitrification takes place in a natural porous soil, only nitrates are produced. Nitrites appear in soil only as products of reduction when air is excluded by an excess of water. When nitrification is started in a solution by the addition of soil, the oxidation may be purely nitric in character, or nitrites may be abundantly formed in the earlier stages of the process—especially if the solution is strong, alkaline, and at a relatively high temperature—but in the end the nitrites are all converted into nitrates. If, however, successive cultures are made in sterilised ammoniacal solutions, starting with a solution nitrified by soil, a point is soon reached at which nitrites only are produced, and these nitrites never change into nitrates. An alkaline condition of the solution is highly favourable to this change in the character of the process. Some difference is thus established in the agent, and it is quite possible by seeding solutions from different sources to obtain a purely nitrous and a purely nitric process of oxidation in similar solutions and under identical external conditions. That the nitrites are not here a product of reduction is shown by their special formation in solutions of ammonium carbonate destitute of organic matter (*v.* also Munro's experiments, C. N. 56, 1887, 62). The nitrifying organism separated both by P. F. Frankland and by Winogradsky is found to be only capable of yielding nitrous acid. From these facts we must conclude, either that the oxidation of ammonia to nitrites, and of nitrites to nitrates, is a distinct process, performed by different organisms, or that the original organism producing nitric acid in the soil becomes weakened by continued cultivation in certain solutions, and loses its faculty of converting nitrites into nitrates. The true explanation is not yet known.

The oxidising power of the organisms in soil is by no means limited to the oxidation of ammonia or of organic matter. Müntz (A. Ch., May 1887) has shown that iodides may be converted into hypoiodites and iodates, and that bromides undergo a similar change. The oxidation of iodides is not apparently a secondary reaction of nitrification, for it may take place in the absence of nitrifiable matter. It is interesting to observe in this connection that iodates occur in the deposits of sodium nitrate in Peru.

The conditions under which nitrification takes place have been pretty well ascertained. For the nitrifying organism to act with vigour the substances necessary for its nutrition must be present. We should suppose, according to the accepted ideas respecting the nutrition of such organisms, that a supply of organic carbonaceous matter would be necessary; we have already stated, however, that the nitrifying organism has been found to flourish, and actively discharge its functions in purely inorganic solutions. Winogradsky has recently established this fact by rigorous experiments, and has shown, by determinations of carbon in the solutions, that the nitrifying organism is capable of producing organic matter from carbonic acid and ammonia without the aid of light. He suggests that, as in the animal body ammonium carbonate is converted into urea, so in this organism an amide may be the first compound produced.

For the nutrition of a living organism the presence of certain ash constituents is essential. It has been shown that nitrification cannot take place in the absence of phosphates (C. J. 45, 641). The necessity for other ash constituents has not yet been made the subject of experiment.

The presence of free oxygen is essential to nitrification. Schloesing (C. R. 77, 203, 353) has determined the rate of nitrification in soil containing different proportions of water, and maintained in atmospheres containing various proportions of oxygen. With soil holding 16 p.c. of water, a considerable amount of nitrification took place when 1½ p.c. of oxygen was present in the atmosphere, but the rate of nitrification increased fourfold when 21 p.c. of oxygen were present. An increase in the proportion of water to 24 p.c. raised the rate of nitrification in atmospheres containing a small percentage of oxygen, the quantity of *dissolved* oxygen being thus increased.

For nitrification to take place there must be some base with which the nitrous and nitric acid produced may combine. When a solution of ammonium carbonate or urea is nitrified, the action proceeds till one half of the nitrogen is oxidised, and then stops, ammonium nitrite or nitrate being the final product. The whole of the ammonia is nitrified only when an excess of base is present. The substance which acts best for this purpose is calcium carbonate; this is also the base usually present in soils. If the solution to be nitrified contains a soluble alkali, nitrification is hindered if the alkalinity exceeds a very small amount, and does not commence at all when the alkalinity is still further increased. The highest degree of alkalinity which has been found compatible with nitrification corresponded to 368 parts of nitrogen, as ammonium carbonate, per million of solution. With sodium monocarbonate the limit was nearly the same; with disodium carbonate a much smaller degree of alkalinity sufficed to prevent nitrification. The same distinction was found to exist between the basic and acid carbonates of ammonium.

It follows from what has been just stated that only weak urine solutions can be nitrified. In Warington's experiments a 12 p.c. solution was the maximum strength nitrifiable. This fact must be borne in mind when liquid manure or gas liquor is applied to land. If, however, an excess of gypsum is added to urine before the introduction of soil, solutions of far greater strength may be nitrified, the gypsum reacting with the ammonium carbonate as soon as it is formed, ammonium sulphate and calcium carbonate being produced (C. J. 45, 653; 47, 758). The favourable influence of gypsum on nitrification has been noticed by several investigators.

The activity of nitrification is largely dependent on temperature. The process has been shown to occur at temperatures as low as 3°. As the temperature rises the rapidity of the action increases, the optimum temperature being, according to Schloesing and Müntz, 37°. Above this point there is, according to the same authorities, a rapid decline, very little nitrification taking place at 50°, and beyond 55° there is no action. The influence of temperature is a point requiring further study.

In the case of solutions, darkness is far more favourable to nitrification than light. When a solution is exposed to a strong light, nitrification ceases altogether.

In a moist, aerated soil, at ordinary temperatures, the nitrification of an ammonium salt commences almost immediately after its application. When, on the other hand, a few milligrams of soil are introduced into a relatively large bulk of a suitable ammoniacal solution, a period of several weeks may elapse before nitric or nitrous acid appears, after which time nitrification will proceed with rapidly increasing speed. This long, so-called 'incubation period,' is probably due to the slow growth of the organism, and the difficulty it finds in adapting itself to altered conditions. If, when nitrification is completed, the solution is decanted, and the bottle filled up again with an ammoniacal solution similar to the first, nitrification will now commence in a comparatively short time, and by repeating this operation nitrification may be brought to begin in a few hours. When two solutions of different degrees of concentration are seeded with soil at the same time, nitrification will always commence first in the weaker solution.

The process of nitrification is suspended by a high temperature (55°), and by the presence of chloroform, carbon disulphide, phenol, mercuric chloride, and other bodies which are injurious to the life of bacteria. The drying of a soil, even at a low temperature, is fatal to the nitrifying organisms which it contains.

If both organic matter and denitrifying organisms are present, all nitrates present may be destroyed; the nitrifying organism is, however, uninjured, and will resume its activity as the organic matter disappears.

Natural soils and river waters usually contain both nitrifying and denitrifying organisms, and the character of the process which occurs is determined by the conditions of the moment. The same soil which rapidly nitrifies when in a moist, aerated condition, becomes a vigorous denitrifying medium when waterlogged. The nitrifying river water becomes denitrifying when polluted with sewage. The products of denitrification are various, according to the nature of the organisms present; nitrites, nitric oxide, nitrous oxide, or nitrogen gas may be produced. In the case of the three last-named products there is, of course, a loss of nitrogen in the form of gas. For the literature of the subject, *v.* C. J. 53, 1888, 742. Müntz has shown that chlorates, bromates, and iodates are reduced equally as nitrates.

The following references may be of use: *The Conditions of Nitrification*—Schloesing (C. R. 77, 203, 353), Warington (C. J. 35, 429; 45, 637), Munro (C. J. 49, 632); *The Nitric Acid in Soils*—Lawes, Gilbert, and Warington (J. R. A. S. 1883, 331), Lawes and Gilbert (C. J. 47, 380), Dehérain (A. a. 1888, 287); *The Nitrification of Manures*—Dehérain (A. a. 1887, 241), Schloesing (C. R. 109, 423, 883); *The Nitric Acid in Drainage and Well Waters*—Lawes, Gilbert, and Warington (J. R. A. S. 1881, 241, 311; 1882, 1; C. J. 51, 500). R. W.

NITROALIZARIN *v.* ALIZARIN AND ALLIED COLOURING MATTERS.

NITROBENZENE $C_6H_5NO_2$ was first prepared by Mitscherlich in 1834 by the action of strong nitric acid upon benzene, and was termed by him 'nitrobenzide.' It is a light-yellow refractive liquid of sp. gr. $\frac{0}{4}$ 1·200, boils at 210°, and solidifies at 3°. Has a peculiar smell of bitter almonds and a sweet, burning taste. Is poisonous. Is very slightly soluble in water but readily soluble in alcohol, ether, benzene, and strong nitric acid. By the further action of strong nitric acid is converted into a mixture of isomeric *dinitrobenzenes* $C_6H_4(NO_2)_2$. *Ortho-dinitrobenzene* crystallises from water or acetic acid in needles, and from alcohol or chloroform in monoclinic tables, m.p. 117°·9. *Meta-dinitrobenzine* crystallises in thin rhombic tables, m.p. 89·9, and is the main constituent of the product obtained by nitrating benzene on the large scale. *Para-dinitrobenzene* forms monoclinic prisms, m.p. 171°. For the preparation of the nitrobenzenes on the large scale *v.* BENZENE AND ITS HOMOLOGUES.

Trinitrobenzene $C_6H_3(NO_2)_3$ is prepared by acting on meta-dinitrobenzene with a mixture of strong nitric acid and fuming sulphuric acid. Forms small rhombic tables, m.p. 121–122°.

NITROCINNAMIC ACID *v.* CINNAMIC ACID.

NITROCRESOL *v. Cresol*, art. PHENOL AND ITS HOMOLOGUES.

NITROGEN. Symbol N. At. w. 14. Nitrogen was discovered in 1772 by Rutherford, Professor of Botany in the University of Edinburgh. He found that when a small animal was allowed to breathe air in a confined space for a time, and the carbon dioxide thereby produced removed by absorption, a gas still remained which was incapable of supporting respiration. Lavoisier first established the individuality of this gas, and clearly demonstrated its existence in the atmosphere. From its incapacity to support life he gave it the name of *azote*; the name nitrogen, denoting that the gas is an essential constituent of nitre, was subsequently given to it by Chaptal.

Occurrence.—Nitrogen is one of the most widely diffused of the elements, and occurs free in the air, of which it constitutes four-fifths by volume. Volcanic gases contain considerable quantities of nitrogen, and the air-bladders of certain fishes, the bone-cavities of many birds, as well as the cavities of plants, all contain the gas in the free state. It occurs in many meteorites. The nebulæ consist, in part, of free nitrogen, and it is contained in the atmosphere of the sun.

Nitrogen, in a state of combination with oxygen, exists in the air as nitric and nitrous acids, and combined with hydrogen as ammonia. Nitrogen is an essential constituent of animal and vegetable organisms, and is found in many minerals, but chiefly in saltpetre or potassium nitrate, and Chili saltpetre or sodium nitrate.

Preparation.—1. By the action of burning phosphorus on a confined portion of air, in a bell-jar standing over water, phosphoric oxide is formed, which easily dissolves in the water. Many other substances which will combine with the oxygen and form compounds easily removed may be employed for preparing nitrogen from air, as a mixture of iron filings and sal-ammoniac moistened with water, moistened lead shavings, and moistened sulphides of the alkaline metals.

2. By passing air over copper heated to redness. In this method a large amount of copper is required, especially when copper turnings are employed, as the coating of oxide formed soon retards and ultimately stops the action. This inconvenience is overcome by mixing the air with ammonia previously to passing it over copper; the cupric oxide being reduced by the ammonia as fast as it is formed, with the production of nitrogen and water. A length of three inches of copper turnings in a glass tube heated by a Bunsen burner, is quite sufficient to effect the decomposition, any excess of air showing itself by tarnishing the surface of the copper (Harcourt).

3. By placing a strong solution of cupric chloride in hydrochloric acid in contact with copper turnings, cuprous chloride is formed, and this absorbs oxygen from the air, the cuprous chloride being reconverted into cupric chloride,

$$Cu_2Cl_2 + 2HCl + O = 2CuCl_2 + OH_2.$$

4. By passing chlorine through a strong solution of ammonia

$$8NH_3 + 3Cl_2 = 6NH_4Cl + N_2.$$

It is necessary in this method to keep the ammonia in excess, otherwise the chlorine reacts on the ammonium chloride and forms nitrogen chloride. According to Anderson (C. N. 5, 246), the nitrogen obtained by this method is always mixed with oxygen. The nitrogen may be washed from admixed ammonia by passing it through sulphuric acid.

5. By adding metallic zinc to fused ammonium nitrate.

6. By saturating oil of vitriol with nitric oxide gas, adding ammonium sulphate, and heating to 130°.

7. By heating ammonium nitrite

$$NO_2NH_4 = 2OH_2 + N_2.$$

8. By heating a mixture of potassium nitrite (more readily obtained than the corresponding ammonium salt) and ammonium chloride

$$KNO_2 + NH_4Cl = KCl + 2OH_2 + N_2.$$

This is the easiest method of obtaining pure nitrogen. The solution of potassium nitrite may be prepared by passing the gases evolved from starch and nitric acid into a solution of caustic potash of sp.gr. 1·38 till it acquires a distinctly acid reaction, when it is to be neutralised by further addition of alkali. This solution undergoes no change by keeping, and, when required to yield nitrogen, may be mixed with three times its volume of concentrated solution of ammonium chloride.

9. By heating a mixture of dry ammonium nitrate and solid ammonium chloride

$$NH_4NO_3 + NH_4Cl = Cl_2 + 12OH_2 + 5N_2.$$

The chlorine may be absorbed by passing the gases through milk of lime.

10. By heating a mixture of potassium dichromate and ammonium chloride

$$K_2Cr_2O_7 + 2NH_4Cl = 2KCl + 4OH_2 + Cr_2O_3 + N_2.$$

11. Pure nitrogen may be obtained by putting in a flask of 10 to 14 litres' capacity about 200 grams of copper turnings and partly covering

them with aqueous ammonia, the flask being then closed by a cork fitted with a safety-tube and a gas delivery-tube stopped at the end with a caoutchouc cap. If the flask be shaken from time to time the whole of the oxygen will be absorbed in a day or two. The nitrogen may then be transferred to another flask by pouring in water previously freed from oxygen by means of copper and ammonia, and washed with sulphuric acid (Berthelot, Bl. [2] 13, 314).

Properties.—Nitrogen is a colourless, inodorous, tasteless, neutral gas, of sp.gr. 0·972 (air = 1); one litre of the gas at 0°C. and 760 mm. weighs 1·256167 grams, or 100 cubic inches at 60°F. and 30 inches barometer pressure weigh 30·052 grains (Regnault). It is slightly soluble in water; 100 vols. of water dissolve 1½ vols. of nitrogen at 15°C. The solubility of nitrogen in water at various temperatures may be expressed by the formula

$$C = 0{\cdot}020346 - 0{\cdot}00053887t + 0{\cdot}00001156t^2.$$

The gas is rather more soluble in alcohol than in water.

Nitrogen is incombustible and does not support combustion; it is not poisonous, but animals when immersed in the gas die for want of oxygen.

Nitrogen has been liquefied by the cold produced by its expansion from a compression of 300 atmospheres at +13°C. Liquid nitrogen boils at −193° under atmospheric pressure. Under a pressure of 60 mm. liquid nitrogen solidifies, the temperature during solidification being −214°, and by further reduction of the pressure the whole of the nitrogen can be solidified to a snow-like mass. Under a pressure of 4 mm. the solid nitrogen has a temperature of −225°, the lowest temperature that has yet been measured (K. Olszewski, C. R. 100, 350–352).

In the free state nitrogen is most remarkable for its inactivity. It may, however, be made to unite directly with boron, silicon, magnesium, titanium, tantalum, and tungsten, and, under certain conditions, with hydrogen, oxygen, and carbon, as, *e.g.*, when a series of electric sparks is passed through oxygen and nitrogen gases standing over a solution of caustic alkali, when a nitrate of the metal is produced. Traces of nitric acid and ammonium nitrate are produced by burning hydrogen gas mixed with nitrogen in an atmosphere of air or oxygen. Nitrogen can unite with hydrogen when one or both the gases are in the nascent state, to form ammonia. Carbon and nitrogen unite directly when nitrogen gas or atmospheric air is passed over an ignited mixture of charcoal and potash, or charcoal and baryta.

There are two characteristic spectra of nitrogen, both obtained by passing the spark from an induction coil through a Geissler's tube containing a small quantity of highly rarefied nitrogen gas. The nitrogen spectrum commonly obtained in this way is a channelled one, exhibiting a large number of bright bands, especially numerous in the violet. If the spark is produced by high tension, as when a Leyden jar is used, a spectrum of numerous fine lines distributed throughout the length of the spectrum will be obtained (Plücker).

Nitrogen is an essential constituent of many of the most potent and valuable medicines, as well as of some of the most powerful poisons, *e.g.*, quinine, morphine, prussic acid, and strychnine. The slight affinity existing between nitrogen and other elements gives a peculiar character to its compounds, many of which are extremely prone to decomposition, as, *e.g.*, azotised principles of animal and vegetable organisms. Many nitrogen compounds, especially those which contain the oxygenated radicle *nitryl* (NO_2), are highly explosive, as in the case of the picrates, certain azo- compounds, gun-cotton, the fulminates of silver and mercury, nitroglycerine, &c.

HALOID COMPOUNDS OF NITROGEN.

Nitrogen chloride NCl_3 may be prepared by electrolysis of a concentrated solution of ammonium chloride, or by passing chlorine into a warm solution of ammonium chloride.

It is also formed as oily drops which fall to the bottom of the vessel, on suspending a fragment of ammonium chloride in a solution of hypochlorous acid, or when a jar of chlorine gas is inverted over a solution of ammonium chloride in a leaden vessel.

Nitrogen chloride is a thin yellowish, volatile, very pungent oil of sp.gr. 1·653, boiling at 71°, and never hitherto solidified (Pelouze and Fremy). It detonates with emission of light when heated to between 93° and 100°, or when brought into contact with organic matters such as turpentine, phosphorus, and oils. Alkalis also determine its detonation, but metals and strong acids, resins, or sugar have not that power. It explodes on exposure to strong light.

In water it decomposes spontaneously with formation of chlorine, nitrogen, hydrochloric and nitrous acids.

This compound appears to be produced by the replacement of all the hydrogen in ammonia by chlorine. The formula NH_2NCl_4 has been attributed to it, but, according to Gattermann (B. 21, 751), it may be obtained of the composition NCl_3 by washing the oil free from ammonia and treating it with a stream of chlorine for some time.

Nitrosyl chloride, *nitrous oxychloride*, or *chloronitrous gas*, NOCl, may be produced by the direct action of nitric oxide on chlorine, or by the action of phosphorus pentachloride on potassium nitrite, and is one of the products obtained by heating a mixture of nitric and hydrochloric acids.

It is an orange-yellow gas condensing to an orange-coloured liquid in a freezing mixture, and boiling at −8°.

Nitrogen iodides. On digesting powdered iodine with aqueous ammonia, a black powder is obtained which, when dried, detonates when touched or heated, with evolution of iodine vapours.

When left in water, or when washed, it slowly decomposes, especially when exposed to sunlight. The presence of ammonia retards the decomposition.

The composition of this body differs with different modes of preparation.

J. W. Mallet (C. N. 39, 257) states that the iodide of composition NI_3 may be prepared as follows:—Iodine is precipitated in a fine state of division from an alcoholic solution by addition of water, and is triturated at 0° with the strongest ammonia, which is then poured off. The residue is washed repeatedly with the strongest ammonia, then with alcohol of 95 p.c., followed by absolute alcohol, and finally by one washing with ether, after which the iodide is dried in a current of air. All the washings are conducted at 0°C.

Nitrogen iodides dissolve in sodium thiosulphate, giving sodium iodide, ammonium sulphate, and free ammonia; and in potassium cyanide with evolution of nitrogen.

See further Guyard (A. Ch. [6] 1, 358) and Raschig (A. 230, 212).

Nitrogen bromides and oxybromides. Nitrogen bromide is a dark-red highly volatile oil, as explosive as the chloride, obtained by addition of potassium bromide to chloride of nitrogen under water.

Three oxychlorides appear to exist—nitrosyl bromide NOBr, boiling at −2° (Landolt); nitrosyl dibromide $NOBr_2$, boiling at 30–50° (Muir); and nitrosyl tribromide $NOBr_3$, boiling at 50–53° (Muir). Frölich (A. 224, 270) regards the two latter compounds as mixtures of nitrosyl monobromide with bromine.

Nitrogen fluoride. By the electrolysis of a solution of ammonium fluoride, H. N. Warren (C. N. 55, 289) has obtained oily drops at the negative pole, which explode violently when connected with the positive pole, or in contact with organic matter, glass, or silica. This compound is doubtless the fluoride.

NITROGEN SULPHUR COMPOUNDS.

Nitrogen sulphide SN or S_2N_2 is obtained in small quantities by passing dry ammonia through a solution of sulphur dichloride in 10 or 12 volumes of carbon bisulphide: $8NH_3 + 3S_2Cl_2 = 6NH_4Cl + 2NS + S_4$.

Nitrogen sulphide crystallises in yellowish-red rhombic prisms, and is stable in dry or moist air. It deflagrates at about 207°, and explodes when struck, but less easily than mercury fulminate.

Nitrogen sulphide combines with sulphur chlorides in several proportions (*v.* Demarçay, C. R. 91, 854, 1066; 92, 726).

A series of compounds derived from *sulphonitro-acids* have been described by Fremy (A. Ch. [3] 15), Claus and Koch (A. 152, 336), Berglund (B. 9, 254, 1896), and Raschig (B. 20, 584; A. 241, 180). They are prepared by the action of sulphurous acid on potassium nitrite, or of potassium nitrite on potassium sulphite, but are of no technical interest.

Nitrosulphonic acid $SO_2.NO_2.OH$ is obtained by passing sulphur dioxide into cold fuming nitric acid: $SO_2 + NO_2OH = SO_2NO_2.OH$; or by passing nitrosyl chloride into sulphuric acid: $NOCl + SO_2(OH)_2 = SO_2NO_2OH + HCl$; or by treating sulphuric acid with nitrogen peroxide: $2NO_2 + SO_2(OH)_2 = SO_2.NO_2.OH + HNO_3$. Forms four-sided rhombic prisms, or nodular masses. M.p. *c.* 30°. Dissolves in concentrated H_2SO_4 without decomposition; solution can be distilled. Decomposed by water into nitrous and sulphuric acids. On heating gives *nitrosulphonic anhydride* $(SO_2)_2O(NO_2)_2$ and H_2SO_4 (Michaelis, B. 7, 1075), which forms colourless quadratic prisms. M.p. 217°; b.p. 360°.

NITROGEN OXIDES AND OXYACIDS.

Nitrous oxide. *Nitrogen monoxide*, or *protoxide; laughing gas*, N_2O.

This gas, which was first obtained by Priestley in 1772, by the action of easily oxidisable substances, such as potassium sulphide, sulphites, &c., on nitric oxide, may be prepared by digesting zinc in a mixture of equal parts of nitric and sulphuric acids diluted with 8 or 10 parts of water, or by dissolving zinc in dilute nitric acid.

According to Campari (C. C. 1888, 1569) a regular evolution of very pure nitrous oxide is obtained by heating to boiling a mixture of 5 parts stannous chloride, 10 parts hydrochloric acid of sp.gr. 1·21, and 0·9 parts of nitric acid of 1·38 sp.gr. These proportions should be adhered to or the gas is liable to be evolved with explosive irregularity.

It is, however, usually prepared by the distillation of ammonium nitrate free from ammonium chloride: $NH_4NO_3 = N_2O + 2H_2O$.

The salt is dried thoroughly below 200°C. and placed in a flask and heated gradually until ebullition occurs. The heat should then be carefully moderated, as the salt is liable to too rapid decomposition and to contain in consequence nitrogen and nitric oxide.

When the nitrate contains ammonium chloride, the gas invariably contains chlorine.

The gas, which is collected over hot water, brine, or mercury, may be freed from nitric oxide &c. by agitation with ferrous sulphate.

Cazeneuve (J. Ph. [5] 11, 67) attributes the irritating action of the impure gas on patients to the presence of hyponitrous acid, which is also absorbed by ferrous sulphate.

Nitrous oxide is a colourless gas of pleasant odour and sweetish taste. At 30 atmospheres pressure and 0° temperature it liquefies to a colourless, mobile liquid, miscible with alcohol and ether, and having a refraction equivalent lower than that of any other liquid. The liquid boils at −92° (760 mm.), and may be frozen to a transparent solid which melts at −99° (Wills). Its density at 0° is 0·9004 according to Wills, and 0·937 according to Andréeff, while, according to Cailletet and Mathias (C. R. 102, 1,202), who have also determined the density of its saturated vapour between −28° and +33·9°, its density at −2·2° is 0·912, at −20·6° is 1·002, and at +23·7 is 0·698.

Ignited charcoal floats and burns brilliantly on the liquid.

Water absorbs 1·3 volumes of the gas at 0°, 0·78 volumes at 15°, and 0·61 volumes at 24°. The gas is also soluble in alcohol and ether, and in fixed and volatile oils.

Nitrous oxide gas supports the combustion of phosphorus, carbon, sulphur, &c., nearly as well as oxygen, provided the combustible has previously been heated to a sufficient temperature to start the decomposition of the gas into its components.

Potassium and sodium, when slightly heated in the gas, produce the peroxides, but when strongly heated they form the nitrates.

Nitrous oxide is a valuable anæsthetic, and is largely employed for producing insensibility during short operations. Prolonged inhalation of the gas causes death. When mixed with about one-fourth its volume of oxygen, inhalation of the gas produces a species of transient intoxication.

Hyponitrites may be regarded as salts of this oxide.

Nitric oxide. *Nitrogen dioxide, deutoxide* or *binoxide*; *nitrosyl* NO.

This gas may be produced by the action of nitric acid on copper, silver, mercury, zinc, &c., or on phosphorus and certain easily oxidisable bodies. It is usually prepared by dissolving copper in nitric acid of sp.gr. 1·2, and washing the gas through water and soda, and collecting over water

$$3Cu + 8HNO_3 = 2NO + 3Cu(NO_3)_2 + 4H_2O.$$

The purest product is obtained by conducting the operation at the lowest possible temperature, but nitrogen and nitrous oxide are always present. The pure gas may be obtained by passing the gas through concentrated ferrous sulphate solution, which produces a soluble compound $2FeSO_4.NO$, from which the gas is re-obtained on heating. Other ferrous salts have a similar action. The gas may also be absorbed by concentrated solutions of alkaline permanganates or chromic acid.

Pure nitric oxide may be obtained by adding potassium nitrate to an acid solution of ferrous chloride obtained by digesting iron filings in concentrated hydrochloric acid until all action ceases, decanting and adding an equal bulk of hydrochloric acid (Pelouze). A mixture of 30 grams of nitric acid and 240 grams of ferrous sulphate is decomposed by pouring upon it 250 c.c. of dilute sulphuric acid (1 to 3).

According to Kaemmerer (B. 18, 3,064) a constant evolution of nitric oxide is produced by adding concentrated sulphuric acid as required to a mixture of copper turnings and cold concentrated ammonium nitrate solution contained in a Woulffe's bottle.

Nitric oxide is a colourless gas of sp.gr. 1·039 (Berard); its odour, on account of its immediate combination with oxygen on exposure to the air, is unknown. It has been liquefied by Cailletet (C. R. 85, 1017) under a pressure of 104 atmospheres at $-11°$, but at $+8°$ cannot be liquefied even at 270 atmospheres, so that the critical point is probably between those temperatures. According to Olzewski (C. R. 100, 940) the liquid solidifies to a snow-like mass at $-153·6°$ at 138 mm. pressure. Its density shows that its formula is NO and not N_2O_2 as formerly supposed. Daccomo and Victor Meyer (B. 20, 1832) have shown that, even at $-100°$ its density corresponds to NO. Nitric oxide is the most stable of the nitrogen oxides, and is not decomposed even at a red heat. When moist, however, it may be decomposed by the electric spark into nitric acid and nitrogen. Carbon, phosphorus, and potassium, burn brilliantly in the gas when fully ignited before immersion; but sodium and sulphur do not burn. A mixture of nitric oxide and carbon bisulphide burns with a bright flash on ignition. The flame is so rich in actinic rays that a lamp in which the mixture burns has been designed by Sells (B. 7, 1,522) for photographic purposes.

Nitric oxide combines with oxygen with production of the ruddy fumes characteristic of the peroxide. Nitric oxide dissolves rapidly in nitric acid, producing a reddish-brown, green, or blue solution, according to the strength of the acid, the blue solution being obtained with the weakest acid. With acid of below 1·15 sp.gr. but little absorption occurs, and the liquid remains colourless.

This oxide has been proposed for use as a disinfectant (Suillot, Bl. [2] 35, 356).

Nitrous anhydride, or **trioxide**, N_2O_3.

This oxide is said to be obtained by passing a mixture of 1 volume dry oxygen and 4 volumes dry nitric oxide through a red-hot tube.

It is, however, usually prepared by heating 1 part of starch in a capacious retort with 8 parts of nitric acid (1·25 sp.gr.) and drying the gas over calcium chloride and liquefying it by passage through a U-tube surrounded by a freezing mixture. Arsenious acid may replace the starch.

According to Lunge (C. J. 1885, 457; and B. 11, 1641), when arsenious acid is used with strong nitric acid (1·5) the gas evolved consists of nine-tenths of nitric peroxide and one-tenth of nitrous anhydride, but Ramsay and Cundall (J. C. S. 1885, 187) prefer to use acid of that strength for preparing the anhydride. According to Lunge (B. 11, 1229), pure nitrous anhydride is obtained by adding nitric acid (1·33 sp.gr. at 20°) to a thick emulsion of starch heated on a water-bath.

Pure nitrous anhydride may be prepared from the bluish-green mixture of nitrous anhydride and nitric peroxide by passing through the warmed liquid a current of nitric oxide and conveying the mixed gases through a heated glass tube, and finally through a U-tube in a freezing mixture. The peroxide is thus said to be reduced to the anhydride, and a liquid which is dark-blue at ordinary temperatures, and indigo-blue at $-10°$, is obtained. This liquid, however, always contains a little peroxide, even after repeated rectification, on account of the decomposition of the anhydride. Moser (P. [2] 2, 139) has shown that the absorption spectra of nitrous anhydride and nitric peroxide are identical, thus indicating at least partial decomposition of the former.

The liquid is highly unstable, and decomposes completely into nitric oxide and peroxide when warmed. Ramsay (J. C. S. March 1890) has shown that it is unstable even at $-90°$.

A small quantity of water at low temperature converts the anhydride into nitrous acid with production of a green liquid, but a larger proportion decomposes it with effervescence into nitric acid and nitric oxide. The anhydride dissolves, however, in a large proportion of ice-cold water with production of nitrous acid.

Nitrous anhydride condenses at $-14·4°$ at 755 mm. pressure. Ramsay (C. J., March 1890) has failed to freeze it even at $-92°$. According to Geuther (A. 245, 97) it boils at 3·5° and has a sp.gr. of 1·449 at 0°.

Passage of oxygen through the liquid anhydride very slowly converts it into the peroxide. The cause of this action is not evident, as an inert gas, such as carbon dioxide, has a similar effect (Ramsay, *l.c.*).

Nitrous anhydride does not appear to exist in the gaseous state. According to Lunge, however, it can exist as gas even in presence of a large excess of air, and at temperatures as elevated as 150°, although the greater part is dissociated on evaporating the liquid.

Lunge (C. J. 1885, 465) considers this oxide to be the carrier of oxygen in the sulphuric acid chamber, according to the equations:—

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2(SO_2.HO.NO_2)$$
$$2SO_2HONO_2 + H_2O = N_2O_3 + 2SO_2(HO)_2.$$

Nitrogen peroxide or **tetroxide.** *Hyponitric acid* N_2O_4 or NO_2. This oxide may be prepared by the combination of nitric oxide with oxygen, or preferably by heating lead nitrate in a glass retort, $Pb(NO_3)_2 = PbO + 2NO_2 + O$, the vapour being condensed by passage through a U-tube in a freezing mixture. A slow current of oxygen is passed through the liquid for a long time to ensure oxidation of any nitrous anhydride when the pure peroxide is required and the liquid is redistilled.

It may also be prepared by heating nitric acid of 1·39 sp.gr. with small lumps of arsenious acid, the distillate being subjected to a current of oxygen and redistilled as above. Groves recommends the use of a mixture of 2 parts of nitric acid and 1 part of sulphuric acid for treating the arsenious oxide.

According to Ramsay (C. J., March 1890) the peroxide is best prepared by adding the liquid distillate from the action of nitric acid on arsenious acid to the solution of nitric anhydride obtained by adding phosphorus pentoxide to nitric acid (*v. Nitric anhydride*). After agitation the upper layer is decanted and redistilled.

Nitrogen peroxide at ordinary temperatures is an orange-coloured liquid boiling at 21·64° at 760 mm. (Thorpe), and solidifying on cooling to colourless crystals, which melt at $-10°$ (Deville and Troost). Its sp.gr. at 0° compared with water at 4° is 1·4903 (Thorpe). At a temperature slightly above its freezing-point the liquid is colourless, but at higher temperatures it passes from greenish yellow to yellow at 10°, orange at 15°, and still darker at higher temperatures.

Addition of water to the liquid peroxide produces a change of colour, passing from its original orange colour through shades of yellow, green, and blue, and finally becoming colourless, while nitric oxide is evolved with production of nitric acid: $2H_2O + 3N_2O_4 = 2NO + 4HNO_3$.

The different tints of the solution are caused by the solution of the nitric oxide in the nitric acid as the strength of the acid increases, as described under *Nitric oxide*. Nitric peroxide is rapidly and completely absorbed by sulphuric acid of 1·71 sp.gr. with production of a mixture of nitrosulphonic and nitric acids (Lunge, B. 12, 357) $N_2O_4 + H_2SO_4 = SO_2HONO_2 + HNO_3$.

The vapour of this oxide has a peculiarly repulsive odour. Potassium burns in it spontaneously. When heated the gas becomes darker and at 38° becomes almost opaque. Richardson (C. J. 1887, 397) has shown that the gas again becomes colourless when heated to 500° at the ordinary pressures. Ramsay (C. J. 1885, 678) had previously observed this change at a red heat.

Richardson attributes the change to the decomposition of the peroxide into nitric oxide and oxygen, for on strongly heating one limb of a bent tube containing the gas, while the other limb is immersed in a freezing mixture, a blue liquid characteristic of nitrous anhydride—produced by the combination between the peroxide and dioxide—is obtained, while free oxygen may be found in the gas if the tube be opened immediately after heating.

The vapour density of the gas is also found to decrease, until at 619°·5 it corresponds to complete dissociation into NO + O.

The vapour density of the gas shows that at different temperatures it contains a mixture of NO_2 and N_2O_4. The experiments of Deville and Troost (J. 1867, 177) prove that at 26·7° the gas contains 20 p.c. of NO_2 and 80 p.c. N_2O_4, while at 140° the whole consists of NO_2. The liquid peroxide has been employed in the manufacture of explosives (Setlick, C. C. 1888, 461).

Nitric anhydride. *Nitrogen pentoxide* N_2O_5. This compound was originally obtained by Deville by passing a slow current of dry chlorine over dry silver nitrate contained in a U-tube, heated in a water-bath to 95°. When the reaction commences the temperature is lowered to 60°, after which the decomposition continues uniformly. The anhydride is condensed in a bulb containing a freezing mixture.

It may, however, be best prepared by adding phosphoric oxide to the strongest nitric acid, with constant cooling. The syrupy liquid produced is poured into a dry retort, and distilled into a receiver surrounded by a freezing mixture. The orange-red distillate separates into two layers, the upper of which is poured into a stoppered tube and cooled in ice. The separated crystals of the anhydride are separated, again melted and crystallised, and again separated from the mother-liquor.

Nitric anhydride forms white, colourless, transparent, brilliant, six-faced prisms, melting at 20–30° (Deville) to a dark-yellow liquid, boiling at 45° to 50°. When heated suddenly the crystals decompose into nitrogen peroxide and oxygen with explosive violence. Such decomposition is sometimes spontaneous. Phosphorus and potassium burn brilliantly on the warmed anhydride. Charcoal does not affect the liquid, but burns in the vapour.

Nitrogen anhydride combines with nitric acid to produce a compound $N_2O_5.2HNO_3$, which is liquid at ordinary temperatures but crystallises at 5°. This body forms the heavy layer in the above distillate obtained in the preparation of the anhydride.

Nitrogen hexoxide NO_3 or N_2O_6. This substance is supposed to be obtained by passage of the silent electric discharge through oxygen containing at least one seventh its volume of nitrogen (*v.* Hautefeuille and Chappuis, C. R. 92, 80 and 94; 946 and 1306).

Nitric acid. *Aqua fortis* HNO_3. The composition of this acid was first shown in 1785 by Cavendish, who obtained it by passage of electric sparks through a mixture of pure nitrogen and oxygen in presence of a solution of caustic potash. The fact that nitric acid contained oxygen had previously been shown by Lavoisier (1776), and Priestley had observed the production, with reduction of volume, of a substance which turned blue litmus red on passage of electric sparks through air.

Nitric acid is also obtained when a hydrogen flame burns in a flask into which oxygen is admitted in quantity insufficient to displace all the air, or when ammonia burns in oxygen.

Boussingault (C. R. 95, 1,121) has found amounts of nitric acid in the rain falling on the Alps up to 0·66 milligram per litre. The rain containing the largest proportion of nitric acid contained also 0·3 milligram of ammonia.

The immense deposits of alkaline nitrates in Chili, &c., are supposed to be produced by putrefaction of nitrogenous organic matters—in many cases of marine origin, as in the deposits of Tarapaca—by conversion into ammonia and oxidation of that substance, in presence of alkalis, into nitrates. Nitrates so produced are usually observable as incrustations on the walls of stables, &c., in dry situations, where putrescible nitrogenous matters accumulate (*v.* further SODIUM NITRATE).

In the laboratory nitric acid is usually prepared by heating dry potassium or sodium nitrate with concentrated sulphuric acid in a retort whose neck passes down the long neck of a carefully-cooled glass receiver. No luting must be used on account of the powerful action of the acid.

The yellowish distillate, which contains nitrogen peroxide and water, is re-distilled with its own volume of concentrated sulphuric acid, and a current of air is passed through the gently-warmed liquid to remove all traces of the tetroxide. Acid may thus be obtained of 99·8 p.c. HNO_3.

The acid known as *fuming nitric acid*, which contains a large proportion of the lower oxides of nitrogen, may be prepared by the following process (Brunner, D. P. J. 159, 385). 100 parts of potassium nitrate is triturated with 3½ parts of starch, and the mixture is covered in a retort with 100 parts of sulphuric acid of 1·85 sp.gr., the retort being of such size as to be then only one-third full. The distillation commences without warming, but a gentle heat may be applied at the end. 60 parts of deep red fuming nitric acid is thus obtained. Other reducing agents, such as sulphur, might replace the starch.

On the manufacturing scale sodium nitrate (Chili saltpetre) is always used, on account of its cheapness and the relatively large proportion of nitric acid which it yields. Cast-iron retorts are used instead of glass vessels, and the temperature employed is much higher than in the laboratory. In England cylindrical retorts 2 feet wide and 5 feet long are usually employed. Their ends, which, to minimise cooling, each consist of a single stone flag, connected with the retort by iron lute (*v.* LUTES), are free, one being fixed and having a pipe for conveying away the vapours, while the other is used for charging and discharging. A small opening serves for the introduction of the nitre, while a pipe, normally closed by a ground-in iron stopper, is employed for running off the fluid residue. A hole and an S-shaped funnel in the main lid permit running in of the acid.

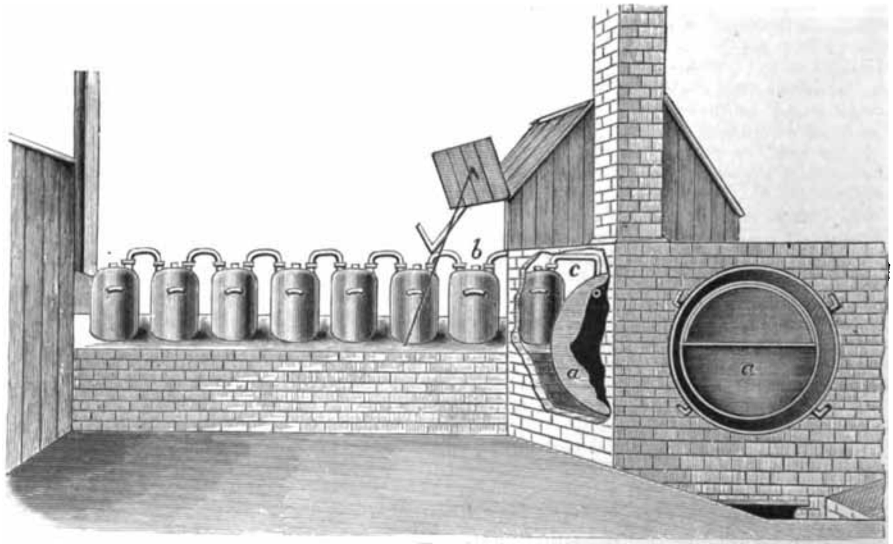

FIG. 1.

Fig. 1 shows a plant commonly employed, *a* being the retort, of which two are heated in each furnace; *b* the receivers, and *c* the tube connecting the retort with the first receiver. The upper part of the retort is sometimes lined with acid-proof bricks, but the acid has no action if the temperature is sufficiently elevated to prevent condensation.

Theoretically, 85 parts of sodium nitrate are decomposed by 49 parts of the strongest sulphuric acid, with production of the normal sodium sulphate and evolution of 63 parts of nitric acid; but to minimise the decomposition of the nitric acid into nitrogen peroxide, it is preferable to use a weaker sulphuric acid, 140–148°Tw. It is also usual to employ 20–30 p.c. more sulphuric acid than the theoretical amount, because the presence of a proportion of the highly fusible sodium *bisulphate* permits the withdrawal of the exhausted charge in a liquid condition, whereas if the residue consists of the less fusible *normal* sulphate it can only be removed in the solid condition after cooling.

When the acid is made at works where salt is decomposed, even more sulphuric acid than the above is employed, the residual 'cylinder cake' or 'nitre cake' being mixed with the salt to be decomposed in the salt cake pans (*v.* Lunge, Sulphuric Acid and Alkali, i. 125).

In the plant illustrated in fig. 1, the charge for one retort comprises 305 kilos. of sodium nitrate and 240 of sulphuric acid, the time occupied by the heating being 18 hours. Sufficient water is usually put in the receivers to produce an acid of 1·35 sp.gr. The amount of nitric acid produced is about 363 kilos.

When stronger acid is required, no water is placed in the receivers. In such a case nitric acid of 77°–82°Tw. is produced from sulphuric acid of 144°Tw. The strongest commercial acid, that of 106°Tw., is prepared from strong vitriol and dried saltpetre.

In some works the retorts are composed of semicylindrical troughs with broad flanges and vertical rims all round, closed by a brick arch or stone slabs.

Fig. 2 shows a plant employed in many continental works. A cast-iron pot C, 4 feet wide and 4 feet high, and having at the top a large aperture closed by a lid, is charged with 250 kilos. of saltpetre and 288 kilos. of sulphuric acid of 66°B. or 300 kilos. of 60°B. The lid is luted on and the fire is lighted. Access to the pot, which is entirely inclosed by the furnace, is obtained through a cover *n*. The pot is connected with the first condenser E by an iron tube having an earthenware lining which enters and is luted in a glass adaptor D. To prevent fracture of the two first condensers by the heated distillate, they are heated at the commencement of the reaction by causing the furnace gases to pass for a time through a flue M instead of through the main flue L.

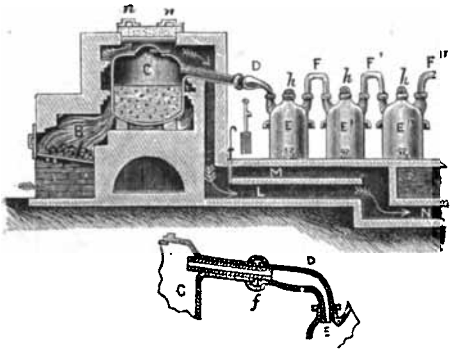

FIG. 2.

With this apparatus the quantity of sulphuric acid used may be only sufficient to produce the normal sulphate, as the solid residue is easily removable through the top.

In a German factory where the strongest acid is made, a cast-iron retort (fig. 3) is used. The charge comprises 700 kilos. sulphuric acid (1·84 sp.gr.) and 650 kilos. sodium nitrate (96 p.c. purity), the yield for each kilo. of the nitrate being 68 parts of acid of 1·5 sp.gr. and 17 parts of weaker acid, *i.e.* about 95 p.c. of the theoretical amount.

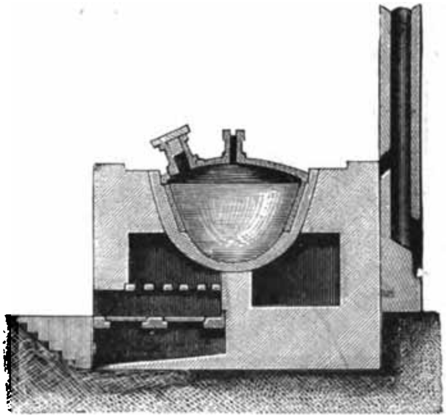

FIG. 3.

Many other processes for preparing nitric acid have been proposed and patented, but none are employed on the manufacturing scale. Among them may be mentioned (1) Wagner's process of heating a mixture of aluminium hydrate and sodium nitrate. (2) J. Walz's process of heating sodium nitrate with chalk and steam. (3) Kühlmann's process in which sodium nitrate is heated with manganous chloride.

The apparatus for condensing the acid admits of considerable variation. Woulffe's bottles arranged in sets of 7 or 9 and each having a tap for running off the contents, are usually employed. The first two receivers contain the strongest but least pure acid.

In order to reduce the number of condensers, the vapours are frequently passed through a stoneware worm condenser before entering the first bottle.

According to a process devised by Göbel (D. P. J. 220, 241) and largely in use, the vapours pass through a straight glass tube lying in cold water and connected at one (bent) end with the glass tube from the retort, and at the other (bent) end with the first receiver. For each ton of nitre decomposed, 4½ tons of water are employed to cool the tube, but the yield of acid is said to be increased by 4¾ p.c. while the number of receivers is considerably diminished.

In another simple arrangement, tapering tubes are fitted one in another to form a condenser which is cooled by the external air only. A length of 10 to 13 feet is required, with sufficient fall to prevent acid from remaining in the joints.

Fig. 4 shows an arrangement of condensers patented by Devers and Plisson. It comprises ten carboys arranged in three superposed sets, the upper six having open funnel-shaped bottoms fitting in the necks of the lower set, which are closed below. A tube M from the retort is connected with a vessel A which condenses a portion of the acid and receives the mechanical impurities. From the lower part of this carboy proceeds a small syphon tube connected with an inclined tube T emptying the carboy through that tube into a vessel A′ when the contents reach a certain height. Into the middle neck of the receiver A is fitted a syphon funnel which supplies water from a bottle F so long as it reaches the level O. The third neck of the vessel A is connected with a receiver B similarly discharging, as do the receivers B′ B″, through a tube T′, into a vessel A″. The manner in which the vapours pass through the remaining condensers is evident from the drawing, the uncondensed vapours passing through a tube K and an earthenware worm through which water constantly trickles, to the chimney. Bottles F′ F″ supply water to maintain the acid at the required density. Tubes H connecting the tubes TT′ with the receiver B″, prevent pressure due to uncondensed gases in the vessels A′ A″.

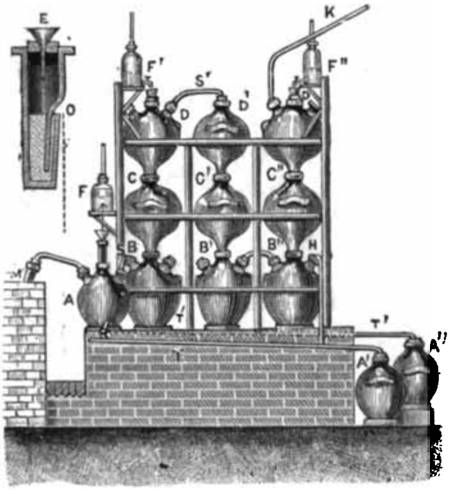

FIG. 4.

Another contrivance comprises a small Gay-Lussac's tower formed of a stack of stoneware pipes filled with coke down which sulphuric acid of 144° to 152°Tw. is continually trickling. The entering gases from the *last* receiver yield up their nitrous vapours to the sulphuric acid and produce a 'nitrous vitriol' which is used in the manufacture of sulphuric acid. A ton of nitre requires $3\frac{1}{4}$ to 4 cwt. of sulphuric acid. The towers are frequently fed with water only. In presence of excess of air, the nitric peroxide is oxidised and converted into nitric acid.

Fig. 5 shows a condensing plant devised by Guttmann (Industries, 9, 242). The vapours from the retorts E traverse zigzag worms A formed of the thinnest possible earthenware pipes and bends, and connected with a Lunge plate-tower F with which the main collector G also communicates. The liquid condensed in the pipes runs from each bend into a collector D, through pipes B fitted with traps and opening into a common discharge pipe C. It is claimed for this arrangement that the acid condensed by the different pipes is of nearly equal strength, so that the whole may be collected in one receiver; that the product contains 93 to 94 p.c. of monohydrate and only 1 to 2 p.c. of peroxide; that the distillation may be conducted at a higher temperature than is permissible with the ordinary plant, and that a charge may be worked through in from twelve to fourteen hours.

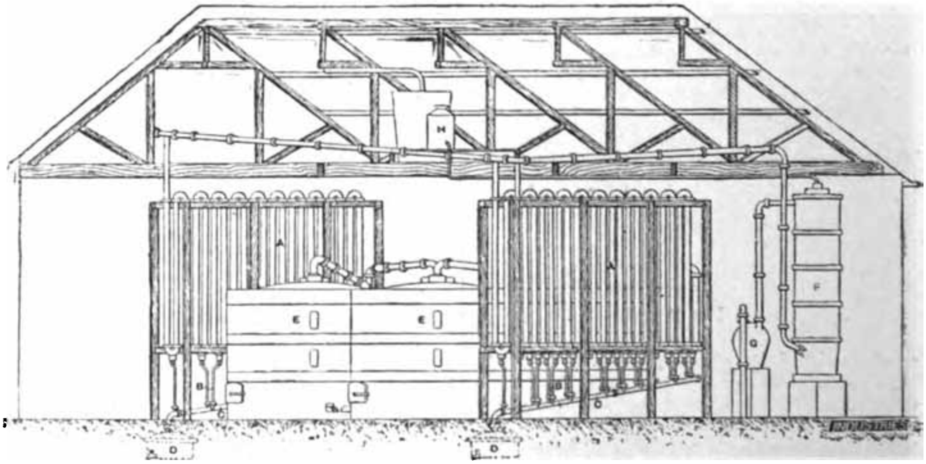

FIG. 5.

The cement employed for the temporary connections of nitric acid plant is usually clay and horsedung. For luting the tubes into the receivers, the following is frequently employed. $\frac{1}{8}$th oz. of finely powdered sulphur is shaken with 5 lbs. of hot linseed oil, and 1 lb. of india-rubber cuttings is added. The whole is boiled until homogeneous, and when cool is mixed and worked into a tough paste with fine barium sulphate.

To produce colourless nitric acid directly, Chevé employs a three-way earthenware cock, the straight branch of which communicates with the retort while the others communicate with separate series of condensers. The distillate is conveyed into one set of condensers until the product, as seen while passing through the glass tubes connecting the condensers, commences to be colourless. The cock is then turned and the remainder of the acid is conveyed into a second series of condensers.

The common impurities in nitric acid are chlorine, hydrochloric acid, iodic acid, nitrogen peroxide, sulphuric acid, sodium sulphate, and iron. To remove these, the acid is distilled in glass retorts, the receiver being changed when the distillate is free from chlorine, which, with the nitrogen peroxide and hydrochloric acid, passes over first. The residue, when most of the acid has been distilled, contains the iodic and sulphuric acids and the non-volatile impurities.

The acid may be rendered colourless by driving off the lower oxides by prolonged heating on a water-bath, or preferably by passing a current of air through the gently heated acid and conducting the air through a small coke tower supplied with water, to minimise loss.

Properties.—Concentrated nitric acid is a colourless liquid, fuming strongly in air and having a powerful oxidising action. It rapidly dissolves or oxidises most metals and oxidises many non-metallic solids such as carbon, iodine, sulphur, phosphorus, arsenic, &c. Sawdust ignites spontaneously sooner or later when impregnated with the acid. Turpentine is oxidised by the strong acid, especially when mixed with sulphuric acid, with evolution of heat and light.

The gaseous products of its action on metals vary with the strength of the acid, the presence or absence of lower oxides of nitrogen, and the nature of the metal. Thus, with copper and warm or hot moderately concentrated nitric acid (1·25 to 1·30 sp.gr.), nitrogen peroxide and nitrogen are evolved, the proportion of the latter increasing with rise of temperature, while at a low temperature and with weak acid nitrogen monoxide and dioxide are produced. The production of these oxides and of ammonia and hydroxylamine, by the action of certain metals on the acid, is attributable to the action of the nascent hydrogen primarily produced by the action between acid and metal on the acid, or by interaction of the other products of the action, rather than to direct action between acid and metal.

Tin, zinc, and some other metals when acting on nitric acid, produce hydroxylamine and ammonia, especially in presence of hydrochloric or sulphuric acid, while silver, copper, mercury, and bismuth produce neither under any circumstances; *v.* also Deville (C. R. 70, 22, and 550), Acworth and Armstrong (C. J. 1877, 2, 54), and Divers (C. J. 1883, 443).

Fuming nitric acid—*i.e.* that containing the peroxide and other nitrogen oxides in solution—has greater oxidising power than the pure acid.

Nitric acid is a monobasic acid and forms a highly crystalline series of salts, all of which are soluble in water and most of which are formed by dissolving the metal or its oxide or carbonate in the acid. These salts will be found described under the various bases.

The following table given by Kolb (Bull. Soc. Ind. de Mullhouse, 1866, 412) shows the composition of nitric acid of different densities:—

Degrees Baumé	Specific gravity	100 parts of water at 0°C. contain		100 parts of water at 15° contain	
		HNO_3	N_2O_5	HNO_3	N_2O_5
0	1·000	0·0	0·0	0·2	0·1
1	1·007	1·1	0·9	1·5	1·3
2	1·014	2·2	1·9	2·6	2·2
3	1·022	3·4	2·9	4·0	3·4
4	1·029	4·5	3·9	5·1	4·4
5	1·036	5·5	4·7	6·3	5·4
6	1·044	6·7	5·7	7·6	6·5
7	1·052	8·0	6·9	9·0	7·7
8	1·060	9·2	7·9	10·2	8·7
9	1·067	10·2	8·7	11·4	9·8
10	1·075	11·4	9·8	12·7	10·9
11	1·083	12·6	10·8	14·0	12·0
12	1·091	13·8	11·8	15·3	13·1
13	1·100	15·2	13·0	16·8	14·4
14	1·108	16·4	14·0	18·0	15·4
15	1·116	17·6	15·1	19·4	16·6
16	1·125	18·9	16·2	20·8	17·8
17	1·134	20·2	17·3	22·2	19·0
18	1·143	21·6	18·5	23·6	20·2
19	1·152	22·9	19·6	24·9	21·3
20	1·161	24·2	20·7	26·3	22·5
21	1·171	25·7	22·0	27·8	23·8
22	1·180	27·0	23·1	29·2	25·0
23	1·190	28·5	24·4	30·7	26·3
24	1·199	29·8	25·5	32·1	27·5
25	1·210	31·4	26·9	33·8	28·9
26	1·221	33·1	28·4	35·5	30·4
27	1·231	34·6	29·7	37·0	31·7
28	1·242	36·2	30·1	38·6	33·1
29	1·252	37·7	32·3	40·2	34·5
30	1·261	39·1	33·5	41·5	35·6
31	1·275	41·1	35·2	43·5	37·3
32	1·286	42·6	36·5	45·0	38·6
33	1·298	44·4	38·0	47·1	40·4
34	1·309	46·1	39·5	48·6	41·7
35	1·321	48·0	41·1	50·7	43·5
36	1·334	50·0	42·9	52·9	45·3
37	1·346	51·9	44·5	55·0	47·1
38	1·359	54·0	46·3	57·3	49·1
39	1·372	56·2	48·2	59·6	51·1
40	1·384	58·4	50·0	61·7	52·9
41	1·398	60·8	52·1	64·5	55·3
42	1·412	63·2	54·2	67·5	57·9
43	1·426	66·2	56·7	70·6	60·5
44	1·440	69·0	59·1	74·4	63·8
45	1·454	72·2	61·9	78·4	67·2
46	1·470	76·1	65·2	83·0	71·1
47	1·485	80·2	68·7	87·1	74·7
48	1·501	84·5	72·4	92·6	79·4
49	1·516	88·4	75·8	96·0	82·3
49·5	1·524	90·5	77·6	98·0	84·0
49·9	1·530	92·2	79·0	100·0	85·71
50·0	1·532	92·7	79·5	—	—
50·5	1·541	95·0	81·4	—	—
51·0	1·549	97·3	83·4	—	—
51·5	1·559	100·0	85·71	—	—

Concentrated nitric acid boils at 86° and melts slightly above −47° (Berthelot). When distilled, it acquires a dark-yellow colour due to partial decomposition into nitrogen peroxide, oxygen, and water. If strongly heated in sealed tubes, the decomposition is more rapid and complete. After distilling about three-fourths of the acid, a colourless residue containing 95·8 p.c. of acid is obtained. Continued distillation of this residue gives a stronger distillate with rise of boiling-point until the residual acid approximates to the formula $2HNO_3 3H_2O$, and contains only 68 p.c. of acid. This boils constantly at 120·5° at 760 mm. and is always produced when either a strong or weak acid is distilled at that pressure. At different pressures, distillates of different composition are produced, but for each pressure there is a distillate of uniform composition.

Passage of a current of dry air through the aqueous acid produces a residue which, according to the temperature and concentration, is stronger or weaker than the original acid. Thus at 100° the final residue is of 66·2 p.c., while at 15° it is of 64·0 p.c.

When mixed with water, a rise of temperature and a decrease of volume is observed, such change attaining a maximum when three molecules of water are mixed with one molecule of nitric acid.

Nitric acid is of great importance in the arts. Amongst its uses may be mentioned the manufacture of sulphuric acid; of coal-tar colours as in the preparation of nitro-benzene, and of nitrates such as those of silver, lead, iron, &c., all of which are employed in the arts. It is also used for etching on stone, steel, and copper by engravers, and for refining gold and silver, &c.

Detection and estimation.—When not too dilute, nitric acid evolves brownish-red fumes when heated with copper turnings. Nitrates give a similar reaction when sulphuric acid is added.

To test for nitrates in dilute solution, the liquid is mixed with sulphuric acid in a test tube, and cooled, and a solution of ferrous sulphate is carefully poured down the side of the inclined test tube upon the top of the liquid. A brown ring is produced where the liquids meet.

The addition of a few drops of brucine to a solution containing even as little as 1 part in 100,000 of a nitrate, with subsequent addition of a few drops of concentrated sulphuric acid, produces a distinct pink colour when viewed against a white background.

According to Bucherer, the following method will detect 1 part of nitrate in 100,000 of water, in the absence of chlorine and bromine. 8 or 10 grams of the solution is placed in a tube 6 or 8 inches long, and a few copper turnings and 3 or 4 drops of concentrated sulphuric acid are added, and the liquid is boiled for a minute. The tube is nearly filled with water, and a few drops of potassium iodide solution are added. The nitrous vapours evolved by the action of the copper and acid set free iodine, which may be detected by shaking up with carbon bisulphide. Free nitric acid is similarly detected without the use of sulphuric acid, and *nitrous acid* or *nitrites* without the use of the copper but with addition of the acid.

The nitric acid in alkaline and other nitrates the bases of which are capable of forming a silicate may be estimated as follows:—2 or 3 grams of finely powdered quartz or silica is heated to redness in a platinum crucible and weighed, and about 0·5 gram of the well-dried, finely powdered nitrate is mixed in with a glass rod. The mixture is then heated for about 30 minutes at a low red heat and weighed. The silica combines with the base and drives off the acid so that the loss gives the weight of N_2O_5.

Nitric acid may be estimated when combined with *any base*, by distillation with sulphuric acid and estimation of the nitric acid in the distillate. The liquid is concentrated with addition of potassium permanganate until a permanent pink colour is produced, to insure conversion of all nitrites into nitrates, if necessary, and is distilled with pure sulphuric acid into a receiver containing barium carbonate suspended in water, until the sulphuric acid commences to distil over. The solution is filtered, and the nitric acid is estimated in the filtrate as usual, the hydrochloric acid being estimated separately and corrected for if necessary.

Nitric acid and nitrates (as also *nitrites*) may be accurately estimated, even in presence of many other substances, by conversion into ammonia by means of the copper-zinc couple (Thorpe, C. J. 26, 541). About 25 to 30 grams of thin sheet zinc is placed in a flask of about 8 oz. capacity and covered with a moderately concentrated solution of copper sulphate. In about 10 minutes the liquid is poured from the zinc, which is now covered with a thick spongy coat of copper, and the 'couple' is well washed and finally covered with about 40 c.c. of pure water.

About 0·5 gram of the nitrate, or a proper quantity of the concentrated solution, is poured into the flask, which is then placed on a sand bath and distilled for about an hour through a condenser, into a flask whose tight-fitting cork receives the condenser tube and is fitted with a U-shaped tube filled with fragments of broken glass moistened with dilute hydrochloric acid. The whole of the nitrate or nitrite is thus reduced and passes over as ammonia into the flask, the contents of which are transferred with the washings from the glass fragments into a dish, and the ammonia is estimated with platinum chloride or by any other method.

The process used for estimating minute quantities of nitrates and nitrites by means of the copper-zinc couple &c. will be found described as applied to Water Analysis in the article on that subject (*v.* also ANALYSIS; NITROMETER).

Nitrous acid HNO_2. Nitrous anhydride dissolves in excess of ice-cold water with production of this acid. The solution, however, is extremely unstable and the acid itself has never been isolated.

Nitrites are found to some extent in nature, and occur in the juices of certain plants. Their universal presence in air has been shown by Schönbein (C. N. 1862, 241) and Warington (C. J. 1881, 229).

All nitrites are soluble in water, and the majority dissolve in alcohol.

According to Le Roy (C. R. 108, 1251) alkaline nitrites are best prepared by projecting 4 parts of finely divided nitrate and one part of barium sulphide in small portions into an iron basin heated to dull redness. The reaction occurs with incandescence. The nitrite is extracted from the barium sulphate by cold water. The individual nitrites will be found described under the various bases.

Detection and estimation.—Certain methods of detecting and estimating nitrites have been given under nitric acid.

For detecting minute traces of nitrites, a test proposed by Griess (B. 1879, 427) and elaborated by Warington (C. J. 1881, 233) may be employed. To 10 c.c. of the liquid to be tested are successively added 1 drop of dilute hydrochloric acid (1 to 4) 1 drop of nearly saturated sulphanilic acid, and 1 drop of saturated solution of naphthylamine hydrochloride. The colour produced varies from a faint pink to a dark ruby-red. A solution containing but 1 part of nitrite in 1,000 million parts of water will give a colour after standing for two hours, when compared with pure water.

An almost equally delicate test is that by means of potassium iodide and starch, as described by Ekin (Ph. 1881, 286). The liquid is acidulated with acetic acid (in preference to hydrochloric or sulphuric acids on account of the difficulty in obtaining them in a state of purity), and the starch and potassium iodide are added. In a few minutes a blue colour is visible when the nitrite amounts to 1 part in 10 millions, while a colour is observable after 48 hours, when the proportion is only 1 in 1,000 millions. Other processes adapted for estimating minute proportions of nitrites will be found described under WATER ANALYSIS; *v.* also ANALYSIS; NITROMETER.

For estimating nitrites in quantity, as in sodium nitrite, Tichborne's process may be employed. Dissolve a weighed quantity (about 2 grams) of the salt in a considerable amount of water and estimate the carbonic acid (due to the presence of carbonate) by addition of decinormal sulphuric acid, adding a drop of the solution at intervals to a solution of starch and potassium iodide until the commencement of the liberation of nitrous acid is indicated by the production of a blue colour.

Three grams of pure potassium bichromate are dissolved in a minimum quantity of water in a flask with a well-ground stopper. An excess of sulphuric acid is then added, and the flask is placed in a freezing mixture composed of sodium sulphate and hydrochloric acid.

The above solution of the nitrite having been preferably similarly cooled, is poured on the surface of the chromic acid without mixing, and the stopper is inserted. The flask is then removed from the freezing mixture, and allowed to reach the ordinary temperature. In half an hour or an hour, the flask contains a mixture of chromic acid and chromic salt, the latter of which represents the amount of nitrite.

The solution is nearly neutralised with potash, and a little ammonia is added, the solution being then boiled until all ammoniacal odour has disappeared. The previously dark-brown colour changes on boiling, the liquid becoming bright yellow, and the precipitate acquiring the bright-green colour characteristic of chromic oxide. This is filtered off, washed, dried, ignited, and weighed as usual. The weight obtained, multiplied by 1·354, gives the weight of *sodium nitrite.*

Hyponitrous acid $(NOH)_2$. This acid is not known in the isolated condition, but its silver, barium (normal and acid salts), calcium, strontium, and alkaline salts have been prepared. Alkaline hyponitrites are prepared by the following methods: (1) By the reduction of alkaline nitrite or nitrate with sodium or potassium amalgam (Divers). (2) By reducing the fused nitrite with iron (Menke). (3) By reducing solution of alkaline nitrite with ferrous hydroxide (Zorn). It may also be obtained by electrolysis of sodium nitrite solution, using mercury as the negative pole. The action appears to be really due to the sodium amalgam produced by the liberation of that metal at the negative pole, since it has been shown that no hyponitrite is formed when mercury is not used. Divers and Haga, and Zorn have failed to prepare hyponitrites by Menke's method.

The silver salt is prepared by neutralising the solution of the alkaline hyponitrite with acetic acid and adding silver nitrate. The yellow precipitate is soluble in dilute acid, and may be re-obtained by crystallisation, but the acid solution decomposes rapidly. According to Divers and Haga and Berthelot and Maquenne, the silver salt cannot be obtained in the pure state; but Zorn, Van der Plaats, and Menke state that it can be so obtained.

The change of nitrates or nitrites into hyponitrites does not appear capable of simple explanation. Divers regards it as directly produced by removal of oxygen, but Dunstan and Dymond (C. J. 1887, 646) suppose that the nitrite first combines with hydrogen and forms a compound $NaN(HO)_2$:

$$Na_2 + H_2O + NaNO_2 = 2NaHO + NaN(HO)_2$$

or

$$Fe(HO)_2 + H_2O + NaNO_2 = Fe(HO)_3 + NaN(HO)_2.$$

The subsequent splitting up of this compound in the one case, and its reduction by hydrogen or ferrous hydrate in the other case, explains the production both of the hyponitrite and the associated hydroxylamine. See further, Divers (Pr. 19, 425), Divers and Haga (C. J. 1884, 78; 1885, 363; and 1889, 772), Zorn (B. 10, 1306; 12, 1509; and 15, 1007 and 1258), Menke (C. J. 1878, 401), Berthelot and Maquenne (C. R. 108, 1286 and 1305), Van der Plaats (B. 10, 1507).

NITROGLYCERIN *v.* EXPLOSIVES.

NITROHYDROCHLORIC ACID *v.* AQUA REGIA.

NITROMAGNITE or **DYNAMAGNITE** *v.* EXPLOSIVES.

NITROMETER *v.* ANALYSIS.

NITROPHENOLS *v.* art. PHENOL AND ITS HOMOLOGUES.

NITROSOPHENOL *v.* art. PHENOL AND ITS HOMOLOGUES.

NITROSORESORCINOL *v. Resorcinol*, art. PHENOL AND ITS HOMOLOGUES.

'NITROSULPHATE' OF IRON *v. Ferric chloride*, art. IRON.

NJIMO WOOD. This wood is obtained from the interior of the Cameroons, and contains a principle which is said to act like pepsin. The drug is found in commerce partly in billets with but little bark, partly as thick circular sections of the root uniformly covered with bark. The wood of both stem and root possesses a beautiful yellow colour, that of the former being dashed with red. It is easily reduced to powder with a rasp, and possesses an odour like musk. It contains numberless circular pores, which contain yellow resin. The alcoholic extract of the drug is yellow by transmitted light, but exhibits a green fluorescence resembling uranium glass. It appears to contain no alkaloid. The resin contains a bitter substance with a faint aromatic smell. The plant itself is not known, and it is even unknown to what family it belongs (Hugo Schulz, Ph. Zeit. 31, 350; S. C. I. 5, 501).

NONDECATOIC ACID *v.* Fatty acids.

NONOIC ACID *v.* Fatty acids.

NONTRONITE. A hydrated ferric silicate of a light-green colour, which, on the expulsion of water, changes to a dark chestnut-brown; opaque, fracture uneven; lustre resinous; unctuous to the touch, and is somewhat harder than talc. Specimens found at Heppenheim, in the Bergstrasse, and at Andreasberg gave numbers agreeing with the formula $Fe_2O_3.3SiO_2.5H_2O$ (Thorpe, Proc. Lit. and Phil. Soc. Manchester, 1869, 1).

NOPEL. The Mexican name of *Cactus opuntia*, the plant upon which the cochineal insect breeds.

NORDHAUSEN ACID. *Fuming oil of vitriol* or *pyrosulphuric acid*, *v.* Sulphuric acid.

NORWAY SPRUCE RESIN *v.* Resins.

NORWEGIUM. Symbol Ng. At. w. 145·95 (NgO) (Dahll). This metal was discovered by Dahll in a copper nickel from the Kragerö. It closely resembles bismuth. Norwegium is a white metal of brownish tinge, as hard as copper. Its sp.gr. is 9·44, its melting-point 350°. It dissolves readily in nitric acid, more difficultly in sulphuric and hydrochloric acids, with formation of blue solutions, which become green on dilution. One oxide NgO (?) and one sulphide are known.

NOTTINGHAM WHITE. *Flake white v.* Pigments.

NOYAU. A liqueur flavoured with peach-stones, or the essential oil of bitter almonds, or, occasionally, with 'essence of mirbane.'

NUCIN or **JUGLONE.** This substance, obtained by Vogel and Reischauer from walnut husks, has been shown by Bernthsen to be an oxynaphtho-quinone $C_{10}H_6O_3$ (B. 1884, 1945).

NUN. This name is given to the fatty product of an insect found in Yucatan. It is a yellowish-brown fatty mass, which has a neutral reaction, absorbs oxygen from the air, melts at 48·9°, and resolidifies between 26·7° and 24·9°; dissolves easily in ether, benzene, chloroform, and oil of turpentine, but is insoluble in alcohol; saponifies with difficulty, yielding a pungent-smelling acid called *nilic acid*, and a volatile oil, together with palmitic and stearic acid. Ammonia colours it red. Its solution in turpentine oil is converted, by exposure to the air, into a resinous syrup (A. Schott, C. N. 22, 110).

NUT-GALLS *v.* Gall-nuts.

NUTMEG (Fr., *Muscade*; Ger., *Muskatennuss*), the fruit of the *Myristica moschata*, a tree growing to the height of 20 to 25 feet, and resembling in appearance the pear-tree. Nutmegs are exported from the Moluccas and from many islands of the Indian Ocean and the West Indies. Being possessed of an agreeable aromatic flavour, the nutmeg is employed as a spice, and is sold under the classification of Penang, Dutch or Batavian, Singapore, and Long or Wild, the relative values being in that order. The fruit is prepared for export by long drying over a slow fire (*v.* Mace).

NUTMEG-OIL (syn. *Oil of Mace*) is the essential oil of the nutmeg, and is extracted by bruising the fruit and submitting the paste to the action of steam; after which the mass is pressed between metal plates, when the oil slowly exudes. The yield of oil reaches 2 to 3 p.c. of the nutmegs so treated. The colour of this oil is reddish-yellow; it possesses the aroma of the nutmeg and is employed for scenting soaps and perfumery; and sometimes also in medicine.

The purest commercial oil of nutmeg is resolvable by fractional distillation into the following bodies:—1. A soft brown resin (about 2 p.c. of the oil) not volatile at 300°, and having the composition $C_{10}H_{20}O_3$. 2. Liquids boiling at 260-280° and 280-290°, whose composition may be represented by the formula $(C_{10}H_{13}O_2)_n$. 3. An oxidised oil, $C_{10}H_{16}O$, boiling at 212-218°. 4. A mixture boiling at 173-179° (about 15 p.c. of the original oil), of a terpene, $C_{10}H_{16}$, with a small quantity of cymene. 5. A hydrocarbon boiling at 163-164°, consisting of a terpene with a trace of cymene, amounting to 70 p.c. of the original oil.

From these results it may be inferred that the hydrocarbon boiling at 167°, called by Gladstone myristicene (C. J. [2] 10, 3), is a mixture of two or more terpenes with perhaps a little cymene.

The oxidised body ($C_{10}H_{16}O$) is myristicol. It is converted by heat into an isomeric (or polymeric) modification boiling at a higher temperature, and subsequently into a resin having the same composition. Myristicol treated with dehydrating agents yields cymene, and when treated with phosphorus pentachloride it is converted into a compound $C_{10}H_{15}Cl$, which is resolved by prolonged boiling into hydrogen chloride and cymene.

The cymene contained in the portion of the nutmeg hydrocarbon which boils at 163-164°, may be isolated by treating the mixture with sulphuric acid so as to polymerise the terpene present (the cymene is not altered by the treatment), then shaking with water and distilling in a current of steam. The cymene thus obtained is quite pure, and amounts to about 8 p.c. of the hydrocarbon boiling at 163-164°.

The terpene of nutmeg-oil may be converted into cymene by combining it with bromine and distilling the resulting dibromide $C_{10}H_{16}Br_2$, whereby it is resolved into 2HBr and $C_{10}H_{14}$ (Wright, C. J. [2] 11, 549), *v.* Oils, essential.

NUX VOMICA (*Noix vomique*, Fr.; *Krähenaugen*, *Brechnuss*, Ger.). Among the numerous species of *Strychnos* distinguished for their toxic properties the best known is *S. Nux vomica* (Linn.), a medium-sized tree which is found throughout Southern and Eastern Asia and in the northern part of Australia. The seeds of the fruit of this tree constitute the nux vomica of commerce. They were introduced into Europe during the sixteenth and seventeenth centuries, and have gradually become an important article of materia medica. They are known in the market as 'Bombay,' 'Cochin,' and 'Madras' seeds. The finest specimens which have been examined are grown in Ceylon. In small doses nux vomica acts as a powerful nervous stimulant affecting certain nerve centres, particularly the medulla oblongata. Other parts of the tree possess similar physiological activity, notably the bark, which has attracted attention as an adulterant of cusparia or angustura and as such is called False Angustura Bark (*v.* CUSPARIA BARK). For further botanical and historical particulars *v.* Fl. a. H. 428; Bentl. a. T. 178; Oberlin a. Schlagdenhauffen (J. Ph. [4] 28, 225); Dunstan a. Short (Ph. [3] 13, 1053; 15, 1 a. 156); Rosoll (M. 5, 94); Greenish (Ph. [3] 15, 60); and Ford, Ho Kai a. Crow (Ph. [3] 17, 927).

The poisonous action of nux vomica depends upon the presence of the two well-known bitter alkaloids, *strychnine* and *brucine*. The former was isolated from the seeds in 1818 by Pelletier and Caventou (A. Ch. [2] 10, 142; 26, 44), and the latter, a year later, from the bark and seeds, by the same chemists (A. Ch. [2] 12, 118; 26, 53). That strychnine is also present in the bark was shown by Shenstone in 1877 (Ph. [3] 8, 445; 9, 154). These alkaloids are widely distributed among the species of the *Strychnos* genus. The *S. Ignatii* (Berg.), a climbing plant of the Philippine Islands, the seeds of which constitute the St. Ignatius' Beans, contains both alkaloids. Strychnine indeed was discovered by Pelletier and Caventou in the seeds of this plant (*cf.* Flückiger a. Meyer, Ph. [3] 12, 1; Fl. a. H. 431; Bentl. a. T. 179; Crow, Ph. [3] 17, 970; and Ford, Ho Kai a. Crow, Ph. [3] 18, 75). Strychnine and brucine are found also in *S. Tieuté* (Lesch.) of Java, the active ingredient in the Upas-Tieuté arrow poison (Pelletier a. Caventou); in *Lignum colubrinum* or snake-wood, from *S. colubrina* (Linn.), a Malabar tree (Berdenis, J. 1866, 710; H. G. Greenish, Ph. [3] 9, 1014), and *S. Gauthieriana* (Piérre), the tree which yields the *hoang-nan* of China (*cf.* Planchon, J. Ph. 1877, 384; Räber, Y.-Bk. Ph. 1881, 138). The Indian drug *bidara laut* derived from *S. ligustrina*, examined by H. G. Greenish, was found to contain brucine only (Ph. [3] 9, 1013). Other poisonous species of *Strychnos* depend upon the alkaloid curarine for their activity (*v.* CURARA); and the African shrub *akazga*, apparently belonging to the same genus, contains a nearly related base *akazgine* (Frazer, J. pr. 104, 51).

For the extraction of the alkaloids from the seeds, besides the process employed by Pelletier and Caventou, numerous other methods have been suggested. The most noteworthy are those of Corriol (J. Ph. [1] 11, 492), Soubeiran (J. Ph. [3] 45, 230), Winckler (Mag. Ph. 19, 261), Neuhaus (N. J. T. 11, 2, 198), Duflos (Berl. J. 28, 2, 208), O. Henry (J. Ph. [2] 16, 752), N. E. Henry (J. Ph. [2] 8, 401), Lebourdais a. Tilloy (J. Ph. [3] 23, 406), Wittstein (Darstell. u. Prüfung, 215), Wittstock (Berz. Lehrb. 3rd ed. 6, 296), and Geiseler (Ar. Ph. [2] 2, 73). Of these that of Wittstein is the best known and has formed the basis of most of the methods now in use. In all cases it is necessary in the first place to reduce the seeds to a powder, an operation which is rendered difficult by their horny nature. Perhaps the best mode of procedure is that recommended by Dunstan a. Short (Ph. [3] 13, 1053). The seeds are split and then subjected to a temperature of 100° for three hours, after which treatment they admit of being powdered in a drug-mill. The powder, according to Wittstein, is exhausted with 40 p.c. alcohol and the solution obtained is distilled and evaporated until the residue is equal in weight to the powder employed. A solution containing one-fiftieth of this weight of normal lead acetate is then added and the precipitated lead salts separated. The filtrate is concentrated to one half, mixed with calcined magnesia and allowed to stand a week, when the alkaloids will have precipitated. They are extracted from the precipitate by treatment with 80 p.c. alcohol, and on evaporating this solution are obtained in an impure condition. Washing with 40 p.c. alcohol removes the brucine and colouring matter and leaves the strychnine. Ammonia is now generally substituted for magnesia, when only twelve hours' standing is necessary (*cf.* Brit. Pharm. 1885, 386). Crude strychnine thus obtained may be purified by further washing with 40 p.c. alcohol, or as suggested by Prescott (Y.-Bk. Pharm. 1879, 97) a weaker alcohol may be advantageously employed until the washings cease to give the colour reaction with nitric acid for brucine. Another plan is to convert it into a salt, such as the nitrate, recrystallise the salt several times and regenerate the base. Strychnine consists of rhombic prisms (Schabus, J. 1854, 516; Kenngott, J. 1855, 567) which melt at 268° (Löbisch a. Schoop, M. 6, 858) and have a sp gr. of 1·359 at 18° (Clarke, B. 12, 1399). Solubility in 100 parts of cold water, 0·014; benzene, 0·607; 95 p.c. alcohol, 0·936; ether, 0·08; fusel oil, 0·55 (Dragendorff, J. 1865, 739; *cf.* Crespi, G. 13, 175). Strychnine citrate (Fischedick, Ph. [3] 17, 170); sulphates (Rammelsberg, B. 14, 1231; Coleman, Am. J. Pharm. [4] 13, 113). Many of the neutral salts of strychnine are almost insoluble in water, and hence precipitation of the alkaloid occurs where, as is sometimes the case, salts of strychnine are prepared for medical administration in aqueous solution together with alkaline bromides or iodides (*cf.* Lyons, Ph. [3] 8, 1048). For other characters and reactions of strychnine *v.* VEGETO-ALKALOIDS.

To obtain brucine from the mixed alkaloids extracted from nux vomica several methods are employed besides those already mentioned, and the seeds are sometimes worked directly for this base. The latter plan was adopted by Shenstone, who prepared brucine quite free from strychnine. The powdered seeds were extracted with alcohol containing one-sixth part of water, and the solution concentrated by distillation and evaporation to the consistence of a thick syrup. From this the alkaloids were extracted by water containing 0·3 p.c. of sulphuric acid. To the acid solution an excess of sodium carbonate was added, and the precipitate, which formed after a few hours, was collected and dissolved in chloroform. The chloroformic solution was then shaken several times with water, to which sulphuric acid was gradually added. The first washings were kept alkaline, but the last ones were made distinctly acid. In this way crystallisation during the operation is prevented. The solution of alkaloidal sulphate was next treated in a shallow dish with an atmosphere of ammonia gas, when some of the base separated in crystals. These were washed with dilute alcohol, which on spontaneous evaporation left brucine, not quite free, however, from traces of strychnine. These were finally removed by conversion into hydriodide and regeneration of the alkaloid (C. J. 39453). The crude alkaloids may also be separated by taking advantage of the different behaviour of brucine and strychnine acetates when heated on a water-bath, when the strychnine salt loses its acid and becomes comparatively insoluble in water (Flückiger, Ar. Ph. [3] 6, 404); or of the action of dilute nitric acid on the picrates (Gerock, Ar. Ph. [3] 27, 158); or of the different solubility of their chromates (Horsley, J. 1856, 758); or of their ferrocyanides (Dunstan a. Short, Ph. [3] 14, 290; *cf.* Beckurts, Ph. Centh. 4, 325). By the last-mentioned process the mixed alkaloids, in a dilute solution containing a slight excess of sulphuric acid, are treated with potassium ferrocyanide, when after standing several hours the whole of the strychnine is precipitated, leaving the brucine in solution. The precipitate is not sufficiently stable to admit of being dried and weighed, and for quantitative purposes it is necessary to isolate the free base, which can be readily done by means of chloroform and strong solution of ammonia (*cf.* Schweissinger, Ar. Ph. [3] 12, 579). Holst and Beckurts have recently proposed a volumetric method based on the same property of the ferrocyanides (Ar. Ph. [3] 25, 313). Brucine crystallises from dilute alcohol in monoclinic prisms or plates containing $4H_2O$ (Lüdecke, B. 10, 838), which lose water at 105° and melt at 178° (Claus a. Röhre, B. 14, 773). The physiological action is similar but less intense than that of strychnine; but, unlike strychnine and like curarine, it is not poisonous when taken into the stomach, but acts fatally when injected under the skin (Brunton, C. J. 47, 143). It is very slightly soluble in cold water, though much more so than strychnine. It is soluble in cold alcohol, chloroform, and volatile oils; but insoluble in ether and fats. For other characters and reactions *v.* VEGETO-ALKALOIDS.

Nux vomica seeds also contain *igasuric acid*, discovered by Pelletier and Caventou (A. Ch. [2] 10, 167; 26, 54), with which the alkaloids are supposed to be combined, and a small proportion of a glucoside, *loganin*, $C_{25}H_{34}O_{14}$, first obtained by Dunstan and Short from the fruit pulp which contains it in larger quantities (Ph. [3] 14, 1025; 15, 4). The 'igasurine' of Desnoix (J. Ph. [3] 25, 202) and Schützenberger (C. R. 46, 1234) has been shown by Jörgensen (J. pr. [2] 3, 175) and Shenstone (C. J. 37, 235; 39, 453) to be impure brucine. Igasuric acid is isolated from the lead precipitate obtained in the preparation of the alkaloids. It is a yellowish-brown amorphous mass, having an astringent taste and acid reaction. It would seem to be a variety of tannic acid (Ludwig, Ar. Ph. [3] 2, 137; Corriol, J. Ph. 19, 155; Marsson, A. 72, 296). Loganin consists of colourless prisms which melt at 215°. It dissolves easily in water and alcohol, but less so in chloroform and benzene. Warmed with sulphuric acid it develops a red colour which changes to purple. Boiled with dilute acids it breaks up into *glucose* and *loganetin*. It occurs in the pulp of the fruit of Ceylon nux vomica to the extent of 5 p.c. (Dunstan a. Short). In addition to these constituents nux vomica seeds contain about 11 p.c. of *proteids* (Fl. a. H.); 4 p.c. of *fat* or fatty oil (Fl. a. H.; Meyer, J. 1875, 856; T. E. Greenish, Ph. [3] 12, 581; Dunstan a. Short) together with *mucilage* and *sugar*.

Several methods have been suggested for the estimation of the alkaloids in nux vomica. The most important are those of Dragendorff (C. Wertbestimmung, St. Petersburg, 1874; Z. [2] 2, 27) and Dunstan a. Short (Ph. [3] 13, 665 a. 1053). Dragendorff's method, which gives accurate results, consists of extracting the powdered seeds with dilute sulphuric acid, nearly neutralising the solution with magnesia, and evaporating to a syrup. From this the alkaloids are extracted by treating it first with 90 p.c. and afterwards with 50 p.c. alcohol. The alcoholic solutions are then distilled until the residue is concentrated to one-fifth of their volume. The slightly acid solution is then shaken with benzene, which removes fat and other substances, but does not dissolve the alkaloidal salts. Treatment with magnesia sets the alkaloids free and they are extracted by benzene or chloroform, the solution evaporated and the residue dried and weighed. The method of Dunstan and Short is simpler. The powdered seeds are exhausted with a mixture of three volumes of chloroform and one volume of alcohol. From this solution the alkaloids are separated by shaking with dilute sulphuric acid, which dissolves them as acid sulphates. By treatment of the acid solution with ammonium hydroxide and chloroform, the free bases are extracted, and on evaporation of the chloroformic solution are obtained in a sufficient state of purity for weighing. Examined by this method, 'Bombay' seeds gave from 3·14 to 3·90 p.c.; 'Cochin' seeds 3·04 and 3·60 p.c., and 'Madras' seeds 2·74 and 3·15 p.c. of total alkaloids (D. a. S.).

The experiments of Siebold (Ph. [3] 7, 283), Dunstan and Short (Ph. [3] 14, 292, 441, a. 443), and Conroy (Ph. [3] 14, 461) proved that the pharmaceutical preparations of nux vomica, the extract and tincture, vary materially in alkaloidal strength. To employ only the alkaloids for medical purposes would obviate this want of uniformity, but they are not believed to possess the whole of the therapeutic activity represented by the extract or tincture. A plan was therefore worked out by Dunstan and Short (Ph. [3] 14, 621, 622 a. 875; 15, 156) by which an extract and tincture can be made to contain a fixed percentage of total alkaloids, and methods similar in principle to that suggested for the estimation of the alkaloids in nux vomica were adapted to the testing of the alkaloidal strength of these preparations (*cf.* Schacht, Ph. [3] 14, 851; Martin, Ph. [3] 17, 254; Beckurts, Ph. [3] 20, 341). A. S.

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