A
TEXT-BOOK OF CHEMISTRY

INTENDED FOR THE USE OF PHARMACEUTICAL AND MEDICAL STUDENTS

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FIFTH EDITION REVISED AND REWRITTEN

PHILADELPHIA & LONDON
J. B. LIPPINCOTT COMPANY

Gift
Medical Library - College of State of South Carolina

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PREFACE TO FIFTH EDITION

The present edition of this pharmaceutical text-book has been in course of preparation for several years, having been begun before the appearance of the 9th Revision of the U. S. Pharmacopœia.

As is well known, chemical manufacturing has undergone quite important changes in recent years, and in particular since the revolution in trade incident to the outbreak of the present great world war. The Editors have sought to bring the book abreast of this changed condition in the chemical world.

The sections on Inorganic Chemistry have been therefore largely rewritten and much that is new introduced, and older statements withdrawn in numerous sections.

This part of the work has been attended to by Professor Coblentz, who has been of recent years in close touch with the manufacturing side of chemistry, and Professor Jeannot Hostmann of the Department of Pharmacy of Columbia University, who is actively engaged in chemical laboratory work.

The section on Elementary Physics has also been largely rewritten by Professor Hostmann.

The section on Organic Chemistry has been brought up to date with the introduction of considerable new matter by Professor Sadtler, who has also contributed the chapter on Electrolysis and its new applications.

Some new and useful tables have, with the permission of the Trustees of the U. S. Pharmacopœia, been inserted for the greater convenience of the pharmaceutical student and for convenient reference for pharmacists using the book.

We believe that the book in its present form is adapted for use in the classes of our Pharmaceutical Schools as a text-book and at the same time is sufficiently complete in its scheme of treatment to make it valuable for the reference libraries of graduates and others who might turn to it as a reference book on chemistry and chemical products.

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September, 1918.

PREFACE TO THE FIRST EDITION.

An experience of some seventeen years as teachers in a professional school, where Chemistry is considered one of the foundation-stones upon which young men must build a technical education, has convinced the authors that the subject must be taught in a way that, while thoroughly scientific, is yet distinctly adapted to the ultimate uses of the students.

The professions of Pharmacy and Medicine are closely related, and their uses for Chemistry are very much alike. The members of these professions must understand the composition and chemical properties and possibilities of the whole *materia medica*, both inorganic and organic, in order safely to maintain the important trusts committed to them,—trusts involving the continued health and life of their fellow-men. The importance of thorough chemical knowledge for these related professions is now recognized in the fullest way in their official publication, the U. S. Pharmacopœia, the last edition of which has embodied throughout the most detailed and exact statements of the chemical nature, properties, and reactions of medicinal substances, together with methods of analysis or assay and tests for purity.

We have sought in the following pages to offer a text-book on Chemistry which should combine scientific accuracy and completeness with that special reference to the needs of the pharmaceutical and medical student, as well as those in active professional practice, which will make it of value for both study and reference. Compounds recognized in the U. S. Pharmacopœia are specially indicated, but they are not taken out of their proper position for such discussion.

A brief outline of Elementary Physics, much of which is absolutely essential for the understanding of chemical methods, forms Part I. The convenient division of the elements into Non-Metals and Metals is followed in the main in Parts II. and III., subject to the limitations made necessary by the chemical relationship as indicated by the valence groups. Part IV. deals with Organic Chemistry. While the arrangement here followed is strictly scientific, it has been sought to give the subject a distinctly practical bearing, and to this end the industrial applications of organic compounds have been noted, and in a number of cases illustrated.

In Part V. a brief outline of Qualitative and Quantitative Analysis is given, the methods being such as have proved of value in our own practice. A number of the Pharmaceutical Assays of the U. S. Pharmacopœia are also added.

The Appendix contains, besides a list of the chemical elements with atomic weights and valences, thermometric scales and the specific gravity tables in most general use.

The authors have made free use of many chemical works, such as Flückiger's "Pharmaceutische Chemie," Schmidt's "Pharmaceutische Chemie," Meyer and Jacobson's "Organische Chemie," Bernthsen's "Organische Chemie," Weyl's "Organische Chemie für Mediciner," Fischer's "Neuere Arzneimittel," Gamgee's "Physiological Chemistry," Pictet's "Alcaloides Végétaux," Power's "Essential Oils," Allen's "Commercial Organic Analysis," Prescott's "Organic Analysis," and Sadtler's "Industrial Organic Chemistry."

Our thanks are due to J. C. Peacock for valuable assistance in the preparation of Parts III. and V., to S. S. Sadtler and H. Blount Hunter for work on the index, and to Edwin Thorpe for the execution of many original drawings for the illustration of the work.

S. P. S.
H. T.

PHILADELPHIA, February, 1895.

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PART I

ELEMENTARY PHYSICS

CHAPTER I

MATTER, FORCE, AND MOTION

1. Introductory.—Science treats of the phenomena associated with matter and the laws governing them. When applied to living matter it is called *biology.*

Matter is that which occupies space and is apprehended by the aid of our senses. Different kinds of matter are called *substances,* while a limited portion of matter is termed a *body.*

Physics embraces the study of the phenomena and laws governing the transformations of energy. It concerns itself with matter and its changes of form, state, and place, while still retaining its fixed composition.

Changes in which the identity of matter undergoes alteration—that is, changes in the molecular constitution—are considered under *Chemistry.*

2. General Properties.—*Divisibility* is that property by virtue of which matter is capable of mechanical subdivision into parts. There is no limit to which subdivision may be carried, for after reaching the apparent limit, the microscope still shows plainly the possibility of further subdivision.

Molecules and Atoms.—The smallest particles of matter which we can conceive of as obtained by this mechanical or physical subdivision we call *molecules.* How large these molecules are, what their shape is, or what their absolute weight is, we do not know. We merely know that they still show the distinctive properties of the masses of matter from which they are derived. Many of these forms of matter, although not capable of resolution into anything different by methods of mechanical subdivision, are capable of decomposition into simpler forms under the influence of chemical reagents. We assume, then, that molecules are made up of still smaller particles, to which the name *atoms* (page 115) has been given. These smallest particles of matter are assumed to be unalterable.

Simple and Compound Matter.—The union of like atoms gives us simple or elementary matter, of which chemists have distinguished some seventy kinds (see page 116), while the union of unlike atoms yields compound matter, the varieties of which are almost infinite.

Conservation of Matter.—If, as stated, the atoms or smallest conceivable portions of matter are final, unalterable particles, it follows that matter is indestructible, whatever the influences to which it may be subjected and the changes of form which it may undergo. Compound matter may, indeed, be resolved into simpler combinations, and ultimately into elemental matter, under the influence of chemical treatment, but the sum total of the products so obtained must always equal that of the matter operated upon. Cases of apparent loss or destruction of matter are all explained upon careful examination of the reaction in its several phases. Changes of outward form take place under the influence of physical agencies alone, so that a solid or liquid may lose in weight by the escape of a gas or vapor, and changes in the method of combinations of the atoms may take place under the influence of chemical reagents, but if the products are examined it will be found that no new atom has been created nor has any been destroyed, and that the *mass* or *quantity of matter* remains the same. In accordance with this, it is asserted that the quantity of matter in the universe is constant. This is sometimes called Lavoisier's Law of the Indestructibility of Matter (see page 114), but it is now generally spoken of as the " Law of the Conservation of Mass."

Three States of Matter.—We recognize three states of aggregation in matter—the *solid,* the *liquid,* and the *gaseous.* In the first of these the molecules are held firmly together by the force of attraction; which is greater than the repellent force which tends to separate them, so that the mass of matter tends to retain its shape, and the exertion of some force is necessary to overcome the adhesion of the molecules and change the shape; in the second the attractive and repellent forces are balanced, the molecules move easily past one another, and the liquid readily assumes the shape of the containing vessel; in the third the repellent is more powerful than the attractive force, the molecules constantly tend to separate and occupy a greater space, and pressure is required to overcome this tendency.

Impenetrability.—As matter occupies space, any particular space cannot be occupied by two different bodies at the same time. Thus, if a solid body, like a bar of metal, be immersed in a tumbler previously filled with water, it will cause some water to overflow. The amount so displaced will exactly equal the volume of the solid immersed. Numerous apparent exceptions to this rule exist, as when a nail is driven into a piece of wood, or water is poured into a tumbler previously filled with dry sand, or a piece of dry wood is dipped into water. But in all such cases we must take account of another property of matter, viz., *porosity.* In the use of this term we mean that the molecules of a substance are never in actual contact, but are separated by spaces relatively large as compared with the size of the molecules themselves. These spaces are called *pores,* and their existence is made evident when pressure is applied and the mass is diminished in bulk. This diminution in the space occupied under increase of pressure shows most notably with gases, which are therefore termed the most compressible, but occurs also in liquids and solids. This is explainable only by the assumption of the porosity of matter.

All bodies are more or less porous. Those pores which form actual cavities or cells, and are visible, are called *sensible pores,* as seen in the structure of such bodies as wood, sponges, unglazed brick, filter-paper, etc. The invisible spaces that separate the molecules of substances are called *physical pores.* A clear illustration of this is had when we mix equal volumes of alcohol and water. Instead of the mixture equalling the sum of the two liquids, it is only about ninety-five per cent. of the combined volume.

Metals contain physical pores, and although these cannot be seen by aid of the most powerful microscope, still they are shown to be pores by the fact that, by means of pressure, liquids and gases can be made to pass through them.

As a proof of and dependent upon the porosity of bodies is the property of *compressibility.* Gases are the most compressible of bodies. In them the molecules are more widely separated than in liquids or solids, and are tending to separate still more widely; but for this very reason they respond more readily to the influence of pressure and can be compressed into smaller space. As we will see later, temperature as well as pressure has much to do with this change of volume.

The compressibility of liquids is but slight; solids, on the other hand, may be very compressible, the change in this case depending, however, largely upon the existence of sensible pores, as in the case of wood, cloth, paper, etc., which readily yield to pressure. Metals are also compressible, as is shown in the process of stamping coins with hardened dies.

Elasticity is the property by virtue of which bodies that have undergone compression tend to resume their original form or volume upon the removal of the compressing force. It generally goes hand in hand with the property of compressibility; hence gases, which are the most compressible of the forms of matter, are also the most elastic. Liquids in the degree that they are compressible under pressure are also elastic. Solids show the property of elasticity in varying degrees. India-rubber, ivory, glass, and tempered steel are highly elastic, while clay and putty have this property only to a very slight degree. The elasticity of cork adapts it for use as stoppers; the elasticity of air renders it a vehicle for the transmission of sound; also this property has been utilized in making air-beds, air-cushions, and in practical mechanics.

3. Volume and Mass.—*Volume.*—As before stated, our most elementary conception of matter is that it occupies space. The amount of space it occupies is termed its volume. We can conceive of its extension in one direction only, which we call space of one dimension, or *length;* of extension in two directions, which we call space of two dimensions.

or *area;* of extension in three directions, which we call space of three dimensions, or *volume.*

Mass is the amount or quantity of matter contained in a body. A pound of cotton may occupy a cubic foot or be compressed to a cubic inch; in either case the number of molecules is the same and the weight the same; hence mass is independent of volume. Mass is determined by weight; two bodies have equal masses when placed on a balance *in vacuo* and they exactly counterpoise each other. While the weight of bodies varies according to the action of gravity upon them (see page 8), their mass is, on the contrary, invariable.

Density is the degree of closeness of the particles of a body. If two cubic inches of air be compressed so as to occupy the space of one cubic inch, then its density will be twice as great. Different bodies having the same volume contain different quantities of matter; for example, a cubic inch of platinum contains 21.5 times as much matter as a cubic inch of water, the same volume of lead 11.2 times, that of iron 7.7 times, and aluminum 2.6 times. Since we are unable to count the number of molecules in a mass, we employ weight as a means of determining this density. The masses of bodies are proportional to their weights. We ascertain the density of solids by comparing the weight of a given volume to the same volume of water taken as standard unit. In the case of gases we compare equal volume-weights of the respective gas and either air or hydrogen as standard. In all cases, the temperatures at which comparison is made must be the same. For further explanation, see pages 23 to 25.

4. Units of Measure.—*Unit of Time.*—The second is $\frac{1}{86400}$ part of a mean (average) solar day, the day is the time required for the earth to turn on its axis once, the hour is one twenty-fourth part of this day, and the minute the sixtieth part of an hour. The second is the time required for a pendulum 39.1398 inches long to make one oscillation; sixty of such constitute a minute, and 86,400 an average solar day.

Unit of Length.—The scientific standard is the *meter,* which represents the length of the standard rod deposited with the U. S. Geodetic Survey in Washington.*

The commercial standard English *foot* represents one-third of the

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* The meter is now universally accepted as a standard unit of length from which the various other units of mass and volume are derived. The length of the meter, which is an arbitrary standard, was adopted in France in 1791, and is represented by the distance between two lines near the ends of a bar of platinum-iridium alloy at the temperature of zero. This unit represents the ten-millionth part of a quadrant of the earth's meridian which is the arc from the equator to north pole.

The meter is divided into tenths called *decimeters* (*dm.*), hundredths called *centimeters* (*cm.*), and thousandths called *millimeters* (*mm.*). The thousandth part of a millimeter is called a *micron* (μ). For measuring long distances, the *kilometer* (1000 meters) is used. The various metric standards of length, volume, and mass are all exact prototypes of the original standards prepared by the International Metric Committee and deposited in the International Bureau of Weights and Measures in Sevres, near Paris.

standard yard, which in turn consists of 36 inches derived from the length of a second's pendulum in London (39.139 inches).

Unit of Volume.—The unit of volume is the *cubic decimeter* (cu. dm. or $dm.^3$) or *liter* (L.). This contains 1000 *cubic centimeters* (c.c. or $cm.^3$). In the United States and British Pharmacopœias the term cubic centimeter has been replaced by the milliliter. According to the U. S. Bureau of Standards, one liter is equivalent to 1.000027 cubic decimeters. Milliliter is abbreviated either mil (U.S.P.) or ml. (Bureau of Standards).

The commercial unit of volume is the *gallon*, which contains 231 cubic inches.

Unit of Mass.—The unit of mass is represented by the weight of one *cubic centimeter* of distilled water at 4° C., and is called the *gram* (gm.). The mass of one *cubic decimeter* (1000 mils) of water constitutes the *kilogram* (1 kg.). The standard kilogram was prepared by the International Metric Committee and deposited with the U. S. Geodetic Survey in Washington.

The commercial unit is the *pound* (avoirdupois), which contains 7000 grains. The standard is kept in the Exchequer office in London. The Troy pound contains 5760 grains.

Tables of the metric system and of English weights and measures will be found in the Appendix.

5. **Motion and Force.**—If a body retains its position in space constant through a period of time, it is in a state of rest; if it is changing, the body is said to be in motion. We must remember that these statements are not to be taken as absolute. The body is at rest with reference to its original position, or in motion with reference to the same, while both the body and the original fixed point may be in motion with reference to some other distant point. Motion and rest are therefore purely relative terms.

Inertia is the tendency which matter has to maintain its state of rest or uniform motion. If in a state of rest, it remains so until disturbed by some force producing motion. If in motion, it will move uniformly in a straight line until some force causes this movement to cease. A rifle bullet would continue its course indefinitely in a straight line were it not for the resistance of the air and the attraction of gravity. It is because the earth is moving in frictionless space that it continues to rotate so regularly upon its axis; because of this the length of the day has not varied a second in centuries. *Mobility* is the property by virtue of which matter yields readily to the exertion of some force, causing it to change its relative position, or inducing motion.

The *velocity* of a particle of matter is the rate of its motion at any given time.

Force is that which by acting upon matter either produces or arrests motion. It is a manifestation of energy, and may be originated in a variety of ways. Thus, we speak of chemical forces, which are manifestations of atomic energy; of molecular forces, which result from molecular energy; and cosmic forces, which illustrate the energy of large masses.

Work is energy applied in overcoming resistance, as when one lifts some article from the ground, where the attraction of gravitation is to be overcome, or when an engine pulls a load, overcoming the resistance due to inertia and friction.

The *unit of work* is the energy expended in raising a unit of weight through a unit of height. As we have already seen, the units of weight and measure differ in the English and the French systems, hence different units must be taken according as one or the other system is used. The *foot-pound,* or the work done in raising one pound avoirdupois one foot, is the English unit, and the *kilogram-meter,* or the energy expended in raising one kilogram one meter, is the French unit. If a person weighing 100 pounds mounts a ladder of 20 feet, he has done 2000 foot-pounds of work. For estimating power a larger unit is taken—namely, the *horsepower.* This is equivalent to the strength of an average horse, or the power sufficient to raise 33,000 pounds vertically one foot in one minute. The capacity of steam engines is generally rated in this manner; thus, an engine is said to be 10 horse-power if it is capable of performing work equivalent to raising 33,000 pounds 10 feet in one minute, or 330,000 pounds one foot in a minute. H. P. = weight in pounds × distance (or height) in feet per minute ÷ by 33,000. For example, if two horses raise a weight weighing 200 pounds at the rate of 300 feet a minute they will exert 1.81+ horse-power.

The *C. G. S.* or *Absolute Units.*—Much inconvenience was caused by various standards of length, time, and mass. For scientific purposes the C. G. S. or *centimeter-gram-second* units are now employed. These units, being independent of gravity ($g.$), are frequently designated *absolute units,* while the older units are called *gravitational units.* The *dyne,* the unit of force of the C. G. S. system, is "that force which will give to unit mass unit acceleration," or, in other words, the force of one dyne will give to a gram mass an acceleration of one centimeter per second.

The *erg* is the C. G. S. unit of work. It is the work done by a force of one dyne acting through a distance of one centimeter, or "unit work done by unit force through unit distance." The force exerted by gravity upon a gram mass is 980 dynes; to lift a gram mass one centimeter against gravity would require 980 ergs. The erg being a very small unit, the *joule* (10^7 ergs) is often used.

The relation between the absolute and gravitational unit of force may be considered as 980 dynes = 1 gram, and the force of 980,000 dynes taken to be the same as the weight of 1 kilogram (1000 grams) is often called a *kilogram weight.*

Energy is capacity for doing work. It is possessed by matter because of its mass and velocity, and its exercise involves motion of some kind. Thus, we have the energy of visible motion of the mass and the energy of the invisible motion of the molecules, which is known to us under the forms of heat, sound, radiant energy or light, and electricity.

Energy may be *potential* or *kinetic* (actual). A weight held up by the hand, or by a support, has the power, because of its position, to fall, and thus do work, if the support be withdrawn. This is *potential energy,* or *energy* of *position.* Numerous applications of this suggest themselves, as the case of a wound-up spring, or an elevated tank or reservoir of water. The same weight descending in consequence of the withdrawal of the support, the spring uncoiling, and the water acting upon a turbine wheel, all represent *kinetic energy,* or the *energy of motion.*

Exact measurements have shown us in the cases of the weight, spring, etc., that the kinetic energy developed exactly equals the potential energy that may have been stored up, and no loss or gain is found when all the elements have been carefully calculated. This principle may, however, be extended not only to all cases of visible energy of motion, but to energy wherever and however manifested. As matter is indestructible, and can be neither created nor destroyed by the changes to which it is subjected, so energy is indestructible, and cannot be created or destroyed. Energy of one form may be changed into energy of another form, but there is no absolute gain or loss in amount. This law is known as the *conservation of energy.*

This change of one form of energy into another without loss of actual amount is one of the most important facts in nature, and one most familiar to us. If we rub our fingers briskly over a surface of cloth or wood, we feel a sensation of warmth. The visible motion of the hand, due to muscular energy, is transformed into that form of molecular energy known as heat. In the steam engine we convert the potential energy of the coal, by combustion, into actual heat energy, and in turn impart visible energy of motion to the piston and connected parts of machinery. This motion, by the aid of a dynamo machine, may be converted into electrical energy, and this in turn into either heat or light energy. This illustrates what is termed the *conservation and correlation of forces,* or, more exactly, *of energy.*

6. Forms of Attraction.—*Gravitation* is the force by virtue of which the particles of matter are attracted towards one another. The strength of the attraction between the particles varies with the mass of each particle, and is inversely as the square of their distance apart. That is, if one body contains twice as much mass as the other, its power of attraction is twice as great as the other. In the second case, when the distance between the two masses is doubled, their attraction is reduced one-fourth; if the distance be trebled, their mutual pull upon each other will be only one-ninth. The earth exerts this force of attraction upon all bodies near it, drawing them towards its center. When this force is unresisted, motion results and the body falls; when resisted, pressure which we call *weight* is produced. This attraction is general throughout the universe, and serves to retain the planets in their orbits. The earth pulls upon every particle of the bodies upon its surface, and by reason of its superior mass tends to draw them towards the center. This force is exerted along a straight line, which, therefore, marks the shortest path towards the earth's center, and is called a *plumb-line*. The weight of a body is proportional to its mass, because the attraction of the earth acts upon each particle which goes to make the mass. Such attraction varies with the distance from the surface of the earth; at the center weight ceases, because the mass is equally attracted on all sides. If a body weighs one kilogram on the earth's surface (4000 miles from its center), at a height of 4000 miles it would weigh 250 grams, or one-fourth as much, in accordance with the law that the attraction varies inversely as the square of the distance.

Weight is the measure of the attraction exerted by the earth upon a given mass.

The *unit of weight* is the same as the unit of mass—one pound avoirdupois in the English system, and one kilogram (or one gram) in the metric system.

The *center of gravity* of a body is the center of weight or attraction. It is that point in a body at which, if supported, the whole mass will remain at rest in any position in which it may be placed. In a sphere of uniform density this center of gravity will exactly accord with the center of the mass; in a cube it will be at the intersection of the diagonals; in a rod or bar, such as is used for the beam of a balance, it is at the center of its axis. In irregular-shaped bodies this center of gravity may be found by attaching a string at one point and allowing the body to hang suspended by this string; the line formed by the string is then projected through the object. This operation is repeated, supporting the mass from other points, and the point of intersection of these lines is the center of gravity.

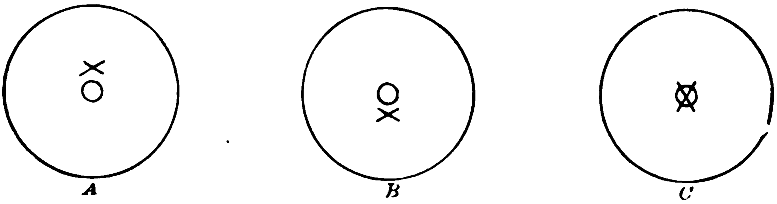
Equilibrium.—When a body is supported and yet free to swing before coming to rest, it will be in equilibrium when the center of gravity is in the same vertical line as the point of support. But to insure stability the center of gravity must also be under the point of support and not above it. According to the relative position of these two points we have the three conditions of equilibrium—*stable, unstable,* and *neutral.* A suspended body is in stable equilibrium, therefore, when the center of gravity is below the point of support, in neutral equilibrium when they coincide. and in unstable equilibrium when the center of gravity is above the point of support.

Fig. 1, consisting of a circle or wheel, illustrates the three conditions respectively. *A* is in *stable* equilibrium when supported at the point *x*, the center of gravity (center of circle) being directly below the point of support; *B* is in unstable equilibrium when supported at *x*, the center of gravity being above the point of support; *C* is in neutral equilibrium when supported at the center of gravity, the circle remaining in neutral equilibrium whenever it is moved.

The chemical balance is an important application of the foregoing principles. This consists of a beam supported in the center by a triangular-shaped steel or agate knife edge so as to oscillate with the slightest amount of friction. To the ends of the beam are attached supports for the pans, on which the weights and articles to be weighed are placed. The center of gravity of the combined mass of all parts of the apparatus must be directly below the middle knife edge. By means of a screw adjustment the center of gravity of the beam can be raised or lowered slightly, which thereby increases or decreases the sensitiveness accordingly. The conditions for delicate working of a balance are as follows:

First, the two arms of the beam—that is, its length from the point of support (fulcrum) to either of the edges of support of the beam—should be of equal length and weight.

FIG. 1.



Second, the weight of the beam should be as small as is allowable, while preserving rigidity.

Third, the center of gravity of the beam should be as near as possible to the point of support and beneath it.

Fourth, when the pans are empty the pointer should indicate the zero of the scale.

The arms of the balance should be relatively long; length increases delicacy.

A balance is said to be *delicate* when a very small difference between the weights in the pans causes a perceptible deflection of the pointer.

The weight of a substance in air, as usually stated, is its *apparent weight.* When weight is to be determined with great accuracy, the operation is carried out *in vacuo,* in order to avoid the buoyant effect of the atmosphere (see Baroscope, page 33). This is known as *absolute weight.*

Molecular Attraction and Repulsion.—Just as the masses of matter, whether large or small, are influenced by the power of gravitation, so the molecules which make up the mass are held together with greater or less firmness by the force of molecular attraction. The intensity of this force determines also the physical state of the matter concerned. In solids the power of molecular attraction is most strongly exerted, in liquids it is weaker, and in gases it seems to be overcome by a force of repulsion which tends to separate the molecules.

We distinguish in ordinary usage between the terms *cohesion,* where molecules of like composition are held together, as the particles of iron in a bar of that metal, and *adhesion,* where bodies of unlike composition are held together, as when a glass rod is dipped into water, the force of adhesion causes the liquid to adhere to the solid.

7. **Motion.**—A body passing from one position to another is said to have *motion*. If the position of a body remains unchanged it is said to be at *rest*. These terms are entirely relative. A person in a moving vehicle may be considered at rest, but is in motion with respect to the earth. A person at rest with reference to the earth is in motion with reference to the planets. When describing ordinary motions certain points on the earth are considered to be at rest.

Motion may be translatory (straight or rectilinear), oscillatory, rotary, centrifugal or centripetal.

TRANSLATORY MOTION is that described by a body in moving from one place to another in a free path. If in a straight line, the motion is rectilinear; if in a curved line, it is called curvilinear motion. The best example of absolute rectilinear motion is that offered by falling bodies responding to the force of gravitation.

Laws of Falling Bodies.—When bodies starting from a state of rest are allowed to fall without resistance (*in vacuo*), they comply with three laws:

1. All bodies fall equally fast.

Since bodies fall in consequence of the earth's attraction upon each of their particles, it would follow that all bodies, regardless of size, would fall equally fast. The fact that a piece of metal falls more rapidly than a feather is solely due to the unequal resistance offered by the air. This is especially manifest with the feather, which is usually driven from its rectilinear course. If we remove this resistance by placing the bodies in a tube which has been exhausted of air, they will then fall equally fast. Therefore the velocity of falling bodies can be correctly measured only in a vacuum.

2. The distances traversed are proportional to the squares of the times occupied in falling.

The space which a body falling *in vacuo* traverses is about 16.1 feet at the end of the first second.

To ascertain the space traversed by a falling body during any given number of seconds, we multiply the space traversed during the first second (16.1 feet) by the square of the number of seconds. Thus, if a body falls three seconds it will have traversed 9 × 16.1 feet, or 144.9 feet.

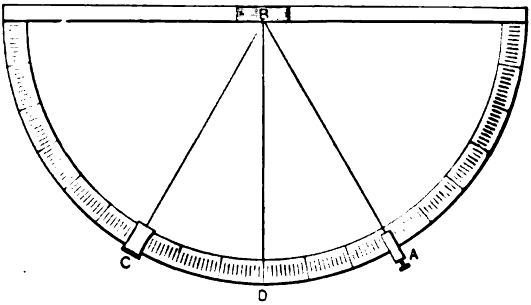
If the body pass through one space during the *first* second, then in consequence of its acquired (increasing) velocity it would pass through two such spaces during the *second* second, which, in addition to the action of gravity that carries it through one space, makes a total of *three* spaces. For the *third* second, the body will have attained a velocity that carries it through four spaces, which, with one space for the action of gravity, makes a total of *five* spaces traversed. The spaces further traversed will be 3, 5, 7, 9, 11, etc., respectively.

3. The velocities acquired during the fall are proportional to the times occupied in falling.

If a body falls from a state of rest it will constantly gain in velocity, and this will, at the *end* of the first second, be at the rate of about 32.2 feet per second. This factor is known as the *acceleration of gravity.* The velocity at the end of the third second will be 3 × 32.2, or 96.6 feet; its average velocity for any given time will be one-half its final velocity.

Momentum.—The momentum of a moving body is the product of its weight (mass) and its velocity. The momentum of a 50-pound cannon-ball moving at the rate of 500 feet per second would be 50 × 500 = 25,000. The gain in momentum by a falling body weighing, for example, 150 pounds, would be as follows:

FIG. 2.



Reflected motion.

Time of Fall	Distance Traversed	Velocity	Momentum
First second	16.1 feet	32.2 feet	4,830
Second second	64.4 "	64.4 "	9,600
Third second	144.9 "	96.6 "	14,490

Reflected Motion.—When an elastic body is thrown against a hard, smooth surface, reaction causes it to rebound; if it strikes the surface perpendicularly, it rebounds back over the same path; if it strikes obliquely (*the line of incidence,* A, B, Fig. 2), it will be reflected back (*line of reflection,* B, C), in an opposite direction. The angle (A B D) described between the line of incidence and the perpendicular to the surface is called the angle of incidence, and the angle (D B C) described between the line of reflection and the perpendicular is the angle of reflection. The law is, *the angle of reflection is equal to the angle of incidence.* This law is applicable to the reflection of sound and light.

Oscillatory Motion.—While translatory motion is continuous in direction, oscillatory (vibratory) is alternate, such as is observed in the motions of a swinging pendulum, the movement of the balance-wheel of a watch, or of a sounding tuning-fork.

The Pendulum.—A pendulum is a weight (bob) suspended from a horizontal axis. If a leaden ball be suspended by a fine thread of about 3½ feet in length, it will nearly beat seconds of time in its oscillations. If, while beating, the thread be caught half-way between the point of suspension and weight, the oscillations will be more rapid, this increasing as we shorten the length of the thread, so that the shorter the pendulum the more rapid is its oscillation. Upon restoring this pendulum to motion again with full length of string, and noting the time required to make an oscillation, we will find that so long as the amplitude of oscillation (that is, the length of the arc through which it beats) does not exceed 5 degrees, the time of beat is invariably the same (isochronal). If the pendulum bob be drawn aside from its state of equilibrium, the force of gravity tends to draw it back, and, upon releasing, it falls to its lowest position; however, in consequence of its inertia and acquired velocity, it does not stop, but moves on in the opposite direction, forming an arc of a circle. By virtue of its new position the weight possesses potential energy, and again swings back over the same course.

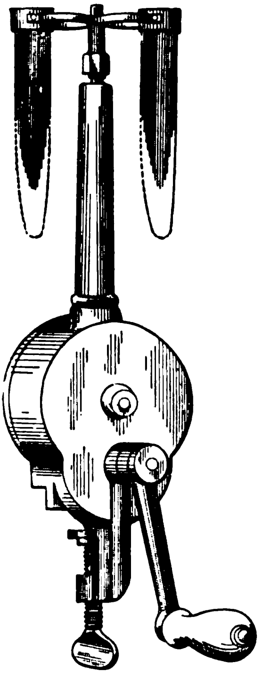
We have learned that the degree of attraction of the earth varies in different latitudes, and that this same attractive force is the cause of the oscillation of the pendulum; hence the length of a pendulum beating seconds of time must vary in different latitudes—that is, a seconds pendulum in New York must be lengthened as we proceed towards the poles and shortened as the equator is approached. If the earth were a true sphere a given body would be equally attracted anywhere upon its surface, but owing to its flattened condition at the poles (the polar diameter being about 43 kilometers less than the equatorial diameter), these polar regions are nearer to the center of gravity than the equatorial, hence attraction at the equator is somewhat less than at the poles. Also, in consequence of the earth's rapid rotation, a certain portion of this force of attraction is employed in retaining the body upon its surface; otherwise it would be deflected off in consequence of centrifugal motion. The combined effect of these two causes—flattening at the poles and centrifugal force—lessens the attraction of gravitation at the equator to the extent of about $^1/_{192}$ part of its value at the poles.

The length of the seconds pendulum being known, the acceleration of gravity can readily be calculated; the relationship may be seen in the following table. The acceleration of gravity = length of the seconds pendulum × the square of 3.14159.

	Latitude	Length of Pendulum	Acceleration of Gravity	
Cape of Good Hope..	30° 55′ S.	39.0780 inches	32.1404 feet	9.7962 meters
New York	40° 43′ N.	39.1012 "	32.1504 "	9.8019 "
Hammerfest	70° 40′ N.	39.1948 "	32.2364 "	9.8258 "

Compensating Pendulum.—Owing to the effect of heat and cold in causing metals to expand or contract, a compensating arrangement must be provided for in the pendulums of accurate time-keepers; otherwise, owing to their expansion or contraction, they will require constant readjustment.* This may be provided for by using two different metals attached in such a way that the downward expansion of one will be exactly counteracted by the upward expansion of the other, thus keeping the length of the pendulum always the same. Another form consists in employing a tall jar of mercury supported in a stirrup as the pendulum bob. As the pendulum rod expands and lowers the center of oscillation, the mercury by its upward expansion in the jar raises it, and the equilibrium is maintained.

FIG. 3.



Centrifuge.

CENTRIFUGAL AND CENTRIPETAL FORCES (MOTIONS).—*Centrifugal* force is simply a manifestation of inertia, and signifies flying from a center of motion. If a weight attached to a string be whirled about the hand it has a continual tendency to fly off in a straight line. This tendency is also seen in mud flying off from a rapidly revolving carriage-wheel. So great is this centrifugal force that not infrequently grindstones and fly-wheels, when their rate of revolution is very rapid, are torn asunder and the parts thrown about with destructive violence. Owing to this force, in the construction of the sharp curves in a race-course, or railroad, the outside track is raised higher than the inside, so that the moving object is inclined inward. In consequence of this the weight and centrifugal force are perpendicular to the path.

Centripetal force is that which resists centrifugal, and means moving toward the center of motion. The attraction of gravity which draws all bodies towards the earth's center is an example of centripetal force;

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* A rise of about 15° C. causes a lengthening of about ¼ millimeter ($^1/_{100}$ inch) of a common pendulum, and this will cause the clock to err about 10 seconds in 24 hours.

this prevents the centrifugal force, resulting from the earth's rapid rotation, from ejecting bodies into space. As already stated, centrifugal force causes a lessening ($^1/_{289}$) in the attraction of gravity (weight) at the equator; for here this force is greatest, and as we approach either of the poles it grows feebler. The flattening of the earth at the poles is the effect of centrifugal motion. It is the attraction or centripetal force of the sun that retains the earth in its orbit.

If a sponge full of water be attached to a string and rapidly whirled about, centrifugal action throws off the water, leaving it almost dry. This principle is practically applied in the *centrifuge,* which commonly consists of a drum-like receptacle perforated around the sides and with a solid bottom, which revolves on an axis. This centrifuge revolves inside a stationary drum, somewhat larger, which serves to collect and drain off the fluid ejected. Into this centrifuge is placed the material to be dried, and then it is caused to revolve at the rate of from 1200 to 2500 revolutions a minute. All fluids are thereby forcibly ejected. In this manner the adhering wash-water may be removed in the preparation of absorbent cotton, the uncrystallizable molasses from sugar, and the mother liquor from crystallized chemicals. This same principle is employed in the centrifugal clothes-wringer and the cream separator. Precipitation in fluids, whether for the collection of precipitates or bacteria, may be greatly facilitated by placing them in test-tubes and rotating rapidly in a centrifuge of the form shown in Fig. 3, on the preceding page.

8. Machines.—*Machines* are devices used for the purpose of employing to better advantage the natural forces. They are sometimes said to be "labor savers," and although at times there appears to be more work "got out" than is "put in," this, of course, cannot be, since "energy cannot be created nor destroyed."

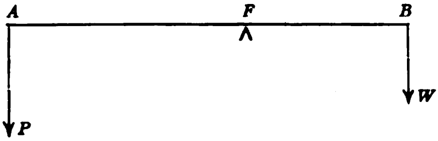
The General Law of Machines.—The work done by a machine in overcoming a force is called *resistance* or *weight,* while the terms *effort* or *power* are given to the force used to operate the machine. If we remember that energy is regarded as work or force times space, then it becomes evident that with a given amount of energy the force may be *increased* in the same ratio that the distance through which it acts is *decreased.* This principle, known as the general law of machines, may be stated thus: *the force applied multiplied by its acting distance is equal to the force exerted multiplied by its acting distance,* or *the power* (*effort*) *times the distance through which it acts is equal to the resistance* (*weight*) *times the distance through which it is moved;* or $Pd = RD$; or Work in = Work out. Due to friction, there can be no perfect machine; that is, one where there is not some waste of energy. In elementary study this loss or waste due to friction may be disregarded. Although there exists for each machine a specific law, the above general law holds good in all cases.

Simple Machines or Mechanical Powers.—The six elementary machines are the *lever,* the *pulley,* the *inclined plane,* the *wedge,* the *wheel and axle,* and the *screw.* As mentioned above, there can be no gain in actual work done through the use of a machine. Whatever is gained in force is lost in speed, and, *vice versa,* whatever is gained in speed is lost in force. The real advantage gained in causing a greater force to act through a lesser distance by the application of lesser force acting over a greater distance is called the *mechanical advantage.*

The *lever* is a rigid bar moving on a fixed point called the *fulcrum.* The " see-saw " and the equal armed balance are examples of an *equal armed lever.* With this type of lever no mechanical advantage is gained. The two arms being of equal length and the weights being equal, it follows that *power times its distance = weight times its distance.*

Levers with Unequal Arms.—(a) *Levers of the first class;* fulcrum (F) between power (P) and weight (W). Examples, a crowbar or a pair of scissors.

FIG. 4.

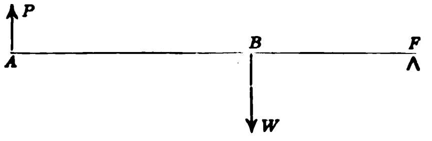


Lever of first class.

The mechanical advantage may be either of force, if AF (power arm) is greater than BF (weight arm); or of speed, if AF is less than BF. If we have a crowbar with which we wish to raise a stone weighing 200 pounds and the distance between the fulcrum and hands (power arm) is 5 feet and the distance from the fulcrum to the stone (weight arm) is 1 foot, then it will take a power of 40 pounds to raise the stone. This is in accordance with the *law of the lever,* Power : Weight :: Weight arm : Power Arm. While the weight of 200 pounds is being raised, say, 1 foot the power of 40 pounds must act through a distance of 5 feet. Work out = work in. 200 × 1 = 40 × 5.

(b) *Levers of the second class;* weight (W) between fulcrum (F) and power (P). Examples, a nutcracker or a wheelbarrow. The mechanical advantage is always one of force. This class differs from the foregoing in that the power arm is the whole length of the lever and that power and weight act in opposite directions instead of in the same direction.

FIG. 5.



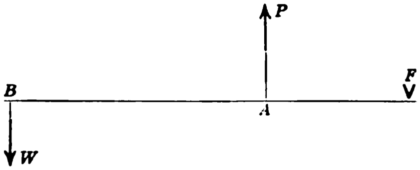
Lever of second class.

(c) *Levers of the third class;* power (P) between weight (W) and fulcrum (F). Examples, a pair of tweezers or the forearm. The mechanical advantage is always one of speed, as the power arm is longer than the weight arm.

The pulley is a small wheel turning freely about an axis. A fixed pulley simply changes the direction of the applied force. It is a modified equal armed lever. With a movable pulley in combination with a fixed one (block and tackle) the mechanical advantage gained is equal to the number of cords *supporting the weight.*

The Inclined Plane.—A pair of skids or a plank used to roll a barrel into a wagon is an example of an inclined plane. The mechanical advantage is one of force. It is *easier* to push a barrel up a gradual incline into the wagon than to lift it vertically. The law of the inclined plane, *power : weight : : height : length,* again demonstrates that *work in = work out.* If we have a plane 15 feet long (L) and 5 feet high (H) and we wish to raise a box weighing 300 pounds (W), it will require a force of 100 pounds (P) to accomplish this (friction being disregarded).

FIG. 6.



Lever of third class.

The *wedge* is a modified inclined plane and may be considered as two inclined planes placed base to base. The *screw* is also a modified inclined plane, while the *wheel and axle* is a modified lever.

CHAPTER II

SPECIAL PROPERTIES OF MATTER

(A) Special Properties of Solids

It is obvious from the definition of solids as contrasted with liquids and gases (see page 2) that they must have properties which are distinctive, and are not shared in any notable degree by the other forms of matter.

Hardness is the resistance to wearing by friction, such as scratching or rubbing, shown by a solid. It is possessed in the highest degree by the diamond, which is, therefore, capable of scratching any other solid. Hard bodies are often used as polishing powders, as diamond dust, emery, pumice, and tripoli. Great hardness may be imparted to steel and other bodies by a process called tempering; that is, cooling them suddenly from a high temperature. Under these circumstances, however, they usually become more brittle.

Brittleness is inability to withstand compression or a blow, and indicates a want of tenacity or cohesive power between the particles of the solid. It may accompany great hardness, as in the diamond and glass.

Tenacity is the resistance to a tearing or pulling strain exerted upon solids. It may vary in different directions in the same body, as in the case of wood, where it is greater in the direction of the fibres than transversely to them. Tenacity varies with different substances and also with the form of the body. The mass being the same, the hollow cylinder possesses a greater tenacity than a solid one. A strand of wires is stronger than a solid rod of the same section. Among all metals cast steel has the greatest tenacity, followed in order by platinum, copper, silver, and lead.

Ductility is the capability of being drawn out into wire or threads, and is possessed especially by certain metals, like gold, platinum, iron, and copper. Glass and waxes when hot can also be drawn out into fine threads. The most ductile metal is platinum.

Malleability is the property by virtue of which bodies are flattened into thin sheets or films under the influence of hammering or rolling. It is possessed especially by metals, such as gold and copper. Lead and tin, while very malleable, possess very little ductility.

Elasticity.—Matter is said to be elastic if after a temporary alteration of shape or volume the displaced particles tend to revert to their original position. This is shared by solids, liquids, and gases, although in unequal degrees. Elasticity of traction, or that developed by a stretching force; elasticity of torsion, or that developed by a twisting force, and elasticity of flexure, or that developed by a bending force or weight, are other phases of elasticity belonging to solids. Elasticity of torsion is represented in the torsion balance, which measures weight by balancing against the twisting force of a wire. The elasticity of flexure is applied in the steel spring coil, the carriage spring, also the spring spiral balance. This latter consists of a coiled spring fixed at its upper end, which from its elongation indicates the weight of a body placed in a scale-pan suspended from the lower end of the spring.

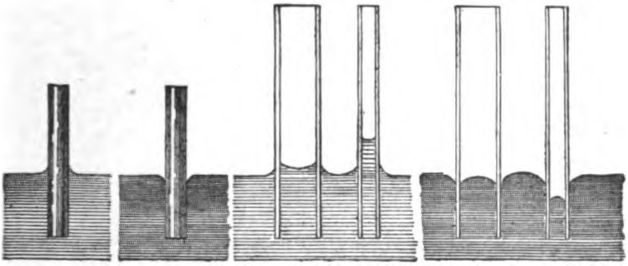
Structure of Solids.—A solid is distinguished from a liquid or gas by possessing definite shape independent of the containing vessel. When we examine more closely the structure of solids, we observe notable differences. Certain substances, for instance, on passing from the liquid to the solid condition, assume characteristic shapes, as alum, nitre, sugar, ice, etc., while others become solid without assuming distinctive shapes, as fats, waxes, and flocculent and gelatinous precipitates. The former are called crystalline bodies and the latter amorphous. Again, crystalline bodies have differences of structure, due to cleavage, as in mica, rock-salt, etc., or to confused crystallization, as in granular minerals like marble, emery, etc. The several systems under which all crystalline bodies may be classified will be referred to later (see page 52).

(B) SPECIAL PROPERTIES OF LIQUIDS

1. Attraction and Repulsion in Liquids.—*Capillary Phenomena.*—We have already referred to the adhesion of liquids to solids, in speaking of the moistening of a rod of glass with water as illustrative of the force of adhesion (see page 10). Not all liquids show this attraction. Some even show a repulsion of the solid, as when a glass rod is dipped into mercury. Instead of a curving upward of the surface of the liquid on all sides of the glass rod, as with water, a depression of the surface occurs immediately around the rod, showing that repulsion exists between the mercury and the glass. The water is drawn upward around the rod because its adhesion to the glass distinctly exceeds the cohesion of the liquid; the mercury adheres to glass much less strongly than it coheres, and hence it curves away from the rod. These attractions and repulsions have an interesting illustration in the phenomena known as *capillarity,* observed when tubes of relatively fine diameter are dipped into liquids. If a glass tube be dipped into a liquid which wets it (or adheres), as in the case of water, the liquid will rise in the tube to a higher level than the surrounding surface, and the height is the greater the smaller the diameter. If, on the other hand, the tube be dipped into a liquid which does not wet it (or adhere), as in the case of mercury, the liquid will be depressed in the tube below the surrounding surface, and the smaller the diameter of the tube the greater the depression. These phenomena with rods and tubes are illustrated in Fig. 7. Many natural phenomena, such as the rise of moisture in rootlets and stems of plants, the rise of oil in a lamp-wick, the absorption of water by filter-paper or sponges, are to be considered as illustrations of the principle of capillarity.

Diffusion of Liquids.—Closely connected with capillary phenomena are those of diffusion. If two liquids of different densities, but capable of admixture, be placed one above the other in the same vessel, they will begin to mix or diffuse through each other, even if the upper liquid be of less density than the lower. This will also take place though they be separated by porous partitions of various materials. But it is found that the rate of diffusion differs greatly for different substances. Many solids when in solution will diffuse rapidly, while others will diffuse with great slowness. The former class will be found to include most crystallizable solids, like salt, sugar, magnesium sulphate, etc., while the latter class includes uncrystallizable or amorphous substances, like starch, gum gelatin, or glue. To the former class the term *crystalloids* has been given, and to the latter term *colloids* (from the Greek word for glue).

FIG. 7.



Capillary attraction and repulsion.

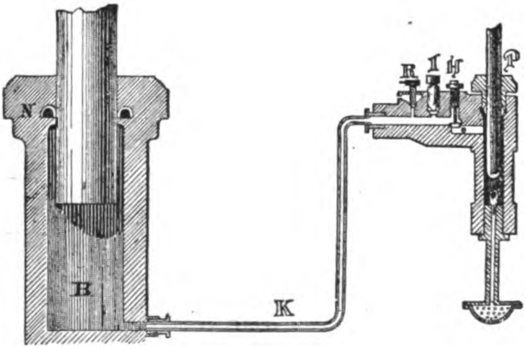
Graham founded upon this property of unequal diffusibility through porous membranes now called *osmosis* the process of *dialysis.* A sheet of bladder or parchment paper is stretched tightly over the lower end of an open cylinder or inverted glass funnel. The mixture of liquids to be separated by dialysis is poured in above, and the dialyser supported with the lower end immersed in pure water contained in a larger outer vessel. The crystalloid substances will diffuse through the membrane, and be found in solution in the outer vessel, while the colloids will remain in the inner vessel, or dialyser.

2. **Pressure of Liquids.**—Liquids are but slightly compressible, and with the removal of the force causing pressure recover immediately their original volume. For this reason and because of the ease with which their molecules are free to move, they readily transmit pressure throughout their entire mass. This pressure is transmitted throughout the liquid equally in all directions, whether it is that in which the force is applied or at an angle to it.

This is illustrated in the case of the sprinkling nozzle of a garden hose, or similar apparatus, where the water is seen to issue with equal force from all the apertures. Of course, if the pressure in the one case is exerted over a larger area of surface than in the other, a different total force is felt in consequence. Here we must multiply the intensity of the pressure per *unit* of *surface* by the *area* of *surface* to get the total force exerted. Hence a pressure of five pounds per *square inch* exerted over a *surface* of *sixteen square inches* would be felt as a pressure of eighty pounds upon that *surface*.

An important application of this principle of transmission of pressure, and exertion of the same over a larger surface than that where it was applied, is found in the hydraulic press. This, as shown in Fig. 8, consists of a small force-pump, in which works a solid piston, P. When this piston is depressed by means of a lever the valve *o* in the bottom of the cylinder is closed and the water is forced over through the connecting tube, K, into the larger cylinder, B. Here the pressure of the water upon the piston is exerted over an area perhaps a hundred times greater than that of the piston of the small pump, and hence the pressure is multiplied a hundred-fold. It must be remembered, however, that in our definition of energy and statement of the law of the conservation of energy (see page 7) we said that energy could not be created any more than it could be destroyed. So in the hydraulic press the energy developed in the larger cylinder is only seemingly greater than that exerted in the smaller cylinder. Though the pressure on the larger piston is one hundred times that applied to the smaller piston, the former moves through $\frac{1}{100}$ of a foot while the latter moves through one foot. The hydraulic press is of great value in compressing cotton, hay, and other loose but bulky material, and in lifting heavy weights or moving machinery, also for the removal of oil from seeds.

FIG. 8

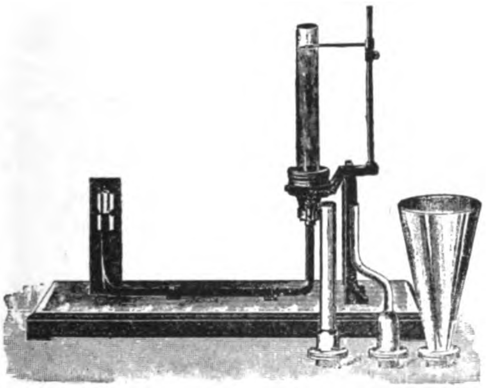


Hydraulic press.

Vertical Downward Pressure.—In considering the pressure exerted throughout the body of a liquid we have so far disregarded the weight of the liquid itself. It is obvious that the weight of the upper layers of the liquid bears upon the layers immediately under them, and that the bottom layer therefore supports considerable weight. But because of the perfect mobility of the liquid molecules and the equal transmission of pressure in all directions, this pressure will be felt equally in all parts of the same horizontal layer, on the sides of the containing vessel, as well as upward and downward from that level. The pressure exerted by a liquid upon the horizontal bottom of a vessel is entirely independent of its shape, and is equal to the weight of a vertical column of the liquid, whose diameter is equal to that of the horizontal bottom and height of the liquid in the vessel.

A small body of water may exert as great a pressure upon the bottom of the containing vessel as a much larger body of water, if the height of the liquid is the same in the two cases. This is true, although the two bodies of liquid may weigh differently because of the difference in amount. This may be illustrated (Fig. 9) by means of a wide U-shaped tube, to the upper right arm of which can be fitted tubes of various sizes and shapes. The lower tube is filled with mercury until it reaches a point indicated near the top of the left extremity. If a tube of any given diameter is attached to the right arm and filled to a certain height with water (indicated by a movable needle), the weight of this will force the mercury column up a certain distance. If this tube of water is substituted by others, the bottom diameter and height of the column being the same, the pressure exerted will be identical, irrespective of the shape of the vessel and the quantity of water it may hold.

FIG. 9.



Pressure on bottom of vessels.

Upward Pressure. Buoyancy.—That the pressure in any horizontal layer of a liquid is exerted equally upward as well as downward or laterally is an important fact, and is capable of a simple demonstration. If we take a glass cylinder, open at both ends (an Argand lamp chimney with one end ground perfectly flat will do), and, closing one end with an accurately fitting glass or metal plate, lower it into a vessel filled with water, we find that the plate is held in position by the upward pressure. Water may then be poured into the glass cylinder until the level inside nearly or quite equals the level outside, when, the upward pressure having been compensated for, the plate will drop off, because of its weight.

Lateral Pressure.—This is the pressure exerted upon the sides of the containing vessel, and is equal to the weight of a column of liquid which has a given portion or the entire side for its base, and whose height is the vertical distance from the center of gravity of that portion to the surface of the liquid. In view of this, it is better to construct tanks for water with a considerable area of bottom and moderate height, so as to relieve the sides of the great pressure.

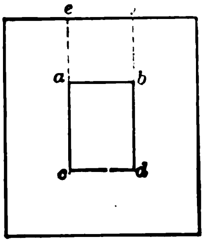
Equilibrium of Liquids.—As every molecule in the body of a liquid is free to move, it is obvious that the force of gravity will act upon all parts of the liquid equally, and the liquid will come to rest only when each part of the liquid is in a position of stable equilibrium. This is attained when the surface of the liquid assumes a position at right angles to the perpendicular or line in which the force of gravity is felt. We call the position so assumed a horizontal line, and the surface of a liquid free to respond to this force therefore will always be horizontal, no matter what the shape of the containing vessel. The level in several communicating vessels will also speedily become the same, as equality of pressure soon establishes itself throughout the entire body of liquid, and the several surfaces come to rest in the same horizontal plane.

Just as the plumb-line is a practical device for quickly and easily determining the perpendicular line, so we have in the spirit-level a ready means of determining whether a surface is perfectly horizontal. It consists of a glass tube nearly filled with alcohol, a bubble of air only remaining. When this tube is mounted in a wooden or metal case, and the latter placed upon a horizontal surface, the air-bubble shows exactly in the middle of the upper surface of the tube, upon which a scale is marked. If the surface upon which the level is placed is not perfectly horizontal, the bubble moves towards one end or the other of the scale instead of remaining in the middle.

3. **Pressure upon Bodies Immersed in Liquids.**—If a body be immersed in a liquid, every particle of its surface will be exposed to a pressure. As the lateral pressures act from all sides, they are equal and hence neutralize each other. The upward pressure against the under surface (*c, d,* Fig. 10), which is equal to the weight of the liquid column (*c, d, e, f*) from the surface to the bottom of the body, *exceeds* that

of the downward pressure, exerted upon the upper end of the body, which is equal to the weight of the column (*a, b, e, f*) from the surface of the liquid. Hence the solid will be pushed upward by a pressure equal to the excess of the former weight over the latter, which is equivalent to the weight of a column of the liquid occupying the same volume as the submerged body (*a, b, c, d*). This excess of upward pressure (*buoyancy*) reduces the weight of the immersed body in amount equal to the weight of the same volume of water displaced. Expressed in the principle of Archimedes: *a body immersed in a liquid loses a part of its weight equal to the weight of the displaced liquid.*

FIG. 10.

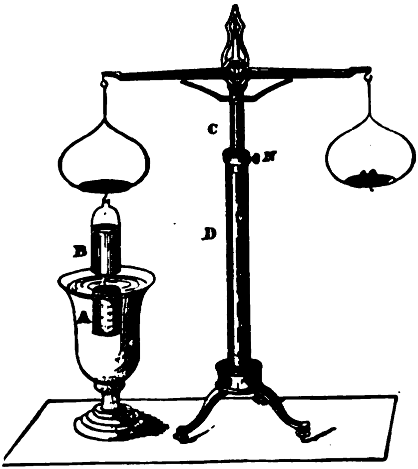


This statement may be demonstrated by the hydrostatic balance, as shown in Fig. 11. The solid brass cylinder A fits exactly in the brass cup B. The two are hooked together, suspended from the one pan of a balance, and counterbalanced exactly by weights placed in the other pan. A glass globe, or other vessel, is now placed in position around the brass cylinder, and water poured in gradually. The buoyant effect of the water causes the cylinder A to rise, so that the two pans of the balance no longer show equilibrium. If, however, water is poured into the brass cup B, the cylinder sinks, and when the cup has been filled, it will be found that the cylinder is just immersed, and that the two sides of the balance are exactly in equilibrium. Obviously the brass cylinder lost a portion of its weight exactly equal to the weight of an equal volume of water.

This so-called principle of Archimedes gives us a convenient means of determining the volume of any solid which is not soluble in water. By weighing the solid first in air and then when immersed in water, we arrive at the weight of the equal volume of water displaced, and, as the relations of weight and volume of water are known (1 cubic decimeter of water at 4° C. weighing 1 kilogram), we get the volume of the body which displaced the water.

Its most important application, however, is in determining the relative weight of different solids and liquids, or, as it is termed, their *specific gravity* or density. The density or specific gravity of a body represents the relative degree of closeness of the particles which make up its mass (see page 4). In order to ascertain this, comparison is made between the weight of a given volume of the body and an equal volume of some standard. For solids and fluids, distilled water (at either 4°, 15.6°, or 25° C.) is selected; for gases, hydrogen or pure air is selected; their density being calculated to

FIG. 11.



Hydrostatic balance.

0° C. and 760 mm. We say the specific gravity of iron is 7.7; this means that it is 7.7 times denser than water. The density of ether is 0.725—that is, where a certain volume of water weighs 1000 grams, the same volume of ether would weigh 725 grams; it is, therefore, lighter than water.

Owing to the difficulties attending the taking of specific gravity at 4° (water being 1.000 at this temperature), the operation is usually carried out either at 15.6° or 25°, comparing the weight of the substance to that of the same volume of water, at either of these temperatures. In such cases the results are indicated by the figures $\frac{15.6^\circ}{15.6^\circ}$ or $\frac{25^\circ}{25^\circ}$. If it is desired to compare (calculate) the gravity to that of water at 4° (indicated by figures $\frac{15.6^\circ}{4^\circ}$ or $\frac{25^\circ}{4^\circ}$), the results are multiplied by the specific gravity of water (see footnote page 45) at 15.6° (0.99907) or 25° (0.99707).

Specific Gravity of Solids.—Weigh the body in air, then weigh again when immersed in water, and the weight in air divided by the loss of weight when weighed in water will give the specific gravity.

In carrying out the specific gravity determinations of solids practically we have several methods to choose from. We may use the specific gravity balance, in which case the solid is suspended from one arm of the balance by a hair or silken filament, and weighed first in air and then immersed in a small cup of water supported independently of the balance-pan and not touching it. Or, for powdered solids, the specific gravity flask may conveniently be used. This is a small glass-stoppered bottle, the weight of which, both empty and filled with distilled water, at the standard temperature has been determined. For greater accuracy the ground-glass stopper is perforated, so that in fitting it in the bottle any excess of water may be forced out and wiped off with a piece of soft paper. In making a determination, the bottle is carefully dried, and, the powder having been placed in it, is weighed. This gives the weight of the solid in air. The bottle is then filled up with water, the excess being wiped off from the top of the stopper, and weighed. The weight found is that of the powder, the bottle, and the original volume of water minus what has been displaced by the powder, which, of course, gives us the weight needed for the specific gravity calculation. In this determination by the aid of the specific gravity bottle, the water must be previously boiled to expel the air.

In the case of solids soluble in water, some other liquid, like naphtha or oil of turpentine, the specific gravity of which is already known, may be used. The solid is weighed in air and then immersed in the liquid chosen and the weight again taken. We are thus able to determine its specific gravity with reference to the liquid chosen. If the known specific gravity of this liquid based upon water be then multiplied by the specific gravity found, we will have the true specific gravity of the solid based upon water.

Specific Gravity of Liquids.—The specific gravity or density of liquids is usually ascertained by means of the specific gravity bottle. The exact weight capacity of these in distilled water is indicated on the outside. This is usually an even quantity, as 100, 50, 25, or 10 grams. All that is necessary, then, is to fill the bottle up to the indicated mark with the liquid to be examined (at 15.6° or 25° C.), and divide this by the weight capacity of the bottle. Thus, a bottle which holds, when filled, exactly 100 grams of distilled water (at 25° C.), will, when filled with glycerin at the same temperature, weigh 124.9 grams; with alcohol, 81.0 grams; hence their specific gravities would be

$$\frac{124.9}{100} = 1.249 \text{ and } \frac{81}{100} = 0.810$$

In practice, specific gravity is more conveniently, though less accurately, determined by the aid of what are termed *hydrometers.* These are long glass tubes with two bulbs blown at one end. The lower (smaller) bulb is weighted with mercury or shot to cause the tube to float upright, the upper (larger) bulb is to impart buoyancy. On the stem is marked a scale of degrees or equal parts. It is obvious that if one of these hydrometers sink to a certain depth of water, it will sink still deeper in a liquid lighter than water, or float higher in one heavier than water. If then the point to which it sinks in water be marked 1 of the scale, the distance above this would be marked in decimal fractions less than 1, while the distance below would be marked in fractions greater than 1. In order to mark slight differences more accurately, a number of hydrometers are used in a set, of which several are weighted and graduated for liquids lighter than water and several for liquids heavier than water. Arbitrary scales are also in use for hydrometers, such as that of Baumé for liquids heavier than water, and also lighter, also those of Tralles, Twaddell, Gay-Lussac, Beck, etc. Special forms for particular liquids are also used, as alcoholmeters, salinometers, saccharometers, lactometers, etc.

Density of Gases.—The density of a gas or vapor* is the amount of matter contained in the unit of volume, or it is the number which expresses how many times heavier or lighter it is than an equal volume of hydrogen or oxygen or air (specific gravity) at the same temperature (0°) and pressure (760 mm.). Density may be calculated by dividing the molecular weight of the gas by that of the standard. Thus the density of carbon dioxide (H = 1) would be $\frac{43.67}{2} = 21.835$, since,

Mol. wt. of H.		Mol. wt. of CO_2.		Density of H.		Density of CO_2.
2	:	43.67	::	1	:	x

$x = 21.835$

---

* The term vapor is applied to the gaseous form of substances that at normal temperature and pressure exist in the solid or liquid state. As examples we have the gaseous halogen acids, sulphur trioxide, nitrogen tri- or tetra-oxide.

If the density is compared to air = 1, we divide the molecular weight of the given gas by 28.75 or 28.95 (calculated mol. wt. of air, referring to $H_2 = 2$ or $O_2 = 32$). In the case of carbon dioxide $\frac{44}{28.95} = 1.519$. The density of air corresponds to its molecular weight (28.75 or 28.95), for,

Wt. of 1 L. O.		Wt. of 1 L. air.		Mol. wt. of O.		Mol. wt. of air.
1.4296	:	1.2934	::	32	:	x

$x = 28.753$

The density of a gas may also be ascertained by dividing the weight of 1 liter of it by the weight of 1 liter of the gas (hydrogen or oxygen) selected as unit. Oxygen is $\frac{1.4296}{0.089873} = 15.9$ times and air is $\frac{1.293}{0.089873} = 14.39+$ times heavier than hydrogen, and oxygen is $\frac{1.4296}{1.293} = 1.105+$ times heavier than air.

(C) GENERAL PROPERTIES OF GASES

1. **Attraction and Repulsion in Gases.**—*Physical Properties.*—As already stated, a gas is matter in such a condition that the repellent forces are superior to the cohesive among its molecules; hence gases tend to expand and diffuse unless confined. They are therefore distinguished from liquids by this tendency of indefinite expansion. The molecules of gases are in a constant state of activity, flying about in every conceivable direction, constantly colliding with one another with enormous velocities. As a result, gases exert a pressure (tension*) equal in all directions, which increases with the decrease of their confined space.

Since heat acts as a repellent force among molecules, the volume of gases will necessarily be subject to temperature changes—that is, expanding or contracting regularly with an increase or decrease of temperature (see Law of Charles, page 46). Likewise, the volume of a gas readily responds to an increase or decrease of pressure. This expansive force of gaseous bodies may be illustrated by placing a small rubber balloon partially distended with air or gas, but securely closed to prevent the escape of gas, under the receiver of an air-pump. Upon exhausting the air from within the receiver, the balloon immediately distends and swells to several times its original bulk. This is, of course, due to the expansion of the gas under diminished pressure, for when the air is admitted again to the receiver of the pump the balloon contracts to its original dimensions.

The law governing this change of volume under variations in pressure is known as *Boyle-Mariotte's law,* and is thus expressed: *The temperature remaining the same, the volume of a given quantity of a gas is inversely as the pressure it bears, also its density and tension* (*elastic*

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* The term *tension* as employed here means "elastic force" or "pressure."

force)*—that is, the less the pressure the greater the volume, and the greater the pressure the less the volume. Thus, if the pressure on a confined volume of a gas be *doubled,* its volume will be reduced *one-half,* and, as a consequence of this, the density (degree of closeness of its molecules) and tension (elastic force) of the gas will be doubled. In other words, the greater the tension the greater is the elastic force and the smaller the volume of the gas. It should be noted, however, that there are limits to this contraction in volume under the influence of pressure. Every gas, when sufficiently cooled, will at some definite pressure assume a liquid condition. No amount of pressure at any point above this temperature will cause liquefaction. This temperature of liquefaction is called the *critical temperature.* The pressure exerted by a gas at the critical temperature (at which it would condense at once if the temperature were lowered) is known as the *critical pressure.*

Owing to the great variations in volume produced by temperature and pressure, all calculations and comparisons are reduced to a *standard temperature* of 0° C. and *pressure* of 760 millimeters (page 30).

Diffusion of Gases.—All gases expand indefinitely, distributing themselves throughout the space of the containing vessel irrespective of the presence of other gases, provided there is no chemical reaction between them. This process of distribution is called *diffusion.* If, for example, two cylinders are placed one above the other, mouth to mouth, the upper one containing hydrogen, and the lower one carbon dioxide, although the latter is 22 times heavier than the hydrogen, the two will, after a time, become uniformly distributed throughout the two cylinders. To this property of gases we owe the uniformity of the mixture of oxygen and nitrogen as present everywhere in our atmosphere. If two gases be separated by a porous diaphragm such as parchment, rubber, unglazed porcelain, they will diffuse through, the lighter gas passing more rapidly than the heavier.

The rapidity of diffusion of two gases of different densities is *inversely as the square root of the densities of the gases.* Thus, as hydrogen is about 14.5 times lighter than air, it will diffuse nearly four times faster than air.

Collection of Gases and Vapors.—Gases and vapors are collected, according to their density, either over fluids or by displacement. (1) *Collection over fluids:* a jar or tube is filled with water and then inverted in a trough of water, keeping its mouth just below the surface. The

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* Hence the volume (v) of a mass of gas multiplied by the pressure upon it (p) is equal to the new volume (V) of the same mass of gas multiplied by the new pressure (P).

$$V \times P = v \times p \text{ or } V = \frac{vp}{P}.$$

If 100 mils of a gas under a pressure of 720 mm. be subjected to an increased pressure of 780 mm., what will be its new volume?

$$V = \frac{100 \times 720}{780} = 92.3+ \text{ mils.}$$

Compare with Law of Charles, page 46.

gas, escaping from a generator, is allowed to bubble upward, displacing the water. Such relative light gases as hydrogen, oxygen, nitrogen, marsh gas, and carbon monoxide are thus collected. Soluble vapors, as those of ammonia and hydrochloric acid, may either be collected over mercury or by (2) *Displacement:* this consists either in introducing the gas by a tube into the bottom of the jar, the entering gas displacing the air, when it is called *downward displacement,* or in passing the gas up to the top of an inverted jar, when it is called *upward displacement.* The height to which the vessel is filled may be judged in some cases by the color of the gas (as chlorine and nitrogen trioxide), in others by means of chemical tests, as the extinguishing of a lighted taper (as carbon dioxide, sulphur dioxide, ammonia). Carbon dioxide is so heavy that it can readily be poured from one vessel into another.

Absorption of Gases by Liquids and Solids.—The solubility of gases in water [*] conforms to the following laws:

1. *The quantity of gas absorbed decreases with the rise of temperature;* that is, as the temperature is lowered the amount of gas absorbed increases. For example, 1 volume of water dissolves 1 volume of carbon dioxide at 14° C.; at 0° C. it takes up 1.8 volumes. One volume of water dissolves 730 volumes of ammonia at 15° C. and 1150 volumes at 0° C. On raising the temperature of such solutions the excess of gas passes off.

2. *The quantity of gas dissolved increases or decreases with the pressure* (the temperature remaining the same). Thus, at the temperature of 14° C., 1 volume of water absorbs 1 volume of carbon dioxide under the pressure of 1 atmosphere; under 2 atmospheres, 2 volumes of the gas; under 3 atmospheres, 3 volumes. A solution of 5 volumes, under 5 atmospheres, is called " soda water." On removing this pressure the excess of gas escapes.

3. *The quantity of a gas which a liquid can dissolve is independent of the nature and quantity of other gases which it already holds in solution.* Thus, when air—a mixture of 1 part of oxygen and 4 parts of nitrogen—is dissolved in water, the gases are absorbed in the same proportion as though each were alone present—namely, 1 to 1.87—that is, a saturated aqueous solution of oxygen will take up nitrogen (or any other gas) as readily as though the former were not present.

Numerous examples of the solubility of gases will be found in the discussion of the chemical elements.

It will be noted that vapors—as ammonia, sulphur dioxide, hydrochloric acid gas, etc., which are more easily liquefied—are far more soluble in water than the true gases.

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[*] At the temperature of 0° C. and pressure of 760 millimeters, one volume of water dissolves of

Nitrogen	0.020 vol.	Sulphur dioxide	79.80 vol.
Oxygen	0.041 "	Hydrochloric acid gas	505.00 "
Carbonic oxide	1.800 "	Ammonia gas	1150.00 "
Sulphuretted hydrogen	4.37 "		

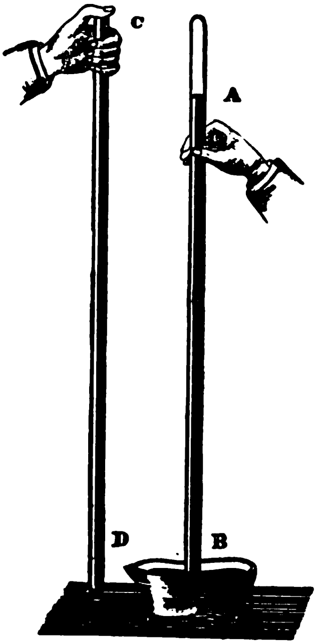
Porous bodies (meerschaum, charcoal) which expose an immensely increased surface in proportion to their size readily absorb large volumes of gas; for example, fresh wood charcoal will absorb 90 times its volume of ammonia gas, 55 volumes of sulphuretted hydrogen gas, 35 volumes of carbon dioxide, and so on. This explains the disinfecting power of charcoal.

Occlusion.—Certain metals, like silver or palladium, possess the power of taking up or occluding many times their volume of certain gases; for example, melted silver absorbs about twenty-two times its volume of oxygen from the air. This is expelled on cooling. At 100° C. palladium will absorb about 650 volumes of hydrogen. Platinum, in the form of powder (platinum black, or sponge), possesses high absorbent power; it will, for example, condense upon its surface two hundred and fifty times its volume of oxygen. Advantage is frequently taken of this, in order to bring about chemical combination between gaseous elements (see page 153).

2. **Atmospheric Pressure.**—*The Atmosphere and its Pressure.*—The atmosphere is a gaseous envelope that surrounds the earth; it is held by the attraction of gravity and attends the earth in its rotation. At the equator the velocity of the earth is over one thousand miles an hour. There are constant local disturbances in this gaseous ocean, which are chiefly due to changes in temperature, and, as a result, winds are produced which reëstablish this equilibrium. Since the atmosphere possesses weight, it consequently exerts a pressure upon all bodies. This pressure decreases as we ascend. The *downward pressure* may be simply illustrated by means of the leather sucker, which consists of a circular piece of thick, wet leather through the center of which a stout string is tied. This disk is then securely pressed against a flat object, removing all air from the under surface. A heavy object may thus be raised, since the downward pressure of the atmosphere binds the leather securely to the weight. The *upward pressure* can be demonstrated by filling a tumbler with water and covering with a piece of cardboard. Care should be taken that no air is admitted under the card. The card is held in position until the tumbler has been inverted, then, on removing the hand, the water will remain in the inverted glass, being held there by the upward air pressure. That the atmosphere *exerts a pressure equal in all directions* may be illustrated by the Madgeburg hemispheres, which consist of two metallic hemispheres, the edges of which have been accurately ground. When placed together a hollow sphere is formed, which can be exhausted of air through the stem of one of the hemispheres, which is provided with a stop-cock. After exhausting the air from the interior by means of an air-pump, the stop-cock is closed, and it will then be found that, on account of the pressure of the atmosphere upon the surface of the sphere, only by the exertion of a force greater than this pressure can the two hemispheres be separated.

These experiments show that the atmosphere exerts a pressure upon everything on the earth's surface with a weight which must be quite considerable. How much this pressure measures was first shown in the experiment of Torricelli illustrated in Fig. 12. A glass tube about a meter long and sealed at one end is filled with mercury. Having closed the open end of the tube with the thumb, the tube is inverted and dipped into a small vessel filled with mercury. The column of mercury is seen to fall, and after some slight oscillation remains stationary at 760 millimeters (about thirty inches) above the level of the mercury in the outer vessel. No matter how long the tube may be, or what its diameter, this height of the mercury column is always observed. Only one explanation of this fact is possible. It is that the atmospheric pressure will support a column of mercury 760 millimeters (about 30 inches) in height and no more. The space above the mercury in the inverted tube is a vacuum, and hence there is no counterbalancing pressure upon the mercury at this point. If the upper or closed end of the tube be provided with a stop-cock and air be admitted, the mercury in the tube will immediately fall to the same level as that in the outer vessel.

FIG. 12.

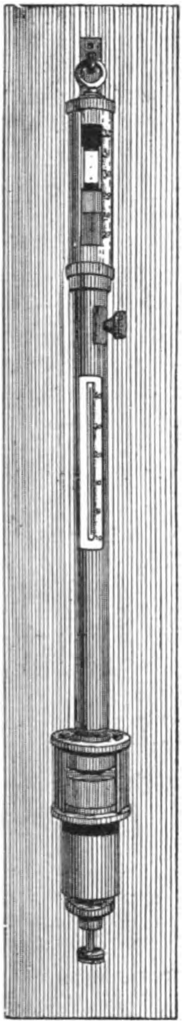


Torricellian tube and vacuum.

When water is used instead of mercury, it is found that the atmospheric pressure will support a column 10.36 meters (34 feet) in height, which is about 13.6 times as high as the mercury column. But mercury is 13.6 times heavier than water, so that the weight of the two columns is the same in the two cases, and is supported by the same pressure. To calculate the pressure necessary to sustain such a column, we will assume that the cross-section of our tubes is 1 sq. cm. (or, in another instance, 1 sq. inch), and the column of mercury is 76 cm. (760 mm.—in the second case about 30 inches) high. Since 1 cu. cm. of mercury weighs 13.6 gm. (or 1 cu. in. 0.4916 ℔), the weight of the column would then be $76 \times 13.6 = 1033$ gm., a little over 1 kg. (or $30 \times 0.49 = 14.7$ ℔). Consequently the atmosphere exerts a pressure of about 1 kg. on each sq. centimeter of surface (or 14.7 ℔ upon each square inch). Assuming that there is 1 sq. meter of surface to the human body, it must then be exposed to the pressure of 10,000 kg. Such a pressure is not perceptible, since it is exerted equally in all directions. The instruments used for measuring atmospheric pressure are called

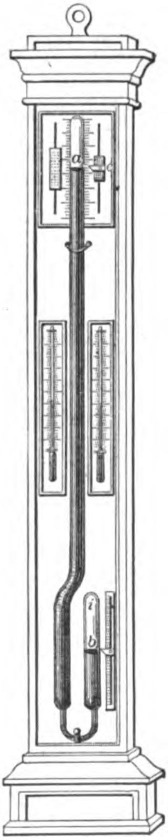
Barometers.—The simplest form of barometer, of course, is the straight tube of Torricelli, as just described. This tube, suitably mounted in a frame on which a scale has been constructed, and dipping into a small cup filled with mercury, constitutes the cistern barometer. A small opening is made in the cistern (Fig. 13) to allow the air access to the mercury. Another form, preferred for many purposes, is the siphon barometer, shown in Fig. 14. In this case the tube has two unequal branches, of which the longer is closed, and the shorter, acting as the

Fig. 13.



Cistern barometer.

Fig. 14.



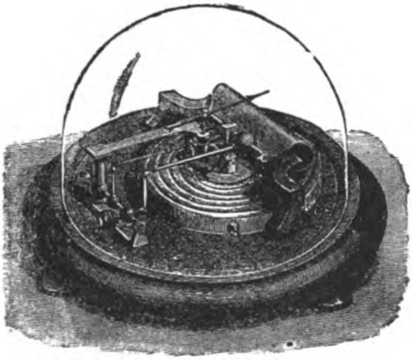
Siphon barometer.

cistern, has an opening communicating with the air. There are two scales, one at either end, so as to note the height of the mercury in either branch. The distance between the upper and lower levels constitutes the barometric column. In order that the instrument may be transported horizontally, a very fine calibrated tube connects the two columns, which prevents any air from penetrating into the longer arm. At the sea-level the normal barometric column measures almost thirty (29.92) inches of the English scale, or 760 millimeters of the metric scale. Since the lower layers of the atmosphere are denser than the upper, the barometric column will fall as we proceed upward. For each 10.5 m. elevation through which the barometer is raised, the mercury falls about 1 mm. To calculate the elevation, the difference in height in meters, D, between two places at T° C. and H mm., and t° C. and h mm., we apply the formula,

$$D = 16{,}000\left(1 + \frac{2(T + t)}{1000}\right) \times \frac{H - h}{H + h}.$$

Still another form of barometer (Figs. 15 and 16), and the one most generally used by travellers in determining the height of mountains on account of its lightness and portable character, is the ***aneroid barometer.*** This is a flat, thin-walled, circular box of corrugated metal partially exhausted of air and then hermetically sealed. The variations of the atmospheric pressure upon the surface of this box cause it to expand or collapse slightly, whereby a system of levers connected to a needle running over a graduated dial face registers the pressure. The graduation must, of course, be made by comparison with a standard mercurial barometer.

FIG. 15.



Aneroid barometer, mechanism.

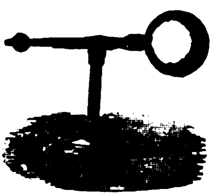
FIG. 16.

Aneroid barometer.

Barometric variations are usually opposite to those of the thermometer—that is, when the former rises the latter falls, and *vice versa.* The barometer indicates changes in the density and weight of the air caused by its expansion or contraction. Such changes, attended by a rise in the barometer, indicate conditions favorable to fair weather, while a continued fall of the column indicates precipitation.* However, weather conditions are largely influenced by the degree of humidity and the direction and force of the prevalent winds. Slight variations of the barometer take place daily.

3. **Buoyancy of Gases.**—The principle of Archimedes (see page 23), whereby a body immersed in a liquid loses a portion of its weight equal to the weight of the displaced liquid, is equally true of gases, and that they possess buoyancy or supporting power upon bodies immersed in them is easily shown. A small scale-beam is taken, capable of being put under the bell-jar of an air-pump, and from one arm of this a hollow sphere is suspended, counterbalanced by a small weight attached to the other arm. When this is put under the bell-jar and the air exhausted, the hollow sphere, deprived of the buoyant effect of the air, sinks and appears to be heavier than the small weight, which feels the buoyant effect of the air much less because of its smaller bulk. The apparatus employed for illustrating this phenomenon is called the baroscope (Fig. 17). Owing to this buoyant effect of the air, very accurate weighings are made in a vacuum.

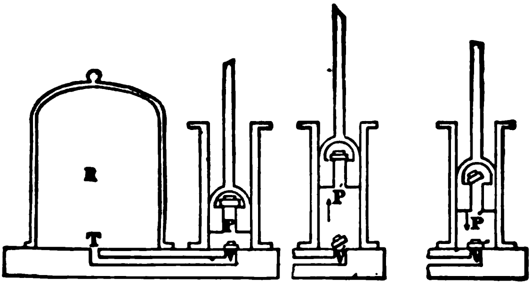
FIG. 17.



Baroscope.

4. **Apparatus Based upon Atmospheric Pressure.**—*The Air-Pump.*—The exhaustion of the air from any given space or the removal of the atmospheric pressure not only is important as allowing us to demonstrate the effects of this pressure, but is a necessary operation in many manufacturing processes, as in evaporation of liquids *in vacuo,* the exhaustion of globes for incandescent electric lamps, operating the condensers of steam-engines, etc. We will refer only to the portable forms of exhausting pumps for production of a vacuum. Fig. 18 gives a sectional view of the common form of air-pump. If we start with the piston P at the bottom of the cylinder, as it is drawn up the valve V′ opens upward and

FIG. 18



Air-pump.

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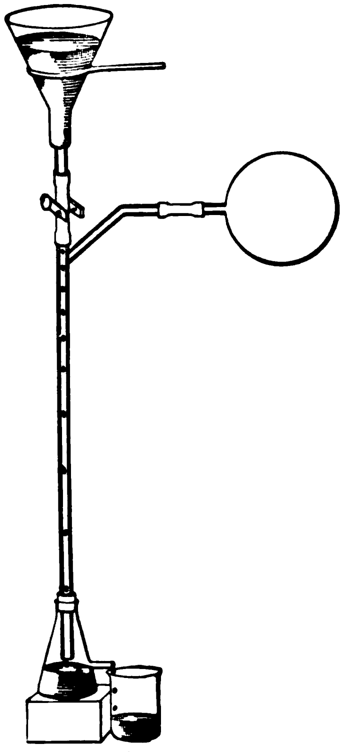
* The indications usually recorded on the dial face of aneroid barometers are:

31 inches,	787	millimeters—Very dry.
30⅔ inches,	779	millimeters—Settled weather.
30⅓ inches,	770.7	millimeters—Fine weather.
30 inches,	762	millimeters—Variable.
29⅔ inches,	753	millimeters—Rain or wind.
29⅓ inches,	744.7	millimeters—Much rain.
29 inches,	736	millimeters—Tempestuous.

air is drawn out of the receiver R. When the piston begins to descend, the valve V″ closes and the valve in piston P″ opens, letting the air escape into the space above the piston. The air can thus be considerably rarefied by a few strokes, but it is impossible to produce a perfect vacuum, owing to the difficulty of securing perfectly fitting joints for the apparatus.

A more perfect vacuum is attained by the aid of the Sprengel mercury pump. A simplified form is shown in Fig. 19. The Bunsen filter pump, which is much used in chemical and pharmaceutical laboratories, is constructed upon this same principle. It is attached to the water-tap, and water is forced through under considerable pressure. As high a degree of vacuum is not attainable with this as with the mercury pump. This consists simply of a vertical tube of narrow bore, something over a yard in height, a few inches from the top of which a lateral tube is made to connect perfectly air-tight. If now mercury be poured into the vertical tube by the aid of a funnel, in falling it draws the air from the vessel connected with the lateral tube until almost a complete vacuum has been established therein. These pumps are used in producing the vacuum needed for incandescent electric-light globes.

FIG. 19.



Mercury pump.

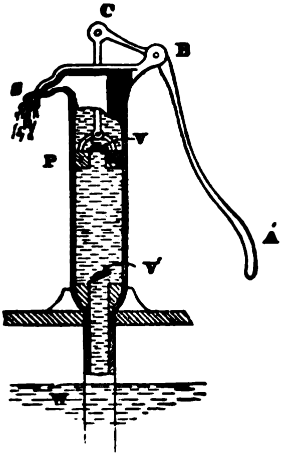
Condensing Pumps.—An air-pump with valves which draws in air when the piston rises, and forces it into a receiver when it sinks, the valve closing from inside pressure, is called a *condenser*.

Compressed air has many applications as a substitute for steam; also in tunnelling, laying of submarine caissons, air-brakes, in conjunction with air-pumps, in operating pneumatic mail tubes, etc. A condensing pump is also useful in condensing other gases than air, as in forcing carbon dioxide under pressure into solutions.

Lifting and Suction Pumps.—An important application of the principle of atmospheric pressure is seen in the pumps devised for the lifting of water from wells and cisterns. One of the common forms is illustrated in Fig. 20. The action here exactly corresponds to that in the cylinder of the air-pump. As the piston P is drawn up, the valve V′, known as a clack-valve, opens upward, and air with water following it is drawn up into the cylinder. As the piston descends, the valve V′ closes and V opens. After a few strokes the water is lifted by this action from the depth W to the cylinder and there remains, filling the whole length of the tube. It is obvious that the action of the piston first exhausts the cylinder of air, and that the water rises into the vacuum thus formed, where it remains unless the leakage of air in the cylinder causes the water to fall again to the level of that below. Other forms of pumps combine the principle of exhaustion and pressure, and thus can deliver a continuous stream of water.

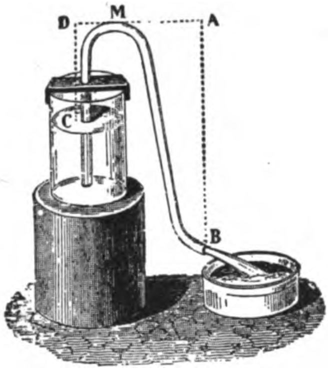
The Siphon.—This is simply a tube bent at an acute angle, open at both ends, and with legs of unequal length. If the siphon be filled with liquid and the longer end closed temporarily, on dipping the shorter leg into the liquid contained in an open vessel a flow begins when the longer leg of the tube is opened, and the liquid will drain from the vessel until the level falls below the end of the short leg. The explanation of the action of the siphon is simple, and is readily had from a consideration of Fig. 21.

FIG. 20.



Lifting pump.

FIG. 21.



Siphon.

The continuous flow is caused by the difference in pressure at C and at B. The pressure at C is the atmospheric pressure minus a column of liquid, C D; while at B it is the atmospheric pressure minus A B. And as this latter pressure is less than the other, the force depending on the ***difference in level,*** acting on the surface of the liquid at C drives the water out. The flow, moreover, is more rapid the greater the difference in level between the two ends of the siphon. The flow continues until the mouth of the siphon in the upper vessel no longer dips beneath the surface, or until the surface of the liquid in the upper vessel reaches the same level as that at B.

CHAPTER III

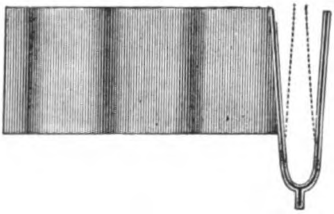
ACOUSTICS

1. Vibrations and Undulations.—*Acoustics* treats of the laws of generation, propagation, and comparison of sound.

Sound originates with vibrations of elastic matter. These vibrations excite undulations in the air, whereby they are communicated to the ear.

Vibrations.—All sounding bodies vibrate. These vibrations are oscillatory movements, like the swinging to and fro of the prongs of a sounding tuning-fork.

FIG. 22.

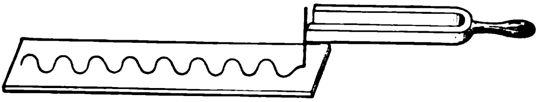


Vibration with wave production.

Undulations or Sound-Waves.—Vibrations are communicated to the ear by means of undulations or sound-waves in the air. Just as a pebble dropping upon the surface of still water produces wave-like rings due to vertical undulations, a vibratory body produces by its rapid backward and forward movement alternate condensed and rarefied air strata, which represent waves. Fig. 22 represents the formation of these sound-waves, as above described, while by means of an attached needle and drawing a vibrating fork over the surface of smoked glass the wave-motion described by these movements may be recorded, as shown in Fig. 23.

The length of a sound-wave is the distance from the middle of one condensation to the middle of the next—that is, from one wave-crest to the next crest. This represents one complete to-and-fro movement of the vibrating body. The height of a sound wave, or the distance from the middle point to either of its extreme positions, is known as its *amplitude*.

FIG. 23.



Sound-waves.

2. General Properties of Sound.—*A musical sound* consists of harmonic motion—that is, it is the result of a succession of vibrations at equal intervals and of sufficient rapidity. The human ear is limited in its range of hearing of musical sounds. The low limit is about 16 vibrations, while the high is about 38,000 per second. These extremes produce notes so low and acutely high that they are not appreciable to many: the average limits are usually placed from 40 to 5000 per second. The highest note produced by the piccolo is 4752 vibrations per second.

Propagation of Sound.—For the propagation of sound an elastic medium like the air is absolutely necessary. This is proved by suspending a bell in a glass globe from which the air has been removed by means of an air-pump. As the exhaustion proceeds the sound of the bell grows feebler, until it ceases altogether. Sound may be propagated to a great distance through the air. Cannonading has been heard fifty or more miles under favorable conditions. Sound travels still farther and more distinctly through the earth's surface; instances have been recorded in which it has been carried a distance of 370 miles.

Velocity of Sound.—That it requires an appreciable time for sound to travel from point to point may be seen in the difference of time elapsing between the flash of a distant gun and the report, or between the blows of a hammer and the time the sounds reach the ear. Experiments have shown that at 16° the velocity of sound is about 342 meters, or 1125 feet, per second. Since temperature affects the density of air, the velocity of sound increases about 60 cm. for each degree C. Moist air, being less dense than dry air, will likewise increase the velocity. Sound travels more rapidly in liquids and solids, owing to their greater elasticity. Thus—

In *water,* sound travels about 4 times as fast as in air.
In *lead,* sound travels about 4 times as fast as in air.
In *wood,* sound travels about 10–18 times as fast as in air.
In *steel,* sound travels about 16 times as fast as in air.
In *glass,* sound travels about 16 times as fast as in air.

Speaking-Tubes.—Sound-waves are propagated in every direction in open spaces, hence rapidly lose in intensity at a distance. However, on speaking into a trumpet (megaphone) or speaking-tube, the sound-waves issuing from the mouthpiece are reflected forcibly by the walls of the tube, and directly, without loss in intensity, in one direction a long distance. The ear-trumpet employed by deaf persons is a reversed speaking-trumpet; it serves to collect and concentrate the sound-waves. Based on this same principle is the *stethoscope,* an instrument used by physicians for locating sounds in the human body. This consists of a small, wide funnel made of metal or hard rubber, to the neck of which is attached a rubber tube, which can be adjusted to the ear. By means of this instrument feeble sounds are condensed and accurately transmitted.

Echoes and Resonance.—An *echo* is a reflected sound. When the distance of the reflecting surface is very short, the sound is strengthened and gives rise to *resonance.* A tuning-fork which has been struck sounds very much louder when the handle is placed on a box or is held in front of its open end. The same effect will be produced if held over the mouth of a wide tube closed at one end, or a cylinder. These are called resonant tubes or boxes, and the cause of their reinforcing effect is that the confined column of air vibrates sympathetically with the sounding object. This principle is employed in the construction of such musical instruments as the violin, zither, and piano; also the resonance of columns of air is the chief source of sound in wind instruments, as flutes, horns, organ-pipes. The openings in the flute and the valves in the horn regulate the length of the column of resonant air, while the pitch of the organ-pipe depends on its length. In those instruments based upon the vibration of cords or wires, as the violin, harp, or piano, the pitch of tone is governed by the number of vibrations, which, in turn, are controlled by the tension, length, size, and density of the cords. These conditions are formulated as laws:

1. *The number of vibrations is inversely as the length of the cord.* Thus, if a given cord makes 18 vibrations per second, it will make 36 (an octave higher) if its length be reduced one-half, or 54 when reduced to one-third.

2. *The pitch varies as the square root of the tension.* If the tension of a cord which gives a certain note be quadrupled, it will render a note an octave higher.

3. *The pitch varies inversely as the diameter.* Small cords vibrate more rapidly than large ones, hence render more acute sounds. A cord of any given size will give twice as many vibrations (an octave higher) as one double its size.

CHAPTER IV

RADIANT ENERGY.—1. HEAT

I. THE NATURE OF HEAT

HEAT is a form of energy due to molecular vibration. This vibration seems to be taking place in greater or less degree in all bodies, and, when communicated to the ether which fills all space around the vibrating body, is transmitted to the nerves of sensation, and so is felt as heat. The presence of air is not essential for this transmission of heat vibrations, as they are transmitted equally *in vacuo* as in air. When these vibrations are sufficiently rapid the heated body becomes luminous, and this manifestation of radiant energy is called light. Electrical energy seems to be due to vibrations of the same nature, but of still greater rapidity of movement. Such is the undulatory or vibratory theory of heat and light. The fact that one of these related forms of energy can be changed readily into the others, and that all of them can be produced from mechanical energy, renders this theory a very probable explanation of the observed phenomena.

II. SOURCES OF HEAT

1. **Physical Sources.**—It is to solar radiation absorbed and transformed that we owe primarily all the various manifestations of energy that take place on our planet. It is the energy of sunlight that sustains all forms of life and supplies us with food and fuel. According to Helmholtz, the earth receives only $\frac{1}{2,300,000,000}$ part of the whole solar radiation, and the source of the sun's heat is due to its contraction from a nebular state. Another theory is that the sun's heat is due to the energy of radio-activity. This is based upon the presence of enormous quantities of the element helium, which is a decomposition product of radio-active matter.

The earth possesses also a heat of its own, readily noted as we descend to any considerable depth below its surface, and made evident to us in hot springs and volcanoes. The rise in temperature is about 1° for every 30 meters of descent. The explanation most generally accepted for this is that the earth has cooled from a much more highly heated state, probably that of an incandescent gas, and that, while a hard crust has formed upon the surface, the interior of the globe is yet in a molten state.

Another explanation is that the earth is self-heating, due to the presence of radio-active matter. It is estimated that one gram of radium generates 864,000 calories per year. Since all matter (soil, water, air) is radio-active, Rutherford argues that this is of sufficient magnitude to balance the loss of the earth's heat into space.

2. **Chemical Sources.**—Most forms of chemical combination, as we will see later, are accompanied by the development of heat in definite amounts, or are *exothermic*. Hence every case of combustion going on about us in nature contributes to the development of heat. This includes the rapid combustion of all forms of fuel, and the slow combustion or decay of organic matter. It includes also the respiration of animals and the processes of assimilation of food, equally due to chemical and heat-producing changes. Those forms of fuel which are richest in the elements carbon and hydrogen possess the greatest value as fuel, as by the oxidation of these elements the maximum of heat can be developed. Hence the value for heating purposes of the several varieties of coal, of petroleum, of hydrocarbon gases, and of so-called " water-gas."

2. **Mechanical Sources.**—Friction and percussion are among the commonest of the methods by which heat is developed. The old device of obtaining sparks from a piece of flint and a steel, and the still older one of the savage of rubbing together two dry sticks to kindle a fire, are illustrations of the development of heat by friction. The " hot-box " on a railway car, where the heat developed by the friction of the car-axle in its box often suffices to ignite the oil-soaked waste, is also an illustration. The striking of the blacksmith's hammer upon the anvil readily illustrates the heat developed by percussion. In this case the energy of the mass of the hammer in descending is changed when it strikes into the molecular energy of the particles known and recognizable by the senses as heat (sparks).

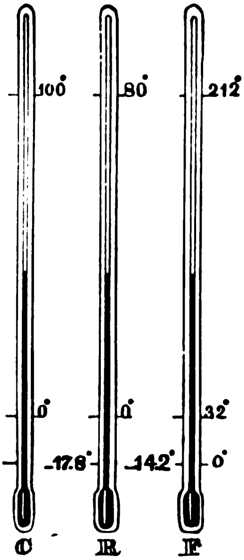
Mechanical Equivalent of Heat.—As already illustrated, heat, which is molecular kinetic energy, can be produced from mass kinetic energy (motion). The degree of heat generated is proportional to the energy of motion of its molecules. The first law of thermodynamics states that when mechanical energy is converted into heat, or when heat is converted into mechanical energy, the quantity of mechanical energy is equivalent to the quantity of heat energy. In the case of the descending hammer, should this weigh 1 kg. and it is raised 1 meter high, the work expended is equivalent to 1 kilogram-meter. The energy expended is distributed as heat in the hammer and anvil and in the propagation of the sound in the air.

Experiments have shown that a work of 424 kg. is consumed in heating 1 kg. of water through 1° C. The number 424 kg. is termed the *mechanical equivalent of the heat unit.* It expresses the intimate relation between work (energy) and heat, by the aid of which one may be transformed into the other.

III. Effects of Heat

The three states of matter, solid, liquid, and gaseous, are dependent upon temperature, which as a form of kinetic energy influences the internal forces of cohesion. In a solid, the molecules are in immediate contact, the relative positions of these are only altered by the action of external forces. Since temperature is proportional to the energy of molecular motion, then through heating a body we set its molecules to vibrating, the body expands, and if the temperature be sufficiently high, we overcome the force of cohesion and the molecules become more and more widely separated until fusion takes place. So long as the influx of heat energy is continued, cohesion will not be sufficiently strong to retain the vibrating molecules in their original positions of equilibrium. If we raise the temperature still further, we increase the intensity of molecular vibration until the fluid assumes the gaseous state. The heat energy consumed in changing the aggregate condition of matter from the solid to liquid or gaseous state is again liberated when the reverse process takes place.

FIG. 24.



Comparison of thermometer scales.

1. Measurement of Temperature.—By temperature we mean the thermal condition of a body with reference to its ability to communicate heat to surrounding objects. If two bodies of different temperature be brought into contact there will be an interchange of heat and cold until both reach the same temperature. Estimates of temperature based on the sense of touch are extremely inaccurate and variable, since they depend upon the sensibility of the individual. Temperature cannot be measured directly, hence we estimate it by its effects upon the volume of certain solids, fluids, or gases. Since expansion and temperature are in direct ratio to one another, we employ one for measuring the other. Instruments employed for this purpose are termed ***thermometers*** (heat measurers).

The ordinary thermometer is that in which mercury is used. It consists of a glass bulb of spherical or cylindrical shape connected with a fine capillary tube or stem. The bulb and part of the stem are filled with mercury, which is boiled to expel the air, and then the upper end of the tube is sealed. To establish a scale for the thermometer when thus filled, two fixed points are needed. One is obtained by immersing the bulb in melting ice, and the other by suspending it in steam from water boiling at normal pressure; these points are then permanently marked upon the glass. Between these two points the tube is divided into divisions, or degrees.

Three scales have been proposed and are now in more or less common use. The Fahrenheit (used commonly in England and the United States), the Réaumur (the domestic thermometer of Germany, Sweden, and Denmark), and the Centigrade or Celsius (used generally in Europe, but more particularly in scientific work). The two fixed points before referred to serve equally for all of these, but the method of dividing the space between the two points is different in each of them. The distinction between the several scales is shown in Fig. 24. In the Centigrade and the Réaumur scales the lower fixed point (the melting point of ice) is called zero, while in the Fahrenheit scale it is put at the 32d division of a scale which starts lower. The upper fixed point (the boiling point of water) is taken as 100 degrees of the Centigrade scale, as 80 degrees of the Réaumur scale, and as 212 degrees of the Fahrenheit scale. Consequently, the space between the two fixed points is divided into 100 degrees in the Centigrade scale, into 80 degrees in the Réaumur scale, and into 180 degrees in the Fahrenheit scale. Divisions of the same value are continued both above and below the fixed points upon each of the several scales, degrees below zero being indicated by the sign minus. One degree of the Centigrade scale (expressed 1° C.) will equal $^4/_5$ of a degree Réaumur (1° R.) and $^9/_5$ degrees Fahrenheit (1° F.).

The conversion of readings of the Centigrade scale into the corresponding readings of the Réaumur scale, and *vice versa*, is easily affected by the aid of this fraction, using the expressions $C.^\circ \times {}^4/_5 = R.^\circ$, and $R.^\circ \times {}^5/_4 = C.^\circ$.

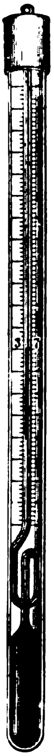
In the case of the Fahrenheit scale the problem is not quite so simple, as the zero of this scale does not agree with that of the other two, and instead of the lower fixed point of the scale being placed at zero it is 32 degrees above zero. To convert Fahrenheit readings into Centigrade we use the expression $(F.^\circ - 32)\ {}^5/_9 = C.^\circ$, and to convert Centigrade readings into Fahrenheit, ${}^9/_5\ C.^\circ + 32 = F.^\circ$ When the minus sign is prefixed to a reading, this must be taken into account in adding or subtracting the 32.

The Centigrade scale has displaced the others in exact and scientific work.

The limits of use of the mercurial thermometer are reached as we approach the freezing or the boiling point of mercury. The lower limit of accuracy is —36° C., as mercury freezes at —40° C.; the upper limit is about 300° C., as mercury boils at 350° C. If, however, that part of the capillary above the mercury column be filled with an inert gas, boiling of the mercury will be prevented by the resulting pressure, and the thermometer may be used for temperatures as high as 550° C.

Mercury thermometers increase their readings with age, and during the first year after their manufacture this increase amounts to as much as one degree or more. This change is due to the slow contraction of the glass bulb which takes place after blowing. Very accurate thermometers are filled at least two years before graduating. A thermometer is said to be *delicate* when it indicates very small differences of temperature. This depends on the ratio of the size of the bulb to the diameter of the capillary; for if the volume of mercury is large and the capillary small, a minute change of temperature will cause the column to rise through an appreciable distance. Thermometers are ***sensitive*** when they quickly assume the temperature of the surrounding medium. This depends upon the surface-area of the bulb. On account of its very uniform rate of expansion, mercury is preferred to all other fillings when it can be used.

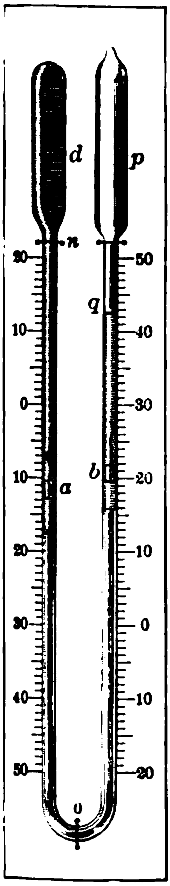
FIG. 26.



Fever thermometer.

Maximum and minimum thermometers are employed for recording extremes of temperature which have been reached during any period of time.

FIG. 25.



Maximum and minimum thermometer of Sixe.

The most convenient form is that of Sixe (Fig. 25), which consists of a U-shaped thermometer tube, the bend of which contains the mercury column. The left arm (above the mercury) and bulb are filled with alcohol, and the right is nearly full of alcohol. With rise of temperature, the alcohol in the left bulb (*d*) expands, and depresses the mercury column, which rises in the right, pushing a small wire (index *b*) covered with glass before it. With a lowering of temperature, the alcohol in the left bulb (*d*) contracts, and in consequence of the pressure from the compressed air in the right bulb (*p*), the column is pushed down the right and up the left arm, registering with the wire index *a*. The index in the left arm indicates the lowest and that in the right the highest attained temperatures. The indices are set by drawing down with a magnet.

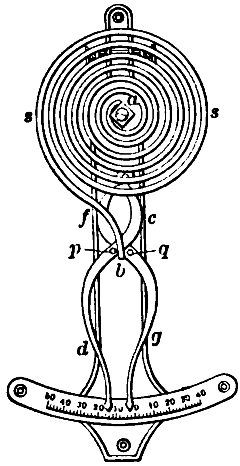
The *Clinical Thermometer* (Fig. 26), which is employed for determining the temperature of the human body, is graduated from 32° to 45° C., the normal body temperature being 37.2° C. A small thread of mercury, separated from the main column by an air bubble, serves to register the maximum temperature as the thread fails to recede with the column. Before using, the upper thread of mercury is shaken down by a sharp jerk of the thermometer.

Alcohol Thermometers.—Colored alcohol is used in place of mercury for such thermometers as are employed in recording extremely low temperatures. Alcohol solidifies at — 130° C. and boils at 78° C.

Metallic Thermometers.—These dial thermometers are in common use, and consist of a double strip composed of steel and brass riveted together, usually bent into the form of a coil (Fig. 27). The inside extremity is secured to the back of the instrument, while the other movable extremity is attached to the needle of the dial. Owing to the unequal expansion and contraction of the two metals, the coil closes or opens, moving the needle accordingly.

Air Thermometers.—These are based on the expansion or contraction of a closed volume of air. They are exceedingly sensitive, and are used to measure very small differences of temperature. Air thermometers are employed in standardizing mercurial thermometers; also for measuring high temperatures. They consist of a large bulb of glass, porcelain, or platinum filled with dry air, connected with an open capillary tube which contains a small index of colored sulphuric acid, which moves along or recedes as the air expands or contracts. A millimeter scale records the volume of contraction or expansion.

FIG. 27.



Metal maximum and minimum thermometer.

Pyrometers are used for measuring extremely high or low temperatures. They are based on the influence of heat affecting the electrical conductivity of a heavy platinum wire. From the resistance in ohms the temperature in degrees may be calculated. Another form is based on the influence of temperature upon the juncture of two dissimilar metals (platinum and palladium or platinum-rhodium alloy), whereby a thermo-electric current is generated, which is readily measured and converted into temperature readings. Pyrometers based on the expansion of metals through heat are no longer used for recording high temperatures.

2. **Expansion.**—This is brought about through the influence of heat, which weakens the force of cohesion and causes a more rapid vibration of the molecules of a substance, whereby they tend to separate more widely.

Solids.—All solids expand more or less under the influence of heat. The extent of this expansion depends on the amplitude of vibration of the individual molecules. Expansion may be either *linear* (length) or *cubical* (volume). The increase in length of many substances caused by a rise of 1° C. has been carefully measured, and differs considerably, but is always uniform for the same substance. The rate of increase for a unit of length when its temperature rises through 1° C. is known as the *coefficient of linear expansion.* This is ascertained by making two marks on a rod of the substance, and accurately noting its length at 0° C., then at 100° C. Dividing the total expansion by the temperature change (100° C.), we have the expansion for 1° C. The quotient obtained by dividing this by the initial length is called the coefficient.* The coefficient of linear expansion multiplied by 3 gives that of *cubical expansion.*

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* COEFFICIENTS OF LINEAR EXPANSION OF SOLIDS BETWEEN 0° AND 100° C.

Pine	0.00000608	Iron	0.0000122
Quartz	0.0000013	Copper	0.0000171
Glass	0.00000837	Porcelain	0.0000025
Platinum	0.00000857	Ebonite	0.0000842

We meet with numerous practical illustrations and applications of the expansion of solids. Furnace bars must not be fastened tightly into masonry at both ends, lest they split the masonry by expanding; water pipes are provided with telescopic joints to allow of expansion; in laying rails for railways, space must be left between two connecting rails for expansion; iron tires are put upon wagon wheels while highly heated, so that in contracting they may tighten all parts of the wheel; hot liquids cannot be poured into vessels of thick glass without danger of breaking, because of the unequal expansion of the glass.

Liquids.—Owing to the slighter degree of cohesion among the molecules of liquids, they expand to a greater degree and more rapidly, though less uniformly, than solids. This expansion differs greatly with different liquids: thus, the cubical volume expansion of chloroform is ten times that of mercury.[*] For this reason, an air space should always be left in all containers for fluids. In measuring the expansion of liquids we must distinguish between the *apparent* expansion, which is that of the liquid with its container—which also expands—and the *absolute* or *real* expansion of the liquid itself, irrespective of that of the containing vessel. The coefficient of cubical expansion for glass is about 0.000025.

Water presents an important exception to the rule that liquids expand uniformly with the increase of heat and contract with cold. When water is cooled down gradually from the ordinary temperature, it contracts until 4° C. (39° F.) is reached, when it begins to expand, and continues to increase in volume until it freezes at 0° C. (32° F.), when 100 volumes become 109 volumes of ice, the specific gravity of which is 0.9173. Water attains its maximum density at 4° C., hence its specific gravity has been placed as 1.000 at this temperature.[†] As the water in lakes and rivers cools in winter, it contracts and sinks until the temperature of 4° is reached. After this the cooler layer becomes lighter and remains on the surface, where it congeals and forms ice, which in time protects the water below from the extreme low temperature to which the air may be reduced. In this way fish are able to live through severe winters without experiencing any lower temperature than 4° C. The expansion of water in cooling to form ice also plays a very important part in the operations of nature. More than any other force it reduces rocks to fragments by freezing in crevices and splitting off small particles.

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[*] COEFFICIENTS OF CUBICAL EXPANSION OF LIQUIDS

Mercury	0.00018	Ether	0.00015
Fixed oils	0.00080	Alcohol	0.00106
Sulphuric acid	0.00063	Chloroform	0.00111

[†] DENSITY OF WATER AT CERTAIN TEMPERATURES

0°	0.99987	6°	0.99997
1°	0.99993	8°	0.99988
2°	0.99997	10°	0.99973
3°	0.99999	15°	0.99913
4°	1.00000	20°	0.99823
5°	0.99999	25°	0.99707

It bursts iron and leaden pipes and other vessels in which it may be when these are exposed to low temperatures.

Gases.—Since there is no coherence between the molecules of a gas to be overcome, heat will cause a far greater expansion than among solids or liquids. While the rate of expansion among solids and liquids varies greatly, with all gases it is constant. Owing to the volume sensibility of gases to pressure and temperature changes, it is necessary in accurate measurements to observe certain standards for comparison. *The standard temperature is 0° Centigrade, and the standard pressure 760 millimeters.* The influence of pressure is explained by the law of Boyle-Mariotte (page 26), while that of temperature is governed by the law of Charles *—namely, *the volume of a gas is proportional to its absolute temperature;* that is, gases expand or contract equally in volume by heat or cold. Further, this expansion or contraction is 0.003665, or $^1/_{273}$ of its volume for each degree Centigrade; and if it were possible to cool a gas to a temperature of $-273°$ C. all molecular movement would cease, and a gaseous tension would no longer exist. This temperature is known as *absolute zero,* which means a total absence of any degree of heat. A gas at 0° C. may be regarded as having been heated through 273° C.; a temperature of $-30°$ C. is 243° of absolute temperature; a temperature of $+30°$ C. is 303° of absolute temperature.

According to this law, 273 vol. of a gas at 0° C. increase by one volume for every 1° C. through which they are heated.

That is, 273 vol. of gas at 0° C. become at 1° C., $273 + 1$ vol.
273 vol. of gas at 0° C. become at $t°$ C., $273 + t$ vol.
273 vol. of gas at 0° C, become at T° C., $273 + T$ vol.
(t and T = degrees Centigrade.)

Then, $273 + t$ vol. of gas at $t°$ C. become at T° C. $273 + T$ vol.

Or, 1 vol. of gas at $t°$ C. becomes at T° C. $\frac{273+T}{273+t}$ vol.

v vol. of gas at $t°$ C. become at T° C. $v \times \frac{273+T}{273+t}$ vol.

If v represents any given volume of a gas, and V the new volume resulting from the temperature change from $t°$ to $T°$, then $V = \frac{v\,(273+T)}{273+t}$.

Example.†—If 100 mils of a gas at 10° C. be heated to 25° C., what would be its new volume?

$$V = \frac{100\,(273+25)}{273+10} = \frac{100 \times 298}{283} = 105.3+ \text{ mils}.$$

Combining this formula with that of Boyle (page 26), the volume of a gas at normal pressure and temperature would be $V = \frac{v\,(273+T°)}{273+t°} \times \frac{760}{P}$.

Calorimetry.—This is the process of measuring the quantity of heat absorbed or given off by substances; the instruments employed are called *calorimeters.* We employ calorimetry to measure the quantity of heat energy which results from various chemical changes (*thermochemistry*), also to measure the amount of heat required to raise the

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* Sometimes called Gay-Lussac's Law.

† For other problems involving the influence of temperature, pressure, and vapor tension on volume, see page 157.

temperature of a given body through a given number of degrees (*thermal capacity*). As a standard of measurement (*thermal unit*), we employ the *calorie,* which represents the quantity of heat required to raise the temperature of 1 gm. of water through 1° C. (a large calorie is 1000 times this).

Specific Heat.—Different substances have different capacities for heat—that is, the same weights of different substances require different quantities of heat to warm them equally. The amount of heat which will raise one gram of water through 1° Centigrade will raise the same mass of ice through 2° C., the same of iron about 11° C., and of mercury 32° C. For example, if bullets of iron, copper, tin, and lead of exactly the same weight are all heated to the same temperature in boiling water, and then quickly dropped on a disk of wax, the iron ball melts its way through first, followed by the copper and tin in order, while the lead, if the cake is not too thin, will remain embedded in the wax. *The specific heat (thermal capacity) of a body is the quantity of heat, expressed in heat units (small calories), required to raise the temperature of 1 gm. of that body by 1°.* As standard for comparison, the specific heat of water is taken as unity or 1; that of any other substance by comparing the quantity of heat required to raise its temperature 1° with that required to raise the temperature of the same weight of water 1°.

If we mix one kilo of water at 0° C. with one kilo of mercury at 100° C., the two bodies will interchange heat and assume a common temperature of 3.2° C. The mercury has cooled 96.8° C. (100° — 3.2° C.), and given off 3.2 calories (heat units). To furnish the 3.2 heat units (*calories*) necessary to heat 1 kilo of water from 0° to 3.2°, the temperature of the kilo of mercury must consequently fall 96.8°. Conversely, these 3.2 thermal units will suffice to heat 1 kilo of mercury by 96.8°, then to heat 1 kilo of mercury through 1°, $\frac{3.2}{96.8}$ or 0.0332 thermal units are necessary, hence the specific heat of mercury will be 0.0332. This is known as the method of mixtures. Another, adapted for gases as well as solids, depends on the use of the ice calorimeter, a copper vessel filled with ice, in which is imbedded a copper cup (or coil for gases) for the reception of the heated body. Since 80 thermal units (page 49) are required to melt 1 kilo of ice, the quantity of heat given off by the body while cooling (measuring by the weight of water from the melted ice) is readily computed.

The specific heat of the various elements has been ascertained. This knowledge has become of great importance in consequence of the discovery by Dulong and Petit of the law *that the product of the specific heat of an element, and its atomic weight, is approximately a constant number*—namely, about 6.4. This product is known as the *atomic heat* of an element.* By the aid of this constant, the atomic weight of

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* A few examples are cited for illustration:

	Specific Heat	Atomic Weight	Atomic Heat
Bromine	0.0843	79.9	6.73
Iron	0.119	55.8	6.64
Mercury	0.0331	200.6	6.64
Nickel	0.109	58.7	6.4
Platinum	0.0323	197.2	6.31
Potassium	0.1728	39.1	6.75
Tin	0.0559	119	6.65

any new element may approximately be ascertained by dividing 6.4 by its specific heat $\left(\frac{6.4}{\text{sp. heat}} = \text{at. wt.}\right)$. The accuracy of this result may subsequently be verified by chemical analysis.

3. **Changes of Condition.**—The three states of matter already described—namely, solid, liquid, and gaseous—depend upon the relations of the forces of cohesion and repulsion. Heat opposes the former, and tends to change solids to liquids or gases by increasing the rate and amplitude of vibration among the molecules. When a solid passes into a liquid state it is said to undergo—

Fusion (melting or liquefaction).—Some substances are very refractory, or incapable of fusion except at excessively high temperatures; others, such as paper, wood, vegetables and animal fibres and tissues, are decomposed without fusion. With these exceptions, we may consider fusion a regular change which solids will undergo when the proper temperature is reached. Fusion is governed by the following laws:

(1) Every substance begins to fuse at a certain temperature, which is invariable for each substance if the pressure be constant.

(2) Whatever the intensity of the source of heat, from the moment fusion commences the temperature of the body ceases to rise and remains constant until the fusion is complete.

The range of temperature shown in the fusing points of solids is very great, varying from —38.8° C. for mercury to 2290° C. for iridium.

Some substances show no definite melting point, as glass and iron, which soften gradually until liquefaction is reached. Such is called *vitreous fusion*. Generally solids expand on fusing; however, there are some exceptions, as, for example, ice, type-metal, and cast iron, which contract in volume during liquefaction.

When metals are fused together they generally form a homogeneous mixture which often possesses properties quite different from those possessed by either of the metals singly. Such mixtures are called *alloys*. They are generally more fusible than either of the metals of which they are composed. For instance, Rose's fusible metal, consisting of 4 parts of bismuth, 1 part of lead, and 1 part of tin, melts at 94° C., while its most fusible constituent, tin, melts at 233° C. Wood's fusible metal, consisting of 1 or 2 parts of cadmium, 2 parts of tin, 4 parts of lead, and 7 or 8 parts of bismuth, melts between 66° and 71° C.

Latent Heat of Fusion.—In accordance with the second law noted above, bodies which are capable of fusion cannot be heated any higher until fusion is complete, no matter how intense the source of heat may be. For example, the mercury column of a thermometer placed in snow will remain stationary at 0° C., when placed in a vessel over a flame, until the snow has completely melted to water at 0°, after which the temperature rises. The (kinetic) heat added has disappeared (become latent), having been consumed in transforming the snow at 0°

into water at 0°. If a kilo of water at 80° C. be mixed with a kilo of dry snow at 0° C., the two kilos of water obtained will have a temperature of 0° C. The kilo of snow in melting has used up the 80 degrees of heat originally possessed by the kilo of water; or to melt 1 kilo of ice, the same quantity of heat is necessary as is required to raise 1 kilo of water from 0° to 80°. The quantity of heat necessary to raise 1 kilo of water by 1° is the heat unit or *large calorie.* The latent heat of ice is then 80 calories or heat units. But, as before stated, energy cannot be destroyed. It must, therefore, still be present, although stored up as potential energy under the name of *the latent heat of fusion.* That these 80 degrees of heat have been temporarily absorbed without raising the temperature of the water produced from the ice is capable of proof, as when the kilo of water again becomes ice (crystallizes) this absorbed heat is all given out, and can by measurement be shown to be the equal of that which disappeared before. Every liquid has its own latent heat. That of water, as established by the above experiment, is 80 calories.

Dissociation.—If certain chemicals be heated to a temperature sufficiently high, they break up into simpler molecules, which, upon lowering the temperature, again reunite. Dissociation (thermal) exists only so long as the temperature applied continues (see page 138).

Regelation.—When two pieces of ice are firmly pressed together they unite at the surface of contact. The pressure exerted liquefies the ice at the point of contact; but as the latent heat of fusion is absorbed and conducted away, the water is converted into ice. The formation of the snow-ball depends on regelation.

Solution of Solids in Liquids.—When brought in contact with liquids, the cohesion among the molecules of many solids is broken up, and the result is a homogeneous fluid mixture called a solution. The solubility of a solid in a fluid depends upon the nature of the solid, the temperature, and the solvent. When the latter has taken up all that it is capable of dissolving at a certain temperature, it is said to be *saturated*—when less, it is *unsaturated.* If a saturated solution be concentrated, or the temperature is lowered before crystallization begins, the solution is said to be *supersaturated.* If such solutions are agitated, or a crystal be added, crystallization takes place at once and the supersaturated solution becomes a saturated one. Pressure increases the solubility of solids to a slight extent. The number of grams of a substance which at a certain temperature will dissolve in 100 grams of water is known as the *coefficient of solubility* of that substance.

As a rule, crystalline inorganic bodies dissolve more readily in water; metals in mercury (amalgams); fats, resins, oils, and organic crystalline bodies in alcohol. Increase of temperature increases the degree of solubility, with few exceptions; as, for example, calcium hydroxide, sulphate, and citrate are less soluble in hot than in cold water. When two or more salts are dissolved in water without chemical action on one another the solubility of each individual salt is not as great as when present alone, the total quantity of salts dissolved is greater than if one alone had been used, and the quantity of each salt held in solution is less than if it were alone present, although the sum total dissolved is greater than if only one had been used.

If the point of saturation of any one of the dissolved salts in the mixed solution is exceeded, this one will separate from the other. Hence, in evaporating a mixture of salts, that salt whose point of saturation has been reached will separate out first, followed by the others in succession. Should two salts tend to crystallize out at the same time (because of like solubilities), the concentration of the solution is carried on at a higher temperature, and the one which is less soluble under these conditions is then deposited.

The freezing point as well as the boiling point of a solvent is altered by the presence of a dissolved salt.

When the solution of a solid is attended by a chemical action, a *rise in temperature* follows, evidenced by dissolving such salts as potassium hydroxide, zinc chloride, or calcium oxide in water. These substances form hydrated salts, and, since the quantity of heat set free in the formation of such salts exceeds that necessary for solution, heat is liberated.

When crystalline solids are dissolved in water (as also in the case of fusion), a certain quantity of heat is absorbed or rendered latent, and the mixture becomes very cold. Advantage is taken of this in preparing—

Freezing Mixtures, by means of which various degrees of cold may be produced. Thus, a mixture of two parts of powdered ice or snow and one part of salt will rapidly reduce the temperature of substances around which it may be packed. The salt forces the liquefaction of the ice, thereby lowering the temperature; the water resulting from this dissolves the salt, again lowering the temperature; so that their combined action produces a temperature of zero Fahrenheit.*

Solidification of Liquids.—Just as change of condition takes place when solid bodies fuse under the influence of heat or dissolve in liquids,

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* The following table gives a list of salts which, when mixed with solvents, reduce temperature, owing to rapidity of liquefaction. The colder the solvent the lower will be the temperature produced.

Sodium sulphate 8 parts + hydrochloric acid 5 parts reduces from +10° C. to about —17° C.
Snow 2 parts + salt 1 part reduces from +10° C. to about —18° C.
Sodium sulphate 3 parts + dilute nitric acid 2 parts reduces from +10° C. to about —19° C.
Sodium sulphate 6 parts + ammonium nitrate 5 parts reduces from +10° C. to about —26° C.
Sodium phosphate 9 parts + dilute nitric acid 4 parts reduces from +10° C. to about —30° C.

so the reverse change may take place, whereby the liquid may resume the solid form, either from fusion or from solution. For this change the following laws, analogous to those before stated for fusion, may be given:

(1) Every body under the same pressure solidifies at a fixed temperature, which is the same as that of fusion.

(2) From the commencement to the end of the solidification the temperature of a liquid remains constant.

This second law, it will be seen, is the counterpart of the law of fusion already explained involving the absorption or storing up of heat. Just as in the other case, no matter what the heat applied, the temperature of the melting solid remained constant until the operation was completed; so in this reverse change, no matter how intense the cold, the giving out of the potential heat energy stored up in the liquid prevents any lowering of the temperature until the solidification is complete.

This principle of the storing up of heat in the liquefaction of a solid and giving it out in the reverse change of solidification of the liquid has a great importance in the economy of nature. The first severe cold of winter does not cause the streams and lakes to freeze up suddenly and completely, because for every pound of ice produced eighty heat units are given out and have a notable retarding influence upon the freezing operation; similarly the first warm days of spring do not instantly melt the accumulated snow and ice of the mountain valleys, because for every pound of ice melted eighty heat units must be taken up and withdrawn from present effect upon the temperature.

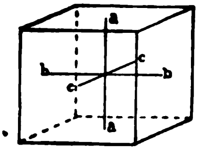
It is obvious that, as the phenomena of solution are analogous to those of fusion, so we may have as the counterpart of solidification from fusion a solidification from solution. In the former case change of temperature is the occasion of the solidification; in the latter, besides this cause, we may have the removal, by evaporation or otherwise, of the solvent as the determining cause of the solidification.

4. **Crystallization.**—Generally speaking, bodies in passing from the liquid or vaporous condition to the solid state assume regular geometric forms. Such regular forms, bounded by plane faces and definite angles, are called *crystals*. Such bodies as do not conform to the above—that is, do not crystallize—are called *amorphous* (as chalk, glue, acacia, etc.). The plane surfaces which bound a crystal are called *faces* or *planes*. The intersection of two adjacent faces (planes) forms an *edge*. When two or more lines or planes intersect, their edges form an *angle*. In order to classify and compare the various forms of crystals, we express the relative position and inclination of their planes by referring them to certain systems of axes. These axes (*a, b, c, d* of Figs. 28, 29, 30, 31, 32, and 33) are called crystallographic axes; they are imaginary lines, which, if drawn through, would intersect

at the center of the crystal. The positions of the different faces (planes) of the crystal are fixed by, and expressed in, the relative lengths of their intercepts on these axes. For the purpose of comparing the different crystal planes, systems of symbols have been devised, which aim to locate the position of each plane, with reference to its relation to the crystallographic axes. Since every crystalline body has its own peculiar form, it will readily be seen that we have an immense number of these in all possible varieties. However, in the face of this, according to their greater or less degree of symmetry, they are divided into six different classes or systems. Each one of these systems has its imaginary crystallographic axis, to which the different planes (faces) bear a fixed symmetrical position. According to the relative position, number, and size of these different planes, we distinguish the following *six* different systems:

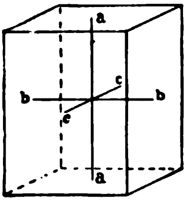
1. The *Regular* (isometric, monometric) *System* (Fig. 28). All forms have *three* axes of *equal* length, which intersect at angles of 90°. To this system belong the cube and octahedron with their many modifications. In this system crystallize the diamond, the various alums, sodium chloride, potassium iodide, bromide, and chloride, etc.

FIG. 28.



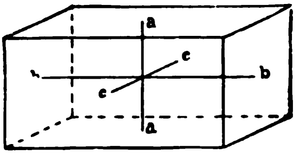
Regular system cf crystallization.

FIG. 29.



Tetragonal system of crystallization.

FIG. 30.



Rhombic system of crystallization

2. The *Tetragonal* (dimetric, quadratic) *System* (Fig. 29) has *three* axes, which intersect at angles of 90°; two of these (lateral) being of equal length, the other (principal axis) is either longer or shorter. To this system belong the square pyramid and prism, and in it crystallize potassium ferrocyanide, tinstone, nickel sulphate, etc.

3. The *Rhombic* (orthorhombic, trimetric, prismatic) *System* (Fig. 30) has *three* axes of *unequal* length, all intersecting at right angles. To this system belong the rhombic pyramid and prism, and in it crystallize barytes, sulphur, saltpetre, zinc sulphate, citric acid, etc.

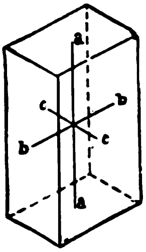
4. The *Monoclinic* (oblique, prismatic) *System* (Fig. 31) has *three* axes of *unequal* length, two of which intersect at an oblique angle and are perpendicular to the third. To this system belong the oblique pyramid and prism, and in it crystallize oxalic acid, tartaric acid, sodium sulphate, ferrous sulphate, sulphur (fused), etc.

5. The *Triclinic* (asymmetric) *System* (Fig. 32) has *three* axes of unequal length, all oblique to one another. The most common form is

the doubly oblique pyramid, and in it crystallize copper sulphate, potassium dichromate, etc.

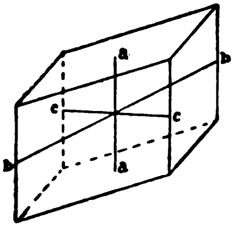
6. The *Hexagonal System* (Fig. 33) has *four* axes; three of these, of equal length, are lateral, and intersect the principal axis at angles of 90°, and one another at angles of 60°. The principal axis may be longer or shorter than the lateral axes. To this system belong the hexagonal pyramid and prism, and in it crystallize quartz, Iceland spar, thymol, bismuth, antimony, etc.

FIG. 31.



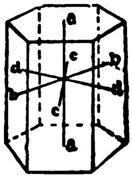
Monoclinic system of crystallization.

FIG. 32.



Triclinic system of crystallization.

FIG. 33.



Hexagonal system of crystallisation.

5. **Vaporization.**—*Solids.*—Some chemicals, as arsenous oxide, iodine, corrosive sublimate, camphor, etc., when heated, pass directly into vapor form without liquefaction. This is called *sublimation,* and is due to relative vapor pressure (tension). If the vapor pressure (page 54) of the substance being heated is less than that to which it is exposed, fusion takes place; but if greater, then it passes directly into the vapor form.

For example, the vapor tension of arsenous oxide is between 1 and 2 atmospheres, hence can only be liquefied when heated in a sealed tube where a pressure greater than 2 atmospheres is generated. On the other hand, ice, with a vapor tension of 4.5 mm., will vaporize without melting if warmed in a vacuum of less than 4.5 mm.

Liquids.—The conversion of a liquid into a state of vapor is designated as *vaporization.* If this vaporization takes place slowly from

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*VAPOR PRESSURE (TENSION) OF DIFFERENT LIQUIDS

	Temp.	Pressure in mm.
Mercury	0°	0.0004
Mercury	60°	0.03
Alcohol	0°	13.
Alcohol	50°	220.
Ether	0°	184.4
Ether	60°	1725.
Water	0°	4.6
Water	10°	9.2
Water	15°	12.7
Water	20°	17.4
Water	25°	23.6
Water	50°	92.
Water	100°	760.

The above temperatures represent the boiling points of the substances at their corresponding pressures.

the surface of a liquid, it is called *evaporation*, while if the vapor is produced rapidly throughout the mass of fluid, it is termed *ebullition* (boiling). When a fluid is heated, the atmosphere resting immediately upon its surface soon becomes saturated with vapor, and as the temperature increases the tension (elastic force) of this vapor layer gradually increases until it equals that of the atmosphere; this is the normal *ebullition* (boiling) *point* of the fluid. All fluids (including mercury) exert a definite vapor tension which varies according to the nature of the substance, and increases with the temperature (see note, p. 53).

If a little water or any other fluid be introduced into the Torricellian vacuum of a barometer, it at once begins to vaporize and saturates the space with vapor, depressing the mercury column according to the temperature of the tube. If we subtract the height of this mercury column from that of a normal barometer, we obtain the vapor pressure of the fluid.

The laws governing ebullition are as follows:

1. *The temperature of ebullition, or the boiling point, increases with the pressure.* The influence of pressure is of far greater importance here than in the case of the fusion of a solid. This is because of the readiness with which a gas or vapor responds to difference of pressure, and of the fact that slow evaporation passes by gradual stages into rapid evaporation, or boiling. We may generalize this statement by saying that a liquid boils when the tension of its vapor is equal to or exceeds the pressure it supports. Hence, as the pressure increases or diminishes, the tension of the vapor, and, therefore, the temperature necessary for boiling, must increase or diminish, it being borne in mind that the temperature of a liquid cannot be raised above its boiling point.

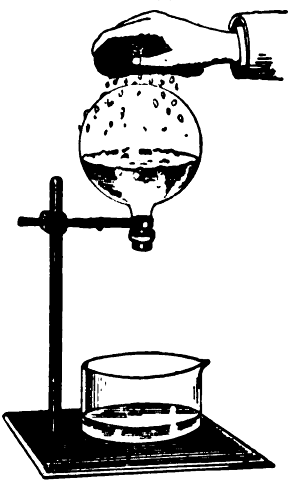
The close relation between boiling temperature and pressure may be shown by the experiment illustrated in Fig. 34. In a round-bottomed glass flask water is boiled for some time, and when the steam has been coming off sufficiently long to have driven out all of the air, the heat is withdrawn and the flask closed by a tight-fitting cork. It is then inverted and clamped, as shown in the figure. If the bottom is then cooled by wringing out cold water from a sponge, the water begins to boil again. The explanation is as follows: When the flask was closed and inverted, the space above the water was filled, not with air, but with vapor of water. When the upper part of the flask was cooled by the application of cold water from without, its first effect was to condense a portion of this steam. Hence the pressure upon the surface of the water was much reduced, and the water started to boil because the tension of the vapor at its surface was greater than the pressure for the time being. As soon as boiling liberates more steam the pressure becomes greater again and boiling ceases.

An important application of the fact that water and other liquids evaporate more rapidly under reduced pressure is found in the use of vacuum-pans and apparatus for concentration of liquids *in vacuo*.

If a fluid be heated in a confined space, the tension of its vapors will increase with the rise in temperature and consequently will exert a pressure upon the surface of the liquid, raising its boiling temperature accordingly. Such tensions are expressed directly in "atmospheres," each being equal to 760 mm. pressure.[*] Based on this principle is the *autoclave*, a cylindrical cast-iron vessel which is used in chemical operations in which a substance is to be extracted, or two or more compounds react on one another under high pressure and temperature. By means of a vacuum-pump water may be made to boil at any temperature from 100° C. down; in an absolute vacuum it would boil at 0° C.

2. *For a given pressure, every liquid has a definite constant boiling point.* This law is analogous to that governing the fusing point of solids. As a consequence of this law we are able not only to identify, but to separate various fluids from one another by means of their boiling points.

FIG. 34.



Boiling under reduced pressure.

3. ***Whatever be the intensity of the source of heat, as soon as ebullition begins the temperature of the liquid remains stationary.*** On introducing a thermometer into the vapor[†] of a boiling fluid, the mercury will rise until it assumes the temperature of the surrounding vapor; it will then remain constant until the entire fluid has been vaporized. Should there be a mixture of miscible liquids, as water and alcohol, the boiling point will cover several intermediate degrees between those of its constituents. If the fluids are immiscible, the boiling point of the mixture will be lower than either of its constituents. Advantage is taken of this fact in removing the essential oils (which have high boiling points) from plants by distillation with steam.

Additional Causes Accelerating Evaporation.—The rate of evaporation depends (1) on *temperature,* for increase of temperature accelerates evaporation by increasing the elastic force of the vapors. (2) *Increased surface:* the larger the area of surface the greater the number of exposed points from which vapors may be formed. For this reason fluids are stirred constantly or exposed in thin layers while evaporating. (3) *Removal of moist air* from the surface of an aqueous liquid facilitates evaporation, because vaporization cannot take place in an atmosphere al-

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[*] TENSION OF WATER VAPOR AT HIGHER TEMPERATURES, OR BOILING POINT OF WATER UNDER VARIOUS PRESSURES

Temperature.	Tension	Temperature	Tension
100°	1 atmosphere	159.2	6 atmospheres
120.6	2 atmospheres	165.3	7 atmospheres
134.	3 atmospheres	180.8	10 atmospheres
144.	4 atmospheres	213.	20 atmospheres
152.2	5 atmospheres	266.	50 atmospheres

[†] The temperature of the boiling fluid may vary according to the nature of the vessel and the presence of dissolved matter, while that of the vapor remains constant.

ready saturated with the vapor of the same fluid; hence the vapor-laden atmosphere should continually be removed and replaced by fresh dry air through fanning.

Influence of Dissolved Substances on Boiling Point.—The presence of dissolved saline matter raises the boiling point of a solvent, and as the proportion of this increases, the rate of vaporization is retarded accordingly. Water saturated with common salt boils at 102° C., with calcium chloride at 179° C. During evaporation, as the solution becomes more concentrated, a saline pellicle forms upon the surface which effectually prevents any further evaporation unless continually broken by stirring.

Nature of the Vessel.—While the temperature of boiling water, when heated in a good heat conductor, as a metallic vessel, is 100° C., it will rise as high as 105° C. in vessels of such poor conductive material as glass or porcelain. The temperature of the fluid in the latter may be lowered to 100° C. by placing a piece of metal in the bottom of the vessel.

Production of Cold by Vaporization.—If a volatile liquid like alcohol or ether be poured on the hand, a cooling sensation is produced; the more rapid the vaporization and the more volatile the liquid the greater the intensity of cold. The explanation of this is that when a change of a solid into a liquid, or a liquid into a vapor, takes place, an absorption of heat follows: thus, when ether evaporates, the heat necessary for vaporization is absorbed from the surrounding objects, thereby producing cold. The heat absorbed in vaporization is far in excess of that required for liquefaction: thus, 1 gram of ice requires only 80 calories to melt it, while 1 gram of water requires 537 calories for vaporization; or, stated in other terms, the *latent heat of the liquefaction* of ice is 80 calories, while the *latent heat of the vaporization* of water is 537 calories. The most effective forms of refrigerating apparatus are based on this fact; in these, the rapid volatilization of such liquefied gases as ammonia or sulphur dioxide is facilitated by aid of condensing pumps. Solutions of brine cooled by these rapidly vaporizing liquids may be carried for distances through coils and utilized for cold storage. Beginning with an easily liquefiable gas, and utilizing the low temperature produced by its vaporization under reduced pressure, then by the application of pressure, other more refractory gases are liquefied, and these in turn are employed for the liquefaction of still others; thus, step by step, physicists have succeeded in liquefying every known gas.

Condensation of Vapors.—This is the reverse of evaporation. It takes place whenever the temperature of the vapor drops below the boiling point of the liquid. It may, however, be also effected by pressure or through the chemical affinity of the vapors for some other substance. By combining the influences of cooling and pressure, the most volatile of vapors have been condensed.

Distillation is an operation by which, taking advantage of the volatility of a liquid, we may separate it from dissolved or admixed solids or other liquids of higher boiling point.

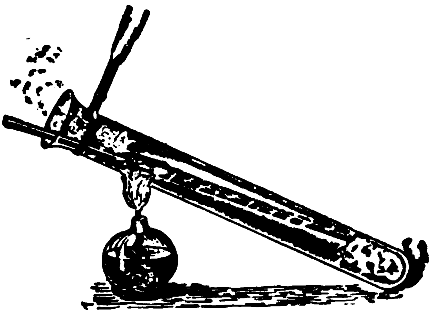
IV. Transmission of Heat

Both heat and light vibrations travel through the ether from the source of heat or light without raising the temperature of the intervening space. When they strike upon a body to which these vibrations can be communicated, it feels the effects of heat and the temperature is raised. Such heat is called *radiant* heat, and it is said to be radiated from the source of heat.

If, however, the end of a metal bar is heated, a rise of temperature is soon recognized some distance from the heated spot, and it may extend throughout the entire length of the bar. The heat is here transmitted through the particles of the metal, and the molecular vibration is not merely an instantaneous one passed on, as in the case of heat rays radiating through air or ether, but continues for some time, and shows its effect in the rise of temperature. The heat in this case is propagated by *conduction.*

1. Conduction of Heat.—We find great differences in the ease with which bodies conduct heat. Metals,* while they differ considerably as to their relative conductivities, are the best conductors, while glass, resins, and wood are poor conductors. Liquids and gases are also poor conductors of heat. Cotton wool, straw, and bran are all bad conductors. The relatively poor conducting power of liquids is shown in the experiment illustrated in Fig. 35. Snow may be packed in a test-tube and water put above it. On inclining the tube, as shown in the cut, and applying the heat at the top of the liquid, the water may be made to boil without melting the snow. Poor conductors of heat are used both for the purpose of retaining heat and shutting it out from bodies or spaces to be kept cool. Thus, steam-pipes at all times and water-pipes in winter are packed in asbestos, magnesium carbonate, straw, felt, and other non-conducting materials, to prevent the loss of heat. Ice, on the other hand, is packed in sawdust or shavings to keep out the heat and prevent its rapid melting. Fire-

FIG. 35.



Water a non-conductor.

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* Relative Conductivity of Metals Compared to Silver (Approximate)

Silver	1000	Iron	120
Copper	736	Lead	85
Gold	532	Platinum	84
Brass	231	Bismuth	18
Zinc	190		

proof safes have the spaces between the inner and outer plates packed with non-conducting material, so that, while the outer frame may be heated red-hot, the inner frame does not become heated sufficiently to injure the books and papers that the safe may contain. Snow is a bad conductor of heat, and a layer of snow is capable of keeping the earth under it warm.

2. Radiation of Heat.—That heat rays are propagated without raising the temperature of the intervening space is demonstrated by interposing a screen in the path of the rays. The sensation of heat at once disappears, as the surrounding air has not been heated by the heat rays passing through it. That radiant heat is propagated *in vacuo* can also be shown by experiment, and is in accordance with probability, as the radiant heat of the sun comes to us through space outside of the earth's atmosphere.

Of the laws governing the intensity of radiant heat we need only note the one that the intensity is inversely as the square of the distance. We will see later that this accords exactly with the observation of the nature of the light rays, and shows the close relationship between them. Radiant heat, when it strikes upon a body, may be reflected, diffused, absorbed, or transmitted. From polished surfaces, whether plane or curved, the heat rays are reflected or thrown back. But this reflection is never complete. Some of the rays are irregularly reflected or diffused. On the other hand, bodies which are poor reflectors absorb the heat rays in large amount. Such bodies, like lampblack, white lead, and other finely divided substances, absorb the bulk of the rays which strike upon them. Among transparent substances, a notable difference exists in the readiness with which they transmit the heat rays. Rock-salt in transparent plates transmits the heat rays very perfectly; alum, on the other hand, absorbs the rays and transmits only very few.

3. Convection.—Liquids, as before stated and illustrated, are poor conductors of heat. When heat is applied to a liquid like water, the conductivity is so slight that, as shown in Fig. 35, ice or snow contained in the same vessel will not be melted, although the water may be brought to boiling at the top of the vessel. It is different, however, when heat is applied at the bottom of a vessel containing water or other liquid. The layer of the liquid nearest the point where the heat is applied becomes heated and at once moves upward, while a current of colder liquid moves downward to take its place. It is by these currents, which move the particles of the liquid from one place to another continuously, that the heat is mainly distributed, and not by the conductivity of the liquid. These ascending and descending currents may be made visible by putting a little bran or sawdust into the water before applying the heat. This mode of transmitting heat is called *convection*. Heat is also propagated in gases in the same way, as their conductivity is equally slight.

CHAPTER V

MAGNETISM

I. Magnets, Natural and Artificial

A certain black mineral, magnetite (ferroso-ferric oxide, Fe_3O_4), was early known to possess the property of attracting iron or steel. It was known as *magnes,* from the city of Magnesia, in Asia Minor, near which it was first discovered. It was called *lodestone* (from the Saxon *loedan,* to lead) because of the property of leading or pointing north and south when freely suspended. Fragments of this mineral are now known as native magnets, and the property thus manifested is called magnetism. Native magnets, however, as a rule, have been replaced in experimental work by the smaller and more convenient artificial magnets of steel. Soft iron can also be magnetized, but, as we will see later, is not adapted for permanent artificial magnets, as it does not retain the power as well as steel. These magnets are commonly known by the designations bar magnets, magnetic needles, and horseshoe magnets. The latter have the convenience that because of their shape the two ends of the magnet are near each other, and can be readily covered by a piece of soft iron, known as an armature, which tends to strengthen and preserve the full magnetic power of the magnet. It is found, moreover, that in a steel magnet the magnetic effect does not penetrate very far, so that several bar or horseshoe magnets, separately magnetized and then riveted together, are more powerful than a single magnet of the same size as the compound one. Most powerful are the *electro-magnets* (page 77).

II. Properties of Magnets

The most important property possessed by the magnet, either natural or artificial, is the power of drawing to it or lifting up pieces of iron. Iron is not the only metal thus drawn to the magnet. Nickel and cobalt are also attracted, although in a lesser degree. This influence of the magnet is not dependent upon the presence of air, nor is it hindered by the interposition of solids, like wood or glass. The attraction takes place *in vacuo* and through non-magnetic solids as readily as under normal conditions.

Polarity.—A piece of iron is attracted with unequal intensity by the different parts of a magnet. The two ends possess this power in the highest degree, while the middle of the bar or horseshoe is destitute of attractive influence. This is seen to advantage if a bar magnet or needle is dipped into iron filings. Thick bunches of the filings will adhere at either end, while the central part of the bar is bare and free from filings. The ends of the magnets, or points, in which the magnetic power is concentrated, are called the *poles,* and the part of the magnet which is destitute of attractive power is called the *neutral line* or *equator.* Again, if a magnetic needle or bar magnet be suspended freely, we shall find that one pole will always point to the north and the other to the south. Hence we designate one as the *north pole* and the other as the *south pole* of the magnet. On bar magnets they are usually marked N and S, while on the magnetic needle the north pole is usually arrow-pointed.

III. Laws of Magnetism

1. **Attraction and Repulsion.**—If the two poles marked N of two bar magnets be brought close to each other, we find no evidence of any attraction, and if, instead of two bar magnets, we take a freely suspended or oscillating magnetic needle and approach its pointed (north) end with the north pole of a bar magnet, we find an actual repulsion—the north pole of the needle is repelled while the two are yet some distance apart. If, on the other hand, the pole of a magnet marked N be approached by the pole of another magnet marked S, the two are attracted, and on touching hold together strongly. In the case of the oscillating magnetic needle, a pole of a magnet will cause the end of the needle of opposite name to swing violently toward the approaching magnet. These observations are summarized in the law of magnetic attraction: *Like poles repel and unlike attract each other.*

2. **Location of the Magnetic Power.**—If a steel bar magnet be broken in two at the neutral zone, the two pieces will show the same polarities as the original magnet, and if this subdivision be continued until broken into the minutest pieces, the same condition exists in each of the fragments. According to this, magnetic influence must reside in the molecules themselves, so that no mechanical subdivision can deprive them of this property.

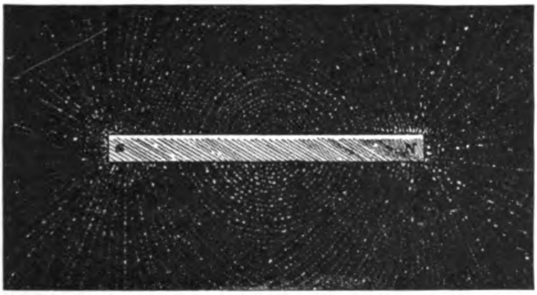
3. **Magnetic Induction.**—A piece of soft iron brought close to a strong magnet is affected by it more strongly than appears in the simple attraction. While under the influence of the original magnet it becomes a magnet itself, and is capable of attracting and repelling another piece of iron, according to the laws of magnetic attraction. This is due to what is termed *magnetic induction.* The end of the piece of iron next to the inducing magnet is given a polarity the opposite of that possessed by the pole exerting the influence, while the end of the iron farthest from the inducing magnet shows a polarity the same as that of the pole with which the iron is in contact. This induction takes place through glass or paper or other non-magnetic substance, without appreciable loss.

The influence in the case of soft iron is only temporary, and when detached or removed from the inducing magnet it loses its power at once. In the case of steel, on the other hand, this power is not immediately or wholly lost on detaching it from the inducing magnet. This is due to the fact that while steel has considerable magnetic retentivity, or coercive force, soft iron has very little. Hence permanent magnets are made of steel, while electro-magnets (see page 77) are made of soft iron.

4. **Methods of Magnetization.**—A bar of steel may be magnetized either by *stroking*, which consists in moving one pole of a powerful magnet from one end of the bar to the other a number of times, always in the same direction, or by means of the *electric current*. This latter is the method usually employed, in which the steel bar is placed inside a tube of glass or brass (non-magnetic material) which is wound with many turns of insulated copper wire. Through this wire an electric current is passed, giving a more or less powerful magnet according to the number of turns of wire and strength of the current (page 77).

5. **Lines of Magnetic Force.**—If a bar magnet be laid upon a horizontal surface like a table, and covered by a glass plate or a sheet of card-board, upon sifting over the glass or card-board fine iron filings we will find that they arrange themselves in peculiar curves, as illustrated in Fig. 36. These are known as the *lines of magnetic force*, and indicate the lines in which the influence of the magnet is felt. It will be noticed that they seem to radiate out from the neighborhood of the two poles, and that the curved lines from the two poles join and make a series of circles enclosing the neutral line of the magnet. These curves thus formed by the iron filings, however, do not indicate that the magnetic force is felt in narrow lines only, but they mark its direction. The entire space around each of the poles is permeated by this influence, and is, therefore, known as the *magnetic field*. The strength of the attraction within this field is governed by a law of distance similar to those noted under heat and light. It is expressed as follows: *Magnetic attraction or repulsion varies inversely as the square of the distance through which it acts.*

FIG. 36.



Magnetic curves.

IV. THE EARTH AS A MAGNET

If a needle be suspended so as to hang horizontally, then when magnetized it will dip downward. If we follow a line approximately near the equator, the needle will rest in a horizontal position (magnetic equator, or aclinic line). If we proceed northwards, then the north pole of the needle will begin to dip (incline downwards), which increases as we approach the north magnetic pole. In the southern hemisphere the dipping of the needle takes place in the contrary direction—that is, the south pole of the needle dips below the horizontal line. The angle which the magnetic needle makes with the horizontal line is called its *inclination* or *dip*. The *magnetic poles* of the earth (not geographical) are those places where the dipping needle assumes a vertical position (90°). The north magnetic pole has been located near Melville peninsula, in the Arctic ocean, while the south pole is about 154° east longitude and 75½° south latitude. It will be seen that the magnetic poles of the earth do not agree in position with the geographical poles. Hence the needle does not in most places point due north and south or in a line determined by the north star. The angle which the needle makes with the geographical meridian is known as the *angle of declination*. It is found that this angle differs at different places, and that for any one place it changes slightly from year to year. The magnetic axis of the earth is slowly oscillating.

V. APPLICATIONS OF MAGNETISM

Permanent magnetism has few applications compared with those that have been found for electro-magnets. These will be noticed farther on. The most important application of the permanent magnet is in the form of the *mariner's compass*. In this the freely oscillating magnetic needle is mounted in such a way that under the influence of the earth's directive action it is made to indicate the direction in which a ship is moving. For this purpose one or more magnetic needles are attached to the under surface of a circular disk of card-board or mica, upon the upper surface of which are marked the thirty-two points of the compass. This disk is supported upon a delicate pivot moving in an agate cup, so that it responds to the slightest change of course of the ship. With the general introduction of iron and steel ships the use of the compass would seem to be attended with great difficulty, because of the local attraction for the needle. It has been found possible, however, to correct this local influence so as not to interfere with the accuracy of the directive action of the needle. The compass is supposed to have been known to the Chinese long before its introduction into Europe in the twelfth century.

Permanent magnets, as well as electro-magnets, are also used in separating magnetic iron ore from accompanying sand and crushed rock material, and in picking out small particles of scrap iron from malt and grain before crushing.

CHAPTER VI

ELECTRICITY

ELECTRICITY is known to us only by its effects and various manifestations. Like energy, it can neither be created nor destroyed, but is capable of being moved from one place to another and put under stress. In some of its deportments it is like an incompressible fluid pervading all space, in others a highly attenuated ether, and, if not identical, it is closely related to luminiferous ether. According to Maxwell, light itself is an electric phenomenon and light waves are electro-magnetic waves. The importance of electricity may be measured by the fact that an expenditure of energy of one kind (mechanical or chemical) can be made to reappear as electrical energy readily convertible into heat, light, or other useful form of energy.

According to its methods of production and various manifestations, electricity will be considered under the following heads—namely, ***static***, ***dynamic***, and *thermal*.

(A) STATIC OR FRICTIONAL ELECTRICITY

Thales of Miletus (500 B.C.) was probably the first who mentioned that when amber is rubbed it acquires the property of attracting light bodies, such as bits of paper, feathers, pith balls, etc. It was not until the sixteenth century that Dr. Gilbert, an English physician, showed that many other substances, as sulphur, resin, shellac, glass, rock-crystal, etc., possess like properties with amber. He applied the name *electrics, from* ηλεκτρου (elektron), the Greek name for amber, to all such substances.

1. **Conditions of Production.**—If a stick of sealing-wax, sulphur, or hard resin be rubbed briskly with a piece of flannel, it will acquire the property of attracting light bodies, like slips of paper, feathers, pith balls, etc. A glass tube carefully dried and rubbed with a silk handkerchief will show similar phenomena. In a dark room the bodies so rubbed often appear slightly luminous, and sparks are sometimes given off when they are touched. It is evident that these are manifestations of a new form of energy developed by the friction of the two bodies and distinct from heat, which may be developed at the same time. The generally received explanation of this change of energy into a new form is that friction and the other means referred to disturb the neutral condition in which the molecules of bodies ordinarily exist, and develop therefrom two opposing influences, which give us the so-called "electrical" phenomena. These influences may be designated as ***positive*** and ***negative***, or ***vitreous*** and ***resinous*** electricity.

The development of electricity of either kind in a body is said to give it a certain *potential* as compared with another body, either electrified or unelectrified. A body charged with positive electricity is said to have a positive potential, while a body negatively charged has a negative potential. These opposing charges may be equal, in which case, when the two bodies are brought into contact, they neutralize each other, and leave the bodies unelectrified, or they may differ in potential, in which case a residue remains of the stronger charge.

If instead of rubbing resin or glass we rub metals with flannel or silk, apparently no electrical effects are produced. This want of electrical excitement is, however, only apparent. If a metal tube is provided with a glass handle by which it may be held and is then rubbed with silk or flannel, it becomes charged with static electricity. Its seeming inability to become electrified is due to the fact that it is a *conductor* of electricity, and hence the charge passes off rapidly into the hand or the object with which it was in contact. We may, therefore, distinguish two classes: *conductors,* like metals, water and aqueous solutions, plants and animals, and *non-conductors,* like silk, glass, resins, rubber, and dry air. Non-conductors are also often called *insulators,* as they prevent the loss or dissipation of a charge of electricity accumulated upon a conductor. Glass and hard rubber are thus used in practice. When a stick of shellac is rubbed with a piece of flannel, both become electrified, the shellac taking the negative charge of electricity and the flannel the positive charge. On the other hand, when glass is rubbed with silk, both likewise are electrified, but the glass takes the positive electricity and the silk the negative electricity. Both these results are, however, explained if we arrange the substances referred to consecutively in what is known as a potential series. In this list the substances are named in such order that any one becomes positively electrified when rubbed with one of the bodies following, but negatively when rubbed with one of those which precede it:

1. Cat's skin.
2. Flannel.
3. Ivory.
4. Rock-crystal.
5. Glass.
6. Cotton.
7. Silk.
8. The hand.
9. Wood.
10. Metals.
11. Caoutchouc.
12. Sealing-wax.
13. Resin.
14. Sulphur.
15. Gutta-percha.
16. Gun-cotton.

2. **Laws of Electrical Attraction and Repulsion.**—In order to ascertain whether a body is electrified or not, we employ either the *electric pendulum* or *electroscope*[*] (Fig. 37). By means of these we are also

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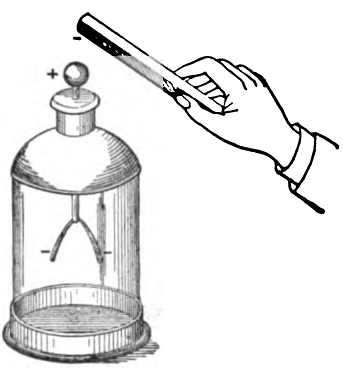
[*] The gold- or silver-leaf electroscope is far more sensitive than the pith ball. It consists of a glass jar closed at the top with a cork through which passes a metallic rod surmounted with a ball of metal, and at the lower extremity are attached two gold- or silver-leaf strips. The jar itself is covered with a non-conducting varnish. If an electrified body is brought *near* to the ball of electroscope, the former acts on the latter by induction, attracting the opposite kind of electricity into the ball and repelling the same kind (as the excited

able to distinguish between positive (+) and negative (—) electrification. If a warm dry glass tube be rubbed with a piece of silk and then presented to the electrical pendulum, which consists of a pith ball suspended by a silk thread, it will be attracted at first, whereby it receives a positive charge from the glass, then, almost immediately afterwards, the ball is repelled, since it has become charged with the same kind of electricity as the glass. If now a stick of sealing-wax be excited with a piece of flannel and be brought near to the charged pith ball, the latter is attracted to the former because the wax is negatively charged. From these experiments we will observe that unelectrified bodies are attracted by electrified ones, and that when both are charged with the same kind of electricity repulsion takes place; when the charges are of opposite kind attraction results.* The laws of electrical attraction and repulsion are as follows:

1. Electrical charges of like name repel each other; electrical charges of opposite name attract each other.

FIG. 37.



Electroscope

2. The force with which each of the two charges attracts or repels the other is directly proportional to the product of the two quantities of electricity and inversely as the square of the distance between them.†

3. **Electrification by Influence.**—A body charged with either positive or negative electricity will exert an influence upon unelectrified bodies in the neighborhood and decompose the neutral condition existing in them, attracting to the surface next to the electrified body a charge the opposite to that which it contains (see Electroscope, Fig. 37). At the same time the decomposition of the neutral condition sets free both kinds of electricity, and while one is drawn towards

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body) into the gold or silver leaves, both of which, being charged alike, will diverge. To ascertain the *kind* of electricity in a body, the electroscope is electrified with the body in question, then with the finger touch the top knob while the leaves are diverging, and remove the finger before taking away the exciting body. When this latter has been removed the electricity retained in the ball spreads over the rod and leaves, causing them to diverge. Now excite a glass rod (+) with a piece of silk and let it touch the electroscope ball; if the leaves diverge more, their charge was positive and that of the body in question was negative; if the leaves collapse, the body must have been charged positive.

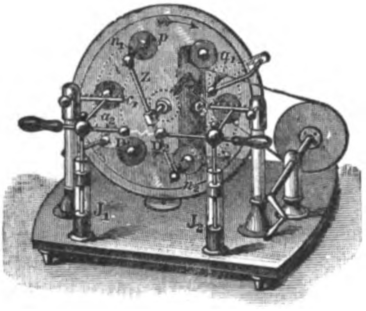
* The electrical charge of a pith ball or electroscope may be removed by touching with the finger, provided it is not within the influence of an electrified body.

† In the first case, if we have one body given a charge of 2 and another one of 3, the force between them will be $3 \times 2 = 6$ times as great as if each had a charge of 1. In the second case, if two small electrified bodies 1 centimeter apart repel each other with a certain force, and this distance is increased to 2 centimeters, the force exerted will be only ¼ as great, and at 10 centimeters it will be only $^1/_{100}$ part. This law of inverse squares is true for small bodies only.

the original electrified body, the other is driven towards the farther extremity of the body which comes under its influence. Such action is called *induction*, and by its means a body once electrified by friction is capable of exerting an influence upon surrounding bodies and developing in them corresponding charges. If this induced electricity is drawn off by suitable conductors and the body again presented in the neutral condition, fresh inductive action will develop fresh charges, and in this way notable charges of both positive and negative electricity can be accumulated. The various newer forms of frictional electrical machines are based upon the principle of repeated induction developing anew fresh electrical charges.

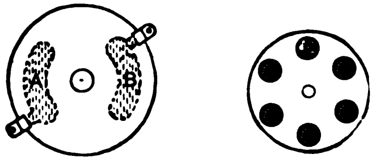
4. **Electrical Machines.**—In the older forms of electrical machines we have simply a circular plate or hollow cylinder of glass, which is rotated rapidly while pressing against pads of silk or leather. These latter are coated with an amalgam or with a bronze powder (stannic sulphide), and by their friction with the glass develop electricity. The plate becomes charged with positive electricity, which is taken off by a metallic comb and accumulates on a brass knob known as the prime conductor, while the pad which presses on the glass plate receives a negative charge which accumulates on a second insulated metallic conductor. A spark may now be taken from either of the insulated conductors. If, however, the conductor which received the negative charge be "grounded"—that is, connected with the floor or table by a metallic chain—the potential of the positive conductor becomes greater, and longer sparks can be taken from it. A newer and more powerful form of frictional machine is the Toepler-Holtz (see Fig. 38), which is in reality a combination of two induction machines. On the back of a stationary glass plate are two cards, A and B, which act as inductors, and on a smaller revolving glass plate in front of the former are pasted a series of tin-foil carriers (see Fig. 39), each of which has in its center a button designed to serve as a contact. A stationary metal rod, *z*, crosses diagonally in front of the moving

Fig. 38.



Toepler-Holtz electrostatic machine.

Fig. 39.



Back fixed disk with field plates on back.

Front rotating disk with carriers on front.

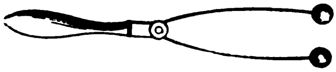
plate, and to this are attached flexible wire brushes, n_1 n_2. As the movable glass plate revolves, these brushes touch the two tin-foil carriers, which are at diagonally opposite positions on the plate, and remove the induced charges from them. As these carriers come around in front of the inductor cards they touch metallic brushes, c_1 c_2, which make contact with the inductors through metallic rods, and thus recharge them with positive and negative electricity respectively. The cards then act inductively upon the revolving glass plate again and communicate to it fresh quantities of the two forms of electricity to be taken up by the brushes of the diagonal rod. The metallic conductors attached to the stationary plate terminate in knobs, D_1 D_2, between which a discharge of sparks is kept up while the other plate is in revolution. These conductors are provided with insulating handles of hard rubber, and are made to slide in and out of metallic sockets, so that the distance between the discharging knobs can be lengthened or shortened according as the difference of potential between the positive and negative charges becomes greater or smaller. The discharging knobs, D_1 and D_2, communicate also with two small Leyden jars, J_1 and J_2, the purpose of which is to accumulate the charges before any discharge takes place. Without them the discharges between the knobs of the prime conductors are continuous and short, while with them the sparks are longer, more brilliant, and louder.

5. Electrical Condensers.—If two metallic surfaces be brought near to each other and yet be kept apart by some insulating medium, we may, by charging one with either positive or negative electricity, cause a charge of opposite name to accumulate in the other by induction. Hence such a combination is called an electrical accumulator, or condenser of electricity. The simplest form would be a pane of glass coated on either side to within an inch of the edge with sheets of tin-foil. More generally a glass jar is used, and this is coated within and without with tin-foil for about two-thirds of its height. Through a cork or wooden cap passes a metal rod terminating above in a knob and ending below in a metallic chain which is long enough to touch the inner tin-foil on the bottom of the jar. Such is known as a *Leyden jar*. It may be charged by grasping it in the hand around the side and then holding the projecting knob to one of the prime conductors of the electrical machine. This charges the inner coating with that kind of electricity which had accumulated on the prime conductor, and at the same time the outer coating by induction takes a charge of the opposing kind. The jar may then be placed upon a table and the charges will remain with little loss for quite a length of time, but if contact is made between the inner and the outer coatings by metallic conductor (Fig. 41) or through the body, the two opposing

FIG 40.

Leyden jar.

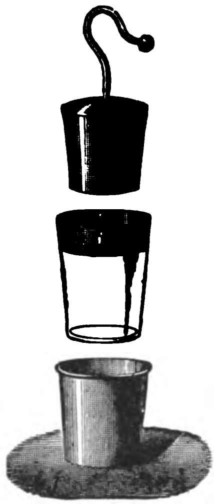
FIG. 41.



Leyden jar discharger.

electricities at once unite and the jar is discharged. The charge of the Leyden jar resides on the outside and inside surfaces of the glass and not on the metallic coating. This may be proven by means of a dissected jar, as shown in Fig. 42, in which two tin cups serve as substitutes for the outer and inner coating of tin-foil. When the cups are in place the jar is charged and set on an insulated surface (glass or rubber), then the inner cup with hook is removed, and by inverting the glass tumbler is removed from the outer tin cup. It will be found on testing with a pith ball that the two surfaces of the glass are oppositely electrified, while no trace exists on either of the two tin cups. On putting together again the jar will be found to be still highly charged. When a Leyden jar is heavily charged, care must be taken in handling, to avoid touching the knob with one hand while holding with the other, as the shock experienced may be very severe.

FIG. 42.



Dissected Leyden jar.

6. Electrical Discharge and its Effects.—The effect of the spark discharge depends very much upon the nature of the body through which the discharge takes place. Its mechanical effects are seen most readily in the case of bad conductors. These are often shattered. Thus it is possible to pierce card-board or leather readily with the aid of the discharge from the Holtz machine. A glass plate may also be pierced in this way. The discharge of atmospheric electricity during a thunder-storm, as seen in the lightning flashes, however, gives us the mechanical effects on the grandest scale. The thunder-cloud and the earth constitute the two parts of a huge condenser. When the difference in potential has become sufficiently great to cause the discharge to take place through the intervening air, we have the lightning stroke which rends the tallest trees as well as buildings which stand out prominently or in exposed positions. Protection against this lightning discharge is sought in the case of tall edifices by the use of metallic conductors, which, while insulated from the building, are connected with the ground. These serve to withdraw an electrical charge of opposite kind to that of the storm cloud, from the earth, restoring thereby the cloud to its neutral state.

The physiological effects of the spark discharge consist in sudden vibrating shocks felt when a Leyden jar is discharged through the person, and in a sharp, prickling sensation felt on the knuckles or fingers when the prime conductors of a plate machine are touched. With large jars or a strong induction machine the spark discharge may be quite dangerous. As will be seen later, this peculiar physiological effect belongs to the spark discharge, whether from the friction machine, the Leyden jar, or the secondary current of the induction machine, because in all these cases the electricity is manifested under high difference of potential or tension.

The luminous effects of a spark discharge vary with the potential of the two kinds of electricity and the medium through which the spark passes. Thus, in ordinary air the spark is white and brilliant, in rarefied air it is reddish, and *in vacuo* it is violet. Rarefied gases, like hydrogen, nitrogen, and carbon dioxide, also cause the spark to show in different colors (see page 85).

The spark passed through inflammable liquids, like alcohol or ether, inflames them; the spark will ignite ordinary illuminating gas, as is seen in many forms of domestic gas-lighting apparatus; when the spark is passed continuously through a wire, although relatively a conductor, the wire still becomes heated. Magnetic effects are also observed. A steel bar or needle may be magnetized if placed inside a tube around which is coiled a wire, through which the spark discharge is made to pass. We will see later, under Voltaic Electricity, that powerful electro-magnets are made in an analogous manner.

Lastly, the chemical effects of the spark discharge are the effecting of chemical decompositions and recombinations of the elements. Thus, if the spark is passed for a time through dry ammonia gas, this is decomposed into hydrogen and nitrogen. On the other hand, the spark discharge will cause the union of hydrogen and chlorine or hydrogen and oxygen when admixed as gases. Among chemical effects must also be noticed the ozonizing of the oxygen of the air through which the discharge takes place. This is readily recognized by the odor which is aways noticed in the neighborhood of the plate electrical machine.

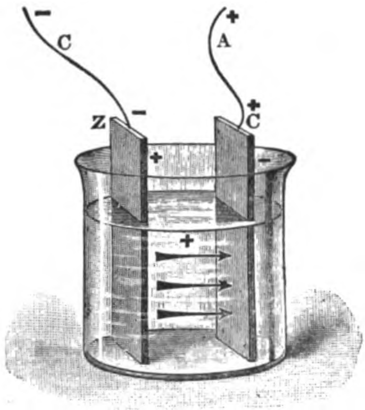
(B) DYNAMIC ELECTRICITY

The electricity hitherto spoken of is known either as *static electricity,* because it remains, when collected, upon the object charged, or electricity of *high tension,* because it accumulates upon neighboring conductors until a high tension or difference of potential is reached, when it is discharged by the passage of the spark. Differing from this in its form and manifestations, although not in identity, is *dynamic* (from δύναμις, power), or electricity of chemical action, so termed because of its various manifestations of power. Synonymously we also employ the terms *galvanic, voltaic, current,* and *chemical* electricity. Under this general heading *magneto-* and *thermo-*currents will be considered.

Galvani, an Italian, was the first (1780) to discover this new method of generating electricity, and Volta the first to construct a battery, known as Volta's Pile, which consisted of a series of alternate zinc and copper plates placed one above the other and separated by felt moistened with brine.

1. Simple Voltaic Cell or Couple.—After a century of constant experiment, scientists still employ the same metals and arrangement in series as Volta, only superseding the moist felt with an acid fluid. If a plate of zinc, Z (see Fig. 43), and one of copper, C, are dipped in dilute sulphuric acid, bubbles of hydrogen gas will collect on the surface of the zinc, which after a time gradually disappear. If we now connect the two plates by means of a wire, the chemical action becomes more violent and a greater amount of hydrogen is liberated; but this time it is disengaged at the surface of the copper instead of the zinc. The latter serves as fuel for generating, while the former collects the current. The production of a current in this case is entirely due to the chemical action which ensues when two dissimilar metals are moistened with the same fluid, one metal being more susceptible to the action of the fluid than the other. If the two wires attached to the plates be separated, electrical action ceases; if they are brought near enough together in the dark, a small spark is seen to pass between them. The joining of the two wires—that is, the establishment of communication between the metals of a cell—is called *closing the circuit;* the separation of these, *breaking* or *opening* it. The metal which is the more energetically acted on by the liquid (in this case the zinc) is called the *generating* (or soluble) plate, while the other (the copper) is the *conducting* plate. The current passes through the liquid from the zinc to the copper, and above through the wires from the copper to the zinc, thus forming a complete circuit. The ends of the wires, A C, leading from the plates are called the *poles* or *electrodes;* the one connected with the zinc, or generating element, is called the ***cathode*** or ***negative*** (—) ***pole,*** while that of the copper, or conducting element, is the ***anode*** or ***positive*** (+) ***pole.***

Fig. 43.



Simple voltaic cell.

2. Electro-motive Series.—As already stated, a current results when two different metals are placed in a fluid which acts on one more strongly than the other. The generating plate is of higher ***potential,**** while the collecting plate is of lower potential. This difference of potential produces *electro-motive force,** which varies between

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* *Potential,* in the physical sense, is that condition of matter by virtue of which it is capable of exerting physical force. Thus, a body of water may, by the expenditure of a definite amount of energy, be forced to some height into a reservoir. This mass of water, by virtue of its position, retains the same energy which has been expended upon it. It has acquired the power to do work; it possesses potential energy. As this water in returning to its former state of equilibrium flows from a higher to a lower level, so electricity flows from

different metals. Various metals have been arranged in a series which expresses their relations to one another in this respect. Such a table is called the electro-motive force series.

+ 1. Zinc.
2. Cadmium.
3. Tin.
4. Lead.
5. Iron.
6. Nickel.
7. Bismuth.
8. Antimony.
9. Copper.
10. Silver.
11. Platinum.
12. Graphite (gas carbon).—

These elements are arranged with the electro-positive at one end and the electro-negative at the other. If any two of these be placed in dilute acid, the current will pass from the lower to the higher (number). Thus, iron is electro-negative to zinc and positive to copper, while silver is negative to zinc and positive to platinum. The E.M.F. is greater in proportion as the metals are distant from each other in the series; for this reason batteries of zinc and platinum (or carbon) give the greatest electro-motive force.

3. **Local Action and Polarization.**—Zinc when placed in water decomposes it, forming zinc oxide, and hydrogen is set free. This action is of very short duration, owing to the coating of the metal with an insoluble film of oxide. The employment of dilute sulphuric acid obviates this by dissolving the oxide as rapidly as it is formed, leaving the surface free. Chemically pure zinc does not react with dilute sulphuric acid until the circuit of the cell is closed. Commercial zinc, which is very impure, reacts constantly with the acid, whether the circuit is open or closed; hence a great waste takes place without contributing anything to the quantity of electricity generated. The presence of these impurities, which usually consist of iron, lead, cadmium, etc., induces the generation of local currents independent of the copper, because these metals are electro-negative to the zinc. This waste of local action may be prevented by *amalgamation,* which consists in rubbing the surface of the zinc plates (which have been cleaned with soap and dilute acid) with mercury.

Polarization is a troublesome feature of the simple voltaic cell. It is due to the accumulation of a film of bubbles of liberated hydrogen over the surface of the copper plate. As this increases, the current weakens and finally ceases. The chief cause of this weakening of the current is the setting up of an opposing electro-motive action, for the hydrogen gas is electro-positive to the copper, and tends to start a current in the opposite direction to the regular one. To avoid this polarization it is necessary to suppress the accumulation of hydrogen. This is usually accomplished by chemical means, which consists in introducing into the cell some substance that possesses a

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bodies of a higher to those of a lower potential. We measure the heat potential of a body by the effect it can produce on temperature, the electrical potential of a body by the electrical force or pressure it is capable of exerting. This force or power which tends to move electricity from one place to another, due to a difference of potentials, is called the *electro-motive force* (E.M.F.). The unit of E.M.F. is the volt, which represents the power of a current to overcome resistance.

strong chemical affinity for the hydrogen, thereby removing it without interfering with the working of the cell. The various means whereby this is accomplished will be explained under the individual cells, which, in view of this, are divided into two general classes—namely, *one-* and *two-*fluid.

4. Voltaic Cells.

ONE-FLUID CELLS.—Though simpler than the two-fluid cells, these are subject to polarization to a greater or lesser degree. However, if allowed to rest at frequent intervals, they rapidly regain their original strength. These one-fluid batteries are especially adapted for "open-circuit" service, such as electric bells, signal circuits, etc., where the current is required only momentarily.

FIG. 44.

Bichromate cells.

The Bichromate Cell.—A convenient form is known as the Grenet Dip Battery (Fig. 44). This consists of two carbon plates, c c, with a zinc, z. This latter is attached to a sliding rod, so that it can be raised out of the fluid when not in use. The exciting fluid consists of potassium bichromate (9 parts), sulphuric acid (25 parts), and water (66 parts). Polarization is prevented through the reducing action of the liberated hydrogen on the chromic oxide.*

The E.M.F. of this cell is about 2 volts. It loses in intensity when used for long periods, but regains it when allowed to remain out of action for a time.

The Leclanché Cell (Fig. 45).—This consists of an inner porous earthen cup which contains a carbon plate packed in fragments of coke and manganese dioxide. The top is covered with a layer of pitch. The positive plate is a rod of zinc, which dips in an exciting fluid consisting of a saturated solution (6 ounces to a quart jar) of sal ammoniac contained in the outer glass jar. Through the action of the salt on the zinc a double chloride of zinc and ammonium is formed, while ammonia and hydrogen gases are liberated at the carbon pole. The hydrogen combines with the oxygen evolved by chemical action from the depolarizer (manganese dioxide), and forms water. If electric action is continued for too long a time, excessive quantities of hydrogen collect and polarization ensues, for the oxygen is not developed with sufficient rapidity; hence short periods of rest are necessary. The great popularity of this cell may be judged from the variety of forms in which it appears on

FIG. 45

Leclanché cell.

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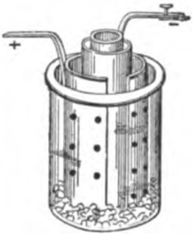
* The chemical action in the exciting solution is $K_2Cr_2O_7 + 7H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O + 6H_2SO_4$. When in action it is as follows:

(a) $3Zn + 3H_2SO_4 = 3ZnSO_4 + 3H_2$.
(b) $2CrO_3 + 3H_2 = Cr_2O_3 + 3H_2O$.
(c) $Cr_2O_3 + 3H_2SO_4 = Cr_2(SO_4)_3 + 3H_2O$.

the market. It does not require renewing for months, or even years. The E.M.F. of this cell is about 1.43 volts. Other kinds of one-fluid cells are the Smee, Wollaston, and mercuric sulphate batteries.

TWO-FLUID CELLS.—These are known as "closed circuit" or "constant" batteries, because of the constancy of their action when in continuous use, such as is required in telegraphy, electro-plating, etc. In these cells the conducting element (copper, platinum, or carbon) is immersed in a fluid which is capable of suppressing the hydrogen, while the soluble element (zinc) is surrounded by a fluid capable of combining with it.

FIG. 46.



Daniell cell.

The Daniell Cell (Fig. 46).—This is one of the oldest and best two-fluid cells in use. The outer glass vessel contains a solution of copper-sulphate kept saturated by adding some crystals of the salt. In this is placed a perforated cylinder of copper. Inside of this cylinder is set the porous earthenware cup containing dilute sulphuric acid and a small cylinder or rod of amalgamated zinc. The chemical reaction, when in use, is as follows: Hydrogen is liberated by the oxidation of the zinc, and passes through the porous cup to the copper sulphate solution, which it decomposes into metallic copper and sulphuric acid. The former is deposited on the copper element, while the latter passes to the zinc to replace that already consumed in forming zinc sulphate. This reaction with the current will continue as long as the outer vessel is provided with copper sulphate. The hydrogen is thus entirely suppressed and depolarization is complete. The E.M.F. of this cell is 1.1 volts. The Meidinger and Crowfoot cells are modifications of this.

FIG. 47.

Bunsen cell.

The Bunsen Cell (Fig. 47).—This consists of an amalgamated zinc cylinder immersed in dilute sulphuric acid contained in a jar. Within this is a porous cup containing a rod of hard gas carbon immersed in strong nitric acid. The "Grove" cell differs from this only in the replacement of the carbon by a strip of platinum. The hydrogen liberated by the zinc passes through the cell and unites with a portion of the nitric acid, forming water and decomposing the acid. The production of fumes (N_2O_4) is the chief objection to this excellent and powerful cell. The E.M.F. is 1.93 volts.

5. Electrical Units.—When electricity is passing, even though it be through what we call a conductor, it meets with resistance.* For purpose of comparison it is desirable to have a uniform method

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*Various metals differ materially as conductors; thus, silver is the best, and is followed in order by copper, aluminum, zinc, brass, iron, etc. The better the conductor the less the resistance. Again, a difference in dimensions of a given conductor offers differences in resistance; for example, taking two round copper wires of the same diameter, one 100 feet in length will offer *twice* as much resistance as will one of 50 feet. If we have two round copof measuring this. The unit of *resistance* is called the *Ohm*, and is the resistance of a column of pure mercury, having a section of one square millimeter and a length of 106.3 centimeters, at a temperature of 0° C. For convenience, coils of wire with a known resistance in ohms are used. These are known as resistance coils, and are prepared in sets, so that any resistance within quite wide limits can be measured with their aid. It is by such means that the location of a break in the ocean telegraph cable can be ascertained so that the cable may be grappled for and repaired.

The unit of current *strength* is called the *Ampere*. It is the rate of flow of a current which under the electro-motive force (pressure) of one volt flows through a circuit which offers a resistance of one ohm. An ampere of current will deposit 0.327 milligram of copper a second, or 1.177 grams per hour. The current is also often measured by the amount of hydrogen and oxygen liberated within a given time by the electrolysis of water.

The *pressure*, or difference of potential, which causes the electricity generated in a battery or cell to overcome the resistance of the circuit and so effect its passage, is called its *electro-motive force*. The unit of electro-motive force is called the *Volt*. It is the pressure required to maintain a current of one ampere through a resistance of an ohm; practically, it is represented by the E.M.F. of the Daniell cell.

The instruments employed for measuring the amperage and voltage of currents are called *ammeters* (ampere-meters) and *voltmeters*, and are explained on page 79. The relation of these three units is expressed in Ohm's law. The Current (in amperes) is equal to the Electro-motive Force (in volts) divided by the Resistance (in ohms). Any two terms being known, the third can be calculated; for, if

$$C = \frac{E}{R}, \text{ then } E = C \times R \text{ and } R = \frac{E}{C}\dagger$$

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per wires each 50 feet long, and one has twice the diameter of the other, the smaller one will have *twice* the resistance. So the greater the length the greater will be the resistance, and the greater the diameter the less the resistance.

† Examples:

1. What will be the resistance of a conductor through which a current of 5 amperes is passing under a pressure of 30 volts?

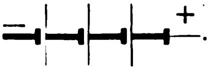
$$R = \frac{30}{5} = 6 \text{ ohms.}$$

2. How many amperes will flow through a conductor having a resistance of 10 ohms under a pressure of 110 volts?

$$C = \frac{110}{10} = 11 \text{ amperes.}$$

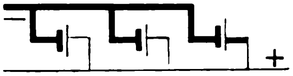
3. How many volts of pressure will be necessary to force 10 amperes through a resistance of 2 ohms?

$$E = 10 \times 2 = 20 \text{ volts.}$$

6. Battery Formation.—A number of voltaic cells may be coupled together for the purpose of increasing the quantity and intensity of the current. Such an arrangement is called a *voltaic battery*. The coupling may be effected in several ways. Two methods, however, demand attention—namely, the *series* and *parallel* couplings. When joined "in series," each zinc is joined to the copper or carbon of the next cell, and so on to the end of the line, the one terminal being a zinc and the other a carbon or copper plate; thus, .

If the external circuit resistance (R) is great, the intensity is proportional to the number (n) of cells; $C = \frac{nE}{R}$.

If the external resistance is small, series coupling presents no advantage over *one* cell, for $C = \frac{E}{r}$ (r = internal cell resistance).

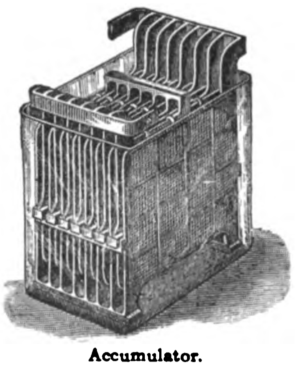
When joined "parallel," all the zincs are coupled together and all the coppers or carbons together.  This arrangement does not give any greater E.M.F. (voltage) than one cell, for the conditions are as though we had but one huge cell with very large zinc and copper (carbon) plates.

If the external resistance is great, the intensity is the same as one cell, for $C = \frac{E}{R}$. If the internal resistance is small to that of the cells (r), the current is proportional to their number, for $C = \frac{nE}{n + r}$.

If the external resistance is great, the elements are arranged in series. If small, then parallel, to get as great intensity as possible.

7. Accumulators, Secondary or Storage Batteries (Fig. 48).—In these the electrical energy furnished is due to an expenditure of chemical energy within the cell. Chemical energy, and not electricity, is stored. The form of accumulator more commonly in use is made by filling the openings of two leaden grids with a paste of red lead (Pb_3O_4) and dilute sulphuric acid. When this has hardened, the plates are placed in a vat of acidulated water and a dynamo current is passed through, the direction of which is changed from time to time, until the red lead on the anode plate has been converted into a semi-porous film of brown peroxide (PbO_2), and that on the cathode plate has assumed a state of spongy metallic lead (Pb). We now have two *different* elements (PbO_2 and Pb), which may be coupled with others, if desirable, and placed in a container with dilute sulphuric acid as excitant.

FIG. 48.



Accumulator.

A layer of felt may be placed between the grids. The chemical reaction that takes place during the discharge is the transferrence of one atom of oxygen from one plate (PbO_2) to the other (Pb), whereby lead oxide (PbO) is produced; and as soon as both plates are alike (PbO) the current ceases. The sulphuric acid present converts the lead oxide of both plates into lead sulphate. The plates are recharged by immersing in acidulated water and passing the current through in alternate directions, whereby the lead sulphate is reconverted into lead peroxide and spongy lead with liberation of sulphuric acid. The capacity of an accumulator is measured in terms of *ampere-hours.* A cell of the capacity of 100 ampere-hours will furnish a current of 1 ampere for 100 hours or 2 amperes for 50 hours or 4 for 25 hours (see page 452).

The cheap *Dry Cell,* which has become popular for running electric bells and circuits, is based on that of Obach, which consists of an outer cylinder of zinc, which serves as a case. This is lined inside with a layer of plaster of Paris, saturated with sal ammoniac, kept separate from the inside contents by a layer of paper. The core, or central portion, contains a carbon cathode embedded in a mixture of manganese dioxide (MnO_2) and ground retort carbon.

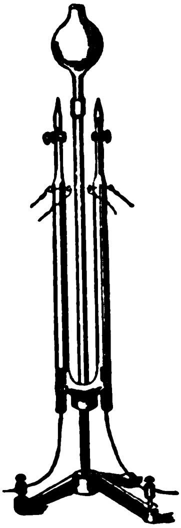
8. Effects of Current Electricity.—The main distinctions between the frictional current or discharge and the current developed by voltaic action are in tension or difference of potential and in amount of the current. Frictional electricity is of high tension but small in total amount, while the voltaic current is of low tension but greater in amount as measured in amperes. Hence the effects will differ somewhat. The mechanical effects of voltaic electricity are very slight as compared with those of frictional electricity. The physiological effects are also, as a rule, very much milder than those of the spark discharge. The wires from a voltaic battery of a dozen cells may be held in the hands without appreciable shock, but a tingling sensation is felt from very strong currents, and prolonged contact with the wires has an exciting effect upon the nerves. The heating effects are dependent, of course, upon the resistance which the circuit offers to the passage of the current and to the amount of current passing. With good conductors like copper, of sufficient section, the heating effect is slight; with wires of insufficient section, or with poor conductors, like platinum, iron, or German silver, the resistance becomes relatively great and the wire becomes strongly heated. It is thus possible, with relatively moderate currents, to fuse a thin platinum wire which may be interposed in the circuit. The luminous effects of voltaic electricity are obtained under two distinct conditions: First, when two wires from the electrodes of a battery are brought together, thus closing the circuit, a spark is seen at the point of contact, often of great brilliancy. This is also seen on breaking the circuit. Secondly, the resistance offered to the passage of the current through a poor conductor often heats the latter to such a degree that it becomes luminous. Both of these methods of obtaining luminous effects, we will see later, are practically applied in electric lighting.

The chemical effects of the battery current are notably more important than are those of frictional electricity, because the greater amount of electricity and the duration of the current in the first case make possible effects not to be attained in the other case. Thus, the current passed through acidified water, as shown in Fig. 49, will decompose it into its constituents, hydrogen and oxygen gases, by a process termed *electrolysis*. Similar results are obtained with solutions of many chemical salts. This will be more fully treated of later under the electro-deposition of the metals, or electro-metallurgy.

ELECTRO-MAGNETICS

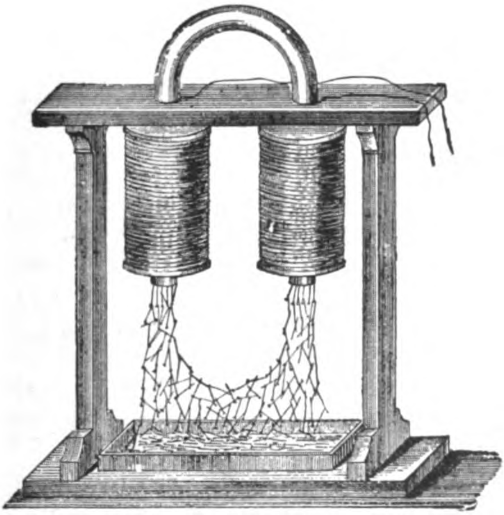
9. The Electro-Magnet.—Soft iron bars become magnetic when brought near to wires carrying a galvanic current, the magnetism lasting as long as the current continues, while steel becomes permanently magnetic. If an insulated wire be coiled around the bar, the magnetic effect will be increased in proportion to the number of coils. To make a powerful horseshoe magnet, therefore, it is only necessary to take a bent or two short bars of soft iron joined at one end by a cross-piece of similar metal, surround these bars by coils or bobbins of insulated wire, and pass a current through the coils. While the current passes we have, as shown in Fig. 50, a powerful magnet,

FIG. 49.



Electrolysis.

FIG. 50.

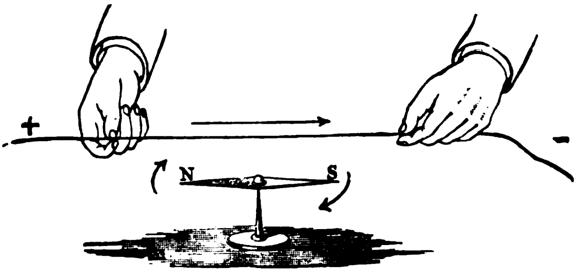


Electro-magnet.

but, as soft iron has little or no coercive force, the moment the current ceases the magnetism of the iron cores disappears. The coils should be wound or connected so that the current passes around one coil in one direction and around the other in the opposite direction, in order that one shall form a north pole and the other a south pole. Electro-magnets are used in almost all forms of practical electrical aparatus.

The Galvanometer.—In 1819 Oersted made the discovery that a magnetic needle tends to set itself at right angles to a wire which carries an electric current, and that this deflection is governed by the direction of the current. For example, if an insulated copper wire attached to both poles of a battery is held above and parallel to a magnetic needle, and the current flows along from north to south, it will cause the north end of the needle to turn eastward (Fig. 51); if the current flows from the south to the north in the wire, the north end of the needle will be deflected westward. If the wire is held below the needle, the movements of the needle will be reversed—that is, the current flowing from north to south will cause the north pole of the magnet to turn westward.*

FIG. 51.



Influence of current on compass.

If instead of using a straight wire it is bent in the form of a loop so that the current will pass above and below the needle (Fig. 52), the deflecting force of the current will be doubled, for the current flows above and below in opposite directions; hence both deflect the needle in the same direction. Such an arrangement is called a *galvanoscope,* and serves in a rough way to indicate the presence and direction of weak currents. To render this instrument more sensitive and adapt it for quantitative use, the number of turns of insulated wire around the needle must be increased, the effect upon the needle being multiplied as many times as there are turns or coils, also the directive force of the earth's magnetism, which tends to keep the

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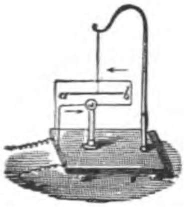
* In order to retain these movements we cite the rule of Ampère—namely, *the observer imagines a small human figure swimming with the current, its face being constantly towards the needle and its arms extended. The* **left** *hand will indicate the direction of the north pole's deflection.*

needle pointed north and south, must be decreased by some compensating arrangement. This usually consists in suspending, by means of the same silk thread or hair, a magnetic needle above, with its poles reversed to the one in the coil below; such a contrivance is known as an *astatic combination* (Fig. 53), and the instrument as a *galvanometer.*[*]

Voltmeters and Ammeters.—For measuring the pressure and intensity of currents, instruments are used based upon the principle that a piece of soft iron suspended inside of a coil of insulated wire through which the current passes strives to place itself in the strongest part of the magnetic field, and according to the strength of the current the degree of attraction varies.

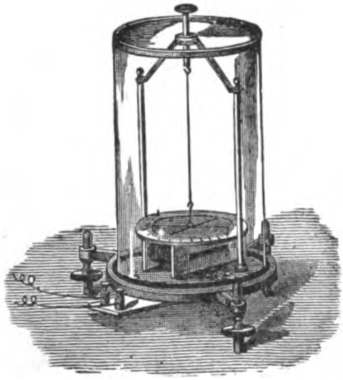
The *amperemeter* (*ammeter*) consists of a wooden spool around which are wound a few turns of thick (low resistance) insulated wire. Inside this spool is suspended a light soft iron core attached to a wire indicator. The stronger the current flowing through the coil, the deeper will the iron core be drawn down, carrying the indicator along the scale accordingly (see Fig. 54).

FIG. 52.



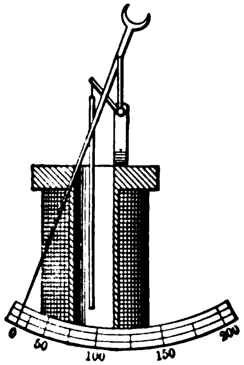
Galvanoscope.

FIG. 53.



Galvanometer.

FIG. 54.



Ammeter.

The *voltmeter* is similarly constructed, excepting that the spool is covered with many windings of thin insulated wire of high resistance; very little current will flow through it; however, what current does flow will be exactly proportional to the potential difference between the two poles of the circuit; hence will indicate pressure or voltage of the current. Other instruments depend on the magnetizing influence of the current on strips of iron, whereby one, attached to an indicator, is attracted or repelled by the other.

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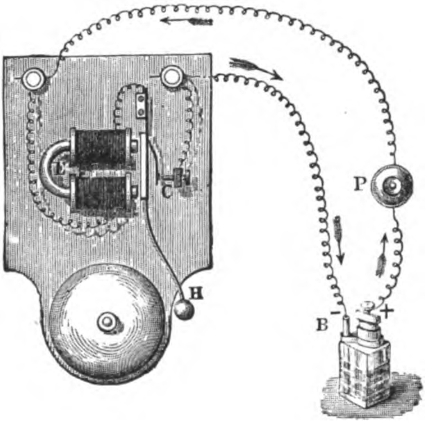
[*] A galvanometer for measuring very minute currents must have many windings of fine wire, for the current must circulate hundreds or thousands of times around the needle in order to multiply its effects so as to turn the needle; this must also be the case if the current has passed through a long circuit or one of high resistance, as, for example, the telegraph. Large currents need a coil of thick wire of but few turns.

Applications of Electro-Magnetism

10. Electric Bells.—These are based on the principle of the electro-magnet, which, by attracting and releasing an armature, to which is attached a hammer, causes a backward and forward movement, striking a bell. The working of these is shown in Fig. 55, in which the electro-magnet, E, is controlled by a Leclanché or dry cell. The instant that the circuit is closed by pressing the button, P, the current flows through the coils and causes the electro-magnet to attract the armature with hammer, H. This forward movement of the armature breaks the circuit, for the current passes through it and the spring contact-breaker resting against the tip of the screw, C, from whence it passes back to the zinc pole of the battery. The circuit having been broken, the electro-magnet ceases to attract, but the momentum already imparted carries the hammer forward. Immediately afterwards, however, the spring forces it back to its original position. These movements are repeated in rapid succession as long as the circuit is kept closed.

Fig. 55.



Electric bell system.

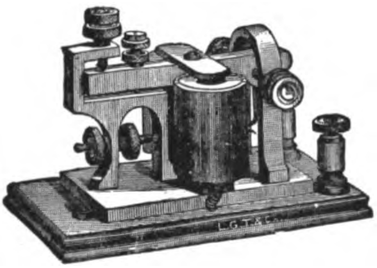
11. Electric Clocks.—By means of a standard central clock which is in electric connection with a circuit containing any number of dials, the circuit is made and broken periodically by the oscillations of its pendulum. These transmitted currents attract an armature behind each dial on the circuit, which controls the movement of a ratchet wheel, permitting it to move forward through one tooth at the specified interval, so that the hands of all the clocks move simultaneously with those of the standard clock.

12. Telegraphy.—The telegraph cannot be assigned to any particular inventor, for it has passed through successive stages to its present state of perfection. Lesage (Geneva, 1774) was the first to construct a telegraph, in which 24 wires were employed, each wire being connected with a pith-ball electroscope representing a letter of the alphabet. Joemmering (Munich, 1808) employed 35 eudiometer tubes, each separately connected, and the electrolytic decomposition of the water contained in each served as a signal. Weber and Gauss (Goettingen, 1833) employed the right and left deflections of a galvanometer needle to indicate a code of signals. Steinheil (Munich, 1837) discovered that the current could be carried by a single wire, the earth being used in place of a return wire. Henry (New York, 1831) utilized the attraction of an electro-magnet on an armature to produce sound signals, and Morse (1835) devised a code of alphabetic signals, consisting of dots and dashes, which were made on moving strips of paper. The telegraphic apparatus consists of—

1. *The Battery and the Wire Circuit.*—The kind of battery employed varies in different countries, but is usually some modification of the Daniell cell. A galvanized iron wire connects the different stations, while the return current is provided for by ground plates sunk in the earth, which acts as a common reservoir, giving and receiving electric energy rather than conducting it.

2. *The Communicator, or Key.*—This consists of a horizontal lever, by means of which the sender controls the current and can establish or break contact by pressure of the finger, producing at the receiving station the clicks or signals.

FIG. 56.



Telegraphic receiver (sounder).

3. *The Sounder* (Fig. 56) is the receiving instrument, which is an electro-magnet. This, when the current passes through the coils, attracts an armature for a longer or shorter period of time. This instrument can be arranged as a "sounder," in which the movements of the armature cause a clicking sound by striking against a stop; or as a "register," in which case the armature, by means of an attached pin, prints dots and dashes upon a strip of paper drawn through the instrument by means of clock-work. The Morse system, which is universally employed, uses as alphabet a series of dots and dashes, indicated by longer or shorter clicks, as heard from the sounder or imprinted on paper.

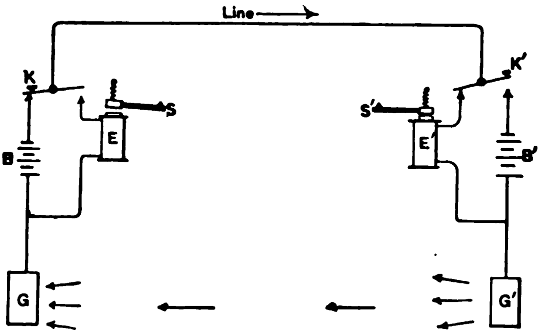
4. *The Relay.*—On lines of not over thirty miles in length the sounders can be operated by the current generated by the batteries of the terminal stations, but on longer lines the resistance weakens the current to such an extent that a relay, or repeater, which consists of an additional electro-magnet with a local battery, must be inserted.

Fig. 57 illustrates the simplest possible case of an open single-current method of telegraphing. On depressing the key K, the current flows from the battery, B, through the line and enters the receiving instrument, causing the electro-magnet, E′, to attract the sounder, S′, returning through the ground plate, G′, to G and the battery whence it started. If key K′ is depressed, the reverse action takes place.

Duplex, Diplex, and Quadruplex Telegraphy.—Two messages sent through the same wire simultaneously from opposite terminals constitute "duplex" telegraphy; when both are transmitted through the same wire in the same direction, "diplex"; while "quadruplex" telegraphy combines both the duplex and the diplex systems.*

Cable or Submarine Telegraphy.—The transmitting cable is made of seven or more No. 16 copper wires, protected, first, by a layer of gutta-percha, then by a woven coating of jute. Outside of this is a layer of at least ten steel wires, which are still further protected by wrapping in hemp. Strong currents cannot be employed, for the cable and its non-conducting sheath, when immersed in water, produce excessive electro-static charges, like those of the Leyden jar, which impede electric transmissions. For each signal a current is sent into the cable, followed by a reactive opposing current, which again discharges it. Since the currents transmitted are very weak, it is necessary that an exceedingly sensitive receiving apparatus be employed. This is a galvanometer, called Lord Kelvin's Siphon Recorder, which consists of a coil of wire suspended between the poles of a powerful magnet. To this coil is attached a fine glass siphon, one extremity of which dips into a vessel of ink, and as the coil oscillates backward and forward like the needle of an ordinary galvanometer the ink flows from the siphon, producing on a moving strip of paper a wavy line, having short and long waves for dots and dashes. The duplex system is used on all cables. The rate of speed for messages varies according to the length of the cable; the cable between Newfoundland and Ire-

FIG. 57.



Principle of telegraph.

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* For explanation of these systems, see "Electricity and Magnetism," by S. P. Thompson, published by the Macmillan Company.

land admits 100 letters (about 25 words) per minute, the speed decreasing inversely with the square of the distance.

Wireless Telegraphy is based on the transmission of electric waves through space. Messages are now readily transmitted to a distance of over 3000 miles. The transmitting instrument is a vertical pole carrying a wire from 50 to 100 feet high; with it is connected one of the knobs of an induction coil, while the other knob communicates with the ground or water. Every spark which passes between the knobs at the bottom of the pole answers as a signal dot, while a short succession of sparks indicates a dash. These sparks produce electric pulsations in the vertical wire, which are communicated as waves in every direction through space. The receiver is a live aerial wire connected to the earth through a simple apparatus called a "coherer"; the wire terminals of this are also joined to a circuit connected to a relay or telephone. The instant the transmitted electric waves fall on the vertical wire connected with this coherer its resistance is reduced, and a current flows through the circuit and operates the electro-magnet of the receiver, producing dots and dashes of the Morse code. More sensitive is the microphone receiver (coherer), which consists of an iron and carbon rod separated by a globule of mercury enclosed in a glass tube and connected with a telephone.*

VOLTAIC INDUCTION

13. Induction Currents.—Faraday (1831) made the discovery that instantaneous currents of electricity are produced in closed circuits by the movement of a magnet in proximity to them; also by a similar movement of a conductor traversed by an electric current; a current whose strength is changing will produce the same effect. Such currents are known as *faradic* or *induced* currents, and on this principle are based the induction coil, dynamo machines, alternate current transformers, etc.

(*a*) *Induction of Currents by Currents.*—To illustrate this, two coils of insulated wire, wound on spools, are selected. One of these, known as the *primary* or *inducing current* coil, is made sufficiently small to fit inside of the other, and its terminals are connected with a battery. The terminals of the larger coil, which is called the *secondary* or *induced current* coil, are connected with a galvanometer. If the primary (smaller) coil is introduced inside of the secondary (larger) the galvanometer will show that a reverse current of momentary duration has been induced in the latter, moving in the opposite direction to that circulating in the primary. The instant the primary current ceases to flow or the coil is withdrawn, a direct current is induced in the secondary coil, moving in the same direction as that of the primary.

(*b*) *Induction of Currents by Magnets.*—If in the above experiment

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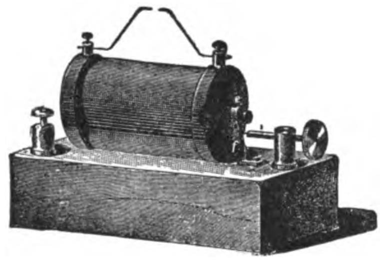
*For details see "Wireless Telegraph and Telephone," by Laughter.

the primary coil is substituted by a magnet, it will be found that on inserting a bar magnet inside of the secondary coil the needle of the galvanometer will be deflected, showing thereby that an electric current has been induced. This current is of momentary duration only, and when the magnet is withdrawn the needle will be deflected in the opposite direction, showing the induction of a reverse current. If the poles of the magnet be reversed the direction of each current will be reversed. This subject will be further explained under magneto-electric currents, on page 88.

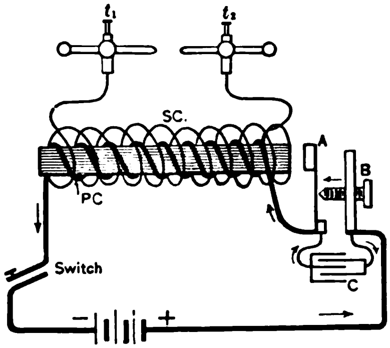
The Induction or *Ruhmkorff Coil* is a practical application of the preceding principles. By means of this we are able, within a few voltaic cells, to produce an exceedingly high E.M.F. or potential difference, which in a large coil is equivalent to many thousand volts. For example, a battery of 600,000 Daniell cells would be required to produce a spark of 6 inches, while by aid of an induction coil the same may be accomplished with perhaps 10 cells. An induction coil (Fig. 58) consists of a central core made of a bundle of soft iron wires * around which are wound a few turns of heavy insulated copper wire (PC, Fig. 59) of low resistance, in order that it may carry strong magnetizing currents. The one terminal of this coil connects with a switch and this with the negative pole of a battery; the other is attached to the spring of the ***vibrator*** or ***contact breaker***, A, resting against the set-screw, B, which communicates with the positive pole of the battery. This is called the ***primary circuit***.

FIG. 58



Induction coil.

FIG. 59.



Outlined induction coil.

On closing the circuit (by means of the switch) the electro-magnet core of the primary coil attracts the vibrator, A, which, the instant

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* A bundle of soft iron wires is employed as electro-magnet in preference to one of solid iron, because of the rapidity with which the wires can be magnetized and demagnetized; solid soft iron always retains (after cessation of the current) a small amount of residual magnetism which would interfere with the rapid making and breaking of the current.

it leaves the set-screw, B, breaks the circuit. The core loses thereby its magnetism, and the vibrator is forced back to its original position by its spring, which again closes the circuit as before. The make and break thus produced take place with great rapidity, giving rise to a series of *primary intermittent* currents. By means of the set-screw, B, the amplitude of the vibrations may be regulated. Around the primary coil, and insulated from it by means of a hard-rubber casing, is the *secondary circuit*, SC, which consists of many turns of very fine wire. For example, a giant coil which gives a spark of about 1 meter contains 480 kilometers (300 miles) of wire in its secondary circuit, with a resistance of over 100,000 ohms. The terminals of this coil end in the knobs, t_1 and t_2, across the points of which, when adjusted to the proper distance, brilliant, snappy sparks will pass. Every "make" of the intermittent current in the primary circuit results in the induction of a momentary *inverse* current in the outer secondary circuit, and at every "break" a powerful momentary *direct* current; thus *alternating intermittent secondary currents* of high potential follow in rapid succession. Connected with the primary circuit is a condenser, C, made of alternate layers of tin-foil and paraffin paper, into which the extra current flows when the circuit is broken, thereby increasing the E.M.F. at the "break." Small induction coils are employed in treating nervous diseases; also for electric gas-lighting, exploding mines, and bringing about chemical union between gases and in wireless telegraphy.

The passage of a spark* between the terminals t_1 and t_2 is accompanied by a loud snapping noise, which is due to the resistance offered by the air; if, however, this discharge is made to take place between two platinum electrodes sealed in the extremities of glass tubes which have been rarefied to the extent of $\cdot\frac{1}{1000}$ part of an atmosphere, a beautiful luminous phenomenon is produced, the color and appearance varying with the degree of exhaustion, diameter of the tube, and nature of the rarefied gas remaining. Such tubes are known as *Geissler tubes*, and, besides being rarefied, they are often made of fluorescent (uranium) glass or the outer walls filled with fluorescent liquids. If the exhaustion of such tube be carried to a very high degree, so that only about $\frac{1}{1000000}$ part of the air originally contained remains, we will find, on connecting with the terminals of a 5- to 6-inch coil, that no electric discharge as heretofore seen takes place; but a purplish ray is seen about the cathode, while the interior of the tube remains dark and the glass walls become fluorescent. It was found that the discharge from only one of the electrodes—namely, the cathode (— pole), irrespective of the position of the anode (+ pole)—was capable of producing this fluorescence of the glass walls of the tube, and that when directed on powdered alumina, rubies, and diamonds it caused them to become phosphorescent. Tubes specially constructed for this

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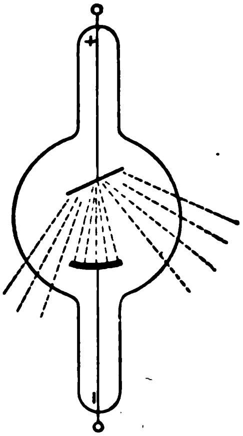
* This differs only in degree from that furnished by the frictional machine or Leyden jar.

purpose are known as *Crookes tubes* (Fig. 60). In the Geissler tube the discharge passes between the anode and the cathode, while in the Crookes tube the cathode rays are projected in straight lines from its surface, their presence being noted by the fluorescence of the walls of the tube opposite the negative terminal.

To Professor Roentgen is due the credit of the discovery that this cathode discharge (called by him "X-rays") is capable of penetrating opaque bodies and exciting certain fluorescent substances. Of these the two best adapted are platino-cyanide of barium and calcium tungstate. If a piece of pasteboard is covered with a layer of either of these chemicals * and is held so that the "X-rays" are directed upon the screen, its surface will become uniformly illuminated. If now any opaque or semi-opaque object is placed between it and the Crookes tube, the rays will either be uniformly intercepted or some more intercepted than others; hence shadows will result. For example, the bones of the hand intercept the rays more than the fleshy parts; hence cast shadows whereby they may be distinguished. The cathode is usually cup-shaped, in order to focus the rays upon a flat, disk-shaped anode, which acts as a reflector.

FIG 60



Crookes tube, showing reflection of "X-rays."

While glass is relatively opaque, wood, paper, and most organic tissues are transparent, and allow the passage of these rays. They act upon the photographic plate, and admit photographs being taken through wood and most organic tissues. The metals, with the exception of aluminum and tin, are more or less opaque to them.

It has been shown that the cathode rays consist of streams of negative electrified material particles, called *corpuscles*, whose mass is only one two-thousandth the mass of the hydrogen atom, and velocity from one- to four-tenths that of light. These corpuscles are the constituents of all atoms and molecules (see page 116).

The Telephone is a practical application of the principles of induction. By its means speech may be transmitted through long distances by the intervention of a magnet and induced currents in a coil of wire surrounding the magnet. The essential parts of the Bell telephone can be seen in Fig. 61. Enclosed in the case, F, is a magnet, M, having at one end a coil of very fine wire, and a diaphragm of very thin sheet-iron, G G, which is placed close in front of the magnet. The coil of wire connects by the two wires C C with binding screws, D D, at the other end of the instrument. When a person speaks into the mouthpiece, E, the diaphragm of thin metal vibrates immediately before

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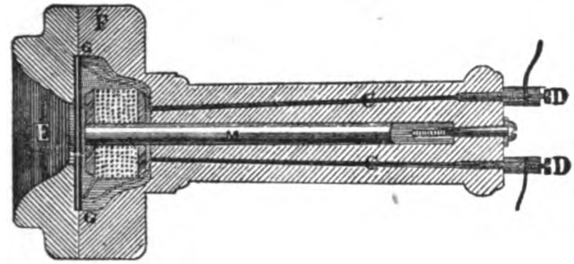
* Such a screen was named by Edison the Fluoroscope.

the magnet and causes changes in the lines of magnetic force and the electric currents in the coil which surrounds it. These currents passing over the line affect the strength of the magnet in a corresponding instrument at the other end, and in turn cause the diaphragm in front of it to vibrate, producing sound waves which will perfectly correspond with those generated by the person speaking. The Bell telephone may therefore serve either as a "receiver" or a "transmitter."

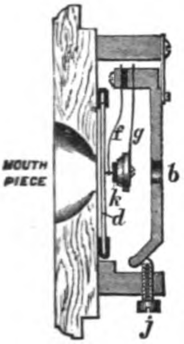
Fig. 61.



Telephone.

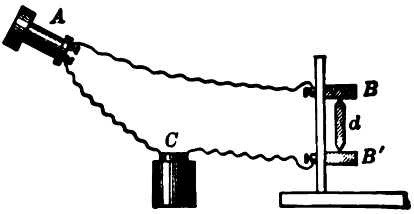
In modern telephones the Blake (microphone) transmitter (Fig. 62) is employed. In this the voice-vibrations directed into the mouthpiece fall upon the thin iron diaphragm, *d*, which is held in place by a soft-rubber ring. The vibrations of this are transmitted by the insulated spring-needle, *f*, to a carbon plug, *k*, attached to a spring, and the current passes to the contact point by one spring and passes off through the other.

Fig. 62.



Blake transmitter.

Fig. 63.



Microphone

In its simpler form, the microphone (Fig. 63) consists of a small pencil of carbon (*d*) held gently in contact with two other pieces of carbon, B and B', which are connected by means of a battery to a telephone receiver. Words or noises near the instrument produce an alteration in the contact of the carbons, and consequently variations in the galvanic resistance, which cause sounds to be heard in the telephone.

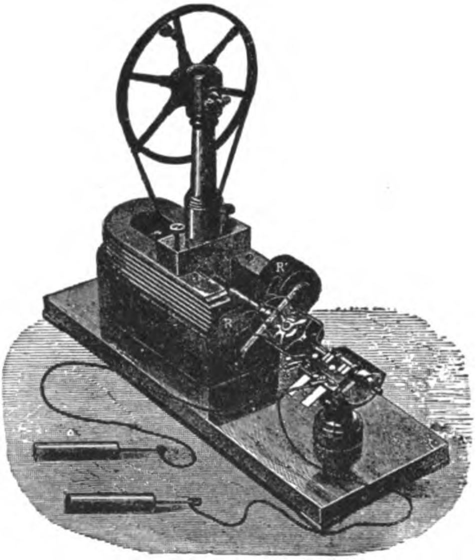
CHAPTER VII

MAGNETO-ELECTRIC AND DYNAMO-ELECTRIC GENERATORS

By means of machines we are able to convert mechanical energy into electrical energy. This involves an expenditure of force in producing relative motion between magnets and conductors, which consists, in most instances, in rotating coils of wire in the field of a magnet or electro-magnet, or in other cases the latter are made to revolve.

Simple Magneto-Electric Machine.—The discovery of Faraday, that if a coil of wire is moved across the field of a magnet, electric currents are induced (see page 83), first suggested the construction of the magneto-electric machine, whereby electric currents could be generated by mechanical power. Such a machine is shown in Fig. 64. In front of a powerful horseshoe magnet, and as near as possible, rotates an armature consisting of two soft iron cores, R R′, each of which has been bound with a coil of insulated copper wire; the ends of the wires connect with the axis, and from this, by means of two springs, the currents are taken up and carried to the handles. When the armature revolves, the soft iron cores, as they pass in front of the north and south poles of the magnet, become magnetic by induction; this induces in each of the coils transient currents which are alternately inverse and direct. Since the poles change twice in every revolution, the direction of the current will necessarily change twice. In order that

FIG. 64.

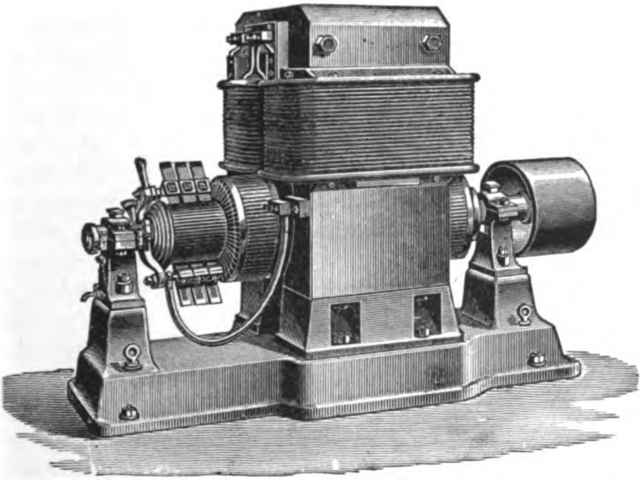


Magneto-electric machine.

the currents may all flow in the same direction, as in the galvanic battery, a *commutator* is fixed on the axis; this consists of two semi-cylindrical segments of copper, each insulated from the axis and connected with the ends of the separate coils. When rotating, these two plates are out of contact with the springs during the break, and are brought into reversed contact at the instant of current reversal, which occurs at each half revolution. Their position with reference to the springs is reversed as the currents are reversed; hence the latter flow in the same direction. Thus, by means of a commutator, direct currents can be made up from alternating ones, with, however, a perceptible intermission at each make and break; this lessens with the rapidity of rotation.

The Dynamo-Electric Machine.—This machine (Fig. 65) differs from the preceding in that the permanent magnet is replaced by an electro-magnet, which is excited by the current generated. In proportion as the strength of the current circulating around the electro-magnet increases the magnetic forces multiply, which in turn induce still stronger currents in the coils which rotate within the field of influence. The number of magnetic poles is frequently increased from two to four and even eight; such are known as multipolar dynamos. Between the poles, or field magnets, of the dynamo rotates an armature of soft iron, made either in the form of a ring, over which the insulated coils of wire are wound, known as the *Grammes ring,* or the armature and its coil are drum shaped, and called the *Siemens armature.* The ends of the armature coils all terminate in a number of copper strips attached to the axis, but insulated from one another, and from these the current is taken up by two sets of brushes, which consist of a number of copper bars set close to the commutators. If the

FIG. 65.

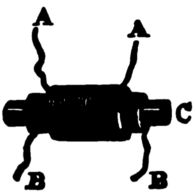


Dynamo-electric machine.

transient currents generated by the rotating armature pass into the external circuit without communication, a continuous *alternating* current is produced, and machines having such a construction are called alternating-current dynamos. The advantages of this kind of a dynamo, with its currents, are several: for example, the resistance and wasteful sparking of the split ring commutator are avoided; it gives currents of higher potential and less internal resistance than the direct-current dynamo; also, it is possible to carry such currents to distances with comparatively small wires and at less cost. A *motor* is a machine which is utilized in converting electrical energy into mechanical; the dynamo, as shown in Fig. 65, can be used as a motor if supplied with a proper current.

Transformers or *Converters* are necessary in the distribution of alternating currents. Their function is to transform currents of high pressure and low quantity into induced currents of low pressure and larger quantity. For instance, a high-pressure current of from 1000 to 50,000 volts flowing through the mains must be cut down to 50 or 100 volts for incandescent lighting in the various branches. These transformers (Fig. 66) are simply inverted induction coils, in which the primary coil consists of many turns of fine wire, which receives a small current of high pressure from the main. Insulated from this is the secondary coil of a few turns of coarse wire of low resistance, which gives out a large current of low pressure. If the primary coil has 2000 turns and the secondary 100 turns (ratio of 20 to 1), in order to take out of the latter a current of 100 amperes and 50 volts, we must put into the primary coil (from the main) at least 5 amperes at 1000 volts pressure. By selecting the proper number of turns, the E.M.F. can be transformed up or down.

Fig. 66.



Transformer.

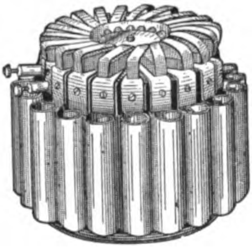
A simple device for adapting the alternating current for use with an induction coil is the electric interrupter. It consists of a beaker glass containing dilute sulphuric acid, into which are immersed strips of platinum to serve as anode, while the cathode consists of a short piece of platinum wire fixed into the end of a glass tube bent at an angle at the lower end. The tube is then filled partly with mercury to enable the wire from the circuit to make electrical contact with the platinum point. Bubbles of hydrogen gas are continuously discharged from this platinum point, and an intermittent current is thus sent into the coil.

Change of Electrical Energy into Heat.—We have already referred to the heating effect of the voltaic current. The heat generated by the powerful currents of the dynamo machine, when passing through poor conductors or encountering electrical resistance in any way, is correspondingly greater. Two effects of this heating may be noticed: *electrical furnaces* for carrying out metallurgical operations which require an intense heat, as in the Cowles furnace for the production of aluminum by the reduction of its oxide by charcoal; and *electric welding*, in which case two pieces of metal are welded together by bringing them in contact and passing a powerful electric current through the juncture. Iron, steel, brass, and copper may be readily welded in this way.

Change of Electrical Energy into Light.—The heating effect of powerful currents may be utilized for lighting purposes in one of two ways. If the two electrodes of the current from a powerful battery or dynamo be brought to within a short distance of each other, a brilliant arc light is formed, spanning the interval between the two terminals. The ends of the wires are raised to a white heat, and most metals melt or volatilize in consequence. If, however, the terminals are pencils of hard carbon, which is infusible, we have the brilliant white light known as the *arc light.* The carbon, of course, burns away gradually, and provision must be made for keeping the distance between the two pencils constant, which is done automatically by a suitable electro-magnetic mechanism attached to the lamp.

The current is also utilized for lighting effects in a still simpler way. This is to interpose at some point in the circuit a conductor of such resisting power that the passage of the current renders it white-hot. This is effected in the *incandescent lamp,* and the substance utilized here is likewise carbon. An extremely fine filament of carbon is enclosed in an exhausted glass globe. This filament or horseshoe of carbonized bamboo is connected at either end by fine platinum wires, which are fused into the glass and pass through, connecting with the brass fitting of the socket into which the lamp is screwed.

FIG. 67.



Thermopile.

In the later incandescent bulbs filaments of tungsten are employed in an atmosphere of nitrogen and argon.

Arc lamps require a very high electro-motive force, usually from 1000 to 3000 volts. Incandescent lamps, on the other hand, require only from 50 to 120 volts. The former voltage is likely to be fatal to life if by accident a naked wire is touched; the other is not.

Thermo-Electric Currents.—If two dissimilar metals are soldered together, and either heated or cooled at their point of contact, an electric current is produced; such currents are termed *thermo-electric currents.* The two bars of metal producing the current constitute the *thermal element.* A number of such elements or metal bars thus joined and arranged side by side in couples, with each pair of ends soldered together in alternate order, form a *thermopile,* one form of which is shown in Fig. 67. For various reasons, very few metals are available for this purpose. Those combinations usually employed consist of either bismuth and antimony, or German silver with an alloy of antimony and zinc. Thermo-currents are of extremely low potential and very constant. The thermopile, when connected with a sensitive galvanometer, affords accurate means for detecting very minute differences of temperature, but has no other practical application.

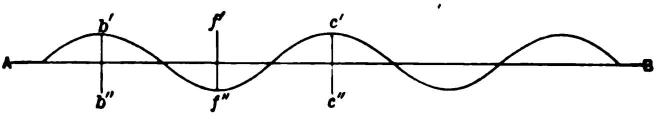
CHAPTER VIII

RADIANT ENERGY.—II. LIGHT

I. NATURE OF LIGHT

1. Comparison of Heat and Light.—We have already referred to the undulations or vibrations which, radiating out from sources of light like the sun, are communicated to the ether, an exceedingly attenuated elastic medium which fills space, and are thus propagated until they strike upon bodies whose molecules are capable of taking up the vibrations and developing what we call heat energy. We saw also that chemical combination or combustion, friction, and other causes were capable of initiating these vibrations and serving as sources of heat. The sun, the great source of these heat vibrations, and most other sources of heat are also capable of radiating undulations of a more systematic, wave-like character, which have one or both of two different effects. They may act upon the retina of the eye, and when communicated by the optic nerve may produce upon the brain the sensation of vision, or they may act upon certain chemical salts, decomposing them, because of what is called actinic power. Most generally, sources of heat become sources of light when the molecular vibration becomes more rapid, as the light undulations are more rapid and of shorter wave-length than the heat rays. Thus, a bar of metal, when heated, gives off at first only heat vibrations recognizable by the rise in temperature. After a time a red glow begins to appear and light rays of greatest length and slowest time of vibration are emitted. When the iron is still further heated it becomes white-hot and the waves are now of shortest wave-length and quickest vibration. The wave-motion communicated by heat and light to ether consists of vibrations which are perpendicular to the line of propagation. As shown in Fig. 68, the wave line represents the motion of the ether molecules in the direction A B, the distance b' c', from one wave-crest to the next, is a *wave-length,* while one-half of the distances b' b'', f' f'', c' c'' represent the *amplitudes* of vibration.

FIG. 68.



Wave-motion.

Theory assigns no limit to the length of ether waves, for the optic nerve is sensitive to only a limited number, the shortest being 0.000039 centimeter long, corresponding to 757 million million vibration-frequencies per second, while the longest is 0.000076 centimeter, with 392 million million vibrations. All vibration-frequencies which lie between these limits constitute light. Each wave-length with its vibration-frequency represents a particular kind of light, which produces the sensation of color. Color is then simply the impression resulting from some or more particular wave-frequencies.[*] Waves of minimum vibration-frequency produce the sensation of red, while those of maximum frequency that of violet; those lying between these produce sensations of red, orange, yellow, green, and blue. Such a succession of colors, beginning with red and shading gradually from one to the other and finally to blue, is called a *spectrum.* Those colors at the red end of the spectrum (ultra-red to yellow) are the richest in heat and poorest in actinic rays, those at the violet end (blue to ultra-violet) give no heat, but are very active chemically (actinic) (see page 139), and those nearest yellow give the most light. If a portion of light consists of waves of the same length, it is termed homogeneous or *monochromatic.* If it consists of a mixture of long and short waves, uniformly *distributed,* white light results.

A *luminous* body is one which emits light rays. Bodies may be self-luminous or original sources of light, like the sun, a candle-flame or gas-jet, and a fire-fly, or merely illuminated bodies which shine by reflected light, like the moon and bodies lighted by ordinary daylight.

Fluorescence and Phosphorescence.—Certain fluids and solids are said to *fluoresce* when, on exposure to light radiations in the form of short waves invisible to the eye (ultra-violet), they deliver them in longer visible waves (violet, blue, green)—that is, these bodies render visible otherwise invisible radiation. Fluorescence is limited in duration, lasting as long as the substance is exposed to the proper light radiation. Solutions of quinine sulphate, gelsemic acid, eosin, fluorescein, chlorophyll, etc., belong to this class, and emit different colors according as they are viewed by either transmitted or reflected light. Thus, an ethereal solution of chlorophyll is green and an aqueous solution of eosin is red by transmitted light, while by reflected light the former is red and the latter is yellow. Phosphorescent bodies are those which, after exposure to the light, continue to shine for some time in the dark. This is due to oxidation, as in the glowing of phosphorus or the sulphides of calcium or barium, or to friction, as in the cleavage of crystals. In the animal or vegetable kingdom we find that the glow-worm, fire-fly, marine luminous infusoria, certain fungi or decaying wood, emit light. This is due in the former instances to nerve energy, while in the latter, possibly oxidation.

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[*] LIGHT WAVES

Color.	Vibration-frequency.	Wave-length.
Ultra-red	370 million million	0.0000810 cm.
Red	428 million million	.0000700 cm.
Orange	502 million million	.0000597 cm.
Yellow	516 million million	.0000580 cm.
Green	569 million million	.0000527 cm.
Blue	634 million million	.0000473 cm.
Violet	739 million million	.0000406 cm.
Ultra-violet	833 million million	.0000360 cm.

Iridescence is produced by the reflection of light from both upper and lower surfaces of a very thin transparent layer of varying thickness.

Transparent bodies are those which readily transmit the luminous rays. *Translucent* bodies transmit light less readily, so that at most the outlines of bodies can be seen through them. *Opaque* bodies do not transmit light at all, and cut off the light rays completely. Some bodies, like metals, which are opaque in bulk, become translucent or even transparent when in very thin layers. A *shadow* is the space where the light rays have been intercepted by an opaque body lying in their path.

2. Transmission, Velocity, and Intensity of Light.—In a homogeneous medium the light rays are always propagated in a straight line. This is illustrated when a beam of sunlight enters a dark room. Its path is revealed by illuminated particles of dust and shown to be in a straight line.

Light travels through space with the velocity of about 300,000 km. (186,000 miles) per second.

The intensity of illumination on a given surface is inversely as the square of its distance from the source of light. That is, a given unit of surface at twice the distance from the source of light of another surface will receive one-fourth the light.

Photometers are instruments for measuring the relative intensities of light. The form in common use is the Bunsen photometer. It consists of a screen of paper mounted in a box which slides to and fro on a graduated bar. The paper screen has a central spot saturated with paraffin. Fixed at one end of the bar is a standard light, usually a sperm candle, of definite size and weight, while the light to be standardized is placed at the other end of the bar. If the two lights are of equal intensity, the grease-spot does not show on the paper. When one side is more strongly illuminated the spot appears dark on that side and light on the other. It is then necessary to move the box containing the paper screen until the spot just becomes invisible. Its position on the bar is then noted, and the relative distance from the two ends taken for the calculation. The result is usually referred to a standard candle and expressed in what is called candle-power.*

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* The standard of comparison is a sperm candle burning 120 grains per hour. If the distance from the illuminated spot to the standard candle be 2 feet, and to the light to be standardized 6 feet, the candle-power of the light would be 9. For, according to the law, the *intensity of illumination from a luminous point is inversely proportional to the square of the distance of the illuminated surface from that point*, then $\frac{6^2}{2^2} = \frac{36}{4} = 9$. The following table gives the relative brightness of several sources of light:

Standard candle	1 candle-power
Gas-jet	12 to 18 candle-power
Welsbach burner	30 to 50 candle-power
Electric arc, average	800 candle-power

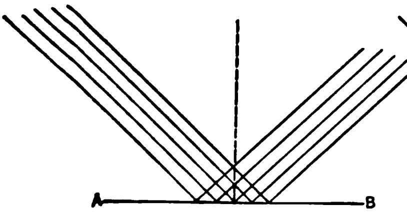
II. REFLECTION OF LIGHT

We have before declared the path of a ray of light entering a dark room, as shown by the illuminated particles of dust, to be a straight line. If this ray strike obliquely upon a horizontally placed mirror or polished surface, we will also notice that a ray of light is thrown off or *reflected* from the mirror, and on measuring the angle made by the entering ray and the imaginary perpendicular to the horizontal mirror, and that made by the reflected ray and the perpendicular, they will be found to be equal (Fig. 69). From the experiment we may deduce the following two laws of the reflection of light:

1. The angle of reflection is equal to the angle of incidence.
2. The incident and the reflected ray are both in the same plane, which is perpendicular to the reflecting surface.

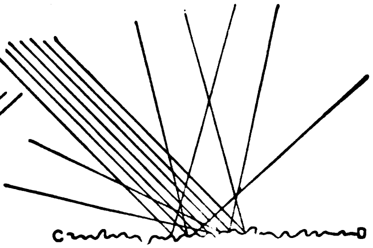
Not all of the light of the incident ray or beam is reflected in this way. Unless the reflecting surface be an absolutely smooth one, some of the light is irregularly reflected or diffused. It is this which enables us to see objects. Well-polished surfaces like that of a mirror reflect light in a definite direction (A B, Fig. 69), while rough or dull surfaces scatter or diffuse the light: C D, Fig. 70, represents the roughness of the surface of paper very much exaggerated. This diffused light renders it visible in all directions. If a reflecting surface were absolutely smooth, it would be invisible. We would simply see in it the image of other objects. Objects about us are thus illuminated by the diffused light reflected from clouds, the air, and other surfaces, and so they become visible, although they may not receive the direct rays of light from the sun. There are, in fact, many days when, on account of clouds, our illumination comes wholly from this irregularly reflected or diffused light.

FIG. 69.



Reflection of light.

FIG. 70.



Diffusion of light.

Reflection of Light from Polished Surfaces.—*Mirrors* are bodies with polished surfaces which are employed to show by reflection objects placed before them. *Images* of the objects are thus formed. The development of these in the case of plane mirrors is very simple. The rays of light coming from the object before the mirror make with the latter an angle of reflection equal to the angle of incidence, and so come to the eye. But the eye always sees objects in the direction from which the rays reach it, so that the image appears in the prolongation of the reflected ray, and at a distance back of the mirror exactly equal to that of the object from it in the other direction. The image, therefore, is not a *real* one formed by the reflected rays themselves, but an apparent or *virtual* image only. It is also a reversed image as regards right and left, as is shown when printed matter is held before a mirror. Wood-cuts and type must therefore be made in reversed position. Held before a mirror the image shows as a printed impression from the type will appear.

The ordinary glass mirror has in reality two reflecting surfaces, that of the glass and that of the metallic backing of the glass. Ordinarily we see only the one image, because the metallic backing is a much better reflector than the glass surface, but we can readily get the double image by placing the point of a pencil against the glass surface, when the double image allows us to judge of the thickness of the glass.

Transparent bodies the surface of which is smooth may reflect light quite regularly at times, and so form distinct images. An illustration of this is seen in the reflection of foliage and other objects in the still waters of a clear stream or pond.

All the images thus far spoken of have been formed with plane mirrors, and have been virtual images. With concave mirrors of glass or polished metal the reflected rays themselves may be made to unite to form an image, which is therefore a real image and is seen on the same side of the mirror as the object itself. This image, formed by the reflection of the rays themselves, will, however, be inverted, because the rays from different parts of the object after reflection must assume relatively reversed positions with reference to each other. The *focus* of a spherical concave mirror is a point to which the reflected rays tend to converge. If the incident rays are parallel to the axis of the spherical mirror, the focus is called the principal focus. When the object is farther from the mirror than the principal focus, the image will be inverted and real, as well as smaller than the object; when the object is between the principal focus and the mirror, the image is virtual and erect, as well as larger.

With convex mirrors we have virtual images only, appearing behind the mirror, erect and smaller than the object.

III. Refraction of Light

1. **Theory of Refraction.**—When light passes obliquely from one transparent medium into another of different density, as from air to water, it is bent from its course, or *refracted*. The rule for this refraction is, when light passes from one medium into a denser medium, it is

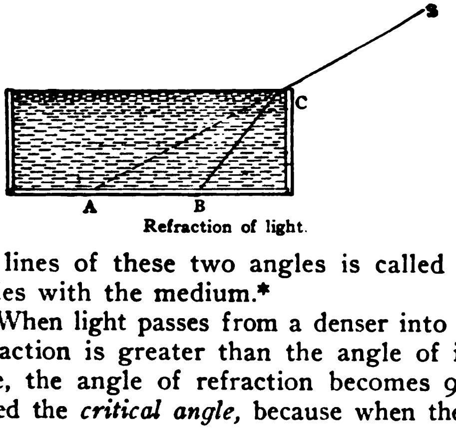
bent *toward* a perpendicular line; when it passes into a rarer medium it is bent *away* from the perpendicular line.

The phenomena of refraction may be illustrated in the experiment shown in Fig. 71. In a vessel, place a coin in such a position (B) that it is just hidden by the edge (at C) from the observer looking obliquely from the side (S), then fill the vessel with water and the coin becomes visible. The reflected ray of vision (B C) on emerging from the water into the air is bent *away* (C S) from the perpendicular, and the eye sees the object in the prolongation of the ray (S C A).

As examples: When a rod is partly immersed obliquely in water, the immersed end appears to be bent towards a line perpendicular to the surface. Owing to the increasing density of the layers of air nearer the earth's surface, the rays of light from the stars and sun (when setting) become bent downward so that these objects appear higher than they really are, being visible even when below the horizon.

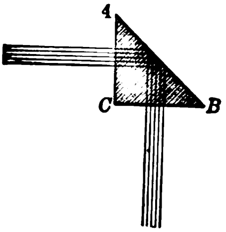
The angle made by the incident ray of light with the perpendicular is called the *angle of incidence;* that made by the refracted ray with the perpendicular is called the *angle of refraction.* The ratio between the lines of these two angles is called the index of refraction, and varies with the medium.*

FIG. 71.



Refraction of light.

FIG. 72.



When light passes from a denser into a rarer medium the angle of refraction is greater than the angle of incidence. When, in such a case, the angle of refraction becomes 90°, the angle of incidence is called the *critical angle,* because when the angle of refraction becomes greater than 90° the refracted ray will not emerge, but will be reflected back again from the surface of the denser medium. This is called *total reflection,* and is more complete than the ordinary reflection of light, where, because of the imperfection of the reflecting surface, some light is always irregularly reflected or diffused. The phenomena of total reflection can be easily shown by means of goblets of water or a glass cube such as is often used for a paper-weight or inkstand. Objects below the goblet or cube are invisible through the side faces, because of this total reflection. Total reflecting prisms (Fig. 72) are frequently used in optical instruments, because they reflect the rays, without loss, in any desired direction.

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* INDEX OF REFRACTION OF—

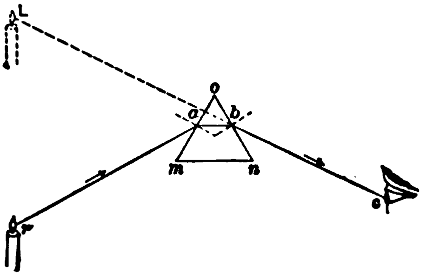
Water	1.33	Crown glass	1.53
Canada balsam	1.36	Diamond	2.49
Carbon disulphide	1.63		

The mirage seen in the desert and at times at sea is an optical illusion, by which inverted images of distant objects are seen as if below the ground or in the atmosphere, and is based upon total reflection, owing to the unequal density of the several layers of the atmosphere through which the rays of light pass.

2. Prisms and Lenses.—A prism is any transparent refracting medium bounded by planes inclined to each other. The angle (*m o n*, Fig. 73) made by the two sides through which the light enters and emerges is called the angle of refraction of the prism. Both flint and crown glass are in use as materials for prisms, but the former possesses the higher refracting power. We may note two effects of prisms upon light passing through them—

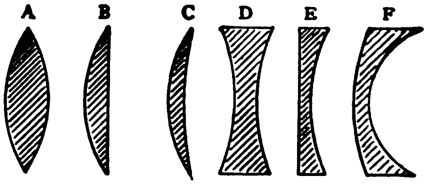
1. Light of any kind is refracted or bent out of its course. A ray of light (*r a*, Fig. 73) falling on the prism, *o m n*, is refracted towards the perpendicular and passes through in the direction *a b;* here, in passing from a denser into a rarer medium, it is refracted from the perpendicular in the direction *b c*. The eye at *c* sees the object *r* backward along the ray *c b*, so that it appears at L.

FIG. 73.



Refraction through prism.

FIG. 74.



Lenses.

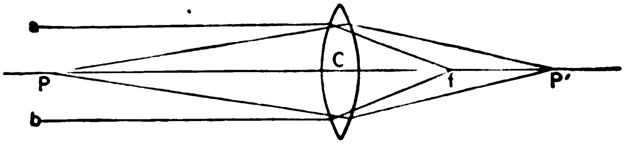
2. White light is dispersed into a band or spectrum of colors. This second effect will be noted on page 100.

Lenses are transparent media, usually of glass, which from the curvature of their surfaces have the power of causing luminous rays either to converge or diverge. The combination of spherical surfaces, either with each other or with plane surfaces, gives rise to six kinds of lenses, which are illustrated in Fig. 74. A is a *double convex*, B a *plano-convex*, C a *concavo-convex* or *converging meniscus*, D a *double concave*, E a *plano-concave*, and F a *convexo-concave* or *diverging meniscus*.

The first three, which are thicker in the center than on the edges, are converging in their effect on rays of light; the others, which are thinner in the center, are diverging.

A line drawn through the center of a lens, as P P′, Fig. 75, is called its *axis;* a double convex lens will bring parallel rays of light *a* and *b* to a point along this axis which is called the *principal focus, f*. The distance from the middle of the lens C to the principal focus *f* is called its *focal length.* This may be ascertained by focussing the rays of sunlight on a piece of paper. Now, if a candle be placed at P, its rays diverge to the lens C, and will be brought to a focus at P′, beyond the principal focus; if the light is placed at P′, the rays focus at P; these two exchangeable foci are called *conjugate foci.* Again, if the source of light be placed at the principal focus of the lens, *f*, the refracted rays *a* and *b* will be *parallel;* if the source of light be inside the principal focus, the refracted rays will *diverge.*

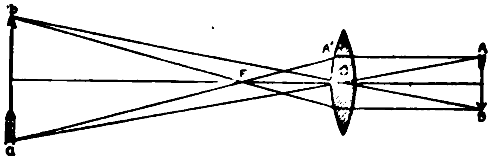
FIG. 75.



Principal and conjugate foci.

Images Produced by Convex and Concave Lenses.—According as the object observed is placed beyond or within the principal focal distance of a convex lens, we observe the following:

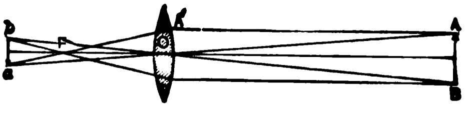
FIG. 76.



Double convex lens image.

1. *A large object at some distance from a convex lens produces a small real inverted image a little beyond the principal focus of the lens.* Thus, in Fig. 76, *a b* represents the object and A B the image. The rays cross one another in passing through the lens; hence the image is inverted. An example of this is the photographic camera. Fig. 77 illustrates the magnification that takes place in the object-glass of a telescope, the object *a b* being at a very great distance beyond the focal distance of the lens.

FIG. 77.



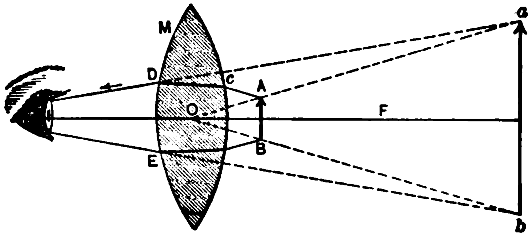
Double convex lens image.

2. *If an object be placed between a convex lens and its principal focus, an enlarged upright virtual image is produced, and is apparently seen*

at a greater distance from the lens than the object. Thus, A B, Fig. 78, represents the object placed within the principal focus, F; the eye observes the image A B, at *a b*, through prolongation of the emergent rays A D and B E to D *a* and E *b*. Such a double convex lens of short focus is called a simple microscope.

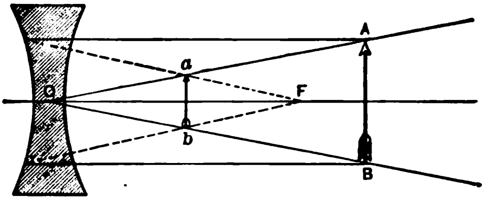
3. *Concave lenses produce virtual erect images smaller than the object.* Thus, A B, Fig. 79, is the object, and the rays coming from A are deviated so as to appear to come from *a*, situated on a line drawn from A to the optical center O; because the rays passing through the lens diverge and the eye following these observes a smaller image at *a b*; likewise, rays from B appear to come from *b*, on the line B O; hence *a b* is the image of the object A B.

FIG. 78.



Simple microscope.

FIG. 79.



Double concave lens image.

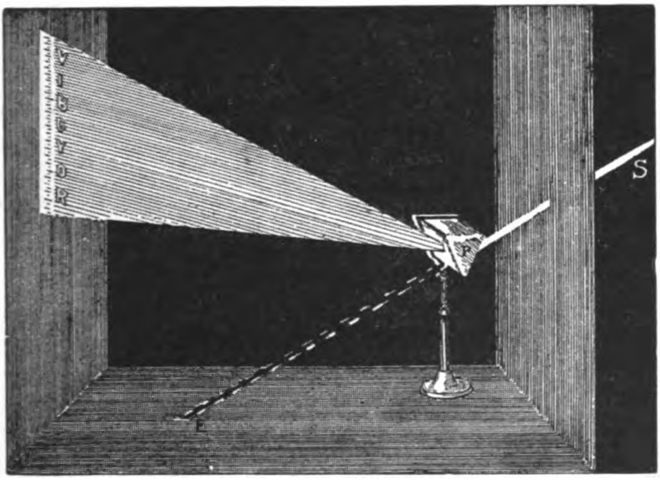
3. **Decomposition of White Light—Spectrum.**—We have already referred to the fact that the effect of a prism upon a beam of light passing through it is twofold—that, in addition to the refraction or bending from its course, white light is decomposed into a series of colored rays. The explanation of this is, that the rays which make up solar and other varieties of white light are not equally refrangible, and hence in passing through a prism they are dispersed and form a band of colors known as a *prismatic spectrum*. The phenomenon is called *dispersion*.

This same spectrum is produced when rays of light are made to pass through narrow interstices, or edges of an opening, or through glass ruled closely with parallel lines. The phenomenon is called *diffraction*, and the spectrum, *diffractive spectrum*.

If a beam of white light, S, be allowed to fall upon a prism, P (Fig. 80), it will undergo dispersion into its component wave-frequencies (of which it is composed), in the order of their respective refrangibilities, the violet being deviated the widest, followed in order by indigo, blue, green, yellow, orange, and red, which is deviated the least. The result is that, instead of a spot of white light appearing on the floor, E, a band of seven colors appears upon the wall or a screen placed at a height above.

While the colors of the solar spectrum merge imperceptibly into one another, so that many tints might be said to exist, the colors cannot be decomposed further, for when the red rays or any of the others are taken singly and passed through a second prism they are uniformly refracted and give a spot of red or other color. These colors are, therefore, homogeneous, and light composed of them is known as *monochromatic* light.

FIG. 80.



Solar spectrum.

If white light consists of a mixture of these variously colored rays (wave-frequencies), then if they be recombined, white light must result. Thus, if the spectrum formed by one prism be allowed to fall upon a second prism of the same material and the same refracting angle as the first, but inverted, the latter reunites the several colors and the emergent pencil is colorless. A concave mirror upon which the spectrum may be cast will also reunite the colors, and a white spot will be formed in the focus of the mirror.

The recomposition of white light from the colors of the spectrum may be shown most strikingly by the aid of Newton's disk. This is a cardboard disk about a foot in diameter, on which are pasted alternate segments of colored paper in the order of the colors of the spectrum. When this is rotated rapidly, the eye receives the impression of white light. This is due to the fact that the sensation is of longer duration than the impression from which it results. If a new impression acts before the sensation arising from the former one has ceased, a sensation results which consists of two impressions. If the time is sufficiently short, several impressions may be mixed with one another. This also explains the phenomenon of the moving lantern pictures, as shown in the cinematograph, bioscope, etc.

Complementary Colors.—While the combination of all the colors of the Newton's disk produces white light, we may by the combination of individual colors get numerous composite shades. Thus, if we remove the red from the set of colors, on combining the remaining colors we get a bluish-green. This is then said to be the complementary color to red, because when united with it white is produced. Similarly, purple is the complementary color to green, and an ultramarine blue to the yellow.

It must not be understood that two pigments showing such colors complementary to each other when mixed yield a white product, but that the two color impressions when superposed give the effect of white light. Thus, if chrome-yellow and ultramarine blue be mixed, the result will be a green pigment, while a yellow and a blue light combine to give us white as the resultant.

The color of bodies depends upon the manner in which they act upon white light. A portion of the rays is absorbed, and that which remains determines the color of the body. If the unabsorbed rays traverse the body, it is colored and transparent; if, on the contrary, they are reflected, the body is colored and opaque. In both cases the kind of light rays (wave-frequencies) that are not absorbed gives the color. If a body absorbs all the colors, it is black; if it reflects or transmits all, it is white or colorless. A body appears blue when it absorbs all the colors except blue.

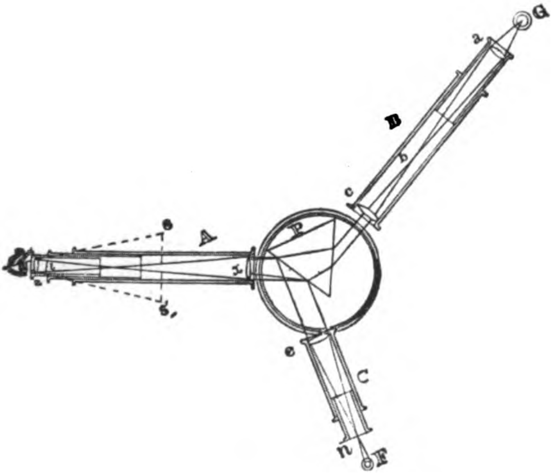
4. **Spectrum Analysis—Spectroscope.**—The examination of the light from different luminous bodies by the aid of a prism has led to important discoveries as to the nature of the light and the luminous bodies. This study has been made possible by the aid of the spectroscope, first proposed by Bunsen and Kirchhoff. A sectional view of this instrument is given in Fig. 81. The rays from the source of light, G, passing through a narrow slit and falling upon the lens *a*, are made to converge at *b*, the principal focus of the lens *c*, so that they are known as parallel rays upon the prism P. After refraction, they fall upon the lens *x*, which forms a real and reversed image of the spectrum at *i*. This is magnified by the eye-piece so that a virtual image is formed at *s s'* much enlarged. The third arm of the instrument, C, is for the purpose of throwing upon the prism, and so into the observing telescope, an image of a micrometer scale which has been photographed upon glass

at *n*. By its means the relative position of lines or bands seen in the spectrum can be determined.

When examined by the aid of such a spectroscope, we find that luminous bodies are capable of yielding three different kinds of spectra.

If the light from a white-hot solid or liquid body be examined, a continuous band of all the colors from red to violet will be observed. Such a spectrum is called a *continuous spectrum*. When the glowing body is in the condition of gas or vapor, we have a series of bright lines or bands against a black background. This is termed a *bright-line spectrum*. When, however, sunlight is examined by the spectroscope, the continuous spectrum appears crossed by hundreds of dark lines. The light from the fixed stars is similar, and such spectra are called *absorption spectra*. The dark lines of the solar spectrum, known as Fraunhofer's lines, were first fully explained by Bunsen and Kirchhoff, who proved that many of them corresponded to the bright lines obtained in the spectra of the vapors of such metals as sodium, calcium, iron, etc.

FIG. 81.



Spectroscope.

They therefore suggested the following explanation of the solar spectrum. The sun is probably an intensely glowing solid or liquid mass (chromosphere). This would give a continuous spectrum without either bright or dark lines. But the glowing mass is surrounded by an atmosphere (photosphere) containing cooler, brilliant metallic vapors. These vapors would absorb light of the same kind as they emit, and hence dark lines show in the spectrum in the same position as those occupied by the ordinary bright lines of these metallic vapors. This theory has been rendered very probable by experiments in which the bright lines of elements like sodium have been reversed and caused to appear as dark lines by passing the light from a very hot sodium flame through a cooler flame of the same vapor. We can also increase the natural absorption by causing the sun's light to pass through more sodium vapor placed in front of the spectroscope slit.

The study of the spectra of various elements, and the accurate mapping of the dark lines of the solar spectrum, show that a large number of the metals known to us on the earth occur as vapors in the sun's atmosphere.

With the aid of this method of spectrum analysis chemists have discovered a number of new and relatively rare metals, such as cæsium, rubidium, thallium, indium, gallium, and scandium. It has also furnished an invaluable means of detecting impurities in chemical preparations which would otherwise escape notice.

Absorption spectra of a somewhat different character are also obtained when solutions of hæmoglobin or coloring matters like chlorophyll, hæmatein, etc., are placed in glass cells and interposed between a source of light and the slit of the spectroscope. Broad absorption bands show, extinguishing at times the whole violet end of the spectrum.

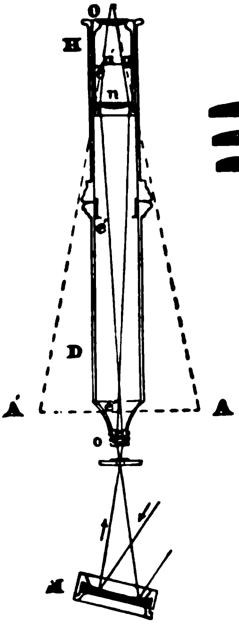
IV. Optical Instruments Based upon the Use of Lenses

1. **The Microscope.**—The simple microscope, as we have seen, is merely a double convex lens of short focus, by means of which we can look at objects placed between the lens and its principal focus. The image produced is an erect and magnified virtual image of the object. In the simple microscope the measure of the linear magnification produced is the ratio of the apparent diameter of the image to that of the object, while the superficial magnification is the square of this ratio. The compound microscope consists essentially of two condensing lenses; one with extremely short focus, called the object-glass or objective, because it comes down immediately over the object; the other acts simply as a means of magnifying the image formed by the first, and is called the eye-piece. The method of combining these lenses and the formation of images by means of them are illustrated in Fig. 82. In this case the objective, *o*, consists of three small condensing lenses, which together act like a single very powerful lens. The object is placed on the stage, and the rays, passing through an additional lens at *n*, inserted here to render the image achromatic, form a real and magnified image at *a a'*. This image is then magnified by the lens o and a much magnified virtual image is formed at A A'. The two lenses *n* and o together constitute in this case the eye-piece, just as the three small lenses, *o*, constitute the objective. The magnifying power of the compound microscope is obtained by multiplying the magnifying power of the objective by that of the eye-piece. Thus, if the magnifying power of the lens *o* is 50 diameters and that of the lens o is 4 diameters, the image seen will be magnified 200 diameters, or the

superficial enlargement will be 40,000 times the natural size of the object. The degree of magnification is often determined experimentally by means of a micrometer eye-piece fitted to the microscope.

Spherical Aberration.—Thus far it has been assumed that all the rays of light in passing through a convex lens meet at the same focal point on the other side. This is correct for lenses whose aperture is not greater than 10°. When larger, it will be found that those rays which pass through the edges of the lens are refracted more than those passing through the center. This results in scattering the rays from the focus, producing an indistinct image. This is called spherical aberration, and can be corrected by placing in front of the lens diaphragms provided with round apertures in the center, called *stops,* which cut off the rays from the edges and allow only the passage of the central ones nearly parallel to the axis. A great sharpness of definition is gained, but brightness of illumination is thereby diminished. Such stops are seen in the caps covering the eye-piece of the microscope; also in the opera-glass and telescope. In the photographic lens the stops are adjustable, owing to the necessity of employing apertures of different sizes.

FIG. 82



Compound telescope.

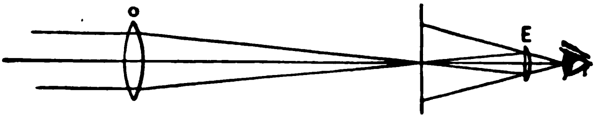
Chromatic Aberration.—Since a lens may be considered as a combination of an infinite number of prisms, it not only refracts light, but also decomposes (disperses) it, like a prism, into different-colored rays of different degrees of refrangibility, which produce a confused coloration of the margins of the images. This scattering of the colored rays to different foci is called chromatic aberration. It may be corrected by employing an *achromatic combination,* in which two lenses of unequal dispersive power are fitted together, one being the double convex (converging) lens of crown glass, while the other is a concave (diverging) lens of flint glass. Such achromatic combinations are seen in L, Fig. 82, which are enlarged representations of the objectives, *o.*

2. **The Telescope** is a combination of two or more lenses to enable one to view distant objects—that is, it increases the angle under which the object is seen. It consists of a large, double convex object-lens, O, Fig. 83, which forms an inverted image of the distant object at its focus. This is in turn enlarged by the plano-convex lens, E, which serves as eye-piece. For astronomical purposes the object-glass is made as large as possible, in order to secure the greatest amount of

light in observing faint, distant objects. The greater the diameter of the objective the longer is its focal length; thus, the Yerkes 40-inch objective has a focal length of about 64 feet. To find the magnifying power, divide the focal length of the object-glass by that of the eye-glass. The *terrestrial* telescope, or spy-glass, differs from the astronomical in having two additional condensing lenses, which restore the inverted image to the erect position. The *Galileo* telescope, now used in the form of the opera-glass, consists of a double convex lens, which collects the rays from an object, and a concave (divergent) eye-piece, which serves to make the convergent rays of the objective parallel, producing an erect, virtual, and magnified image.

3. **The Lantern and Camera.**—The projecting lantern, or stereopticon, is used for throwing magnified images on a screen in a darkened room. It consists of a closed box of metal in which is placed a strong oil lamp provided with a reflector or a lime or arc light. In the front of the box are fixed two plano-convex lenses which converge the light upon the lantern-slide, which is a photograph upon glass. Beyond this a double convex focussing lens is placed so that the slide shall be a little beyond its principal focus. The lens will then produce a real, inverted, and enlarged image upon a screen placed at a suitable distance. To get the image in proper position the lantern-slide is, of course, put in an inverted position. The image on the screen will be the more magnified as the slide approaches the principal focus of the lens, which is, therefore, set so as to be moved to and fro.

FIG. 83.



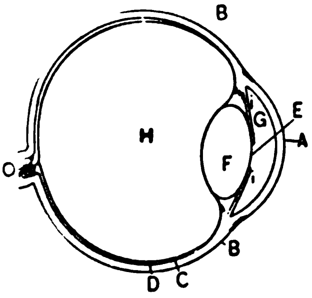
Astronomical telescope.

In the photographic camera we have the reverse of the projecting lantern. It is a dark chamber with a convex lens in front and a screen at the back on which to form an image of objects in front of and outside of the camera. This image is real, inverted, and usually smaller than the object. It is visible to the operator back of the camera, as the screen is made of ground glass, which, when side light is shut out, is semi-transparent. In order to form a sharp image the lens is given a movement to and fro, and the screen at the rear of the camera box is also capable of a forward and backward movement by means of a rack and pinion. When a clearly defined image is obtained, a cap is put in front of the lens, the ground-glass screen is removed, and a plate-holder containing a sensitized glass plate is slipped into its place. This brings the photographic plate exactly in the position of the screen, and the image will be cast upon it. The slide in front of the plate-holder is then drawn out and the cap removed from the lens, when the reflected rays of light quickly act upon the sensitive surface.

4. The Eye as an Optical Instrument.—The human eye is a camera, and the retina the sensitive surface upon which images are constantly formed to be communicated by the optic nerve to the brain.

The outer covering of the eye-ball, the *sclerotic coating* (B, Fig. 84), or white of the eye, is quite firm and constitutes the frame of this camera Inside of this is the *choroid coating,* C, which gives to the interior of the eye the black lining necessary for absorbing all useless or diffused rays. In front we have the transparent *cornea,* A, set in like a watch crystal; the colorless and transparent *aqueous humor,* G, filling the space between the cornea and the *crystalline lens,* F; and back of this the jelly-like *vitreous humor,* H, filling the whole remaining cavity.

FIG. 84.



Cross-section of eye.

In front of the crystalline lens we have the *iris, i, i,* a diaphragm with a circular opening which can be widened or contracted at will by muscular effort, the opening constituting the *pupil* of the eye; and spread out over the rear of the cavity is the *retina,* D, which is the sensitive plate of the camera, and by its connection with the optic nerve conveys its impressions to the brain.

The eye, like the camera, requires to be focused according to the varying distance of the object. This is effected mainly by a change in the curvature of the front of the lens. For instance, by a strong pressure of the ciliary muscles at either edge of the crystalline lens the curvature is increased, thus accommodating the eye for viewing near objects. When this muscular effort is relaxed, the lens again becomes flatter and is in adjustment for more distant objects. The eye is, therefore, rested by fixing it on objects at some distance. If the eye be now considered as an optical instrument, we will see that its crystalline lens, being a double convex lens, must form real and inverted images of objects placed before us. That the images formed on the retina of the eye are inverted, has been shown experimentally with the eyes of albinos, in which, on account of the absence of the choroid coating, the image is visible. The brain restores all these inverted images to the natural position without apparent effort.

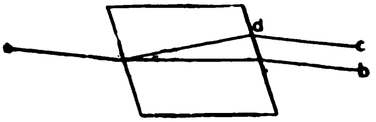
The distance of distinct vision varies greatly in different individuals. For small objects like print the normal distance is from ten to twelve inches.

Persons who see distinctly only at a short distance are called *near-sighted,* and those who see distinctly only at a long distance are called *long-sighted.*. The usual cause of near-sightedness is a too great convexity of the cornea or the crystalline lens, in consequence of which the rays, instead of forming an image on the retina, are focused at a point in front of it. The remedy is found in the use of diverging glasses, which tend to throw the focus farther back and so bring it upon the retina. The cause of long-sightedness is an insufficient convergency of the lens of the eye and consequent formation of images at a point back of the retina. With advancing age especially the crystalline lens tends to become flatter. The remedy is the use of converging glasses, which aid in bringing the rays to a focus exactly upon the retina.

V. Double Refraction and Polarization

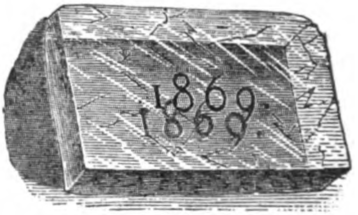
1. Double Refraction.—All crystalline solids not of the regular system possess more or less the property of dividing (bifurcating) an incident ray which passes through them into *two* distinct rays, which undergo unequal refraction and produce two images. This phenomenon, possessed in greatest degree by Iceland spar, is known as double refraction, and is caused by inequalities in the grouping of the molecules of the body which impart different degrees of elasticity in different directions. As a consequence, the transmitted light wave is divided into two parts, which advance with unequal velocities; one (*a d c,* Fig. 85) follows the common law of refraction, and is called the *ordinary ray,* while the other (*a b*) does not, and is called the *extraordinary ray.* This may be illustrated (Fig. 86) by placing a crystal of Iceland spar over a black spot or printed matter, and the images will appear double, the ordinary image seemingly nearer the eye than the other. Now, if the crystal be turned around while still lying on the paper, it will be observed that one image (the ordinary) remains fixed in position and the other (the extraordinary) describes a circle around it.

Fig. 85.



Double refraction.

Fig. 86.



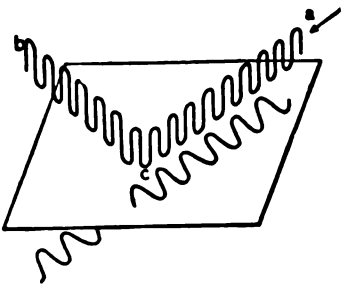
Double refraction

2. Polarization of Light.—According to the undulatory theory of light, the particles of ether through which a ray of light is propagated vibrate in a variety of planes perpendicular to the line of propagation.

When this light is polarized, the vibrations of the ether particles take place in a single plane perpendicular to the line of propagation. The unaided eye cannot distinguish between them, but a variety of means exist by which the difference can be demonstrated.

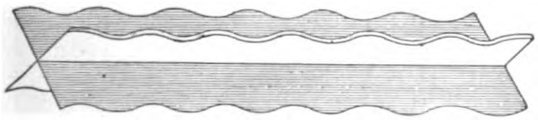
Polarization may be of two kinds, plane or circular, according as the propagating wave is made up of particles vibrating in parallel planes or of those describing circles.

Fig. 87.



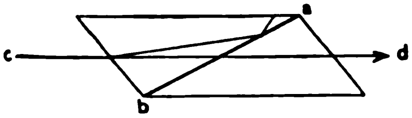
Polarization by reflection.

Fig. 88.



Vibrations of ordinary and extraordinary rays.

Fig. 89.

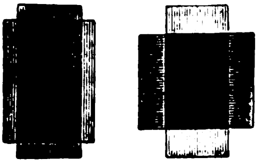


Nicol's prism.

Plane Polarization may be produced by reflection or refraction. (*a*) *By reflection.* When a ray of light falls at an angle on any non-metallic polished surface, such as wood, ivory, unsilvered glass, quartz, etc., it undergoes polarization in the plane of reflection—that is, all the reflected waves (*c b,* Fig. 87) vibrate in the same or parallel planes; hence are polarized. The other waves, vibrating in different planes, pass through or are absorbed. The completeness of polarization depends upon the angle which the incident ray makes with the normal (perpendicular) to the plane surface. For glass this angle is 54° 35′, for water 52° 45′, for diamond 68°. Light is also more or less polarized by reflection from water, from the clouds, and from all objects which aid in diffusing light. (*b*) *By refraction.* It has been shown under double refraction that certain crystals have the power of bifurcating (polarizing) ordinary light into two rays (ordinary and extraordinary), which vibrate in planes at right angles to each other, as shown in Fig. 88. One of these rays (the ordinary), which is more retarded in passing through the crystal, may be entirely suppressed and a single polarized ray transmitted by means of what is known as a Nicol's prism. This consists of a rhombohedron of Iceland spar which has been cut through its short axis *a b* (Fig. 89) and cemented together in the same position with Canada balsam. The light ray enters from *c* and undergoes double refraction, the extraordinary polarized ray passes out at *d,* while the ordinary ray is reflected off at the surface of the balsam near *a*. By means of this Nicol's prism we are able to ascertain whether a source of light is polarized or not; for, on rotating, the light, if polarized, will produce alternately an illuminated or dark field of vision at every turn of 90°. A combination of two of these Nicol's prisms is employed in the polariscope (Fig. 91); one produces the polarized light, and is called the *polarizer;* while the other, which is used for examining this light by rotating, is called the *analyzer.*

Plates cut from the mineral tourmaline also serve for polarizing light. Fig. 90 represents two thin plates, which, if so placed that the axes are parallel, will cause polarization of the beam of light that passes through. Now, if the upper plate (the analyzer) is slowly turned, the polarized light passing through is gradually intercepted and becomes feebler until the axes are perpendicular to each other, when total darkness ensues. These may be used for examining polarized light, like the Nicol's prism.

FIG. 90.



Tourmaline plates.

Circular Polarization.—If a beam of plane polarized light falls upon a plate of quartz which has been cut at right angles to its axis, two equal beams will be produced plane polarized at right angles to each other. Since the extraordinary ray travels over a longer path through the plate than the other, it is one-quarter of a wave in advance. The resulting motion of the two waves will be circular, like that of a turning corkscrew. Circular polarization may be either right-handed (moving in the direction of the hands of the watch)—called dextrogyrate—or left-handed (moving in the opposite direction—called lævogyrate. The various systems of polariscopes in use are all based on circular polarization.

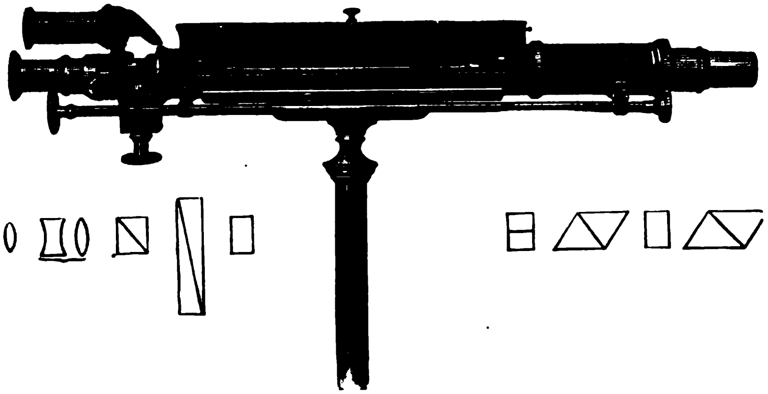
3. **Applications of Polarized Light.**—By the aid of polarized light we are able to distinguish between minerals or salts of different crystallographic systems, and determine to which a given fragment of a crystal may belong. Thin slices of the crystal in question, if examined between two Nicol's prisms or between the tourmaline plates, will show rings of color in case the crystal belongs to any other than the regular system.

Those belonging to the tetragonal or hexagonal systems show circular rings on which appears a cross, which is black or white according to the position of the analyzing prism. Such crystals are called *uniaxial.* Those belonging to the orthorhombic, monoclinic, or triclinic systems show elliptical rings on which appear black or white bands or curves. Such crystals are called *biaxial.*

Beautiful colors are produced by the action of polarized light, even when the object is not definitely crystallized. Microscopes are frequently provided with a set of two Nicol's prisms, one under the stage and the other in the eye-piece, in order that the delicate structure of objects can be studied under polarized light.

Many organic substances, as sugars, essential oils, alkaloids, albumin, etc., show a characteristic action upon the ray of polarized light, rotating it circularly to the right (dextro-rotatory) or left (lævo-rotatory). Such substances are said to be *optically active.* The polariscope (Fig. 91) is an instrument based on this principle, and by its aid the strength or purity of these various substances may accurately be determined. The solution of the substance to be examined, contained in a tube with glass ends, is placed in the instrument between the polarizer (the prism to the right below the figure) and the analyzer (the prism to the left). To the left of the analyzer are the lenses belonging to the eye-piece; to its right are the long quartz wedges of opposite rotatory power. For a description of the various kinds of instruments and methods of operation the reader is referred to special works on this subject.

FIG. 91.



Polariscope.

PART II

CHEMISTRY OF THE NON-METALS

CHAPTER I

THEORETICAL INTRODUCTION

Matter is that which occupies space and is apprehended by the aid of our senses. Close observation teaches us that matter is constantly subject to changes, and these may be of two distinctive characters—namely, *physical* and *chemical.*

Physical Changes.—These are changes of state or condition without alteration of the identity of matter: for example, when water is heated it is converted into vapor or steam; this, on cooling, condenses to water. If we cool water sufficiently it crystallizes—that is, it is converted into ice. Such changes affect only the outward or physical appearances of the water.

Again, on bringing a piece of iron in contact with lodestone it acquires the property of attracting and holding to itself other pieces of iron—that is, it becomes magnetic. This same iron may be heated until it gives off light and heat, yet these changes which the iron has undergone are all of a purely physical character; it has not lost its identity as metallic iron.

Chemical Changes.—In changes of this character which involve the composition of the molecule the substance loses its individual properties, and a new body is formed in its place which possesses entirely new properties. The substance has lost its identity. For example, if we allow the electric current to act upon water it rapidly loses its identity as water in being resolved into two different invisible gases—namely, hydrogen and oxygen. These products no longer possess any characteristics in common with water.

Again, on exposing iron to moist air it soon begins to rust, and if this is allowed to continue sufficiently long, the iron completely disappears, leaving in its stead a deposit of reddish-brown powder, which is infusible and no longer attracted by the magnet. If iron be brought in contact with a liquid known as hydrochloric (muriatic) acid, it rapidly disappears, having been dissolved by this acid, with the production of a new compound. In these two changes just cited we observe that the iron has lost its identity as such—that is, it no longer possesses the characteristics of iron as a metal: it has undergone chemical changes.

Conservation of Mass or Indestructibility of Matter.—Matter cannot be destroyed nor created anew: whenever apparently destroyed it continues to exist in another form. Transformations (physical and chemical) are constantly taking place in nature, but do not involve any increase or decrease in the total amount of matter. This law of the conservation of mass is, *whenever a chemical change takes place, the total mass of the substances after the change is equal to the total mass of the substances entering into the reaction.* In the case of the rusting of iron, the combined masses of the iron and oxygen taking part in the change are exactly equal to the mass of ferric oxide, or the gaseous products (hydrogen and oxygen) of the electrolysis of a known weight of water will weigh exactly the same as the water taken.

Mechanical Mixtures and Chemical Compounds.—If we mix iron filings and sulphur, a gray-colored powder is obtained. This represents a mechanical mixture, so called because the two ingredients can be separated by mechanical means. By the use of a magnet the iron filings may be removed from the sulphur, or the latter may be taken up by means of a solvent, leaving the filings behind.

If this mechanical mixture be heated by direct application of a flame, the entire mass will soon begin to glow, and after cooling a black fused mass remains which no longer resembles either iron or sulphur. Examination with a lens will no longer reveal any particles of either iron or sulphur, nor will the magnet or treatment with a solvent remove either one of the ingredients. These have lost their identity with the formation of a chemical compound known as iron sulphide. Gunpowder is a mechanical mixture of sulphur, saltpetre, and charcoal. By means of the solvent carbon disulphide the sulphur may be removed, while subsequent washing with water eliminates the saltpetre, leaving the charcoal behind. If this mixture be ignited, a flash with explosion results, which is due to the sudden chemical combination which takes place among the ingredients of the mixture.

From this we learn that when substances undergo chemical changes they lose their individual characteristics, which have merged into the new compounds formed. Accompanying these chemical changes there is almost invariably an evolution of heat, sometimes heat with light; also physical changes take place, such as liquid to solid or gaseous state, or *vice versa.*

In the combination of the iron with the sulphur, or the explosion of the gunpowder, we effect chemical changes which result in the production of new substances of essentially different properties. Such changes are the result of a form of energy called chemical affinity. *Chemical affinity is the attraction or force which binds atoms together to form molecules and causes interchanges among these, resulting in the formation of new substances of different properties.* All elements and compounds possess this affinity in a greater or lesser degree, manifesting it differently under different conditions, some combining with great energy, as in the explosion of gunpowder, while others require the aid of physical forces to bring about combination. Still others do not unite at all. The intensity of affinity varies under different conditions in the same element. The various conditions necessary for bringing about chemical union—a result of this attractive force—will be taken up on page 133.

Kinds of Chemical Changes.—The various chemical changes thus far cited are more properly known as *reactions.* These may be divided into two classes—namely, synthetic and analytic.

Synthetic reactions are those in which various elements or compounds unite, with the production of new substances of different properties. As, for example, the combination of sulphur and iron to iron sulphide, or when an electric spark is passed through a mixture of hydrogen and oxygen gases they unite to form water.

Analytic reactions are those which resolve a chemical compound into its various constituents: the reverse of synthetic reactions. For example, by the action of the electric current upon water it is resolved (decomposed) into the invisible gases oxygen and hydrogen. If red precipitate (a compound of mercury and oxygen) be heated, the latter (a gas) is liberated, leaving the mercury behind. These analytic reactions may all be verified by synthetic reactions, whereby the products of the former are again caused to unite.

Chemistry is the science which treats of the composition of matter, together with the study of the phenomena under which changes through the influence of chemical energy take place.

Nature of Matter.—Chemists consider that matter (solid, liquid, or gaseous) is made up of exceedingly minute particles called molecules (*molecula* = a minute mass), which represent the smallest masses that can exist in the free state; they also possess the distinctive properties of the masses from which they are obtained. *A molecule is the smallest particle of matter into which substances can be divided without losing their identity.* When we arrive at our physical limit of subdivision we still find that each molecule is capable of *chemical* subdivision—that is, each ultimate particle is made up of elementary substances called atoms (ἄτομος = indivisible), these being the indivisible constituents of molecules.

An atom is the smallest unit quantity of simple matter which can enter into the composition of a molecule. Excepting in a few instances, atoms are incapable of existing in the free state; hence when liberated by chemical action they unite at once to form molecules. Most elemental molecules consist of two atoms; as exceptions, ozone (a form of oxygen) contains three, while phosphorus, arsenic, and antimony each contain four. The inert gases, as helium, argon, neon, etc., are mono-atomic; that is, their atomic and molecular weights are alike. In various compounds the number of atoms to the molecule may extend to several hundred.

As shown through the investigations of the radio-active elements, such as radium, thorium, and uranium, which undergo spontaneous decomposition, the atom possesses a complex structure. This consists of a positively charged nucleus of exceedingly minute dimensions, surrounded by concentric rings of negative electrons, which are in rapid orbital motion about the nucleus; the entire mass is about $^1/_{2000}$ that of an atom of hydrogen (see page 480).

Elements.—If all the various compounds known to chemists be subjected to analysis, they can be finally resolved into simple substances, called *elements*, of which about 80 have been discovered.

An element is a substance which cannot by any means known to chemists be resolved into anything else essentially different from itself. Thus, chemists have been unable to resolve oxygen gas into anything simpler, nor can sulphur be made to yield any other kind of elementary matter; hence these are termed elements. For table of elements see inside back cover. For sake of convenience these elements are divided into two classes. *metals* and *non-metals*. To the latter class belong the gaseous elements, also bromine, iodine, sulphur, selenium, tellurium, phosphorus, arsenic, carbon, silicon, and boron. These differ greatly in their physical properties.

Names of the Elements.—The names of the elements are usually derived from some distinguishing feature or peculiarity. Thus, *chlorine* (from χλωρός = *yellowish green*) refers to the characteristic color of the gas; *hydrogen* (compounded from ὕδωρ = *water*, and γεννάω = *I produce*) derives its title from the fact that it is a necessary constituent in the production of water; the title *argon* (from αργος = *without energy*) refers to its chemical inertness; such elements as *gallium*, *germanium*, and *scandium* have derived their titles from the old Latin names referring to the nationality of the discoverer. The names of the more recently discovered elements end in *ium* or *on*.

Symbols of the Elements.—In expressing the composition of different chemical substances which are made up of various elements, it is necessary, as a matter of convenience and simplicity, that an abbreviated form of chemical language be employed. This has been provided for through a system of symbols, in which the initial letter of the title of the element is generally selected.* In some cases several elements possess the same initial letter; it is then the custom to assign the single letter to the most important, abundant, or earliest-discovered member of the group, and to the others a second letter. Thus, ten names of elements begin with C. This symbol was selected for Carbon, as the most important; then Ca for Calcium, Cd for Cadmium, Ce for Cerium, Cl for Chlorine, Co for Cobalt, and so on. In a few instances the symbols are selected from the old Latin titles of the elements. Thus, Fe is taken from Ferrum (iron), Pb from Plumbum (lead); K from Kalium (potassium), Au from Aurum (gold), and so on.

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* See Table of Elements, inside back cover.

Atomic Weight, or Mass.—The above symbols possess a quantitative signification. Each one represents one atom of the element in question, this being the smallest quantity of an element which is present in the molecule of its compounds. Thus, Na does not represent any indefinite quantity of sodium, nor Cl any amount of chlorine. These symbols, like those of all the other elements, invariably refer to definite and fixed quantities, as in the above instance to 23 parts of sodium and 35.46 parts of chlorine, so that NaCl, representing a molecule of sodium chloride, always denotes 58.46 parts, the sum of one atom of sodium and one atom of chlorine.

The absolute weight of either atoms or molecules cannot be determined directly; hence they are determined *relatively* by comparison with some standard element. The earliest standard selected was hydrogen. This was chosen because it was the lightest known element and had the smallest combining value. Starting with H = 1.000 as unit, it would follow that if we determined the weights of the various elements which united with one unit of this standard, these figures would represent the *relative* weights of their atoms. Since oxygen has been arbitrarily fixed as standard with a value of 16 compared to H = 1.008, this same ratio prevails. If an element does not combine directly with hydrogen, then its relative weight would be determined by comparison with another element the ratio of which to hydrogen was known. Thus we find that 35.46 p. of chlorine, 79.92 p. of bromine, and 19 p. of fluorine to be the smallest quantity by weight of these elements entering any of their compounds and combining with 1.008 gm. of hydrogen (O = 16); hence we may say that the atomic weights of these three elements are 35.46, 79.92, and 19 respectively. Since the molecule of hydrogen consists of two atoms, then the molecule of chlorine would weigh (35.46 × 2) 70.92 times and the molecule of sodium chloride (23 + 35.46) 58.46 times heavier than the atom of hydrogen. Therefore, the atomic weight of an element is the *relative weight of its atoms as compared with those of oxygen or hydrogen as unity. The molecular weight of an element or compound represents the sum of the weights of the atoms which make up its molecule.*

Oxygen, with the arbitrary standard atomic weight of 16.000, has within recent years been adopted as the unit in place of hydrogen as 1.000. The chief reasons for such a change are (1) that while but very few elements unite directly with hydrogen to form stable compounds which can be analyzed, oxygen combines with nearly all, the composition of which can be readily and accurately determined. Hence we were under the necessity of first determining the relation of most elements to oxygen, and, through this, to hydrogen. With every change in the ratio of oxygen to hydrogen (15.88 to 1), necessitated by new determinations, all the atomic weights referred to hydrogen (through oxygen) must also be changed. But if the number 16 be retained as arbitrary standard for oxygen, and 1.008 for hydrogen, no such recalculations of other numbers will be necessary, since only the value of hydrogen would be affected. (2) The error in the determinations is less with the larger (O = 16) than with the smaller standard (H = 1). The atomic weight figures under O = 16 usually approximate whole numbers, which are more convenient in calculating than the fractional numbers encountered under H = 1.

Chemical Formulæ.—The various chemical compounds are produced by the combination of two or more elements, and are graphically represented by placing the symbols of the constituent elements together. Such an aggregation of symbols (which also represent their respective atomic weights) is designated as a chemical formula. For example, HCl represents a compound made up of one atom of hydrogen (1.008 parts) and one atom of chlorine (35.46 parts); the formula H_2O represents a compound whose molecule is made up of two atoms of hydrogen (2×1.008 parts $= 2.016$ parts) and one of oxygen (16 parts): the small figure placed to the right below the symbol of the element hydrogen indicates the number of atoms of that element which enter into the compounds.* In unabbreviated style the above formula would be HHO; for nitric acid it would be HNOOO, while it is written HNO_3. The advantage of such abbreviations is at once apparent.

The formula $2H_2SO_4$ or $2(H_2SO_4)$ represents two molecules of a compound (sulphuric acid) made up of two atoms of hydrogen (2×1.008 parts $= 2.016$ parts), one of sulphur (32.07 parts), and four of oxygen (4×16 parts $= 64$ parts). The large numeral (2) placed before the formula is called the *coefficient,* and represents the number of molecules of the substance represented. The molecular weight of this would be $2\ (2.016 + 32.07 + 64)$ or $2 \times 98.086 = 196.172$. Sometimes this number will apply to only a portion of the symbols. In such a case the latter are enclosed in parenthesis. Thus, $Fe_2(SO_4)_3$ represents a compound of two atoms of iron and three groups of SO_4; its molecular weight would be calculated thus:

$$\begin{array}{lllcl}
Fe_2 & = & 55.84 \text{ parts} \times 2 & = & 111.68 \text{ parts.} \\
SO_4 & = & \left\{\begin{array}{l} S \ = 32.07 \text{ parts,} \\ O_4 = \underline{64.00 \text{ ``}} \quad (16 \times 4) \end{array}\right. & & \\
(SO_4)_3 & = & \quad 96.07 \text{ parts} \times 3 & = & \underline{288.21 \text{ ``}} \\
Fe_2(SO_4)_3 & = & & & 399.89 \text{ parts.}
\end{array}$$

Chemical Equations.—By means of these chemical formulæ we are able to express the various chemical changes which take place between two or more molecules. Such changes are termed *reactions.* The several substances taking part in these changes are called *reagents.* In expressing these reactions we employ chemical formulæ in which the substances entering into the reaction connected by plus (+) signs are placed to the left of the equality sign (=), and the products of the reaction connected by plus signs to the right. Such combinations of formulæ and algebraic signs are called *chemical equations.* Thus, in accordance with the above the reaction between two molecules, AB and XZ, would be expressed $AB + XZ = AZ + BX$. Should a minus sign be necessary, it would be $ABC - B = AC + B$. The plus sign replaces "and," indicating that the bodies are brought together in reaction; the equality sign means "produces," or "yields."

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* The term *subscript* is sometimes employed for this figure.

Since each symbol entering into a chemical equation represents a definite weight of matter, and the products of the reaction represent an interchange among these symbols, it follows that after the change the quantity of matter must remain the same as before. The sum of the molecular weights of substances on the right of the equality sign must always equal the sum of the molecular weights of those on the left. Thus,

$$\underset{\text{Silver Nitrate.}}{AgNO_3} + \underset{\text{Sodium Chloride.}}{NaCl} = \underset{\text{Silver Chloride.}}{AgCl} + \underset{\text{Sodium Nitrate.}}{NaNO_3}.$$

$$\underbrace{169.89 \qquad 58.46}_{228.35} \qquad \underbrace{143.34 \qquad 85.01}_{228.35}$$

This, like all equations, conforms to the rule that when two or more chemical compounds are brought together under proper conditions an interchange of elements takes place, with the formation of new combinations. In the above example the atom of chlorine of the sodium chloride, owing to its greater affinity, attaches itself to the atom of silver, thereby displacing the molecular group* NO_3, which at once attaches itself to the atom of sodium, forming sodium nitrate. The sum of the molecular weights of the products on the right of the equation (228.35) is the same as that on the left (228.35). Not only must the two sides of the equation balance each other quantitatively, but also qualitatively—that is, all of the elements which enter into the reaction as factors on the left must be accounted for on the right.

Valency of the Elements.—*Valency is the combining, saturating, or replacing power of an element expressed in hydrogen (univalent) units.* The inert gases show no valency, since they do not form compounds.

Upon comparing the various compounds of hydrogen with several of the elements, such as chlorine, oxygen, nitrogen, sulphur, etc., differences will be observed as regards the number of atoms of hydrogen (whose standard valency is I) which combine with these. Thus,

I	II	III	IV
HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si
HF	H_2Se	H_3As	
HI	H_2Te	H_3Sb	

From this we see that, while chlorine combines with *one* atom of hydrogen, oxygen requires *two,* nitrogen *three,* and carbon *four.* Elements which combine with or replace hydrogen atom for atom are known as *monads;* those of which one atom will combine with or replace two atoms of hydrogen are called *dyads.* Similarly, we have the groups *triads, tetrads, pentads, hexads,* etc. As adjective terms we employ univalent, bivalent, trivalent, quadrivalent, quinquivalent, sexivalent, etc.

Thus, chlorine and bromine, which combine with hydrogen atom for atom, are known as monads, while oxygen and sulphur require

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* For explanation of this term, see Radicles, p. 123.

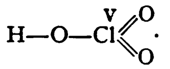
two atoms of hydrogen for saturation and are therefore dyads. Sodium, on the other hand, does not combine directly with hydrogen, but, in reacting with hydrogen chloride (hydrochloric acid), *replaces* hydrogen atom for atom; and so its valence as a monad is established, $Na + HCl = NaCl + H$. Similarly the atom of zinc in the reaction with hydrogen chloride displaces two atoms; hence is a dyad, $Zn + 2HCl = ZnCl_2 + H_2$.

Variations in Valency.—The same element may exhibit a different valence in different compounds. Thus, chlorine, which in combining with hydrogen is a monad, forms a series of compounds with oxygen and hydrogen in which its valence is one, three, five, and seven. Thus,

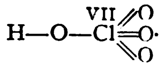
Hypochlorous Acid, $H—O—\overset{I}{Cl}$.

Chlorous Acid, $H—O—\overset{III}{Cl}=O$.

Chloric Acid,



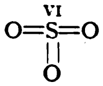
Perchloric Acid,



Sulphur, which combines as a dyad to form hydrogen sulphide, unites with oxygen with the valence of two, four, and six. Thus,

$H—\overset{II}{S}—H$, Hydrogen Sulphide

$O=\overset{IV}{S}=O$, Sulphur Dioxide.



$O=\overset{VI}{S}=O$ with $=O$ below S; Sulphur Trioxide.

This variation in valence increases by increments of two, although there are exceptions to this general rule. Thus, it would be 1, 3, 5, or 7, as in chlorine, bromine, and iodine, or from 3 to 5, as in nitrogen and phosphorus. Among the elements of even valencies they usually vary as 2, 4, or 6, as, for example, in sulphur or selenium.

It should be noted, however, that *the valency of all the elements towards hydrogen is constant and unchangeable, and is known as hydrogen valence.* Thus, when combined with hydrogen, chlorine, bromine, or iodine is always a monad, or when these are combined with metals, as, for example, copper chloride, $\overset{II}{Cu}Cl_2$, or bismuth chloride, $\overset{III}{Bi}Cl_3$. But when various elements are caused to combine with the dyad oxygen or such other elements as chlorine or bromine, variations develop; this is termed *oxygen* or *halogen valence.* Thus, chlorine, bromine, and iodine are always monads, oxygen and sulphur dyads, nitrogen and phosphorus triads, when they are combined with hydrogen. Quite different is the case when some of these and other elements combine with oxygen or the halogens (Cl, Br, I, F) as cited above, in the acids of chlorine or compounds of sulphur, or, as further examples:

$$\overset{\text{III}}{S_2O_3} \quad \overset{\text{IV}}{SO_2} \quad \overset{\text{VI}}{SO_3} \quad \overset{\text{VII}}{S_2O_7}$$

$$\overset{\text{I}}{ICl} \quad \overset{\text{III}}{ICl_3} \quad \overset{\text{V}}{IF_5}$$

$$\overset{\text{II}}{OsO} \quad \overset{\text{IV}}{OsO_2} \quad \overset{\text{VIII}}{OsO_4}$$

From this we learn that the *oxygen (or halogen)* valence of the *elements varies.*

In general, valency depends upon the properties of the reacting elements and the conditions under which they unite.

For instance, valency is largely influenced by temperature; at lower temperatures higher valenced compounds are possible, while at high temperatures these dissociate into compounds of lower valence. Thus, sulphur is a hexad towards oxygen (SO_3) much below 700°, while above this it is a tetrad (SO_2).

When all the bonds of one element have been satisfied or replaced by a like number of another, the resulting compound is said to be *saturated*—*e. g.,* H_2O, PCl_5. But where one of the elements of a compound appears with a valency less than its maximum valence the compound is said to be *unsaturated* (see Radicles, page 123).

Equivalence.—Like valence may be termed equivalence; it also expresses the number of parts by weight of an element which combines with or replaces 8 parts by weight of oxygen or 1.008 parts by weight of hydrogen. The atomic weights are the equivalent weights of the elements or multiples thereof. For example, one atom (35.46 p.) of chlorine combines with one atom (1.008 p.) of hydrogen, hence 35.46 is the equivalent (also atomic) weight of chlorine. One atom of sodium (23 p.) combines with one atom of chlorine (35.46 p.), and since one atom of this gas is equivalent to one of hydrogen, then one atom of sodium (23 p.) must be equivalent to one of hydrogen (1.008 p.). If two atoms of hydrogen are equivalent to (or combine with) one atom of oxygen, then one atom of hydrogen will be equivalent to 8 parts of oxygen. If one atom of nitrogen (14.01 p.) is equivalent to three atoms of hydrogen (3.024 p.), then one atom (1.008 p.) of the latter will be equivalent to $(\frac{14.01}{3.024})$ 4.63 parts of nitrogen. If 2 atoms of silver (2 × 107.88 p.) combine with one atom of oxygen (16 p.), then one atom of *silver* (107.88 p.) is equivalent to 8 p. of *oxygen.*

In various chemical reactions elements or groups of elements may replace one another in the molecules of the reacting compounds. Thus one atom of chlorine (35.46 p.) replaces one atom of iodine (126.92 p.) in hydriodic acid ($Cl + HI = HCl + I$), also one atom of bromine (79.92 p.) in hydrobromic acid ($Cl + HBr = HCl + Br$). The number of atoms of the various elements involved in a reaction depends upon their valency, thus one atom of a bivalent or a trivalent element replaces two or three atoms of a monovalent respectively.

$$\overset{\text{II II}}{ZnO} + 2\overset{\text{I I}}{HCl} = \overset{\text{II I}}{ZnCl_2} + \overset{\text{I II}}{H_2O}.$$

$$\overset{\text{III II}}{Bi_2O_3} + 6\overset{\text{I I}}{HCl} = 2\overset{\text{III I}}{BiCl_3} + 3\overset{\text{I II}}{H_2O}.$$

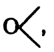
The sum of the valencies replacing one another must always be equal.

Graphic Symbols for Valence.—When it is desired to indicate the valence of an element, a Roman numeral or strokes are placed to the right above the symbol. Thus, $\overset{II}{O}$, $\overset{III}{N}$, $\overset{V}{P}$, or O'', N''', or Cl'. These valence marks are not used ordinarily in writing formulæ or expressing reactions between chemical substances, but only in so-called graphic formulæ. In such instances it is customary to employ lines, called *bonds,* to indicate the linking of atoms to one another. These valence bonds should never be considered as really existing, but merely placed there from purely theoretical considerations.

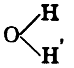
Thus, $O=$ or $-O-$ or $O<$, $N\equiv$ or $-\overset{|}{N}-$, $=C=$ or $>C<$ or $-\overset{|}{\underset{|}{C}}-$.

Examples:

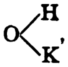
Bivalent Element.



Oxygen Atom.



Hydrogen Oxide or Water Molecule.



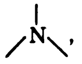
Potassium Hydroxide.

O=O

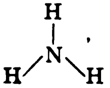
Oxygen Molecule.

Ozone.

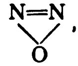
Trivalent Element



Nitrogen Atom.



Nitrogen Hydride or Ammonia.



Nitrogen Monoxide.

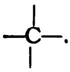
$N\equiv B$,

Nitrogen Boride.

$N\equiv N$

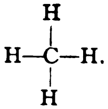
Nitrogen Molecule.

Tetravalent Element.



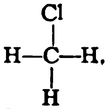
$$-\overset{|}{\underset{|}{C}}-.$$

Carbon Atom.



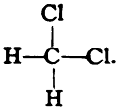
$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H.$$

Methane.



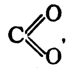
$$H-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-H,$$

Monochlor-methane.

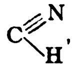


$$H-\overset{\displaystyle Cl}{\underset{\displaystyle H}{C}}-Cl.$$

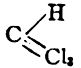
Dichlor-methane.



Carbon dioxide.



Hydrocyanic Acid.



Trichlor-methane.

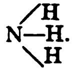
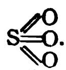
$C\equiv Cl_4$,

Tetrachlor-methane.

$H-C\equiv C-H$.

Acetylene.

The position of the valence strokes is usually a matter of convenience. They are, however, of great value in illustrating the arrangement and relationship which various atoms bear to one another in the formation of chemical compounds. Such formulæ are usually known as *graphic, structural,* or *rational.*

Empirical or Condensed Formulæ.*	Structural or Graphic Formulæ.
Ammonia, NH_3.	
Bismuth Oxide, Bi_2O_3.	Bi=O >O. Bi=O
Sulphur Trioxide, SO_3.	

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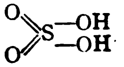
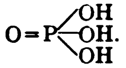
* The empirical or condensed formula simply expresses the kind and relative number of atoms in the molecule.

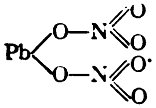
Sulphuric Acid, H_2SO_4.

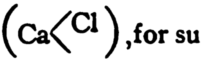
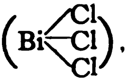
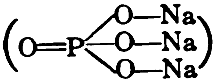
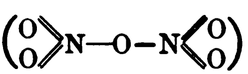


Phosphoric Acid, H_3PO_4.



Lead Nitrate, $Pb(NO_3)_2$.



Radicles.—From the preceding we have learned that the various elements combine in accordance with their affinities and valencies, giving rise to saturated molecules (chemical compounds). Thus, calcium chloride is written $\overset{II}{Ca}\overset{I}{Cl}_2$; it cannot be CaCl (),for such a compound of chlorine and calcium with a free or unsaturated affinity does not exist. For like reasons potassium oxide must be $\overset{I}{K}_2\overset{II}{O}$ (), bismuth chloride $\overset{III}{Bi}\overset{I}{Cl}_3$ (), sodium phosphate $Na_3\overset{V}{P}\overset{II}{O}_4$ (), nitric anhydride $\overset{V}{N}_2\overset{II}{O}_5$ ()

For theoretical reasons we find it convenient to distinguish certain *unsaturated groups of atoms* (with free bonds) *which deport themselves like atoms;* these are called *radicles, residues,* or *rests.* Such radicles result through the removal of an atom from the saturated molecules, their so-called valency being equal to the number of unsaturated bonds. Thus,

II	II	III
$H—O—H$, Hydrogen Oxide.	$H—S—H$, Hydrogen Sulphide.	$H—N{=}H_2$, Ammonia.
$—(OH)$, Hydroxyl.	$—(SH)$, Sulphydryl.	$—(NH_2)$, Amidogen.
IV	IV	V
$H—C{\equiv}H_3$, Methane.	$H—C{\equiv}N$, Hydrogen Cyanide.	$H—NO_2$, Hydrogen Nitrate.
$—(CH_3)$, Methyl.	$—(CN)$, Cyanogen.	$—(NO_2)$, Nitro-Radical.
IV		
$O{=}C{=}O$, Carbon Dioxide.	$(OH)_3{\equiv}P{=}O$, Hydrogen Phosphate.	$O_2{=}S{<}^{OH}_{OH}$, Hydrogen Sulphate
$=(CO)$, Carbonyl.	$\equiv(P{=}O)$, Phosphoryl.	$=(SO_2)$, Sulphuryl.

With but few exceptions, the names of these compound radicles terminate in *yl.* Those of an uneven number of free (unsaturated) bonds do not exist in a free state, but, like atoms, when liberated immediately unite with other atoms to form molecules. Thus, $\overset{I}{(OH)} + H = HOH$ or H_2O; $\overset{I}{(OH)} + \overset{I}{(OH)} = H_2O_2$, hydrogen dioxide; $H + \overset{I}{(CH_3)} = CH_4$, methane; $\overset{I}{(NH_2)} + \overset{I}{(CH_3)} = NH_2CH_3$, methylamine, etc.

An acid radicle or residue remains after abstracting the hydroxyl (OH) from an oxygen acid; *e. g.*, $H_2SO_4 - (OH)_2 = SO_2$, *sulphuryl;* $H_2CO_3 - (OH)_2 = CO$, *carbonyl.* Saturated compounds of these are sulphuryl chloride (SO_2Cl_2) and carbonyl chloride ($CO.Cl_2$).

Such residues as have an even number of bonds, as sulphuryl = (SO_2) and carbonyl = (CO), may exist in a free state, since there is a mutual saturation between the two free bonds. Thus, $<(SO_2)$, $<(CO)$.

In common practice the groups SO_3 and SO_2 are generally referred to as the sulphuric and sulphurous (acid) radicles, although they are acid anhydrides.

In the various reactions of analytic and synthetic chemistry these radicles play an important part; the readiness with which they interchange with atoms may be seen in the following equation:

$$\underset{\text{Silver Nitrate.}}{\overset{\text{I}}{\mathrm{Ag}}\overset{\text{I}}{\mathrm{NO_3}}} + \underset{\text{Sodium Chloride.}}{\overset{\text{I}}{\mathrm{Na}}\overset{\text{I}}{\mathrm{Cl}}} = \underset{\text{Silver Chloride}}{\mathrm{AgCl}} + \underset{\text{Sodium Nitrate.}}{\mathrm{NaNO_3}}.$$

$$\underset{\text{Methyl Iodide.}}{\overset{\text{I}}{\mathrm{CH_3}}\overset{\text{I}}{\mathrm{I}}} + \underset{\text{Silver Hydroxide.}}{\overset{\text{I}}{\mathrm{Ag}}\overset{\text{I}}{\mathrm{OH}}} = \underset{\text{Methyl Hydroxide.}}{\mathrm{CH_3OH}} + \underset{\text{Silver Iodide.}}{\mathrm{AgI}}.$$

$$\underset{\text{Sodium Sulphate.}}{\overset{\text{I}}{\mathrm{Na_2}}\overset{\text{II}}{\mathrm{SO_4}}} + \underset{\text{Barium Nitrate.}}{\overset{\text{II}}{\mathrm{Ba}}\overset{\text{I}}{\mathrm{(NO_3)_2}}} = \underset{\text{Sodium Nitrate.}}{\mathrm{2NaNO_3}} + \underset{\text{Barium Sulphate.}}{\mathrm{BaSO_4}}.$$

$$\underset{\text{Sodium Phosphate.}}{\overset{\text{I}}{\mathrm{2Na_3}}\overset{\text{III}}{\mathrm{PO_4}}} + \underset{\text{Magnesium Sulphate.}}{\overset{\text{II}}{\mathrm{3Mg}}\overset{\text{II}}{\mathrm{SO_4}}} = \underset{\text{Sodium Sulphate.}}{\mathrm{3Na_2SO_4}} + \underset{\text{Magnesium Phosphate.}}{\overset{\text{II}}{\mathrm{Mg_3}}\overset{\text{III}}{\mathrm{(PO_4)_2}}}.$$

Compound Molecules.—Simple molecules (as H_2, P_4) consist of like atoms, while compound molecules are made up of unlike atoms. These may be divided into two classes, namely, *binary* and *ternary.*

Binary Compounds.—These consist of only two kinds of atoms,* as NaCl, FeS, NH_4Cl. In writing their formulæ the electro-positive element is placed first, followed by the electro-negative. Thus, we write NaCl and not ClNa. In naming the compound the same order is observed: the name of the positive atom or radicle is followed by that of the negative, which terminates in *ide.* Thus—

$\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{Cl}}$ = Sodium Chloride.

$\overset{+}{\mathrm{Ca}}\overset{-}{\mathrm{O}}$ = Calcium Oxide.

$\overset{+}{\mathrm{Na}}\overset{-}{\mathrm{OH}}$ = Sodium Hydroxide.

$\overset{+}{\mathrm{(NH_4)}}\overset{-}{\mathrm{Cl}}$ = Ammonium Chloride.

$\overset{+}{\mathrm{(NH_4)}}\overset{-}{\mathrm{CN}}$ = Ammonium Cyanide.

$\overset{+}{\mathrm{(C_2H_5)}}\overset{-}{\mathrm{I}}$ = Ethyl Iodide.

Thus, compounds in which chlorine acts as the electro-negative element are called *chlorides,* with oxygen as *oxides,* with phosphorus as *phosphides,* with the radicle CN as *cyanides.*

The valence of the different elements entering into combination should be carefully observed, in order that there be no free (unsat-

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* Also radicles which act as electro-positive or negative elements.

urated) bonds remaining in the formula. This may be illustrated in the following classification:

a. The atoms unite singly where the valencies are alike—

$\overset{I}{Na}\overset{I}{Cl}$, $\overset{I}{Ag}\overset{I}{Br}$ $\overset{II}{Ca}\overset{II}{O}$, $\overset{III}{B}\overset{III}{N}$, $\overset{IV}{Si}\overset{IV}{C}$.

b. One valence is a multiple of the other—

$\overset{I}{Ag_2}\overset{II}{O}$, $\overset{II}{Ca}\overset{I}{Cl_2}$, $\overset{IV}{C}Cl_4$, $\overset{V}{P}Cl_5$, $\overset{VI}{W}Cl_6$.

c. Combinations of atoms of unequal valencies. In such cases the valencies of the different atoms or atomic groups are exchanged as coefficients—

$\overset{III}{Bi_2}\overset{II}{O_3}$, $\overset{III}{As_2}\overset{II}{S_3}$, $\overset{V}{P_2}\overset{II}{O_5}$, $\overset{VII}{Cl_2}\overset{II}{O_7}$.

Where the two elements form several compounds, the negative element retains its normal valence, while the positive may vary. To distinguish between two compounds of the same two elements, we employ the ending *ous* to indicate the lower valence, or lower state of oxidation, and *ic* the higher. Thus—

$\overset{II}{Fe}\overset{II}{O}$ Ferr*ous* Oxide.

$\overset{III}{Fe_2}\overset{II}{O_3}$ Ferr*ic* Oxide.

$\overset{IV}{S}\overset{II}{O_2}$ Sulphur*ous* Oxide.

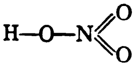
$\overset{VI}{S}\overset{II}{O_3}$ Sulphur*ic* Oxide.

In those cases where two elements form two or more compounds, these may be more appropriately distinguished from one another by means of Greek numeral prefixes added to the name of the negative element.

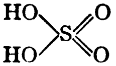
N_2O = Nitrogen *mon*-oxide.*
N_2O_2 = Nitrogen *di*-oxide.†
N_2O_3 = Nitrogen *tri*-oxide.
N_2O_4 = Nitrogen *tetr*-oxide.
N_2O_5 = Nitrogen *pent*-oxide.

SO_2 = Sulphur *di*-oxide (Sulphur*ous* Oxide).
SO_3 = Sulphur *tri*-oxide (Sulphur*ic* Oxide).
P_2O_3 = Phosphorus *tri*-oxide (Phosphor*ous* Oxide).
P_2O_5 = Phosphorus *pent*-oxide (Phosphor*ic* Oxide).

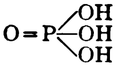
Ternary Compounds.—These consist of three or more different kinds of atoms, one of which serves to unite the two other dissimilar atoms or radicles; for example—


(HNO_3)

Nitric Acid.


(H_2SO_4)

Sulphuric Acid.


(H_3PO_4).

Phosphoric Acid.

Acids, Bases, and Salts.—The only acid (*acidus* = sour) known to the ancients was vinegar. They were acquainted with its solvent action on calcium carbonate (calcareous earth). Later other acids in impure state, as nitric and sulphuric, were prepared, and, owing to their sour taste and similar solvent properties (like vinegar), they were classed as acids.

The ashes of sea weed, called *alkali,* were known to possess detergent properties as well as influence the color of certain plant pigments (as litmus). Later this

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* Also known as Nitrous Oxide.

† Now designated as Nitric Oxide with simple formula NO.

term included all similar compounds possessing like properties. It was noted that certain alkalies effervesced with acids (mild alkalies), while others, possessing the same general properties, were of a caustic nature (caustic alkalies). Another class, which were insoluble in water and yet neutralized acids, were termed *earths*. The products of the neutralization of acids by alkalies were termed *salts*. Originally the term salt was applied to sea-salt obtained by the evaporation of sea-water. Later this name was used for similar products obtained through the interaction of acids and alkalies.

Acids.—Acids are compounds of hydrogen with an electro-negative element or radicle. They usually possess a sour taste when diluted, redden blue litmus, and saturate bases (oxides and hydroxides of metals). In aqueous solution acids dissociate into hydrogen ions which produce the acid reaction and are characteristic of all acids. All acids contain hydrogen, which is readily replaceable by metals, the product being termed a *salt*. Acids may be divided into two classes—namely, the binary or halogen acids, and the ternary or oxygen acids.

Binary or Halogen Acids.—These are compounds of hydrogen and the halogens,* and are—

HCl = Hydrogen chlor*ide*.
HBr = Hydrogen brom*ide*.
HI = Hydrogen iod*ide*.
HF = Hydrogen fluor*ide*.

In naming these, custom has followed another method, which consists in employing the term acid and preceding it by the name of the electro-negative element ending in *ic* with the prefix *hydro;* thus—

HCl = *Hydro*chlor*ic* Acid.
HI = *Hydr*iod*ic* Acid.

Ternary or Oxygen Acids.—These are ternary compounds in which hydrogen is linked by means of oxygen to electro-negative radicles containing oxygen. For example—

$H—O—ClO_2$	$HO—NO_2$	$(HO)_2SO_2$
Chloric Acid.	Nitric Acid.	Sulphuric Acid.

These acids dissociate into hydrogen ions and the oxygenated negative ion complex; thus—

$$HClO_3 = \overset{+}{H} + \overset{-}{ClO_3}. \qquad HNO_3 = \overset{+}{H} + \overset{-}{NO_3}.$$

$$H_2SO_4 = \overset{+}{H} + \overset{+}{H} + \overset{=}{SO_4}$$

As in binary acids, the hydrogen atoms are replaceable by electro-positive atoms or radicles. Also the oxygen acids of lower valence (lower state of oxidation) end in *ous* and the higher ones in *ic*. The compounds of these end in *ite* and *ate* respectively. Thus—

Acids.	Salts.
$H\overset{III}{N}\overset{II}{O_2}$ Hydrogen Nitr*ite* .... or Nitr*ous* Acid.	$NaNO_2$ Sodium Nitr*ite*

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* The halogens are a group of elements consisting of chlorine, bromine, iodine, and fluorine.

$H\overset{V}{N}\overset{II}{O}_3$ Hydrogen Nitr*ate* ....$NaNO_3$ Sodium Nitr*ate*
or Nitr*ic* Acid.

$H_2\overset{IV}{S}\overset{II}{O}_3$ Hydrogen Sulph*ite* ....Na_2SO_3 Sodium Sulph*ite*.
or Sulphur*ous* Acid.

$H_2\overset{VI}{S}\overset{II}{O}_4$ Hydrogen Sulph*ate* ....Na_2SO_4 Sodium Sulph*ate*.
or Sulphur*ic* Acid.

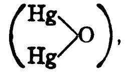
Some elements form several oxygen acids, differing from one another in the number of molecules of oxygen present. For such as contain less oxygen than the *ous*, we employ the prefix "*hypo*," and those containing more than the *ic* the prefix "*per*." Thus—

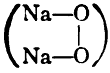
	Acids.	Salts.
$H\overset{I}{Cl}O$	*Hypo*chlor*ous* Acid...............	Sodium *Hypo*chlor*ite*.
$H\overset{III}{Cl}O_2$	Chlor*ous* Acid...............	Sodium Chlor*ite*.
$H\overset{V}{Cl}O_3$	Chlor*ic* Acid................	Sodium Chlor*ate*.
$H\overset{VII}{Cl}O_4$	*Per*chlor*ic* Acid	Sodium *Per*chlor*ate*.

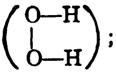
The following represent a number of prefixes, some of which, though antiquated, still find usage:

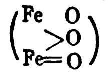
Proto means first of a series; for example, *proto*iodide of mercury (HgI) and *proto*chloride of iron ($FeCl_2$) represent the simplest combinations of these two elements.

Deuto, Di, Bin, or Bi.—These prefixes refer to the number of atoms of the electro-negative element present in the compound. *Deuto-* or *bin*iodide of mercury (HgI_2), *di-* or *bi*chloride of mercury.

Sub means below or under; thus, a *sub*oxide or *sub*chloride refers to the oxide or chloride below the normal. Since normal oxide of mercury is HgO, the suboxide would be Hg_2O  $\left(\begin{array}{l}Hg\diagdown\\ \quad\;\; >O\\ Hg\diagup\end{array}\right)$, the latter compound containing a lower percentage of oxygen. Subchloride of mercury is HgCl (or Hg_2Cl_2), and contains less chlorine than the normal or bichloride ($HgCl_2$).

Super or *Hyper* means "beyond"; thus, a *super-* or *hyper*oxide would be the oxide beyond the normal; or, for example, normal sodium oxide is Na_2O; its next higher or superoxide is Na_2O_2  $\left(\begin{array}{l}Na—O\\ \qquad\;|\\ Na—O\end{array}\right)$. These terms are almost obsolete.

Per.—This prefix, which is frequently employed, indicates that the molecule contains the highest possible percentage of the electro-negative element or group. Thus, we have *per*chloride of iron ($FeCl_3$) as compared with *proto*chloride ($FeCl_2$); hydrogen *per*oxide would be H_2O_2  $\left(\begin{array}{l}O—H\\ |\\ O—H\end{array}\right)$; sodium *per*oxide, Na_2O_2; *per*chloric acid, $HClO_4$.

Sesqui.—This term refers to a ratio of *two* atoms of the electro-positive element to *three* of the electro-negative. Thus, *sesqui*oxide of iron would be Fe_2O_3  $\left(\begin{array}{l}Fe\;\;O\\ \quad >O\\ Fe=O\end{array}\right)$ Sb_2S_3 is *sesqui*sulphide of antimony.

Basicity.—The basicity of acids is represented by the ***number*** of hydrogen atoms which can be replaced by monovalent electro-positive atoms. Examples:

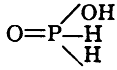
Monobasic acids—hydrogen chloride (HCl) and hydrogen nitrate (HNO_3).

Dibasic acids—hydrogen sulphate (H_2SO_4) and hydrogen oxalate ($H_2C_2O_4$).

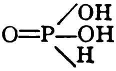
Tribasic acids—hydrogen phosphate (H_3PO_4) and hydrogen borate (H_3BO_3).

Tetrabasic acids—hydrogen pyrophosphate ($H_4P_2O_7$) and hydrogen ferrocyanide [$H_4Fe(CN)_6$].

Polybasic acids. These include all that are of a greater basicity than monobasic. Among the ternary acids are certain ones in which the number of hydrogen atoms contained in the molecule does not indicate their basicity. The replaceable hydrogens are usually linked to the negative atom or group by aid of oxygen, hence the number of hydroxyl (OH) groups determines this.



Hypophosphorous Acid, $\mathrm{O{=}P}\begin{matrix}\diagup \mathrm{OH}\\ -\mathrm{H}\\ \diagdown \mathrm{H}\end{matrix}$ is monobasic.
(HPH_2O_2)



Phosphorous Acid, $\mathrm{O{=}P}\begin{matrix}\diagup \mathrm{OH}\\ -\mathrm{OH}\\ \diagdown \mathrm{H}\end{matrix}$ is dibasic.
(H_2PHO_3)

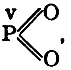
Ortho-, Meta-, and Pyro Acids.—*Ortho*-acids (ὀρθός = true). As already stated, the basicity of oxy-acids depends on the number of hydroxyl groups present. Such acids as contain the same number of hydroxyl (OH) groups as there are affinities or valencies in the negative atom or group are termed ortho-acids. Thus—

Ortho-boric Acid, $\overset{\mathrm{III}}{B}(OH)_3$ ....H_3BO_3.
Ortho-silicic Acid, $\overset{\mathrm{IV}}{Si}(OH)_4$..............$H_4SiO_4$.
Ortho-antimonic Acid, $O = \overset{\mathrm{V}}{Sb}(OH)_3$..........$H_3SbO_4$.
Ortho-phosphoric Acid, $O{=}\overset{\mathrm{V}}{P}(OH)_3$ ....H_3PO_4.

By the removal of one molecule of water, acids containing a minimum of hydrogen result; these are called "***meta-***" (μετα = a change) acids.

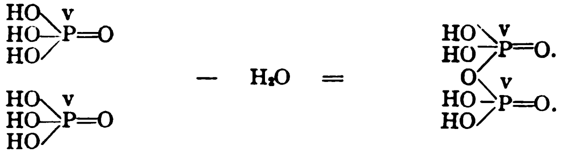
$$\underset{\text{Crtho-boric Acid.}}{\overset{\mathrm{III}}{B}(OH)_3 \text{ or } H_3BO_3} - H_2O = \underset{\text{Meta-boric Acid.}}{(HO)\overset{\mathrm{III}}{B}O \text{ or } HBO_2}.$$

$$\underset{\text{Ortho-silicic Acid.}}{\overset{\mathrm{IV}}{Si}(OH)_4 \text{ or } H_4SiO_4} - H_2O = \underset{\text{Meta-silicic Acid.}}{SiO(OH)_2 \text{ or } H_2SiO_3}.$$



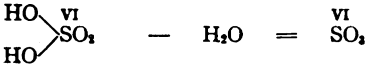
$$\underset{\text{Ortho-phosphoric Acid.}}{(HO)_3\overset{\mathrm{V}}{P}{=}O \text{ or } H_3PO_4} - H_2O = \underset{\text{Meta-phosphoric Acid.}}{(HO)\overset{\mathrm{V}}{P}\begin{matrix}\diagup\!\!\diagup O\\ \diagdown\!\!\diagdown O\end{matrix}, \text{ or } HPO_3}.$$

If one molecule of water is removed from two molecules of an ortho-acid, a *pyro*-acid results—



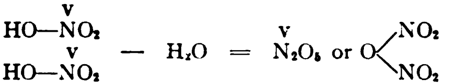
Ortho-phosphoric Acid. $2H_3PO_4$ Pyro-phosphoric Acid. $H_4P_2O_7$

Acid Anhydrides.—These are obtained from acids by removing all of the hydrogen with sufficient oxygen to form water.



Hydrogen Sulphate. Sulphuric Anhydride (Sulphur Trioxide).

In case the number of hydrogen atoms in the acid is uneven, the anhydride is derived from two molecules of the acid.



Nitric Acid. Nitric Anhydride.

$$2H_3PO_4 - 3H_2O = P_2O_5.$$

Phosphoric Acid. Phosphoric anhydride (Phosphorus pentoxide).

The anhydrides may also be considered as oxides (*acidic oxides*), which with water form oxy-acids, *e.g.*, $SO_3 + H_2O = H_2SO_4$. One or two of the anhydrides, while derived from oxy acids by loss of water, are not capable of reversing the reaction, *e.g.*, $H_2N_2O_2 - H_2O = N_2O$. The highest oxides of some metals are known as anhydrides, *e. g.*, chromic anhydride (CrO_3) and permanganic anhydride (Mn_2O_7).

Bases (Hydroxides, Alkalies).—These are compounds in which a positive element or radicle is linked to hydroxyl; when dissolved in water they yield hydroxyl ions. Or they may be considered as being derived from one or more molecules of water, in which one hydrogen of each is replaced by an electro-positive element or radicle. Owing to the presence of the hydroxyl (—OH) group, these compounds are known as *hydroxides* (sometimes incorrectly termed hydrates).

$$\overset{\text{I}}{\text{K}}\text{OH} \qquad \overset{\text{II}}{\text{Ba}}(\text{OH})_2 \qquad \overset{\text{III}}{\text{Bi}}(\text{OH})_3 \qquad \overset{\text{I}}{\text{NH}_4}\text{OH}$$

The number of OH groups present determines the saturating (page 130) power of the base; hence they are termed mono-, di-, or tri-acid or hydric bases. Thus, KOH is a mono-hydric base, since it saturates one molecule of a mono-basic acid—

$$KOH + HCl = KCl + H_2O.$$

$\overset{\text{II}}{\text{Ba}}(\text{OH})_2$ is di-hydric, since it saturates two molecules of a mono-basic acid—

$$Ba(OH)_2 + 2HCl = BaCl_2 + 2H_2O.$$

The oxides of the alkali metals combine with water to form the *alkali hydroxides,* all of which are soluble.

$$Na_2O + H_2O = 2NaOH.$$

The oxides of the alkaline earths unite with water to form the *alkaline earth hydroxides,* which vary in their solubility in water.

$$CaO + H_2O = Ca(OH)_2.$$

Weakly basic hydroxides of such metals as zinc and aluminum, as well as those of the heavy metals, because of their insolubility, are prepared by interaction between solutions of salts of the metals and an alkali hydroxide.

$$ZnSO_4 + 2NaOH = Zn(OH)_2 + Na_2SO_4.$$

Bases through electrolytic dissociation split up into metal cations and hydroxyl (OH) anions. The latter impart the alkaline taste and reaction that turns red litmus blue. Bases are strong or weak according to their degree of dissociation, the strongest being the hydroxides of the alkali metals (K, Na, Rb), which dissociate very readily. Ammonium hydroxide is a very weak base, being about 200 times weaker than potassium hydroxide when the latter is in normal solution (56.11 p. in 1000). The hydroxides of the alkaline earths (Ca, Sr, Ba) are strong bases, but less so than the alkali metals. The hydroxides of the heavy metals are insoluble, hence fail to dissociate.

Salts.—Salts are the product of the interaction between acids and bases or metals. The acidic* hydrogen of the acid has been replaced by a metal or basic radicle (NH_4NO_2). They consist of one or more electro-positive elements or radicles united to one or more electro-negative elements or radicles according to their respective valencies. Thus—

$$\underset{\text{Sodium Hydroxide.}}{\overset{+\,-}{NaOH}} + \underset{\text{Hydrogen Chloride.}}{\overset{+\,-}{HCl}} = \underset{\text{Sodium Chloride.}}{\overset{+\,-}{NaCl}} + \underset{\text{Water.}}{\overset{+\,-}{H_2O}}.$$

$$\underset{\text{Bismuth Oxide.}}{\overset{+\,-}{Bi_2O_3}} + \underset{\text{Hydrogen Sulphate.}}{\overset{+\,-}{3H_2SO_4}} = \underset{\text{Bismuth Sulphate}}{\overset{+\,-}{Bi_2(SO_4)_3}} + \overset{+\,-}{3H_2O}.$$

$$\underset{\text{Magnesium Oxide.}}{\overset{+\,-}{MgO}} + \underset{\text{Hydrogen Sulphate.}}{H_2SO_4} = \underset{\text{Magnesium Sulphate.}}{\overset{+\,-}{MgSO_4}} + \overset{+\,-}{H_2O}.$$

The above reactions serve to illustrate what is known as ***neutralization***—that is, the exact saturation of an acid with an alkali hydroxide or oxide. To ascertain when neutralization (replacement of hydrogen) is complete, we employ litmus paper, which will indicate saturation by change in color, the presence of the slightest excess of acid producing a red, while with an alkali this changes to blue. Salts also result from the action of acid anhydrides upon bases and acids upon metals.

$$\underset{\text{Sodium Hydroxide.}}{\overset{+\,-}{2NaOH}} + \underset{\text{Sulphurous Anhydride.}}{\overset{-}{SO_2}} = \underset{\text{Zinc Sulphite.}}{\overset{+\,-}{Na_2SO_3}} + \overset{+\,-}{H_2O}.$$

$$\underset{\text{Zinc.}}{\overset{+}{Zn}} + \underset{\text{Hydrogen Sulphate.}}{\overset{+\,-}{H_2SO_4}} = \underset{\text{Zinc Sulphate.}}{\overset{+\,-}{ZnSO_4}} + \underset{\text{Hydrogen.}}{H_2}.$$

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* In some acids not all hydrogen can be replaced, *e.g.*, phosphorous acid (H_2PHO_3) and hypophosphorous acid, HPH_2O_2; the former has two and the latter one replaceable hydrogen atom.

$$\underset{\text{Copper.}}{\overset{+}{3Cu}} + \underset{\text{Hydrogen Nitrate.}}{\overset{+\ -}{8HNO_3}} = \underset{\text{Cupric Nitrate.}}{\overset{+\ -}{3Cu(NO_3)_2}} + \underset{\text{Nitrogen Dioxide.}}{\overset{+\ -}{2NO}} + \overset{+\ -}{4H_2O}.$$

Since there is only one replaceable hydrogen in the binary acids, there can be only one class of salts.

Salts of the oxygen or ternary acids may be classified as *normal, acid,* and *basic.*

Normal or Neutral Salts.—These are formed by the replacement of *all* of the hydrogen atoms of an acid by metals. They are usually of neutral reaction.*

$$\underset{\text{Sodium Chloride.}}{\overset{\text{I}}{Na}\overset{\text{I}}{Cl}} \qquad \underset{\text{Zinc Sulphate.}}{\overset{\text{II}}{Zn}\overset{\text{II}}{SO_4}} \qquad \underset{\text{Calcium Phosphate.}}{\overset{\text{II}}{Ca_3}\overset{\text{III}}{(PO_4)_2}}.$$

Acid Salts.—These are derived by the partial replacement of the hydrogen of polybasic acids by metals. They always contain one or more unreplaced hydrogens, and, in consequence, usually have an acid reaction. These compounds are termed *acid, bi,* or *hydrogen* salts. Thus—

$NaHSO_4$ = Sodium *acid* sulphate, or sodium *bi*sulphate, or sodium *hydrogen* sulphate.

The salts of the tribasic acids are named according to the number of hydrogen atoms which have been replaced—namely, primary, secondary, or tertiary, or mono, di, or tribasic salts.

H_3PO_4.	NaH_2PO_4.	Na_2HPO_4.	Na_3PO_4.
Hydrogen Phosphate.	Mono-sodium-di-hydrogen Phosphate. Mono-basic Sodium Phosphate. Primary Sodium Phosphate.	Di-sodium-mono-hydrogen Phosphate. Di-basic Sodium Phosphate. Secondary Sodium Phosphate.	Tri-sodium Phosphate. Tri-basic Sodium Phosphate. Tertiary Sodium Phosphate.

Double Salts.—These are the result of the combination of two salts in molecular proportions. Dilute solutions of the double salts give the same ions as are present in the salts entering into their composition, hence exhibit the reactions of their components. These salts

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* Neutral salts of such weak acids as hydrocyanic (HCN), boric (H_3BO_3), or silicic (H_2SiO_3), may be of alkaline reaction, while the neutral salts of weak bases, as ferric [$Fe(OH)_3$], aluminum [$Al(OH)_3$], and zinc [$(Zn(OH)_2$] hydroxides, may show an acid reaction. This is caused by the dissociating action of the water ions, whereby the salts of the weak acids split up into non-dissociating acids and dissociated bases. For example, sodium cyanide, a compound of a strong base (NaOH) and weak acid (HCN), shows the alkaline reaction of the OH ions of the water, in addition to that of the Na ions, for the compound NaOH dissociates completely. The H ions of the water combine with the CN ions, forming HCN, which is a very weak and slightly dissociable acid.

Ferric chloride ($FeCl_3$), a compound of the strong acid (HCl) and a weak base [$Fe(OH)_3$], shows an acid reaction due to the presence of the H ions of the water and Cl ions of the acid. The alkaline reaction of the OH water ions is not manifested, because they unite with the Fe''' ions to form a non-dissociating compound.

may be derived either (a) from two different metals with the same acid, *e.g.*,

H_2SO_4 Hydrogen Sulphate. $\overset{I}{K}\overset{I}{Na}\overset{II}{SO_4}$ Potassium Sodium Sulphate. $\overset{I}{Na}\overset{I}{NH_4}\overset{II}{SO_4}$. Sodium Ammonium Sulphate.

$KAl(SO_4)_2.12H_2O$ Potassium Aluminum Sulphate. $MgSO_4.K_2SO_4.6H_2O$ Magnesium Potassium Sulphate.

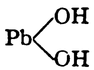
These dissociate in solution into the ions of their components, viz., $K^{\cdot}$, $\overset{\cdot\cdot\cdot}{Al}$, and $\overset{''}{SO_4}$, and $\overset{\cdot\cdot}{Mg}$, $\overset{\cdot}{K}$, and $\overset{''}{SO_4}$; or (b) two different salts of the same metal, *e.g.*, $HgCl_2.2HgS$; or (c) two different metals of two different acids, *e.g.*, $MgSO_4.KCl.3H_2O$.
Kainite.

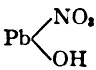
Complex Salts.—These are formed through the mixing of solutions of two single salts (like double salts), but their solutions differ in having the constitution of single salts. The ferrocyanides and cobalticyanides are salts of the complex hydro-ferro-cyanic $[H_4Fe(CN)_6]$ and hydro-cobalti-cyanic $[H_3Co(CN)_6]$ acids. Their solutions do not give the usual characteristic reactions of iron and cobalt, although they are formed through the union of single salts, *e.g.*,

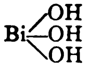
$$\underset{\text{Potassium Cyanide.}}{4KCN} + \underset{\text{Ferrous Cyanide.}}{\overset{II}{Fe}(\overset{I}{CN})_2} = \underset{\text{Potassium Ferrocyanide.}}{K_4\overset{II}{Fe}(\overset{I}{CN})_6}.$$

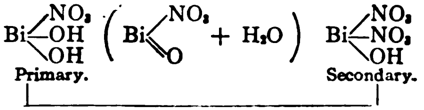
This dissociates into the ions $4\overset{\cdot}{K}$ and $\overset{''''}{Fe(CN)_6}$.

Basic Salts.—These are derived by the replacement of part of the hydroxyl groups of polyhydroxides by acid radicles. That is, the amount of acid used is not sufficient to neutralize the basic hydroxide (*e.g.*, hydroxides of Bi, Zn, Pb, Sb). They may also be considered as compounds of normal salts with metallic oxides or hydroxides. Basic salts are frequently termed *oxy* or *sub* salts.


Lead Hydroxide.


Basic Lead Nitrate, or
Lead Subnitrate, or
Lead Oxynitrate.


Bismuth Hydroxide.


Primary. Secondary.
Basic Bismuth Nitrates.

These basic salts may also be considered as resulting from the replacement of hydrogen atoms of an acid by metallic oxides or hydroxides.

HNO_3 Hydrogen Nitrate. $(\overset{II}{Pb}\overset{I}{OH})—\overset{I}{NO_3}$ Basic Lead Nitrate. $(\overset{III}{Bi}\overset{II}{O})—\overset{I}{NO_3}$. Basic Bismuth Nitrate.

HCl Hydrogen Chloride. $\overset{II}{Zn}\,(\overset{I}{OH})\,\overset{I}{Cl}$ — Basic Zinc Chloride.

Oxidation and Reduction.—When an element combines with oxygen it is said to undergo oxidation (equation 1); when this oxide is deprived of its oxygen it is said to undergo reduction (equation 8). Oxidation, in general, embraces all chemical reactions which result in the addition of electro-negative elements or radicles to an element or compound with a decrease in the relative quantity of the electro-positive element in a molecule, the valence of the electro-positive element usually increasing.

	Compound.		*Oxidizing Agent.*		*Oxidized Product.*
(1)	$\overset{\text{II}}{\mathrm{Mg}}$	+	O	=	$\overset{\text{II}}{\mathrm{MgO}}$
(2)	$\overset{\text{II}}{\mathrm{FeCl_2}}$	+	Cl	=	$\overset{\text{III}}{\mathrm{FeCl_3}}$
(3)	$\overset{\text{II}}{\mathrm{6FeCl_2}}$	+	$\mathrm{6HCl + 2HNO_3}$	=	$\overset{\text{III}}{\mathrm{6FeCl_3}} + \overset{\text{II}}{\mathrm{2NO}} + \mathrm{4H_2O}$.
(4)	$\overset{\text{II}}{\mathrm{PbS}}$	+	$\mathrm{2O_2}$	=	$\overset{\text{II}}{\mathrm{PbSO_4}}$
(5)	$\overset{\text{III}}{\mathrm{PCl_3}}$	+	$\mathrm{Cl_2}$	=	$\overset{\text{V}}{\mathrm{PCl_5}}$
(6)	$\overset{\text{III}}{\mathrm{Cr_2O_3}}$	+	$\mathrm{KClO_3}$	=	$\overset{\text{VI}}{\mathrm{2CrO_3}} + \mathrm{KCl}$

The oxidizing agent undergoes deoxidation (reduction). *Reduction* (the reverse of oxidation) is the abstraction, partial or entire, of electro-negative elements or radicles from compounds, or the increase of electro-positive atoms or radicles in a molecule, the valence of the electro-positive element usually decreasing.

	Compound.		*Reducing Agent.*		*Reduced Compound.*
(7)	$\overset{\text{III}}{\mathrm{2FeCl_3}}$	+	$\mathrm{H_2}$	=	$\overset{\text{II}}{\mathrm{2FeCl_2}} + \mathrm{2HCl}$
(8)	$\overset{\text{III}}{\mathrm{Fe_2O_3}}$	+	$\mathrm{3H_2}$	=	$\overset{\text{II}}{\mathrm{Fe_2}} + \mathrm{3H_2O}$
(9)	$\overset{\text{II}}{\mathrm{2HgCl_2}}$	+	$\mathrm{H_2SO_3 + H_2O}$	=	$\overset{\text{I}}{\mathrm{2HgCl}} + \mathrm{H_2SO_4} + \mathrm{2HCl}$
(10)	$\overset{\text{V}}{\mathrm{KNO_3}}$	+	Pb	=	$\overset{\text{III}}{\mathrm{KNO_2}} + \mathrm{PbO}$
(11)	$\overset{\text{II}}{\mathrm{CuO}}$	+	$\mathrm{H_2}$	=	$\overset{\text{I}}{\mathrm{Cu}} + \mathrm{H_2O}$
(12)	$\overset{\text{VI}}{\mathrm{2CrO_3}}$	+	$\mathrm{3H_2}$	=	$\overset{\text{III}}{\mathrm{Cr_2O_3}} + \mathrm{3H_2O}$

It will be noted that oxidizing and reducing reactions are directly the reverse; that is, they are the same processes, differing only in their direction. The substance that causes reduction is oxidized to the same extent as the one reduced. Thus in equation 2, while the ferr*ous* chloride is oxidized, the chlorine is reduced; in equation 7, the ferr*ic* chloride is reduced and the hydrogen is oxidized. In equation 6, the chromium sesquioxide is oxidized to the trioxide, while the potassium chlorate is reduced (de-oxidized); in equation 12, the chromium trioxide is reduced to the sesquioxide, while the hydrogen is oxidized to water.

Conditions Necessary for Chemical Change.—Chemical changes are the result of chemical action which takes place in response to that attractive force, which holds the constituent parts of a compound together, known as chemical affinity. This latter force varies greatly, not only among the various elements, but also with the same element under different conditions. Some chemical compounds possess such molecular instability that they undergo spontaneous decomposition, sometimes with explosion (as the oxides of chlorine) or upon a slight shock (as nitrogen chloride or iodide). Other elements or compounds require the influence of certain physical forces, such as heat, light, or electricity, in order to bring about reaction. Usually the first condition which is necessary to induce chemical interchange is to secure intimate contact and freedom of motion between the molecules, so as to favor atomic interchange. This is usually accomplished, between solids, by aid of a solvent. Thus, we may mix finely powdered corrosive sublimate ($HgCl_2$) and potassium iodide (KI), and so long as they remain in the dry condition no reaction will take place, but with the addition of water the white powder disappears and a red one forms, thereby indicating that chemical reaction, resulting from an interchange of the several atoms, has taken place.

$$\underset{\substack{\text{Mercuric}\\\text{Chloride.}}}{HgCl_2} + \underset{\substack{\text{Potassium}\\\text{Iodide.}}}{2KI} = \underset{\substack{\text{Mercuric}\\\text{Iodide.}}}{HgI_2} + \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{2KCl.}$$

In gases we find the same freedom of molecular contact and motion as in the solutions of solids. Thus, on mixing chlorine and gaseous hydrogen bromide, bromine is liberated from its compound with hydrogen: $2Cl + 2HBr = 2HCl + 2Br$.

Nitric oxide unites under like circumstances with oxygen to form nitrogen tetroxide, $2NO + O_2 = N_2O_4\ (2NO_2)$.

The union of chlorine and hydrogen may be accomplished by exposing the mixture of the gases, in molecular proportions, to strong sunlight; oxygen and hydrogen combine through application of a flame, while oxygen and nitrogen unite only through the continued action of the electric spark. The union of certain other gases is brought about through the presence of a foreign body, which apparently does not take any part in the reaction. Such a substance is called a catalytic agent (see page 152). For example, sulphur dioxide and oxygen unite in the presence of spongy platinum,* as, for example, in the manufacture of sulphuric acid by the contact process (page 230).

Chemical Changes in Aqueous Solutions.—According to the nature of the reaction they may be divided into the following types:

1. *Metathesis.*—Reactions of this type are the most frequent and may be expressed as follows:

$$AB + CD = AC + BD.$$

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* Asbestos wool is impregnated with a solution of ammonio-platinic chloride, then ignited, whereby finely divided platinum remains distributed over the asbestos.

Upon mixing solutions of chemical compounds, an interchange of atoms or atomic groups (radicles) takes place, resulting in the formation of new compounds; precipitation takes place or not, according to the solubility of these in the given solvent.

Example.—If we mix an almost colorless solution of ferric chloride and a colorless solution of sodium acetate, a dark-red solution results. This change in color is indicative of chemical action, although no precipitation takes place.

$$\underset{\text{Ferric Chloride.}}{FeCl_3} + \underset{\text{Sodium Acetate.}}{3\,NaC_2H_3O_2} = \underset{\text{Sodium Chloride.}}{3NaCl} + \underset{\text{Ferric Acetate.}}{Fe(C_2H_3O_2)_3.}$$

Example.—If we mix solutions of barium chloride and sodium sulphate, a precipitate forms, owing to the insolubility of the newly formed compound barium sulphate, which is the result of an interchange or rearrangement of atoms. Thus—

$$\underset{\text{Barium Chloride.}}{BaCl_2} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Sodium Chloride.}}{2NaCl.}$$

In this manner the element barium may be removed from a solution by the aid of a reagent, with which it forms an insoluble compound. Such reactions which involve precipitation of one of the elements furnish the analyst with a valuable means for their identification and separation.

Example.—If the resulting compounds formed in a reaction of this kind are soluble in the solvent, we must resort to artificial means of removing either the undesirable or the desirable product. This may be accomplished in various ways, depending on the relative solubilities of the two salts present in solution. Advantage is usually taken of variations in the degree of solubility of the dissolved salts at different degrees of concentration and different temperatures. For example, a less soluble salt may be separated from the more soluble while cooling the hot concentrated solution or sometimes by leaching the mixture of the two dry salts with cold water. Since the solubility of two different salts in the same solvent usually varies at different temperatures, separation may be accomplished by fractional crystallization. Thus, we may prepare ammonium bromide by mixing solutions of potassium bromide and ammonium sulphate; as a result, two soluble compounds are produced, as follows:

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Ammonium Bromide.}}{2NH_4Br} + \underset{\text{Potassium Sulphate.}}{K_2SO_4.}$$

In order to separate the inert side-product potassium sulphate from the ammonium bromide, advantage is taken of the fact that the former is practically insoluble in diluted alcohol, while the latter is soluble; hence alcohol is added to the not too dilute fluid mixture, and after standing in a cool place a few hours the solution of the ammonium bromide is drained off from the precipitated potassium sulphate and evaporated. On large scale, the less soluble potassium sulphate is removed by permitting the hot saturated solution to stand, whereby this salt crystallizes out, leaving the readily soluble ammonium bromide in solution, which is then obtained by evaporation of the mother liquor.

The following general rules of solubility for the salts of the more common elements should be noted, since a knowledge of these is indispensable for laboratory work:

1. All normal nitrates are soluble.
2. All chlorides are soluble except those of silver, mercurous mercury, cuprous copper and lead.
3. All sulphates are soluble except those of barium, calcium, strontium, and lead.
4. All phosphates are insoluble except those of the alkali metals (viz., K, Na, Li) and ammonium.
5. All carbonates are insoluble except those of the alkali metals and ammonium.

Such interactions, in which water is the activating element, are termed *hydrolytic decompositions; e.g.*, the decomposition of phosphorus trichloride by water into phosphorous and hydrochloric acids:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl,$$

or acetyl chloride by water into acetic and hydrochloric acids:

$$CH_3COCl + H_2O = HCl + CH_3COOH,$$

or ethyl nitrite (spirit of nitre) by water splitting up into ethyl alcohol and nitrous acid:

$$C_2H_5O.NO + H_2O = C_2H_5OH + HNO_2.$$

2. *Displacement.*—One element of a compound is displaced by another element.

$$\begin{aligned} Fe + 2HCl &= FeCl_2 + H_2. \\ CuSO_4 + Fe &= FeSO_4 + Cu. \\ 2HCl + H_2O_2 &= 2H_2O + Cl_2. \end{aligned}$$

3. *Substitution.*—This is displacement accompanied by chemical union with the displaced element. Such reactions are very frequent in organic chemistry.

$$\underset{\text{Benzene.}}{C_6H_6} + Cl_2 = \underset{\text{Chlor-benzene.}}{C_6H_5Cl} + HCl.$$

$$\underset{\text{Aldehyde.}}{CH_3COH} + 3Cl_2 = \underset{\text{Trichlor-aldehyde.}}{CCl_3COH} + 3HCl.$$

4. *Synthetic Reactions.*—The formation of compound bodies from simple ones:

$$(a)\ SO_3 + H_2O = H_2SO_4.$$

$$(b)\ Cl + F + H_2O = HF + HClO.$$

$$(c)\ \begin{array}{l} 1\ Fe + S = FeS. \\ 2\ \underset{\text{Iron Sulphide.}}{FeS} + \underset{\text{Potassium Cyanide.}}{6KCN} = \underset{\text{Potassium Ferrocyanide.}}{K_4Fe(CN)_6} + \underset{\text{Potassium Sulphide.}}{K_2S}. \end{array}$$

5. *Analytic Reactions.*—These embrace a great variety of reactions the aim of which is the decomposition or separation of elements from their compounds, as carried out by the analyst with view to the formation of insoluble bodies or stable compounds the weight of which may be determined:

$$\underset{\text{Calcium Oxalate.}}{CaC_2O_4} + \text{heat} = \underset{\text{Calcium Oxide.}}{CaO} + \underset{\text{Carbon Monoxide.}}{CO} + \underset{\text{Carbon Dioxide.}}{CO_2}$$

$$\underset{\text{Silver Nitrate.}}{AgNO_3} + HCl = \underset{\text{Silver Chloride.}}{AgCl} + HNO_3$$

In the above reaction either the quantity of the silver or the chlorine present may be determined:

$$\underset{\text{Barium Chloride.}}{BaCl_2} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4} = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Sodium Chloride.}}{2NaCl}$$

This equation represents either a determination of the barium (as $BaSO_4$) or the SO_4 or H_2SO_4 (as Na_2SO_4) present.

Reversible or Reciprocal Reactions.—The previously classified reactions are known as *complete* because *all* of the reacting bodies on the left side of the equation are converted into the products on the right side. A *reversible* reaction is one in which by slightly altering the conditions under which the reaction takes place, the products will react to re-form the original reacting substances. Whether it is the original reacting substances or the products of their reaction which react, the same result obtains—a state of *equilibrium.* Such equations are indicated by the symbol $\rightleftarrows$.

If molecular quantities of iodine and hydrogen are heated to 445° in a sealed vessel, 79 per cent. of hydrogen iodide is formed and 21 per cent. of the gas mixture remains uncombined. If a similar vessel be filled with hydrogen iodide and is heated to the *same* temperature, dissociation to the extent of 21 per cent., into its elements, hydrogen and iodine, will take place; hence this reaction yields the same results whether we start with hydrogen and iodine or hydrogen iodide; the reaction is never complete, hence is called reversible—that is, it occurs in either direction at the same time. If the temperature be kept constant for a time, a period is reached in which both sides of the equation are in equilibrium. An alteration in temperature will cause a new equilibrium stage to be established in which the HI formed will balance the H and I liberated. The equilibrium formed in this equation is expressed thus: $H_2 + I_2 \leftrightarrows 2HI$.

Further, the gradual addition of water to a slightly acid solution of bismuth trichloride causes the precipitation of bismuth oxychloride to begin, continuing until all of the bismuth has been precipitated. If now hydrochloric acid be slowly added to the oxychloride, this will gradually dissolve until all of the bismuth has passed into solution as trichloride. The relative amounts of water and hydrochloric acid present determine the direction of the reaction.

$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl.$$

This represents another type of a *reversible* or *balanced* reaction.

Mass Action.—The result of chemical interaction depends not only upon the nature of the reacting bodies and temperature of the reaction, but also on the relative masses of the substances participating. That is, the trend of a chemical change is frequently influenced by mass action, large masses compensating relatively feeble affinity. Thus, hydrochloric and nitric acids are more volatile than sulphuric acid, hence the latter expels the two former from their salts; but not if diluted sulphuric acid is employed. At the boiling-point of sulphuric acid (338°), phosphoric acid is not volatile, hence at this temperature the weaker phosphoric acid will expel the stronger sulphuric acid from its salts. This is not due to any relative greater affinity of one acid over the other for the base, but because of its subdivision between the two acids being continually upset in favor of the phosphoric acid. The active mass of this latter acid increases over that of the sulphuric acid, which is being continually removed from the reaction because of its volatility. This continues until all of the sulphuric acid has been replaced by the phosphoric acid.

A *small* quantity of potassium chloride is decomposed by a *large* quantity of bromine, yielding potassium bromide, although chlorine possesses a far greater affinity for the base than bromine. Hence, by virtue of its affinity alone, one substance can never completely expel another from its compounds. These considerations are embodied in the Law of Mass Action—namely, *chemical* change is proportional to the active mass of the substances taking part in the reaction. The *active mass* represents the number of molecules of the substance in a unit volume as gram-molecules per liter.

Influence of Various Forms of Energy upon Chemical Affinity.—As already stated, chemical affinity, or attraction, may vary not only between different bodies, but also under the influence of such forces as heat, light, and electricity, it may increase or decrease in intensity, or cease altogether in the same substance.

Heat.—The effect of temperature change upon chemical attraction may be threefold: first, at very low temperatures chemical affinity is so feeble that to all appearances it practically ceases; second, moderate temperatures, as a general rule, assist chemical union; third, sufficiently high temperatures cause a breaking up of chemical compounds into simpler forms, and, finally, if very intense, into their elements: in the sun matter is present only in its elementary state.

For example, mercury when exposed to the air at ordinary temperature undergoes but little change, but if it be heated to near its boiling point (360° C.) it readily unites with the oxygen of the air, forming red mercuric oxide (HgO); if this temperature be increased to 400° C., further attraction between these elements ceases, and the compound decomposes into oxygen and mercury.

Dissociation.—This is a reversible decomposition which differs from a metathetical reaction in that the products of the reaction reunite on altering the physical conditions. This is a splitting up of the molecules of certain chemicals into simpler forms, lasting as long as the favoring conditions continue, and, when they cease, the products of dissociation reunite, forming the original substance. We distinguish between dissociation produced by heat, called *thermal* dissociation, and that resulting from solution, called *electrolytic* dissociation (page 141). Examples of the former class are such compounds as ammonium chloride, which, through heat, splits up into ammonia and hydrogen chloride ($NH_4Cl \rightleftarrows NH_3 + HCl$); sulphuric acid splits into water and sulphur trioxide ($H_2SO \rightleftarrows H_2O + SO_3$); phosphorus pentachloride into its trichloride and chlorine ($PCl_5 \rightleftarrows PCl_3 + Cl_2$); upon cooling, the dissociation products of these several compounds again reunite. The reactions are reversible. We must distinguish between dissociation and chemical *decomposition,* where, in the latter case, the products of the reaction do not unite upon lowering the temperature. For example, potassium chlorate when heated decomposes into potassium chloride and oxygen ($2KClO_3 = 2KCl + 3O_2$), mercuric oxide into mercury and oxygen. This phenomenon of dissociation explains why certain chemicals show abnormal density when attempting to determine their molecular weights. Thus, ammonium chloride should show (if it did not dissociate) a density of 26.75 ($\frac{53.50}{2}$), but in practice (at 350°) it is found to be only half this number, namely, 13.375+; however, if we consider that the salt dissociates into ammonia and hydrogen chloride, and average the density of these two constituents, $NH_3 = 8.515$ and $HCl = 18.235$, we get 13.375+.

The density of sulphur vapor at 500° C. gives this element an atomic weight of 96, there being 6 atoms to the molecule; at 1000° C. these more complex hexatomic molecules dissociate, or break up further, into simpler diatomic molecules—that is, the molecule contains 2 atoms, which gives the accepted atomic weight of $S = 32$.

Light.—Like heat, light also exerts an important influence upon chemical combination and decomposition, varying according to the nature of the substance and the kind of light. Such reactions are known as *photo-chemical.* We find that certain *gases,* as chlorine detonating mixture (chlorine and hydrogen in molecular proportions), may be made to combine with explosive violence; *liquids,* as a solution of chlorine in water, decomposes the latter into hydrogen chloride and oxygen ($Cl_2 + H_2O = 2HCl + O$), and *solids,* as white phosphorus, change into the red modification, or cinnabar (red) turns black through the influence of light energy. The intensity of the photo-chemical reaction depends upon the kind of light—that is, the ultra-violet rays, consisting of the shortest vibrations, are the most active, while the longer infra-red rays are far less so.

Chemical decomposition of aqueous solutions of hydrogen iodide or bromide readily takes place on exposure to light, with separation of iodine or bromine ($2HI + O = H_2O + I$). The yellow iodide of mercury, under like conditions, changes to a dark green, the light having caused a separation of a portion of the mercury from the iodine. The decomposition of the compounds of iodine and bromine with silver by the action of light is the principle upon which the art of photography is based.

The influence of electrical energy upon chemical affinity and other processes demands special consideration.

ELECTRO-CHEMISTRY

Through the induction-spark or electric arc, chemical combination as well as decomposition may be brought about; this is, however, in all probability due to the high temperature produced. On the other hand, the galvanic current induces chemical decomposition only. Such decompositions are termed *electrolytic* and the operation *electrolysis.*[*] As regards their deportment to the electric current, substances may be divided into the following classes: (1) *conductors proper,* or such as conduct the current without decomposition, as metals, alloys, or carbon; (2) *electrolytes,* or substances in the fluid state which permit the passage of the current while undergoing chemical decomposition, as acids, bases, and salts, either fused or in aqueous solution; (3) *non-conductors,* which offer great resistance to the passage of the current, as pure water, aqueous solutions of most organic compounds (excepting well-defined organic acids, bases, and salts), wax, rubber, or glass.

The wires which carry the current into and out of the electrolytes are termed the *electrodes.* The electrode which carries the positive (+) current into the electrolyte is called the *anode,* while the one carrying the negative (—) current is the *cathode.* The products of electrolytic decomposition, known as *ions,* appear at the electrodes, and those attracted to the anode are called *anions,* while those appearing at the cathode are the *cations.* These ions at the instant of their liberation consist either of elementary atoms or atomic complexes (radicles) electrically charged; thus $\overset{+}{\mathrm{Na}}$ (or $\dot{\mathrm{Na}}$) is a univalent positive sodium ion, $\overset{-}{\mathrm{Cl}}$ (or Cl′) a negative chlorine ion, $\overset{=}{\mathrm{SO_4}}$ (or $\mathrm{SO_4}''$) a negative bivalent sulphate ion. The plus signs or dots indicate positive ions and the relative electric charge, or valence, while the minus signs or dashes corresponding negative ionization.[†] Upon subjecting various compounds (either in solution or fused state) to the action of the galvanic current, the ions of the electrolyte move towards the electrodes, the *metallic elements* being attracted to the cathode and are therefore *electro-positive,* while the *non-metallic elements* (as O, S, I, Cl, etc.), as well as their complexes (as $\overset{=}{\mathrm{SO_4}}$, $\overset{-}{\mathrm{NO_3}}$, $\overset{-}{\mathrm{OH}}$, etc.), pass to the anode and are *electro-negative.* The liberated elementary ions (atoms or radicles), as soon as they have lost their electrical charges, immediately unite to form molecules or react with the solvent or the electrodes (page 141).

When pure, water resists the electrolytic action of the strongest currents; however, when slightly acidulated with sulphuric or hydrochloric acid, resistance is reduced and decomposition takes place readily. Since water is employed as the solvent in solutions of chemicals, their electrolysis involves the simultaneous decomposition of the water. This important factor must not be overlooked.

If very dilute hydrochloric acid be electrolyzed, hydrogen collects

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[*] The substance to be electrolyzed must be in a liquid condition, obtained either by solution or by liquefaction. It must be a conductor and a compound.

[†] Bivalent ions carry twice, tervalent ions thrice the charges of the mono-valent ions.

at the cathode, and no chlorine appears at the anode, but in its stead an equivalent amount of oxygen. This is due to the fact that the water is decomposed by the chlorine with formation of hydrogen chloride and oxygen which is liberated at the anode. Such reactions as take place between the products of electrolysis, or by them upon the solvent, are known as *secondary* reactions.

Examples:

(1) The electrolysis of water acidulated with hydrogen chloride or hydrogen sulphate:

(*a*) $4HCl = 2\overset{+}{H_2}$ (cathode) $+ 2\overset{-}{Cl_2}$.

(*b*) $2Cl_2 + 2H_2O = 4HCl + \overset{=}{O_2}$ (anode).

(*a*) $2H_2SO_4 = 2\overset{+}{H_2}$ (cathode) $+ 2\overset{=}{SO_4}$.

(*b*) $2SO_4 + 2H_2O = 2H_2SO_4 + \overset{=}{O_2}$ (anode).

(2) In the electrolysis of a solution of potassium sulphate, the liberated potassium cations $(\overset{+}{K})$ react with the water to form potassium hydroxide, while the $(\overset{=}{SO_4})$ anions, reacting with the latter, liberate hydroxyl $(\overset{-}{OH})$ ions, which break up into water and oxygen. So the final products of electrolysis of this salt would be hydrogen and oxygen.

(*a*) $K_2SO_4 = \overset{+}{K_2} + \overset{=}{SO_4}$.

(*b*) $\overset{+}{K_2} + 2H_2O = 2KOH + \overset{+}{H_2}$ (cathode).

(*c*) $\overset{=}{SO_4} + 2KOH = K_2SO_4 + 2(OH)$.

(*d*) $2(OH) = H_2O + \overset{=}{O}$ (anode).

For further treatment of this subject see page 725.

Electrolytic Dissociation or Ionization.—As already stated, pure water* and solid electrolytes do not conduct the electric current, but if the latter are dissolved in the former, then the water becomes a ready conductor. The fact that exceedingly weak electric currents decompose stable electrolytes, when dissolved in water, suggested the theory (of Arrhenius) that the molecules of acids, bases, and salts are already largely dissociated into their ions (atoms or radicles) through the influence of the solvent, and that some of these ions (the metals) are charged with positive and others (the non-metals as well as their radicles) with negative electricity. The current does not decompose the dissolved electrolyte, but simply causes the cations and anions which are already present and carry electric charges of opposite kinds to drift in opposite directions towards their respective electrodes—that is, the charged atoms migrate from pole to pole, the negative charged cations being repelled from the negative and attracted

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* In addition, such solvents as chloroform, alcohol, and ether, which do not respond to the usual chemical reagents.

by the positive electrode, while the positive charged anions are repelled by the anode and attracted by the cathode. Thus, when we dissolve sodium chloride ($NaCl$) in water, part of this salt will remain undissociated as ordinary molecules, while the greater proportion splits up into sodium ($\overset{+}{Na}$) cations and chlorine ($\overset{-}{Cl}$) anions; in a like manner, sulphuric acid into hydrogen ($\overset{+}{H}$) cations and sulphion ($\overset{=}{SO_4}$) anions; and potassium hydroxide into potassium ($\overset{+}{K}$) cations and hydroxyl ($\overset{-}{OH}$) anions. The undissociated molecules do not conduct the current. Since these ions are electrically charged, they remain invisible and exist in water without acting on the same. A normal sodium atom decomposes water instantly, while the charged sodium ions (atoms) are indifferent until they have given up their positive charge at the cathode, when they at once assume their normal state. The electro-negatively charged chlorine ion is colorless, odorless, and does not bleach; however, as soon as it has given up its charge at the anode it assumes its yellowish-green color, odor, and bleaches. Another method of ion formation is shown by dipping a rod of iron or zinc into a solution of copper sulphate; the copper which is present in solution as positive ions gives up its charge to the zinc or iron atoms, converting them into ions, while the copper passes over into neutral atoms. Thus:

$$\overset{++}{Cu} + \overset{=}{SO_4} + Zn\ (\text{or } Fe) = \overset{++}{Zn}\ (\text{or } \overset{++}{Fe}) + \overset{-}{SO_4} + Cu.$$

Electrolytic dissociation differs from *thermal* dissociation in that compounds under the latter class split up into molecules capable of separate existence ($NH_4Cl + \text{heat} = NH_3 + HCl$), while those under the former break up into atoms or atomic groups (ions), electrically charged and known only in solution. ($NH_4Cl = NH_4$ cations + Cl anions.)

The products of thermal dissociation reunite upon lowering the temperature, while those of electrolytic dissociation remain in this state so long as they are in solution. There is no complete recombination of the oppositely charged ions, unless the solvent be removed, owing to their relatively great separation from one another through the molecules of water which act as insulating agents. The degree of dissociation, as determined by electrical conductivity, increases with the dilution of the solution of the chemical.* An increase in the percentage dissociation and consequent electrical conductivity of an

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* Kohlrausch found the following numbers for sodium chloride:

Concentration, 58.5 Grams in	Molecular Conductivity.	Relative Number of Ions per 100 Molecules of Salt
1 liter	69.5	67.5
10 liters	86.5	84.1
100 liters	96.2	93.5
1000 liters	100.8	98.0
10000 liters	102.9	100.0

electrolyte indicates greater chemical activity; also different ions vary in the relative intensity of their electro-affinity, constituting active and weaker ions; the former dissociate more completely and yield very soluble compounds, while the latter yield less soluble and poorly dissociated ones. Such acids as nitric, hydrochloric, hydrobromic, hydriodic, chloric, iodic, permanganic, etc., undergo extensive dissociation in dilute aqueous solution. Hydrofluoric acid dissociates far less, while nitrous, hydrocyanic, boric, acetic, and most organic acids dissociate very slightly. The polybasic acids dissociate less than the monobasic.

Sulphuric acid dissociates in two stages—

$$(a)\quad H_2SO_4 \rightleftarrows \overset{+}{H} + \overset{-}{HSO_4}$$

$$(b)\quad \overset{-}{HSO_4} \rightleftarrows \overset{+}{H} + \overset{=}{SO_4}$$

in very dilute solutions chiefly according to (*b*), while in the more concentrated according to (*a*). Phosphoric acid dissociates in three stages, and, like sulphuric, with different kinds of anions—

$$(a)\quad H_3PO_4 \rightleftarrows \overset{+}{H} + \overset{-}{H_2PO_4}.$$

$$(b)\quad \overset{-}{H_2PO_4} \rightleftarrows \overset{+}{H} + \overset{=}{HPO_4}.$$

$$(c)\quad \overset{-}{HPO_4} \rightleftarrows \overset{+}{H} + \overset{\equiv}{PO_4}.$$

The hydroxides of the alkali metals dissociate extensively in aqueous solution, while the hydroxides of the alkaline earths, as barium, strontium, and calcium, dissociate to a much lesser degree. Ammonium hydroxide dissociates only slightly, hence is a weak base.

The properties of hydrochloric acid represent those of its ions, namely, hydrogen and chlorine ions; those of solutions of sodium hydroxide depend on its hydroxyl and sodium ions. Hence the reactions of electrolytes in general are those of their ions. Since ions are exceedingly reactive compared to non-ionized molecules, then the greater the degrees of dissociation of acids and bases in solution the greater will be their reactive ability; that is, their relative strength. The stronger the acid or base, the greater its degree of dissociation.*

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* The relative strength or affinity (reactive ability) of various acids and bases, based on degree of ionization, has been tabulated by Kohlrausch as follows:

Nitric Acid	100	Sulphuric Acid	49
Hydrochloric Acid	100	Phosphoric Acid	25
Hydrobromic Acid	89	Tartaric Acid	5
Hydriodic Acid	70	Acetic Acid	3
		Boric Acid	1

Lithium Hydroxide	100
Sodium Hydroxide	98
Potassium Hydroxide	98
Ammonium Hydroxide	2

The wet reactions of analytic chemistry are the result of electrolytic dissociation and the consequent interchange between the various ions. Thus the neutralization of hydrochloric acid by sodium hydroxide, which is usually expressed by the equation:

$$NaOH + HCl = NaCl + H_2O$$

is, according, to the ionic theory, written as follows:

$$\overset{+}{Na} + \overset{-}{OH} + \overset{+}{H} + \overset{-}{Cl} = \overset{+}{Na} + \overset{-}{Cl} + H_2O.$$

Further, interaction between solutions of sodium chloride and silver nitrate proceeds thus:

$$\underbrace{\overset{+}{Na} + \overset{-}{Cl}}_{} + \underbrace{\overset{+}{Ag} + \overset{-}{NO_3}}_{} = AgCl + \overset{+}{Na} + \overset{-}{NO_3}.$$

Owing to the insolubility of the compound, silver chloride, precipitation takes place; therefore all silver compounds which contain a silver ion are detected through the addition of a salt containing a chlorine ion, or the reverse. Most organic compounds which contain halogen ions do not ionize in water, hence these elements cannot be detected by the addition of silver nitrate. Some organic solvents possess this ionizing power to a certain extent—for example, formic acid to 75 per cent., methyl alcohol to 38 per cent., and grain alcohol 25 per cent. that of water.

Ionization explains why we cannot detect the presence of chlorine in chlorates, or in the complex salt Na_2PtCl_6 (sodium hydrochlorplatinate), for the former ionizes into the complex anions ClO_3 and the latter into the anions $PtCl_6$ and cations Na_2, which do *not* form insoluble salts with silver. The dissociation of the double salt sodium magnesium sulphate takes place as follows:

$$Na_2SO_4.MgSO_4 \rightleftarrows 2\overset{+}{Na} + \overset{++}{Mg} + 2\overset{=}{SO_4}.$$

Electrolytic dissociation also explains why such poisonous cations as Cu, Ag, and Hg become less so or even non-toxic when combined with various more or less complex anions; thus, mercuric bromide ($HgBr_2$) is less active than the chloride ($HgCl_2$), and the cyanide [$Hg(CN)_2$] is worthless as an antiseptic. Potassium cyanide (KCN) is a powerful poison because of the presence of the very toxic cyanogen (CN) ion, while the anion ($Fe(CN)_6$) from potassium ferrocyanide [$K_4Fe(CN)_6$] is non-toxic.

Laws Governing Chemical Combination

A study of the phenomena of chemical action demonstrates that chemical combination invariably takes place in conformity with certain laws, all of which are based on the fundamental principle of the indestructibility of matter—that is, the sum total of matter resulting from a reaction is invariably equal to the sum of the weights of all substances entering into such (see page 114).

Law of Definite (Constant) Composition.—This law was demonstrated and proven by Proust during the period 1802–1807. *The elements* *combine with one another in definite and unalterable proportions by weight.* It is immaterial by what method prepared, the composition of a chemical compound is invariably the same—that is, it is made up of the same elements in the same relative proportions by weight.

For example, if we mix sulphur and iron irregardless of proportions, we will find that after chemical union has taken place a portion of either the one or the other will remain uncombined, but if they be mixed in the proportion of their atomic weights, namely, 55.84 parts of iron and 32.07 parts of sulphur, we will find that the combination is perfect, neither iron nor sulphur remaining. Water, regardless of origin, consists invariably of 1.008 parts of hydrogen and 7.943 ($\frac{16}{2.016}$) parts of oxygen, ammonia of 1.008 parts of hydrogen and 4.63+ ($\frac{14.01}{3.024}$) parts of nitrogen, etc.

Laws of Combining Weights.—*The elements combine with one another in the ratios of simple multiples of their combining weights.* By the *combining weight* or equivalent of an element we mean the number of parts by weight of the element that combines with 8 parts by weight of oxygen * or 1.008 parts by weight of hydrogen (page 121).

If 1.008 parts of hydrogen combine with 8 of oxygen to form water, the combining weight of hydrogen is 1.008. If 35.46 parts of chlorine, 79.92 parts of bromine, and 126.92 parts of iodine combine with 1.008 parts of hydrogen, these figures represent the combining weights of their respective elements. Also they are equal or equivalent to one another. In iodine monochloride the ratio of the elements to one another is as 126.92 to 35.46. Further, 35.46 parts of chlorine combine with 23 parts of sodium, 39.10 parts of potassium, 20.035 ($\frac{40.07}{2}$) of calcium, 12.16 parts of magnesium ($\frac{24.32}{2}$), 69.33+ parts of bismuth ($\frac{208}{3}$) and 48.8 parts of platinum ($\frac{195.2}{4}$). If a zinc rod be placed into a solution of copper sulphate, for each 32.685 parts of zinc which dissolve, 31.785 parts of copper separate.

Frequently two elements combine in several ratios; thus 8 parts by weight of oxygen combine with 1.008 parts by weight of hydrogen to form water (H_2O); also 2 × 8 parts of oxygen combine with 1.008 parts of hydrogen to form hydrogen peroxide (H_2O_2).

Dalton, in applying his atomic theory in the study of the compounds of olefine (C_2H_4) and marsh gases (CH_4), found that the former contained twice as much hydrogen to a definite weight of carbon as the latter. Also he found similar ratios of oxygen to carbon in carbon monoxide (CO) and carbon dioxide (CO_2). These observations were later confirmed by Berzelius and others, and finally accepted in the

Law of Multiple Proportions.—*When two elements unite in several different proportions by weight, the higher proportions are invariably simple multiples of the lowest.*

As instances of the application of this law the following examples are cited:

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* This value of 8 for oxygen, which is a dyad, is one-half of its atomic weight (16). Since 2 H atoms are required for one O, then $H = \frac{O}{2}$.

Carbon forms *two* compounds with oxygen; the combining proportions are parts by weight:

	Carbon.	Oxygen.	
Carbon Mon-oxide	12 parts,	16 parts	$= 16 \times 1 =$ CO.
Carbon Di-oxide	12 parts,	32 parts	$= 16 \times 2 = CO_2$.

Oxygen forms *five* compounds with nitrogen according to the following proportions by weight: *

	Nitrogen.	Oxygen.	
Nitrous Oxide	28 parts,	16 parts	$= 16 \times 1 = N_2O$.
Nitric Oxide	28 parts,	32 parts	$= 16 \times 2 = N_2O_2$.
Nitrogen Tri-oxide	28 parts,	48 parts	$= 16 \times 3 = N_2O_3$.
Nitrogen Tetr-oxide ...	28 parts,	64 parts	$= 16 \times 4 = N_2O_4$.
Nitrogen Pent-oxide ...	28 parts,	80 parts	$= 16 \times 5 = N_2O_5$.

It must be distinctly understood that only *whole* atoms, and not fractions, can combine. Thus, no compound can be formed from 28 parts of nitrogen and 24 parts ($16 \times 1\frac{1}{2}$) of oxygen. Any quantities above or below the given whole multiples do not combine, but remain as free oxygen or nitrogen.

Laws of Combination by Volume.—While studying the synthesis of water from hydrogen and oxygen, Gay-Lussac and Humboldt (1805) noted that the volumes of these gases combining were in the ratio of two of hydrogen to one of oxygen. Continuing this study to other gases, Gay-Lussac established in 1808 the following laws:

1. *The ratio in which gases combine by volume is always a simple one, the temperature and pressure remaining the same.*
2. *The volume of the gaseous product obtained in a combination bears a simple ratio to the volumes of its constituents.*

When this law was proposed, there was much uncertainty as to the number of atoms in equal volumes of gases, since the molecular theory as now understood had not been formulated. It was considered that since all gases deport themselves exactly alike under the same conditions of temperature and pressure, they would contain the same number of atoms. However, the synthesis of water presented difficulties in that 3 volumes of hydrogen and oxygen gave 2 volumes of steam, hence the number of atoms per unit volume could not be the same for steam as for the uncombined elements.

According to this law, *one* volume of hydrogen unites with *one* volume of chlorine to form two volumes of hydrogen chloride; *two* volumes of hydrogen unite with *one* volume of oxygen to form *two* volumes of steam; *three* volumes of hydrogen with *one* volume of nitrogen form *two* volumes of ammonia gas. If, for example, as formerly assumed, 1000 atoms are present in a given volume of hydrogen, then an equal volume of chlorine would likewise contain 1000 atoms, and, through their union, 1000 particles of hydrogen chloride, occupying the same volume as the two gases, would result, because experiment had shown that equal volumes of the two gases united without any change in volume. If this were the case, it would then follow that one volume of hydrogen chloride would contain half as many atoms as the same volume of the simple gases.

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* The atomic weight of nitrogen has been rounded off for the sake of convenience.

This contradiction of facts and the law formulated by Gay-Lussac (1808) was later reconciled by Avogadro (1811), who proposed that a distinction be made between *atoms* (indivisible particles) and *molecules* (molecula = mass particles), and that gases should be considered to consist of molecules, which are the smallest constituent particles, and these in turn being made up of atoms.

Avogadro's Hypothesis.—*Equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.*

Although Dalton's conception of an atom was an indivisible ultimate particle of matter, yet this term, up to his time, was applied indiscriminately to compound atoms, now known as molecules, as, for instance, atoms of water, ammonia, or carbon dioxide. Hence Gay-Lussac, in studying the combination of gases by volume, was unable to apply Dalton's atomic theory (see preceding law). This difficulty was overcome by Avogadro in 1811, who proposed the existence of two kinds of ultimate particles of matter, namely—

(a) *Molecules,* which are the physical units of subdivision, or the smallest masses of matter which are capable of existing in the free state.

(b) *Atoms,* the ultimate particles which make up the composition of molecules.

According to Avogadro, the union that takes place between like volumes of chlorine and hydrogen or other reacting gases must not be considered in the sense of atoms reacting with atoms producing atoms, but an exchange of atoms between molecules producing molecules. Thus, for example, one volume of hydrogen, containing 1000 molecules, unites with an equal volume of chlorine, which also must contain 1000 molecules to form two volumes of hydrogen chloride containing 2000 molecules. Since each molecule of hydrogen chloride is halved, that is, made up of one atom of chlorine and one of hydrogen, then in the two volumes containing 2000 molecules, there must be 2000 atoms of chlorine and 2000 atoms of hydrogen.

$$\underset{\text{1 volume.}}{\boxed{\begin{matrix}1000\\ H_2\end{matrix}}} + \underset{\text{1 volume.}}{\boxed{\begin{matrix}1000\\ Cl_2\end{matrix}}} = \underset{\text{2 volumes.}}{\boxed{\begin{matrix}1000\\ HCl\end{matrix}\Big|\begin{matrix}1000\\ HCl\end{matrix}}}$$

In a like manner, one molecule of oxygen splits up into two atoms, each of which unites with two atoms of hydrogen to form one molecule of steam.

$$\underset{\text{1 volume.}}{\boxed{nH_2}} + \underset{\text{1 volume.}}{\boxed{nH_2}} + \underset{\text{1 volume.}}{\boxed{nO_2}} = \underset{\text{2 volumes.}}{\boxed{nH_2O \,\big|\, nH_2O}}$$

In the case of ammonia, each single atom of the molecule of nitrogen unites with three atoms of hydrogen to form one molecule of ammonia gas.

$$\underset{\text{1 volume.}}{\boxed{nH_2}} + \underset{\text{1 volume.}}{\boxed{nH_2}} + \underset{\text{1 volume.}}{\boxed{nH_2}} + \underset{\text{1 volume.}}{\boxed{nN_2}} = \underset{\text{2 volumes.}}{\boxed{nNH_3 \,\big|\, nNH_3}}$$

This hypothesis of Avogadro forms the basis of our system of atomic and molecular weights in that it enables us to determine (*a*) the relative weight of gaseous molecules, that is *molecular weights,* and (*b*) to determine the number of atoms in the molecules from which *atomic weights* are calculated.

Relation of Density to Molecular and Atomic Weight.—From the preceding we may summarize as follows:

1. Matter is made up of exceedingly minute discrete particles called *molecules,* which in turn consist of still smaller parts called *atoms.*
2. Like atoms unite to form *simple* or *elemental* molecules, while unlike ones form *compound* molecules.

If, according to the laws of definite and multiple proportions, the different proportions by weight in which elements combine represent the relative weights of their atoms or multiples of these, and these same elements also combine in definite and simple proportions by volume (Gay-Lussac), then

3. The gas densities must bear the same ratio to one another as their molecular weights (Avogadro's hypothesis); that is, the molecular weights of the gases are proportional to their relative densities. When the density of oxygen is taken as 16 (as unit), the densities of steam and of hydrochloric acid gas would be 9.008 and 18.234 respectively. If we now determine the number of atoms in the molecule, the atomic weights can be readily fixed. Taking the synthesis of hydrogen chloride; by means of density determinations we ascertain the relative molecular weights of various compounds of hydrogen, and, after analysis, calculate the quantity of hydrogen in each molecular weight. It has been found that this is never less than ½ of the molecule of hydrogen (H_2). That is, an atom of hydrogen represents ½ of its molecular weight, hence ½ of the molecular weight, or the density of the element, is equivalent to its atomic weight.

It should be distinctly understood that atomic weights represent *relative* values only, being referred to an arbitrary standard. Formerly hydrogen was employed as the unit for comparison, its atomic weight being represented as 1.000, its molecular weight must then be $H_2 = 2$. If the density of any other gas is y, then the molecular weight of this gas must be $2y$. The molecular weights of compound molecules are obtained by adding together the weights of the constituent atoms. That of hydrogen chloride (HCl) would be $1.008 + 35.46 = 36.468$. Since gas densities of elements, when compared to $H = 1.000$, are equal to their atomic weights, those of compound bodies would be *one-half* of their molecular weight; that of hydrogen chloride would be 18.234 $(\frac{36.468}{2})$.

Since about 1895 it was decided by an International Committee on Atomic Weights to drop the $H = 1.000$ standard and replace this by the standard **Oxygen** $= 16$. The chief practical advantage of this is that there are more compounds of the elements with oxygen than hydrogen, also the atomic weights of most of the more common elements are represented by whole numbers, a useful factor in calculating chemical equations.

With the fixing of the atomic weight of oxygen at 16 as standard in determining atomic weights of the elements, its molecular weight would be $O_2 = 32$. If the density (specific gravity) of a gas based on $O = 16$ is accepted as a, its molecular weight would be $2a$, because that of oxygen is 2×16 (density) $= 32$ (see p. 25).

Hence, to determine the molecular weights of gases, their vapor densities are ascertained compared to oxygen = 16, *and the factors obtained are multiplied by* 2. For example:

Substance.	Vapor Density. $O = 16$	Molecular Weight.
Oxygen	16	32
Water (H_2O)	9.008	18.016
Hydrogen Sulphide (H_2S)	17.043	34.086
Sulphur Dioxide (SO_2)	32.035	64.07
Carbon Monoxide (CO)	14.00	28.00
Carbon Dioxide (CO_2)	22.00	44

The number of atoms contained in the molecule of an element is dependent upon temperature. At lower temperatures the molecules of many elements in the gaseous state are more or less complex, while at higher temperatures they dissociate into simpler ones. For example, in the gaseous state sulphur has a density ($O = 16$) varying from 192 (at 500°) to 32.3 (at 860°), indicating that at the lower temperature its vapor consists of S_8 molecules and at 860° and above only of S_2 molecules. Above 1800° the S_2 molecules begin to dissociate into atoms. The diatomic molecules of Cl_2, Br_2, I_2 dissociate gradually into monatomic molecules with rise in temperature.

Oxygen, nitrogen, and hydrogen consist of diatomic molecules at the highest temperatures. The elements potassium, sodium, zinc, cadmium, mercury, helium, argon, and neon are all monatomic—that is, the molecular and atomic weights are identical. The densities of phosphorus and arsenic indicate the presence of complex molecules; at 313° phosphorus is P_4, while at 1700° there is a large percentage of P_2 molecules present. Arsenic at 644° is equivalent to As_4, while at 1700° the molecules are almost all As_2.

Determination of Molecular and Atomic Weights.—Since, according to Avogadro's hypothesis, molecular weights of gases are proportional to their relative densities, and these are based on the standard of $O = 16$, then to determine the molecular weight of a gaseous substance, *multiply its vapor density by* 2; *the product is the molecular weight.* In determining **atomic weights** we ascertain the quantity of the element contained in the molecule. In such cases where the substances (as H, O, N, CO, CO_2, CH_4, etc.) are gaseous at ordinary temperature the molecular weights can be determined with great accuracy. Liquid and solid substances must be vaporized, and since the gases at high temperatures do not strictly conform to the gas laws, the results are only approximate.

Vapor Densities.—For the exact determination of the density of substances gaseous at ordinary temperature, the method of Regnault may be employed. This consists in filling a glass globe of known capacity, which has been cleaned, dried, and tared, with the gas. The weight of this gas is then determined at 0° and 760 mm. and compared with a like volume of oxygen under the same conditions, or, since 32 gm. of oxygen (O_2) (or the molecular weight of any gas expressed in gms.) occupy at 0° and 760 mm. a volume of 22,400 mils, the molecular weight of another gas will be the weight of 22,400 mils at 0° and 760 mm.*

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* Since 1 liter of oxygen at 0° and 760 mm. weighs 1.4291 gm., the volume (V) of 1 gm. molecule would be $V = \frac{32}{.0014291} = 22{,}400$ mils (22.4 liters).

To determine the vapor density of solids or liquids which can be vaporized without decomposition or dissociation, the method of Victor Meyer (page 508) is usually employed.

Molecular Weights of Non-Volatile Substances in Solution.—These methods are based on the influence exerted by the molecules of the dissolved substance on the physical properties of the solvent.

(*a*) *Lowering the Freezing* (congealing) *Point,* or *Cryoscopic Method* (see page 509).—Through the depression of the congealing point exerted by a dissolved substance upon certain solvents, we obtain figures which closely approximate their molecular weights; the general law being, when molecular quantities of different substances are dissolved in the same amount of solvent, they lower the freezing point of the solvent to the same extent.

(*b*) *Elevation of the Boiling Point of Solutions,* or *Ebullioscopic Method* (see page 510).—The elevation of the boiling point of certain solvents produced by the addition of a weighed quantity of a soluble substance has a fixed relation to its molecular weight which can be readily calculated. If X gm. of a substance be dissolved in 100 gm. of a solvent, the boiling point of the solution will be t° higher than that of the pure solvent.

(*c*) *Specific or Molecular Heat* (see Law of Dulong and Petit). Since the molecular heat of a compound is equal to the sum of the atomic heats of its constituent elements, we have a ready means of determining the atomic heats of such elements which cannot be determined in the vaporized state.

To determine the atomic weight of an element we analyze or synthesize several of its compounds, which must be absolutely pure—that is, free from all foreign elements not belonging to the compound. For this purpose we usually select some compound of the element with either oxygen, chlorine, or silver. Since the ratio of the atomic weights of these is accurately known, the ratio of the value sought to O = 16 can be readily obtained through these compounds. With the knowledge of the exact per cent. of each of the elements present, the smallest quantity of the element in question will represent its equivalent or its atomic weight. The atomic weights can either be the equivalent weights of the elements or multiples of them. In order that we may ascertain whether the figures obtained represent the equivalent or atomic weights, the specific heat or the vapor density of the elements are determined. The figures obtained closely approximate the true atomic weight. In addition, a knowledge of the molecular weight of a compound of the element in question affords us a direct means for confirming the above.

Examples:

(*a*) In the analysis of uranium oxide (UO_3) the equivalent or combining weight of uranium was found to be 39.75. Its valency was found to be 6, from $(\overset{VI}{U}\overset{II}{O}_3)$, hence its atomic weight would be $39.75 \times 6 = 238.5$. This latter figure was further confirmed by determining the specific heat of uranium, which was found to be 0.027. According to the law of Dulong and Petit (page 47), the approximate atomic weight would be $\frac{6.4 \text{ (atomic heat factor)}}{0.027 \text{ (specific heat)}} = 237+$; hence the atomic weight of 238.5 has been accepted.

(*b*) Hydrogen chloride when subjected to electrolysis yields equal volumes of hydrogen and chlorine. When equal volumes of these two gases are caused to unite, two volumes of hydrogen chloride are formed; nothing else remains. The vapor density of hydrogen chloride has been found to be 18.234 (O = 16); its molecular weight would then be $18.234 \times 2 = 36.468$. The analysis of compounds obtained by replacing the hydrogen of hydrogen chloride with such monad elements as Na or K (NaCl, KCl) show further that only *one* atom of hydrogen is combined with the one chlorine. Knowing the molecular weight of the compound to be 36.468 and that one atom of hydrogen is present, then 36.468 − 1.008 (H) = 35.46, the combining (atomic) weight of chlorine. In this instance the combining and atomic weights are the same. If hydrogen chloride contains 2.7646 per cent. of hydrogen and 97.2354 per cent. of chlorine and but one atom of each is present, then the ratio of the combining weights would be as 1.008 to 35.46 (2.7646 : 97.2354 : : 1.008 : X). In a like manner, it has been found that 79.92 parts of bromine or 126.92 parts of iodine combine with 1.008 parts of hydrogen or 23 parts of sodium or 39.10 parts of potassium. Since these are compounds of but two elements in the ratio of but one atom of each, then the combining weights obtained would represent their relative atomic weights.

(*c*) Sulphur forms with hydrogen the compound hydrogen sulphide, of which 94.1 per cent. consists of sulphur and 5.9 per cent. of hydrogen. The combining ratio of the two is 1 to 15.907. The vapor density of this compound is 17.043 (O = 16), hence its molecular weight would be $17.043 \times 2 = 34.086$. If this compound consists of one atom each of hydrogen and sulphur, then the equivalent and atomic weights of sulphur would be the same, namely, $\frac{94.1}{5.9} = 15.9$. This is impossible, because the molecular weight is 34.086. If the compound consists of two atoms of hydrogen, then the atomic weight of sulphur would be approximately $\frac{94.1 \times 2}{5.9} = 32$, which corresponds to the formula $H_2S\,(2.016 + 32.07) = 34.086$. Analysis of other gaseous compounds of sulphur has demonstrated, through their molecular weights, that they contain not less than 32.07 parts of sulphur to each 1.008 parts of hydrogen, or its equivalent in another element.

The Colloidal State

Introductory.—If hydrogen sulphide be passed into an aqueous solution of arsenous oxide, a yellow-colored solution containing arsenous sulphide is obtained, from which the precipitate cannot be removed by simple filtration. If, however, this solution be first acidified by hydrochloric acid, then the arsenous sulphide separates as a yellow precipitate. The yellow color of the former solution is due to a suspension of the sulphide in an extremely fine state of subdivision or colloidal state.

If hydrochloric acid be poured into a solution of sodium silicate (water-glass) the silicic acid precipitates as a gelatinous mass. If the order of mixing be reversed by pouring a dilute solution of the silicate into an excess of the acid, the silicic acid liberated remains in solution. Graham found that by suspending this solution, contained in a bladder or dialyzer, in a vessel of water, the sodium chloride diffused through, leaving the silicic acid behind, thus proving that the latter was not an ordinary aqueous solution. The sodium chloride which diffused through, like all other crystalline bodies, he termed a *crystalloid*, while the silicic acid, which did not diffuse, was classed as a *colloid*. A colloidal solution is termed a *sol;* with water as the dispersive medium, the solution is designated as a *hydrosol*, with glycerol as a *glycerosol*. It was formerly considered that this colloidal state was peculiar to certain nondiffusible bodies, as glue and albumin. It has since been found that so many substances (not necessarily crystalline) can be prepared in the colloidal state that this is now regarded as a general property of matter. The colloidal state represents a suspension of particles of exceedingly fine but variable state of subdivision in media such as water, alcohol, glycerol, or even glass. These particles may be seen and their size determined by means of the ultra-microscope. This is carried out by a transverse illumination of the suspension, placed under the microscope, by means of a horizontal beam of light, so that the eye of the observer is not blinded. The smallest colloidal particle that can be detected under these conditions has a diameter of 4×10^{-6} mm. In a colloidal solution of gold, numerous minute brilliant particles of red, yellow, and green colors may be seen, which, like all other colloidal particles, are in a constant state of zig-zag motion known as the Brownian movement. If this motion be arrested, for example, by the addition of ions carrying a charge opposite to that of the colloid, precipitation ensues. That is, hydrosols carrying opposite electric charges precipitate each other; for example, on adding a colloidal solution of gold to one of stannic acid, a precipitate of metallic gold (purple of Cassius) takes place.

Organic colloids, contrasted to the inorganic, resemble true solutions and are usually free from electric charges and only precipitate through the addition of an excess of electrolytes. Organic colloids give viscid solutions with water and are convertible into a jelly (*Gel*) like gelatin, which is not the case with the inorganic colloids.

Colloids may be classed as *reversible* and *irreversible*. Organic colloids, like gelatin, agar, albumin, and starch, give colloidal solutions on simple contact with water, also colloidal silver (silver nitrate reduced with ferrous sulphate in presence of sodium citrate), dissolves readily in water even after it has been precipitated by means of a solution of ammonium nitrate. Such are known as *reversible* colloids. Emulsions which are permanent suspensions of fats or oils in water, like milk, may be classed in this group. Most inorganic colloids are *irreversible,* because they cannot, after precipitation from solution, be again converted into colloidal solution unless the entire process of preparation be repeated.

Protective Colloids.—The stability of inorganic colloids, as colloidal silver, mercurous chloride, mercuric oxide, etc., may be increased by the addition ot gelatin or proteins; that of graphite by means of tannin.

Of pharmaceutic importance the following colloidal solutions may be cited: Sulphur, phosphorus, mercury, silver, gold, arsenous oxide, aluminum, bismuth, iron and silver hydroxides, the halogen salts of the alkalies, mercurous chloride, sulphate and phosphate of barium.

Preparation of Colloidal Solutions:

Metals.—(*a*) Very dilute solutions of the salts of the metals are treated with reducing agents such as formaldehyde, hydroxylamine, tannin, stannous chloride, ferrous sulphate, etc. If desired in a stable form, the precipitation is made in presence of a protective colloid.

(*b*) By the dispersion of metals under water, using poles of the metal as electrodes with a 110 volt circuit. When the terminals are brought sufficiently near one another to form an arc, minute particles of the metal of the cathode are ejected, forming a colored hydrosol.

Hydroxides and Salts of Metals.—These may be prepared by interaction between a dilute solution of a salt of the metal and an alkali hydroxide or salt in presence of a protective colloid. Example, silver and mercurous chloride, mercuric oxide, bismuth hydroxide, and barium sulphate. The colloidal halogen salts of the alkalies are prepared by interaction in the presence of organic solvents. For example, colloidal potassium bromide is obtained by interaction between ethyl-bromo-acetate and potassium ethyl-malonate.

Ordinary colloids can be separated from their suspensions by filtration through a Bechhold clay filter or by dialysis. Colloidal forms of sodium chloride or sucrose require for their separation a membrane of copper ferrocyanide.

The study and development of colloids has been of great importance in not only theoretic but especially industrial chemistry; in the ceramic, glass, cement, dye, brewing, and soap industries, the purification of sewage, as well as in medicine. Colloidal suspensions of metals and their salts are of especial value in modern medicine.

Catalysis

Many chemical reactions are influenced to a marked degree through the presence of a very small quantity of some "foreign substance" which remains of the same chemical composition after the change as before. Such a substance is termed a "catalyzer" or "contact substance." Catalyzers usually consist of very finely subdivided metals, the most useful of which are platinum, nickel, cobalt, copper, iron, manganese, and zinc. With exception of platinum, these are prepared by reducing the oxide of the metal in a current of hydrogen at about 300°, which serves to produce an extremely fine state of subdivision. The catalyzing oxides are ferric, stannic, cupric, vanadic, manganese, zinc, nickelic, nickelous, and cobaltous oxides. The following examples may be cited which illustrate the varied action of catalyzers. In the preparation of oxygen by heating potassium chlorate, if a little manganese dioxide be added, the decomposition is accelerated, proceeding more readily and uniformly at a much lower temperature (200° instead of 400°), while the manganese dioxide remains unchanged.

Finely divided platinum (platinum black, spongy platinum, or platinized asbestos) is a powerful catalyzer in inducing certain chemical syntheses; thus when a current of hydrogen or coal-gas is directed upon platinum black, ignition takes place through the union of either of these gases with the oxygen of the air. The "contact" process for the manufacture of sulphuric acid (see page 230) is based on the property of platinum black or certain very finely divided metals or their oxides in inducing chemical combination of sulphur dioxide and oxygen (from air). A heated mixture of nitrogen and hydrogen, when passed under pressure over platinum sponge (or finely subdivided iron containing traces of uranium, copper, or bismuth, etc.), combines to form ammonia. In these and other reactions a very small quantity of the catalyzer suffices, its activity remaining unimpaired.

In the Deacon process for the manufacture of chlorine, a mixture consisting of 60 per cent. of air and 40 per cent. of hydrochloric acid is passed over heated porous bricks which have been saturated with a copper salt. A small quantity of the latter suffices to bring into reaction almost unlimited volumes of hydrogen chloride and oxygen with liberation of chlorine (and nitrogen). If a small quantity of a solution of a cobalt salt be added to a solution of chlorinated lime, oxygen is given off. This is due to the catalytic action of cobaltous oxide, which undergoes oxidation from CoO to Co_2O_3, the latter yielding oxygen with the chlorinated lime, whereby it is reduced to CoO again. In the preparation of glucose from starch (see page 593), the inversion takes place through the aid of a small quantity of hydrochloric acid added to the mixture of starch and water; the acid remains undiminished at the end of the reaction.

Catalytic Reduction.—The addition of finely divided platinum to hydrogen peroxide causes instantaneous reduction with liberation of oxygen. Some carbon compounds when mixed with platinum black undergo reduction at moderate temperature. Carbon monoxide and dioxide are reduced to methane and water at 200 to 300°. Ethylene and propylene are reduced to their corresponding paraffins. Aromatic hydrocarbons, as benzene, toluene, xylene, and cymene, yield their hexa-hydro-derivatives. Aliphatic nitro compounds yield (at 150 to 180°) amino derivatives.

Catalytic Oxidation.—Most important among these is the oxidation of primary alcohols into aldehydes and hydrogen when their vapors are passed through a tube containing finely divided iron, zinc, copper, or zinc or ferric and stannic oxides. These reactions are reversible in presence of catalysts:

$$\text{Primary alcohol} \rightleftarrows \text{Aldehyde and } H_2$$
$$\text{Secondary alcohol} \rightleftarrows \text{Ketone and } H_2.$$

If the alcohols are heated with hydrogen under pressure in contact with metallic catalysts, hydrocarbons are produced.

The phenomenon of catalysis is known by its results; no general theory of action can as yet be assigned; however, it is assumed that catalysts form transitive intermediate compounds which react with formation of the final products, while the former (catalyst) reverts back to its original composition.

STOCHIOMETRY

Stochiometry, or chemical arithmetic, is based on the fundamental laws of chemistry. Since chemical formulæ and equations are made up of symbols, and these symbols in turn represent atoms which express definite weights of matter, it is simply a question of calculation to ascertain the percentage of each element entering into the composition of a chemical compound, or the quantities of the chemicals necessary for or resulting from a chemical reaction.

Percentage Composition Calculations.—In order to ascertain the percentage of each of the elements present in the molecule of a compound, we first determine its molecular weight, then multiply the atomic weight of each of the elements by the number of atoms present, and this product by 100; this is then divided by the molecular weight of the compound.

Example 1.—Calculate the percentage composition of sulphuric acid, H_2SO_4.

Hydrogen (H_2) = atomic weight 1.008 × 2 = 2.016 molecular weight.
Sulphur (S) = atomic weight 32.07 × 1 = 32.07 molecular weight.
Oxygen (O_4) = atomic weight 16.00 × 4 = 64.00 molecular weight.

98.086

*Hydrogen in 100 parts would be $\frac{2.016 \times 100}{98.086} = 2.055$ per cent.

Sulphur " " " $\frac{32.07 \times 100}{98.086} = 32.696$ " "

Oxygen " " " $\frac{64 \times 100}{98.086} = 65.249$ " "

100.000

Example 2.—Find the percentage of Fe, SO_4, and H_2O in ferrous sulphate ($FeSO_4 + 7H_2O$).

	Atomic or Molecular Wt.			Percentage.
Fe	= 55.84	÷ 278.012	× 100	= 20.086
SO_4	= 96.07	÷ 278.012	× 100	= 34.552
$7H_2O$	= 126.112	÷ 278.012	× 100	= 45.362
	278.022			100.000

Molecular Formula Calculations.—If the composition of a compound expressed in parts by weight of its various elements or groups of elements be given, the relative number of these present are found by dividing the per cent. weights by the atomic or formula weights.

Example 1.—Given the analysis of ferrous sulphate expressed in percentage of Fe, SO_4, and H_2O, what would be its formula? Dividing the given percentages by their respective atomic or molecular weights, we obtain the ratios in which these are present, and from these figures the simplest ratio figures are obtained by dividing by the lowest number.

	Analysis.	Atomic or Molecular Wt.	Ratio.	Simple Ratio.
Fe	= 20.086	÷ 55.84	= 0.3597	= 1
SO_4	= 34.552	÷ 96.07	= 0.3597	= 1
H_2O	= 45.362	÷ 18.016	= 2.5178	= 7

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*This compound is made up of $\frac{2.016}{98.086}$ parts of H, $\frac{32.07}{98.086}$ parts of S, and $\frac{64}{98.086}$ parts of oxygen. In 100 parts we would have as many parts of hydrogen as

$H_2SO_4 : H_2 : : 100 : x$, of oxygen $H_2SO_4 : O_4 : : 100 : x$
$98.086 : 2.016 : : 100 : x$ $\quad 98.086 : 64 : : 100 : x$

$98.086\,x = 2.016 \times 100$ $\quad 98.086\,x = 64 \times 100$
$x = 2.055$ parts. $\quad x = 65.250$ parts.

The ratio of the atoms and groups would then be Fe, SO_4, and $(H_2O)_7$, or $FeSO_4.7H_2O$.

Example 2.—It frequently occurs that fractional numbers are obtained in the simplest ratio. In such a case it is necessary to multiply both by some number which will round off these fractions into their nearest whole numbers. Ascertain the formula for an oxide of iron after following analysis:

	Analysis.	Atomic Wt.	Ratio.	Ratio.	Final Ratio.
Fe	= 72.36	÷ 55.84	= 1.296	= 1.00	= 3
O	= 27.64	÷ 16.00	= 1.72	= 1.33	= 4

Bv multiplying fractional ratios by 3 we obtain 3 and 4 (3.99), hence the formula would be Fe_3O_4.

Example 3.—In many instances the true formula of the compound is a multiple of that calculated from the analysis, which always represents the simplest ratios of the several possible multiples the compound represents, an approximate knowledge of its molecular weight is necessary, and that multiple which yields a figure nearest is selected.

A compound yields upon analysis 39.988 per cent. of carbon, 6.716 per cent. of hydrogen, and 53.296 per cent. of oxygen, and its molecular weight has been found to be about 60, what is its formula?

	Percentage.		Ratio.	Simple Ratio.
C	39.988	÷ 12.00	= 3.33	= 1
H	6.716	÷ 1.00	= 6.71	= 2
O	53.296	÷ 16.00	= 3.33	= 1
	100.00			

The simple formula deduced from this is CH_2O with a molecular weight of 30.00. With the multiples 2 or 3, the molecular weights would be ($C_2H_4O_2$) 60.00 and ($C_3H_6O_3$) 90.00. Selecting the multiple which yields a figure nearest the found molecular weight (60), the formula would then be $C_2H_4O_2$.

Equation Calculations.—This class of calculations embraces the determination of the quantities of the various substances entering into or resulting from a chemical reaction. In such cases it is first necessary to express the complete reaction with the molecular weights of all the substances. Then make the following proportion. *As the molecular weight of the substance given in the equation is to the molecular weight of the substance required, so is the weight of the substance given in the problem to x, the weight of the substance required.* Three terms of the equation being given, the fourth is ascertained by multiplying the two means (second and third terms) and the two extremes (first and fourth), and dividing the product containing the unknown factor (x) into the other product. The first and third terms and the second and fourth must always be of the same denomination.

Problem.—How much chloride of iron (ferrous chloride) can be prepared from 100 grams of iron?

Equation:

$$\begin{array}{ccccccc} \mathrm{Fe} & + & 2\mathrm{HCl} & = & \mathrm{FeCl_2} & + & \mathrm{H_2}. \\ 55.84 & & 72.936 & & 126.76 & & 2.016 \end{array}$$

Statement:

$$\underset{55.84}{\mathrm{Fe}\left(\begin{smallmatrix}\text{subs. given}\\ \text{in equation}\end{smallmatrix}\right)} : \underset{126.76}{\mathrm{FeCl_2}\left(\begin{smallmatrix}\text{subs.}\\ \text{required}\end{smallmatrix}\right)} :: \underset{100}{\mathrm{Fe}\left(\begin{smallmatrix}\text{subs. given}\\ \text{in problem}\end{smallmatrix}\right)} : \underset{x}{\mathrm{FeCl_2}\left(\begin{smallmatrix}\text{weight of}\\ \text{subs. required}\end{smallmatrix}\right)}$$

$$\begin{aligned} 55.84\,x &= 126.76 \times 100 \\ 55.84\,x &= 12676. \\ x &= 227 \text{ grams.} \end{aligned}$$

Therefore, 227+ grams of ferrous chloride can be prepared from 100 grams of iron.

Problem.—How many grams of iron are necessary for the production of 100 grams of ferrous chloride? If, according to the above equation, 55.84 parts of iron are necessary for the production of 126.76 parts of its chloride, then 44.09+ grams of iron would be necessary for the preparation of 100 grams of chloride, for

$$\begin{array}{ccccccc} \mathrm{Fe} & : & \mathrm{FeCl_2} & :: & \mathrm{Fe} & : & \mathrm{FeCl_2} \\ 55.84 & & 126.75 & & x & & 100 \end{array}$$

$$\begin{aligned} 126.76\,x &= 55.84 \times 100 \\ x &= 44.05+ \text{ grams.} \end{aligned}$$

Problem.—How much potassium iodide (U.S.P.) and tartaric acid (U.S.P.) will be required to prepare 1000 gm. of Acidum Hydriodicum Dilutum? The question resolves itself into the preparation of 100 gm. of absolute hydriodic acid. The reaction involved is as follows:

$$\begin{array}{ccccccc} \mathrm{KI} & + & \mathrm{H_2C_4H_4O_6} & = & \mathrm{KHC_4H_4O_6} & + & \mathrm{HI.} \\ 166 & & 150 & & & & 128^{*} \end{array}$$

If 166 gm. of potassium iodide will yield 128 gm. of hydriodic acid, then to prepare 100 gm. of hydriodic acid, 130 gm. of potassium iodide (100 per cent.) will be required, for

$$\begin{array}{ccccccc} \mathrm{KI} & : & \mathrm{HI} & :: & \mathrm{KI} & : & \mathrm{HI} \\ 166 & & 128 & & x & & 100 \end{array}$$

$$\begin{aligned} 128\,x &= 16600 \\ x &= 130 \text{ gm. of KI (of 100 per cent.).} \end{aligned}$$

Since the U.S.P. KI is of but 99 per cent. purity, then 131.3 gm. must be employed in place of 130 gm. of a 100 per cent. salt.

If 150 gm. of tartaric acid are required for interaction with 166 gm. of potassium iodide, then for 130 gm. of the latter 117.4 gm. of tartaric acid (100 per cent.) will be required, for

$$\begin{array}{ccccccc} \mathrm{H_2C_4H_4O_6} & : & \mathrm{KI} & :: & \mathrm{H_2C_4H_4O_6} & : & \mathrm{KI} \\ 150 & : & 166 & :: & x & : & 130 \end{array}$$

$$\begin{aligned} 166\,x &= 150 \times 130 \\ x &= 19500 \\ x &= 117.4 \text{ gm. tartaric acid.} \end{aligned}$$

Since the U.S.P. tartaric acid is of 99.5 per cent. purity, then 117.98 gm. of this is employed in place of 117.4 gm. of a 100 per cent. acid.

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* The molecular weight figures have been slightly rounded.

Therefore for the preparation of 1000 gm. of dilute hydriodic acid (10 per cent.), 131.3 gm. of U.S.P.KI and 117.98 gm. of U.S.P. $H_2C_4H_4O_6$ are necessary.

Problem.—How much sodium chloride will be required to liberate 10 grams of iodine from sodium iodide by aid of manganese dioxide and sulphuric acid?

The reactions involved are as follows:

$$\begin{array}{c} 4NaCl + 4H_2SO_4 = 4NaHSO_4 + 4HCl \\ 4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2 \\ Cl_2 + 2NaI = 2NaCl + I_2 \end{array}$$

According to the above:

$$\begin{array}{rcl} 4NaCl & = & Cl_2 = I_2 \\ 4NaCl & = & I_2 \\ 2NaCl & = & I \\ 2 \times 58.46 & & 126.92 \end{array}$$

Since 126.92 grams of iodine are liberated by 116.92 (2 × 58.46) grams of sodium chloride, then 10 grams of iodine will require $\frac{116.92}{126.92} \times 10 = 9.212+$ grams of sodium chloride.

Problem.—How many liters of hydrogen gas can be obtained by the action of sulphuric acid on 100 grams of zinc?*

Equation:

$$\begin{array}{lcccccccc} & Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2. \\ & 65.37 & & & & & & 2.016 \end{array}$$

$$\begin{array}{lccccccc} \text{If} & & Zn & : & H_2 & :: & Zn & : & H_2 \\ & & 65.37 & & 2.016 & & 100 & & x \end{array}$$

$$65.37\,x = 2.016 \times 100 \qquad x = 3.084 \text{ grams of hydrogen.}$$

The next question that arises is to convert this 3.084 grams of hydrogen gas into volume liters. Since one liter of dry hydrogen at standard temperature (0° C.) and pressure (760 millimeters) weighs 0.89873 gram, 3.084 grams would measure 34.315+ liters, according to the following proportion:

$$\begin{array}{ccccccc} \text{Weight} & : & \text{volume} & :: & \text{weight} & : & \text{volume} \\ 0.089873 \text{ gram} & & 1 \text{ liter} & & 3.084 \text{ grams} & & x \end{array}$$

$$0.89873\,x = 3.084 \times 1$$

$$x = 34.315+ \text{ liters.}$$

Therefore, 100 grams of zinc yield 34.315 liters of hydrogen gas.

Measurement of Gases.—*Calculations involving volume corrections for variations in temperature, pressure, and vapor tension.*

1. EFFECT OF TEMPERATURE ON VOLUME:

According to the law of Charles (page 46), gases increase or decrease $^1/_{273}$ (0.00367) of their volume for each 1° C., or 273 volumes at 0° increase 1 volume for every 1°.

Thus, 273 volumes of a gas at 0° measure at 1° C. 273 + 1 volume.
273 volumes of a gas at 0° measure at 5° C. 273 + 5 volumes.
273 volumes of a gas at 0° measure at t° C. 273 + t volumes.
273 volumes of a gas at 0° measure at T° C. 273 + T volumes.

---

* It is understood that the reaction is carried on in the presence of water.

If v represents any given volume of a gas, and V the new volume resulting from the temperature change from old temperature $t°$ to new temperature T°, then

$$V = \frac{v\,(273 + T°)}{273 + t°}$$

Problem.—What will be the volume of 100 mils of a gas if heated from 10° to 30° C.?

$$V = \frac{100\,(273 + 30)}{273 + 10} = \frac{100 \times 303}{283} = 107.06+ \text{ mils}$$

Therefore 100 mils of a gas at 10° will measure 107.06+ mils at 30° C.

Problem.—What will be the volume at 25° of 44.5 mils of nitrogen dioxide when measured at 32° C.?

$$V = \frac{44.5\,(273 + 25)}{273 + 32} = \frac{44.5 \times 298}{305} = 43.476+ \text{ mils.}$$

Therefore 44.5 mils of NO at 32° C. measure 43.476+ mils at 25° C.

2. Effect of Pressure on Volume:

According to Boyle's law (page 26), the volume of a gas varies inversely as the pressure, hence the volume (v) of a gas multiplied by the pressure (p) upon it is equal to its new volume (V) multiplied by its new pressure (P), —that is,

$$VP = vp \text{ or } V = \frac{vp}{P}$$

Problem.—What would be the volume of 43.48 mils of nitrogen dioxide measured at 590 mm. pressure, calculated to the normal pressure of 760 mm.?

$$VP = \frac{vp}{P}.\ V = \frac{43.48 \times 590}{760} = 33.75 \text{ mils.}$$

Therefore 43.48 c.c. of NO at 590 mm. pressure will measure 33.75 mils at 760 mm. pressure.

3. Effect of Both Temperature and Pressure on Volume:

If both temperature and pressure are changed, we combine formulas 1 and 2. Thus,

$$V = \frac{v\,(237 + T°)}{237 + t°} \times \frac{p}{P.}$$

Problem.—What will be the corrected volume of 44.5 mils of nitrogen dioxide at 25° C. and 760 mm. when measured at 32° C. and a pressure of 770 mm.?

$$V = \frac{44.5\,(273+25)}{273+32} \times \frac{770}{760} = 44.04+ \text{ mils.}$$

Therefore 44.5 mils of NO at 32° C. and 770 mm. will measure 44.04+ mils at 25° C. and 760 mm.

4. EFFECT OF TEMPERATURE, PRESSURE AND VAPOR TENSION ON VOLUME:

When gases are measured over water (as in assay of ethyl nitrite) they become saturated with water-vapor, which causes an expansion of the gas with its increase in temperature. Hence the pressure of the water-vapor, that is, vapor tension (page 53), at the temperature of observation must be deducted from the prevailing atmospheric pressure in order to find the actual pressure to which the gas is subjected.

$$V = \frac{v(273)}{273 + t^\circ} \times \frac{p - w}{P} \quad w = \text{vapor tension of water at given temperature.}$$

Problem.—Referring to the preceding problem 3, what would be the volume of *dry* nitrogen dioxide, if it measured 44.04+ mils over water at 25° C. and 760 mm.?

The vapor tension of water at 25° C. = 23.6 mm. (see table, page 53).

$$V = \frac{44.04(273)}{273 + 25} \times \frac{760 - 23.6}{760} = \frac{44.05(273)}{298} \times \frac{736.4}{760} = 39.09 + \text{cc.}$$

Therefore 44.05 c.c. of NO, measured over water at 25° C. and 760 mm.. correspond to 39.09+ mils of the *dry* gas at same temperature and pressure.

CHAPTER II

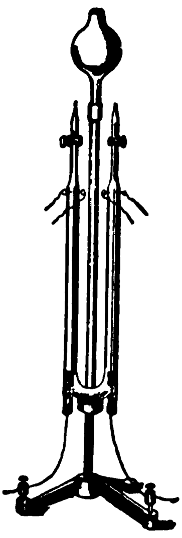
HYDROGEN

Symbol, H. *Atomic Weight,* 1.008. *Valence,* I.

Number of atoms in molecule, 2; *weight of one liter (at* 0° *and* 760 *mm.),* 0.089873 *gm.;* 1 *gram measures* 11.1235 *liters;* 14.4 *times as light as air.*

History.—That an inflammable gas is generated through the action of certain acids upon iron, was known to Paracelsus (1493-1541). This gas was confused with various other inflammable gases until the investigations of Cavendish (1766), who established its elementary character and named it "inflammable air." Lavoisier, some years later, proposed the name hydrogen, which has met with general acceptance.

FIG. 92.



Isolation of hydrogen by electrolysis of water.

Occurrence.—Hydrogen, one of the most widespread of our elements, occurs in the free state in certain volcanic gases, in pockets of the carnallite deposits of the Stassfurt mines, in the natural gas of our oil regions, in the gaseous envelope of the sun, fixed stars, and nebulæ. In combination, hydrogen forms one-ninth of the water of the globe, and is a constituent of nearly all organic matter.

Isolation.—(1) *By the electrolysis of water* (Fig. 92). The addition of one part sulphuric acid to one hundred parts of water assists the process by making the latter a better conductor. The products of the reaction are two volumes of hydrogen (which collects at the negative electrode) and one volume of oxygen (which collects at the positive electrode), according to the following:

$$2H_2O = 2H_2 + O_2.$$

(2) *By the decomposition of water with certain metals.* *a.*—At *ordinary temperature* with the alkali metals, as sodium or potassium. When a small piece of potassium is thrown on water, chemical action takes place at once: the metal melts, and floats about enveloped in a flame of hydrogen, which ignites spontaneously from the heat of the reaction. The flame is of a violet color, imparted by the volatilization of the metal.

Sodium does not react so violently with the water as to cause ignition of the escaping hydrogen, unless it be held in one spot by placing it on a piece of filter paper, when sufficient heat is developed to ignite the gas, which, in this case, burns with a yellow flame, the resulting solution being strongly alkaline.

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium Hydroxide.}}{2NaOH} + \underset{\text{Hydrogen.}}{H_2}.$$

b.—At ***high temperature*** with such metals as iron, zinc, and nickel. If the vapor of water be passed through a tube containing any of the above finely divided metals heated to redness, they combine with the oxygen of the water vapor, forming an oxide of the metal, while the hydrogen passes off and may be collected over water.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Steam.}}{H_2O} = \underset{\text{Zinc Oxide.}}{ZnO} + \underset{\text{Hydrogen.}}{H_2}.$$

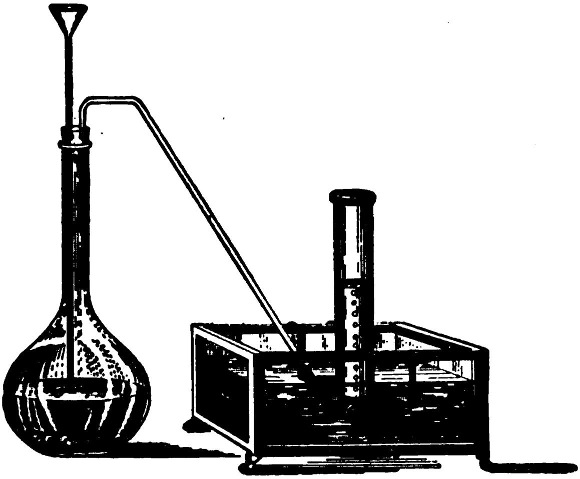
$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Steam.}}{4H_2O} = \underset{\substack{\text{Ferroso-ferric}\\\text{Oxide.}}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}.$$

(3) *By the action of dilute acids on certain metals, usually iron and zinc.*

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Zinc}\\\text{Sulphate.}}}{ZnSO_4} + \underset{\text{Hydrogen.}}{H_2}.$$

Sulphuric acid may be substituted by hydrochloric acid, with similar results. Iron, however, does not yield as pure a gas as zinc, on account of certain carbon impurities contained in it.

FIG. 93.



Preparation of hydrogen.

The above reaction progresses satisfactorily only in the presence of water, which dissolves the zinc sulphate formed, and prevents its collecting on the metal and retarding the further action of the acid. When chemically pure zinc is used the action at first is very slow, but by the addition of a drop or two of platinic chloride or copper sulphate solution a galvanic action is established, which causes a rapid evolution of the gas.

(4) *By the action of concentrated solutions of the alkali hydroxides on certain metals, as zinc, aluminum, magnesium, or iron (finely divided).* It is usually necessary to apply heat to assist the reaction.

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sodium Hydroxide.}}{2NaOH} = \underset{\text{Sodium Zincate.}}{Zn(ONa)_2} + \underset{\text{Hydrogen.}}{H_2}.$$

$$\underset{\text{Aluminum.}}{Al_2} + \underset{\substack{\text{Sodium}\\\text{Hydroxide.}}}{2NaOH} + 2H_2O = \underset{\substack{\text{Sodium}\\\text{Aluminate.}}}{2NaAlO_2} + \underset{\text{Hydrogen.}}{3H_2}$$

With magnesium and aluminum the action takes place at ordinary temperature.

The gas as it escapes from the generator should never be ignited until all traces of air have been removed from the apparatus. This may be ascertained by collecting a test tube full of the escaping gas by displacement and then igniting;

as long as any air remains in the apparatus, this is accompanied by a slight report.

All the foregoing chemical processes yield a gas more or less impure. In order to obtain pure hydrogen from method 3, it should be passed through a solution of lead acetate, to remove hydrogen sulphide; through a solution of silver sulphate, to remove hydrogen phosphide and arsenide; through potassium hydroxide solution, to remove free acid; and, finally, over calcium oxide to remove moisture.

Industrial Preparation.—Owing to the extensive use of hydrogen in various branches of chemical industry, the most important methods of preparation will be outlined.

Linde-Frank-Caro Process.—Compressed water gas is cooled to —193°, whereby all constituents are liquefied except the hydrogen, which is obtained from 97 to 98 per cent. pure.

Steam and Iron Contact Process.—This is based on the well-known decomposition of steam by red-hot spongy iron, $2Fe + 2H_2O = 2FeO + 2H_2$, the resulting iron oxide being reduced each time by a current of water gas (CO and H) $2FeO + H_2 + CO = 2Fe + H_2O + CO_2$. In practice, a mixture of iron oxide and clay or bog iron ore made into briquettes is used; the oxide is reduced by water gas to spongy iron; over this heated iron steam is then passed.

Aluminum Process.—Steam is passed over a mixture of aluminum in powder and lump form. The reaction being $Al_2 + 3H_2O = Al_2O_3 + 3H_2$. One kilo of Al can produce 1300 liters of hydrogen.

Riker-Walter Process.—Oil gas is heated to 1200 to 1400°, whereby it is decomposed into carbon and hydrogen. In this process petroleum is sprayed over hot coke, which retains most of the carbon. The liberated gases consist, chiefly, of hydrogen with impurities, such as CO and H_2S; the latter are removed by passing over soda lime and red-hot bog iron ore. The hydrogen is about 97 per cent. pure.

Electrolysis.—Electrolytic methods are extensively employed and are based upon the electrolysis of water or aqueous solutions of caustic potash or soda, water being replaced gradually as the decomposition proceeds. In the electrolysis of potassium chloride, besides hydrogen, chlorine and caustic potash are obtained.

Physical Properties.—Pure hydrogen is an odorless, colorless, and tasteless gas. It is the lightest substance known; one liter at 0° and 760 mm. atmospheric pressure weighs 0.089873 gram (one crith), and 1 gram measures 11.1235 liters, indicating a density of 0.0695 when air equals 1.000. On comparing the weights of like volumes of oxygen and hydrogen at 0° and 760 mm. pressure, the ratio is 15.88 to 1, or 16 to 1.008. Owing to its lightness ($\frac{1}{14.4}$ of air and $\frac{1}{15.9}$ of oxygen), hydrogen may be collected by "upward displacement," by simply holding a receiver over a tube from which the gas is escaping; or, in view of its insolubility, it may be collected over water. The molecular volume, that is, the volume occupied by the gram molecular weight (2.016), of hydrogen is 22.416 liters.

The great diffusibility of hydrogen is one of the most prominent characters, it being four times as diffusible as oxygen and 3.8 times as air; hence this gas can be kept only in absolutely non-porous vessels.

Hydrogen may be converted, by a pressure of 180 atmospheres and a temperature of —205° C., produced by the vaporization of liquid air in a vacuum, into a steel-blue liquid (density about 0.07), and on suddenly releasing this pressure, the vaporization of the liquid is so rapid that the intense cold thus produced converts a portion of the escaping liquid into solid particles, which almost instantly disappear. The critical temperature of hydrogen gas is —243° C. (Dewar), while its critical pressure is only 19.4 atmospheres. Liquid hydrogen boils at —252.78° C., producing by its evaporation a temperature of —260 or 13° A (absolute zero being —273°). Hydrogen is very slightly soluble in water, 100 mils at 0° dissolving 2.14 mils of the gas.

Certain metals, like platinum and palladium, possess the peculiar property of absorbing, under certain conditions, hydrogen gas, the phenomenon being termed *occlusion*. For example, palladium, when heated to 100° C. and cooled in an atmosphere of hydrogen, will absorb over 982 volumes of this gas; or when this metal serves as the cathode for the electrolysis of water, it absorbs 900 volumes of hydrogen. Platinum in the spongy state will absorb 110 volumes of hydrogen.

Chemical Properties.—Under ordinary conditions, hydrogen shows but little affinity for other substances, owing to the firm linkage between both atoms forming the molecule, considerable energy being necessary to bring about a cleavage. At elevated temperature or in the nascent state, its behavior is quite the reverse. Hydrogen is combustible and burns with a non-luminous but intensely hot flame, combining with the oxygen of the air to form water. The temperature produced through the combustion of 1 gram of hydrogen is sufficient to raise 340 grams of water at 0° C. to the boiling-point; the temperature of the oxy-hydrogen flame (pages 165, 196), which is about 2500° C., is exceeded slightly by the oxy-acetylene flame and considerably by that of the electric furnace.

The great affinity of hydrogen for oxygen may be further illustrated by mixing two volumes of the former with one of the latter and applying a flame, when union of the two gases will take place with a violent explosion. The same occurs when air, in larger volume, is used instead of oxygen, hence the importance of having all the air driven out of a generator before attempting to ignite the escaping gas. When a current of hydrogen is directed upon a mass of finely divided platinum (platinum sponge), the latter becomes incandescent. This phenomenon, which is an evidence of chemical reaction, is due to the fact that oxygen, which is occluded in the finely divided metal, combines readily under these conditions with the hydrogen, while the platinum undergoes no chemical change. Certain other metals as well as chemicals deport themselves similarly. Such chemical reactions that take place, their rate being greatly facilitated through the agency of a third substance, which itself undergoes no chemical change—that is, does not pass into the products of the reaction—are termed *catalytic*. Those substances which accelerate such chemical reactions through their presence are called *catalytic* agents, or *catalyzers*. The process is termed *catalysis* (see page 152). With chlorine and some other halogens, hydrogen combines even more readily than with oxygen, but with most other non-metals it does not unite directly unless in the nascent state.

The affinity of hydrogen for the halogens decreases in proportion to their increase in atomic weight. Thus, fluorine combines with hydrogen in the dark with explosive violence, while chlorine requires the aid of direct sunlight; with bromine a temperature of 200° C. and sunlight are necessary, while iodine and hydrogen combine directly with some difficulty, and the resulting compound is quite unstable. The gaseous elements, at the moment of their generation (*statu nascendi*), act more energetically than after their liberation, for the reason that this *nascent* or specially active state represents the element in its atomic condition—that is, before the atoms have united to form molecules.

While in this nascent state, hydrogen gas is capable of reducing compounds of a higher state of oxidation (*-ic*) to a lower (*-ous*), or metallic oxides or chlorides to their metals, also of converting some compounds free from hydrogen into ones containing this element. Such reactions, in which a part or all of the electro-negative element of a compound is removed, or when the valence of the electro-positive element or group is decreased, are termed ***reducing***, and the substance which accomplishes this a ***reducing agent.***

Thus, on adding zinc or iron filings to a solution of the following chemicals in dilute hydrochloric or sulphuric acid, reduction takes place. In equation 1 the valence of electro-positive Fe‴ is reduced to Fe″; in equations 2 and 3 oxygen is withdrawn from the electro-positive element, and in equation 4 an electro-positive atom is added to the molecule.

$$(1)\ \underset{\text{Ferric Chloride.}}{2\overset{\prime\prime}{\mathrm{Fe}}\,\overset{\prime}{\mathrm{Cl}}_3} + \underset{\text{Hydrogen.}}{\overset{\prime}{\mathrm{H}}_2} = \underset{\text{Ferrous Chloride.}}{2\overset{\prime\prime}{\mathrm{Fe}}\,\overset{\prime}{\mathrm{Cl}}_2} + \underset{\text{Hydrochloric Acid.}}{2\overset{\prime}{\mathrm{H}}\,\overset{\prime}{\mathrm{Cl}}.}$$

$$(2)\ \underset{\text{Sulphurous Acid.}}{\overset{\prime}{\mathrm{H}}_2\overset{\prime\prime\prime\prime}{\mathrm{S}}\,\overset{\prime\prime}{\mathrm{O}}_3} + \underset{\text{Hydrogen.}}{3\overset{\prime}{\mathrm{H}}_2} = \underset{\text{Water.}}{3\overset{\prime}{\mathrm{H}}_2\overset{\prime\prime}{\mathrm{O}}} + \underset{\text{Hydrogen Sulphide.}}{\overset{\prime}{\mathrm{H}}_2\overset{\prime\prime}{\mathrm{S}}}$$

$$(3)\ \underset{\text{Arsenous Oxide.}}{\overset{\prime\prime\prime}{\mathrm{As}}_2\,\overset{\prime\prime}{\mathrm{O}}_3} + \underset{\text{Hydrogen.}}{6\overset{\prime}{\mathrm{H}}_2} = \underset{\text{Arsenous Hydride.}}{2\overset{\prime\prime\prime}{\mathrm{As}}\,\overset{\prime}{\mathrm{H}}_3} + \underset{\text{Water.}}{3\overset{\prime}{\mathrm{H}}_2\overset{\prime\prime}{\mathrm{O}}}$$

$$(4)\ \overset{\prime\prime}{\mathrm{Hg}}\,\overset{\prime}{\mathrm{I}}_2 + \overset{\prime\prime}{\mathrm{Hg}} = 2\overset{\prime}{\mathrm{Hg}}\,\overset{\prime}{\mathrm{I}}$$

Hydrogen occluded in metals, as Pd and Pt, is more active than "nascent hydrogen," often causing combination with explosive violence. When palladium hydrogen is added to solutions of such metals as Ag, Au, Cu, Hg, etc., the metals are precipitated; ferr*ic* solutions are reduced to ferr*ous,* chrom*ic* to chrom*ous,* and chlor*ates* to *hypo*chlor*ites.*

Hydrogen in its ordinary (molecular) state possesses reducing properties through its affinity for such electro-negative elements as oxygen, sulphur, chlorine, etc. In such cases the compound to be reduced is heated, while a current of hydrogen is passed over it. Thus—

$$(1)\ \underset{\text{Ferric Oxide.}}{\overset{\prime\prime\prime}{Fe}_2\,\overset{\prime\prime}{O}_3} \quad + \quad 3\overset{\prime}{H}_2 \quad = \quad 3\overset{\prime}{H}_2\overset{\prime\prime}{O} \quad + \quad \underset{\text{Reduced Iron.}}{\overset{\prime\prime}{Fe}_2.}$$

$$(2)\ \underset{\text{Cupric Oxide.}}{\overset{\prime\prime}{Cu}\,\overset{\prime\prime}{O}} \quad + \quad H_2 \quad = \quad \underset{\text{Copper.}}{\overset{\prime\prime}{Cu}} \quad + \quad \overset{\prime}{H}_2\,\overset{\prime\prime}{O}$$

$$(3)\ \underset{\text{Antimony Pentasulphide.}}{\overset{\text{v}}{Sb}_2\,\overset{\prime\prime}{S}_5} \quad + \quad 2\overset{\prime}{H}_2 \quad = \quad 2\overset{\prime}{H}_2\overset{\prime\prime}{S} \quad + \quad \underset{\text{Antimony Trisulphide}}{\overset{\prime\prime\prime}{Sb}_2\,\overset{\prime}{S}_3.}$$

$$(4)\ \underset{\text{Ferric Chloride.}}{2\overset{\prime\prime\prime}{Fe}\,\overset{\prime}{Cl}_3} \quad + \quad H_2 \quad = \quad \underset{\text{Ferrous Chloride.}}{2\overset{\prime\prime}{Fe}\overset{\prime}{Cl}_2} \quad + \quad 2\overset{\prime}{H}\,\overset{\prime}{Cl}.$$

Uses.—Hydrogen has a number of very important industrial applications: in aeronautics for filling balloons, since it can be readily compressed in cylinders and transported or even be generated when needed. The ascensional power of hydrogen is 1.2 kilos per cubic meter, or 73.5 pounds per 1000 cubic feet. As a high temperature producer when burned in the presence of oxygen (oxy-hydrogen blowpipe), this is variously given from 2100 to 2500°.

The hydrogen flame is employed in the autogenous welding of steel, cast iron, copper and other metals, also in place of riveting. The oxy-hydrogen flame is used in cutting wrought iron and steel; fusing quartz, in which sand is fused and moulded into various forms of laboratory apparatus, such as beakers, crucibles, evaporating dishes, tubing, etc.; in the manufacture of synthetic rubies and sapphires, in which aluminum oxide is fused either alone or with an addition of 2 per cent. of chromic oxide (ruby); the sintering and fusing of tungsten metal powder into rods, fusing of metals of the platinum group. Hydrogen is extensively employed in the hydrogenization of oils.

Hydrogen is used in research work where very low temperatures are required. These are obtained by evaporation of the liquefied gas.

CHAPTER III

THE HALOGENS

CHLORINE, BROMINE, IODINE, FLUORINE

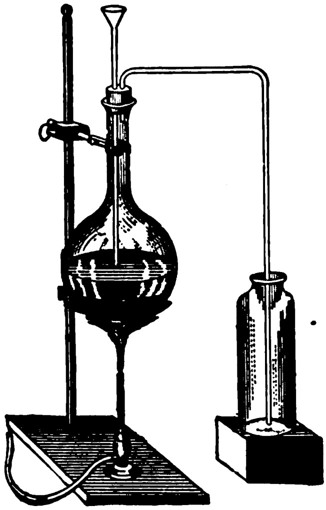
CHLORINE

Symbol, Cl. *Atomic Weight,* 35.46. *Valence,* I, *also* 3, 5 *or* 7.

Number of atoms in molecule, 2; weight of one liter (at 0° *and* 760 *mm.),* 3.22 *gm.; density,* 2.49 *(air* = 1); 1 *gram measures* 310.56 *mils.*

History.—Chlorine was first isolated by Scheele, in 1774, while experimenting with "black magnesia" (an ore consisting largely of manganese dioxide) and hydrochloric acid, but its elementary character was first established by Davy, in 1801, who gave to it the name of chlorine on account of its greenish-yellow color.

FIG. 94.



Isolation of chlorine.

Occurrence.—Chlorine does not occur in the free state in nature, but is found abundantly in combination with sodium in sea-water, and in the salt-wells of the United States; also as rock-salt in the mines of Austria, Spain, and Bavaria, all of which have been worked for centuries. It is also found in certain "horn" minerals, combined with lead, silver, or mercury.

In the vegetable kingdom chlorine is not very abundant, but in the animal kingdom, combined with sodium, it is found more abundantly, being a constituent of most animal secretions.

Isolation.—Chlorine may be isolated by a number of different processes, as follows:

(1) *By the electrolysis of hydrochloric acid or chlorides,* the chlorine gas being liberated at the anode.

(2) *Through the oxidation of hydrochloric acid by means of certain higher metallic oxides.*

(*a*) Heating a mixture of hydrochloric acid and manganese dioxide.

$$\underset{\text{Manganese Dioxide.}}{MnO_2} + \underset{\text{Hydrochloric Acid.}}{4HCl} = \underset{\text{Manganous Chloride.}}{MnCl_2} + 2H_2O + \underset{\text{Chlorine.}}{Cl_2}$$

The liberated gas is usually collected by "downward displacement," as illustrated in Fig. 94.

Care should be taken to mix the acid thoroughly with the powder, to prevent any of the latter from remaining unmoistened on the bottom and causing fracture of the flask on the application of heat. The oxide should be in excess of the acid, and heat should not be applied for some minutes after they are mixed, or the resulting gas will be contaminated with hydrochloric acid. As an additional precaution, it has been recommended to use the oxide in lumps, and have them above the surface of the acid; even then the gas should be passed through a small quantity of water, to remove any traces of acid, before collecting it in the receiver.

(*b*) By heating a mixture of four parts of manganese dioxide, nine parts of sodium chloride, and a mixture of twelve parts of sulphuric acid with six parts of water:

$$\underset{\substack{\text{Manganese}\\\text{Dioxide.}}}{MnO_2} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{2H_2SO_4} = \underset{\substack{\text{Manganous}\\\text{Sulphate.}}}{MnSO_4} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + 2H_2O + Cl_2.$$

(*c*) By gently heating a mixture of potassium dichromate and concentrated hydrochloric acid.

$$\underset{\substack{\text{Potassium}\\\text{Dichromate.}}}{K_2Cr_2O_7} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{14HCl} = \underset{\substack{\text{Chromic}\\\text{Chloride.}}}{2CrCl_3} + \underset{\substack{\text{Potassium}\\\text{Chloride.}}}{2KCl} + 7H_2O + 3Cl_2.$$

(*d*) Upon adding hydrochloric acid to bleaching powder or hypochlorites.

$$\underset{\text{Bleaching Powder.}}{Ca(OCl)Cl.CaO} + 4HCl = \underset{\text{Calcium Chloride.}}{2CaCl_2} + 2H_2O + Cl_2.$$

Because of its extensive uses in the arts as a bleaching agent and solvent, chlorine is prepared industrially on an extensive scale. Only a few of the more important methods are enumerated.

(3) The "*Deacon Process*" is based on the oxidation of hydrochloric acid gas by the oxygen of the air. This is brought about by passing the vapors of the acid, mixed with air, over pieces of brick which have been saturated with copper chloride and heated to about 440° C. In outline, the reaction is as follows:

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

It is presumed that the copper chloride acts as a catalytic agent in the liberation of a portion of its chlorine, and withdrawal of it from the hydrochloric acid, through the influence of the oxygen of the air (see page 152).

(4) The "*Weldon Process*" consists in heating a mixture of hydrochloric acid and manganese dioxide (see Equation 2, *a*). The economical innovation consists in the recovery of the manganese, which is converted from the chloride ($MnCl_2$) back into the oxide (MnO_2). This is accomplished by treating the manganous chloride with milk of lime [$Ca(OH)_2$], whereby manganous hydroxide [$Mn(OH)_2$] is produced; then, upon passing a blast of air through this heated mixture, the latter is converted into manganese dioxide (MnO_2), which is again heated with a fresh portion of hydrochloric acid, as before.

(5) *Electrolytic Processes.* Most of the chlorine manufactured is obtained by the electrolysis of the chlorides of sodium or potassium. These methods are all based upon the decomposition of the alkali chloride by means of the electric current, in which the chlorine separates at the carbon anode and the alkali at the cathode (see Castner process).

Many chemical difficulties have been encountered in the various processes, owing to secondary reactions taking place with the formation of sodium hypochlorite, chlorate, and chloride, caused by the diffusion of the chlorine through the solution.*

---

* (1) $2NaCl = Na_2 + Cl_2.$
(2) $Na_2 + 2H_2O = 2NaOH + H_2.$
(3) $2NaOH + Cl_2 = NaClO + NaCl + H_2O.$
(4) $3NaClO = NaClO_3 + 2NaCl.$
(5) $NaClO_3 + 3H_2 = NaCl + 3H_2O.$

To overcome this difficulty, various devices have been introduced. Most successful is that of Castner (page 730), in which the positive and negative plates are kept apart in water-tight compartments which permit, however, a transfer of one of the products of the reaction from two of the cells to the third.

Physical Properties.—Chlorine is a yellowish-green gas, of a suffocating odor, and when inhaled exerts a corrosive action on the mucous membranes of the air passages. It is about 2.5 times heavier than the air, hence may be readily collected by displacement, the height to which the vessel is filled being noted by the color of the gas. Under ordinary atmospheric pressure, chlorine liquefies at —34° C., or by a pressure of 8.5 atmospheres at 12.5°. Its critical temperature is 146° and its critical pressure 93.5 atmospheres. More usually, however, liquefaction is carried out under a pressure of 8 atmospheres while cooling with water. One liter of Cl weighs 3.22 gm. (0° and 760 mm.). One liter of liquid chlorine corresponds to 300 liters of gas. Commercially chlorine is supplied in liquid state contained in steel cylinders, forming a dark greenish-yellow liquid, immiscible with water, boiling at —33.6° C. at 760 mm. At 25° C. its specific gravity is about 1.40. The solubility of chlorine in water reaches its maximum at 9.6°, when one volume absorbs 3 volumes of the gas.

Chemical Properties.—Next to fluorine, chlorine is the most reactive member of the group of non-metals, and with the exception of the inert gases (N, He, Ar), oxygen, carbon, and some of the rarer metals of the platinum group, chlorine unites readily with all elements. Phosphorus, copper, bismuth, tin, antimony and arsenic inflame when sprinkled in a finely divided condition into a cylinder of chlorine. When mixed with hydrogen, chlorine combines with explosive violence upon the application of a flame, electric spark, or when exposed to the direct rays of the sun, or when brought into contact with platinum sponge. This affinity for hydrogen is illustrated in its behavior towards various compounds. Thus, if tissue paper, moistened with warm turpentine oil ($C_{10}H_{16}$), be plunged into a cylinder of chlorine, the latter combines with the hydrogen of the turpentine, generating sufficient heat to cause ignition of the oil, which burns with a copious evolution of black smoke from the liberated carbon. A candle burns in an atmosphere of chlorine with a smoky flame, caused by the combination of this gas with the hydrogen while excluding the carbon. Because of its intense affinity for hydrogen, chlorine is a powerful oxidizing agent. Thus sulphur and phosphorus may, under certain conditions, be oxidized to their respective acids, and salts of various metals oxidized from the "*ous*" to the "*ic*" state. Chlorine is very extensively employed for making bleaching powder (Chlorinated Lime), hypochlorites (liquid bleach), and chlorates. To secure this bleaching it is necessary that the gas be used in the presence of moisture, or in solution in the form of "bleaching powder," or the "hypochlorites." This depends upon the coöperation of water, which is decomposed by the chlorine with the liberation of oxygen ($Cl_2 + H_2O = 2HCl + O$); this in turn forms colorless oxidation products with organic colored substances. Large quantities of chlorine are employed in the manufacture of chlorinated organics, as trichlor-acetic acid, chloral, phosgene, carbon tetra-chloride, etc. Chlorine is a powerful disinfectant and deodorizer, readily destroying bacteria. It is more commonly employed in the form of chlorinated lime. Chlorine exerts a very irritating action upon the mucous surfaces of the air passages. Air containing not more than about 1 part per million of chlorine can be breathed with safety.

Chlorine Water.—An aqueous solution containing about 0.4 per cent. of chlorine, which may be prepared either by saturating cold water with chlorine gas (U.S.P. test solution) or through the action of diluted hydrochloric acid on potassium chlorate by the aid of heat and dissolving the liberated gases through the addition of water. The following reaction takes place:

$$\underset{\text{Potassium Chlorate.}}{4KClO_3} + 16HCl = 4KCl + 8H_2O + 7Cl_2 + \underset{\text{Chlorine Peroxide.}}{2ClO_2}.$$

The chlorine peroxide breaks up as follows, in the presence of water:

$$3ClO_2 + H_2O = 2HClO_3 + Cl + O.$$
$$2ClO_2 + H_2O = HClO_3 + HClO_2.$$

Consequently such a solution will contain, besides chlorine, chlorous and chloric acids.

Chlorine water is a transparent greenish-yellow liquid, which, because of its instability, should be prepared fresh when desired.

Upon standing, when exposed to sunlight, solutions of chlorine become colorless, decomposing into hydrochloric acid and oxygen:

$$2Cl_2 + 2H_2O = 4HCl + O_2.$$

When exposed to diffused light, hypochlorous and chloric acids are formed:

$$Cl_2 + H_2O = HCl + HClO.$$
$$8HClO = 2HClO_3 + 6HCl + O_2.$$

In addition to its use in medicine as a stimulant and antiseptic, chlorine water is a valuable laboratory reagent, being especially employed for liberating iodine and bromine from their salts, and for oxidizing many metallic compounds. When employed as a reagent for liberating iodine or bromine, care should be observed not to add too great an excess of the chlorine solution, owing to the tendency of this element to form colorless compounds with bromine and iodine.

HYDROGEN AND CHLORINE

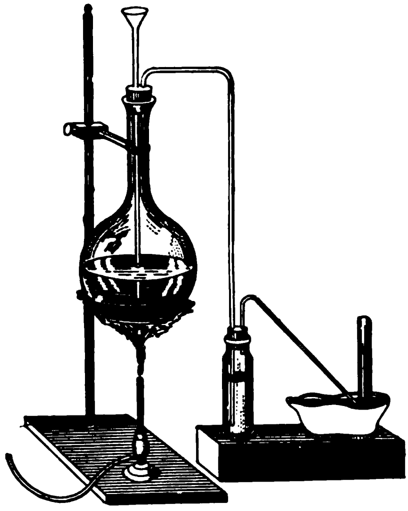
HYDROCHLORIC ACID. HYDROGEN CHLORIDE. MURIATIC ACID.

Formula, HCl. *Molecular Weight*, 36.47.

History.—Hydrochloric acid in solution (first mentioned by Basil Valentinus, in the fifteenth century) was known to the ancients. The alchemists were already familiar with *aqua regia,* obtained by distilling nitre, sal ammoniac, and vitriol together. Glauber, about the year 1648, first prepared the aqueous acid, and gave it the name of *spiritus salis,* which as "spirit of salt" it retains to the present day. Priestley first collected the gas by the use of a pneumatic trough containing mercury. Davy, in 1810, disproved its supposed elementary character, and demonstrated it to be a compound of chlorine and hydrogen.

Occurrence.—Hydrochloric acid gas occurs as one of the gaseous products ejected from volcanoes. It is present in solution (0.1 to 0.4 per cent.) in the normal gastric juice of mammals, along with pepsin and inorganic salts.

FIG. 95.



Preparation of hydrochloric acid.

Preparation.—When equal volumes of chlorine and hydrogen are mixed and exposed to diffused daylight, they slowly combine, forming hydrochloric acid. This combination may be effected at once and with explosion by exposing the mixture to the direct rays of the sun, to the light of the electric arc or burning magnesium, or by the application of a flame. For laboratory purposes the gas may be prepared in a flask with suitable attachments for washing and purifying, as in Fig. 95, by adding to sodium chloride one and a half times its weight of sulphuric acid, previously diluted with half its weight of water, and applying heat. A small quantity of sulphuric acid is put in the wash bottle to remove moisture, and the gas is then collected over mercury. When two molecules of sodium chloride and one molecule of sulphuric acid are taken, the following reaction occurs:

$$\underset{\text{Sodium Chloride.}}{2NaCl} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Sodium Sulphate.}}{Na_2SO_4} + \underset{\text{Hydrochloric Acid.}}{2HCl.}$$

In working on a small scale, however, it is better to use the proportion of one molecule of each, when a more soluble acid sodium sulphate remains in the flask:

$$\underset{\text{Sodium Chloride.}}{NaCl} + \underset{\text{Sulphuric Acid.}}{H_2SO_4} = \underset{\text{Acid Sodium Sulphate.}}{NaHSO_4} + \underset{\text{Hydrochloric Acid.}}{HCl.}$$

This reaction occurs with the aid of less heat than is required in the preceding, and is in other ways more satisfactory.

For laboratory purposes, this gas may be conveniently prepared by adding sulphuric acid (through a separatory funnel) to common salt or ammonium chloride, in broken pieces, contained in a flask and heating.

$$\underset{\text{Ammonium Chloride.}}{2NH_4Cl} + H_2SO_4 = \underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} + 2HCl.$$

No heat need be applied if the alkali chloride be covered with fuming hydrochloric acid before adding the sulphuric acid.

Industrially, hydrochloric acid is obtained as a by-product in the manufacture of "salt cake" (sodium sulphate) (see page 357).

Physical Properties.—Hydrochloric acid is a colorless gas, of a sharp, suffocating odor and an acid taste. It has a density, compared with air, of 1.269, and may therefore be collected like chlorine by downward displacement. One liter of HCl vapor at 0° and 760 mm. weighs 1.639 gm. Its density (grams per mil) at 20° is 0.0974. It has been liquefied by a pressure of 40 atmospheres and a temperature of 10°, its critical temperature is 52° and critical pressure 83 atmospheres.

Chemical Properties.—The dry gas neither acts on metals nor reddens litmus. It fumes in moist air and is very soluble in water; at 0°, one volume (1 liter) of water will absorb about 505 volumes (505 liters, or 816 grams) of the gas; one volume of ethyl-alcohol (0.836 sp. gr.) dissolves 327 volumes of the vapor at 17°. Hydrochloric acid gas is neither combustible nor a supporter of combustion in the general sense; however, it will support the combustion of metallic sodium, potassium, or magnesium, hydrogen gas being evolved and a chloride of the metal formed. Certain other metals react in a similar manner at higher temperature.

$$Fe + 2HCl = \underset{\text{Ferrous Chloride.}}{FeCl_2} + H_2.$$

Hydrochloric acid gas decomposes most metallic oxides, with the formation of water and a chloride.

$$\underset{\text{Ferric Oxide.}}{Fe_2O_3} + 6HCl = \underset{\text{Ferric Chloride.}}{2FeCl_3} + 3H_2O.$$

Acidum Hydrochloricum.—The concentrated aqueous solution of the pure gas forms a colorless, corrosive fluid of very sour taste and penetrating odor, fuming readily in moist air; less concentrated acids do not fume. The concentrated chemically pure (C.P.) acid contains from 35 to 38 per cent. of the anhydrous acid, while that recognized by the U.S.P. should contain not less than 31 nor more than 33 per cent. and has the specific gravity of about 1.155 at 25°.

The "commercially pure" acid is of variable strength and quality. The specific gravity of an acid being known (at 15°), the percentage strength may be approximately ascertained by multiplying its two first decimals by 2; for example, an acid of the gravity 1.12 contains 24 per cent., one of the gravity 1.162 contains 31.9 per cent. of absolute acid.

When heated, concentrated hydrochloric acid evolves the gaseous acid until it reaches a concentration of 20.2 per cent., then it distils unchanged at 110° C. (760 mm.). Conversely, if a weaker acid be distilled, it will lose water until it reaches a concentration of 20.2 per cent.

Most metals dissolve in hydrochloric acid with evolution of hydrogen gas, while the metallic oxides dissolve with separation of water.

Peroxides of the alkalies and alkaline earths are decomposed by hydrochloric acid, yielding hydrogen peroxide,

$$\underset{\text{Barium Peroxide.}}{BaO_2} + 2HCl = BaCl_2 + \underset{\text{Hydrogen Peroxide.}}{H_2O_2}.$$

The commercial acid is one of the by-products in the Leblanc soda process, the first stage of which is the production of sodium sulphate through the action of sulphuric acid on sodium chloride, hydrochloric acid being the side product.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

For this purpose, the salt and crude sulphuric acid are heated together in a specially constructed furnace, and the evolved hydrochloric acid vapors are forced through a system of towers filled with coke, or brick, over which water trickles; or the gas is absorbed in large earthenware Woulfe bottles.

Impurities.—The impurities found in the commercial acid arise from the crude or raw materials employed in its manufacture, as well as contact with exposed parts of the apparatus. This acid is of a pale yellow color, due to the presence of a small amount of ferric chloride. The other impurities consist chiefly of sulphurous and sulphuric acid, chlorine, arsenic, lead, and inorganic salts. The pure (C.P. or U.S.P.) acid is generally prepared from pure sodium chloride and sulphuric acid. The C.P. or Reagent acid varies from 35 to 38 per cent. strength and should yield not more than 0.003 per cent. of non-volatile matter.

Chlorides.—The compounds of hydrochloric acid are known as chlorides, and are usually formed by dissolving the metal, its hydroxide or carbonate in the diluted acid. A few are made by the direct action of chlorine on the metal. Nearly all metallic chlorides are soluble in water, the exceptions being the chlorides of silver, mercury (*ous*), and lead, the last of which is soluble in hot water. Most chlorides are quite stable when subjected to moderate heat. The chlorides of the "noble" metals, as gold and platinum, decompose with liberation of chlorine. When heated with concentrated sulphuric acid, most chlorides decompose into sulphates of the metals and hydrochloric acid vapor. In fact, this takes place at ordinary temperature with nearly all chlorides except Sb, Bi and Cu.

Nitric acid decomposes all metallic chlorides excepting $AgCl$, $HgCl_2$ with formation of nitrates and liberation of HCl. Boric, arsenic and arsenic and phosphoric acids decompose chlorides by aid of heat.

Most metallic chlorides when heated with manganese dioxide and sulphuric acid give off chlorine.

Tests.—The test of identity for free hydrochloric acid is made by heating with manganese dioxide and noting whether chlorine is evolved. If the quantity of acid be very small, the escaping gas should be passed into a diluted solution of potassium iodide and starch paste, whereby a blue color is produced. Hydrochloric acid and chlorides produce insoluble white precipitates with solutions of silver, mercurous mercury, cuprous copper, and lead. The first forms silver chloride, $AgCl$, soluble in ammonium hydroxide; the second mercurous chloride, $HgCl$ (calomel), which blackens on the addition of ammonium hydroxide; the third, $CuCl$, dissolves in an excess of ammonium hydroxide with a blue color, and the fourth, lead chloride, $PbCl_2$, is soluble in hot water.

BROMINE

Symbol, Br. *Atomic Weight,* 79.92. *Valence,* 1, *also* 3, 5 *or* 7.

Number of atoms to the molecule, 2; *specific gravity at* 0°, 3.18; *density of vapor at* 60°, 5.869 (*air* = 1).

History.—This element was discovered in 1826 by Balard, of Montpellier, France, in the bittern or mother liquor from the manufacture of common salt. The name, from *βρῶμος*, stench, was given it because of its disagreeable odor.

Occurrence.—Bromine occurs chiefly as magnesium bromide in sea-water, and as the magnesium, calcium, and sodium salt in many rock-salt deposits and salt-wells. Large quantities of bromine are produced at Stassfurt, also from the brine wells of Michigan and Ohio. Natural salt brine contains bromides and chlorides of sodium, calcium, magnesium, and potassium. Usually less than 0.1 per cent. of bromine is present.

Isolation.—The various methods employed depend on the displacement of bromine by chlorine, the latter being generated either through reaction of the chlorides present in the brine with manganese dioxide and sulphuric acid, or by their electrolysis. The bittern, which is the mother liquor from the crystallization of salt, is concentrated to about 45° B. (sp. gr. 1.45), which causes the separation of the greater part of the more insoluble sulphates and chlorides, and then manganese dioxide and sulphuric acid are added, which cause liberation of the bromine.

The application of heat completes the reaction. The vapors are conducted through a condensing apparatus into well-cooled receivers.

According to the Dow Process for the extraction of bromine, such impurities in the brine (as ferrous salts) as have a reducing action on bromine are first oxidized. This is accomplished by passing air containing traces of chlorine and bromine through the brine. This brine is then subjected to electrolysis till about half of the bromine has been liberated. This is then blown out by means of a current of air, and after passing through purifying towers containing sodium bromide, which serves to retain the chlorine ($NaBr + Cl = NaCl + Br$), the bromine vapor is brought into contact with sodium or potassium hydroxide, whereby a mixture of bromine and bromate is produced. If sodium or potassium bromide is desired, this is evaporated and baked at red heat to remove organic matter and bromate, then taken up with water, filtered and crystallized. This mixture of bromide and bromate when heated with sulphuric acid yields bromine, according to the following equation:

$$5KBr + KBrO_3 + 3H_2SO_4 = 3K_2SO_4 + 3Br_2 + 3H_2O.$$

The brine, from which part of the bromine has been removed, is electrolyzed and the gases (Cl and little Br) blown out by a blast of air and used for oxidizing a fresh lot of brine. Another method, known as the "*continuous process,*" consists in decomposing the bromides of the hot bittern by a current of chlorine and steam. The liberated bromine dissolves in the liquor, from which it is afterwards removed by boiling.

The crude bromine thus obtained contains as chief impurity bromine chloride, with traces of iodine, organic matter, and bromides. It is purified by shaking with ferrous or sodium bromide and distilling from glass retorts, or distilling direct from iron filings, the quantity used depending on the percentage of chlorine present. The reaction is as follows:

$$FeBr_2 + 2BrCl = FeCl_2 + 2Br_2.$$

Physical Properties.—Bromine is a reddish-brown, intensely caustic liquid which freely evolves corrosive orange-red vapors of a suffocating odor resembling that of chlorine. Its specific gravity is about 3.10 (25°). Pure bromine boils at about 63°, and when cooled to —7.3° it solidifies.

Bromine is soluble in 30 parts of water at 25°; the solution is far more stable than the solution of chlorine, yet in time partly decomposes into hydrobromic acid and oxygen. The reaction is incomplete, since the liberated oxygen reacts reversely with the hydrogen bromide.

$$2Br_2 + 2H_2O \rightleftarrows 4HBr + O_2.$$

Bromine is more soluble in alcohol, ether, chloroform, and carbon disulphide, the last three being capable of extracting it from its aqueous solution on agitation. Bromine is very soluble in aqueous solutions of the alkali bromides, hydrobromic acid and hydrochloric acid, forming very stable reddish-brown colored solutions.

Chemical Properties.—Bromine closely resembles chlorine chemically, although it usually reacts with less energy. Thus, while chlorine combines with hydrogen under influence of light, bromine does not. Bromine combines readily with the metalloids and metals, in some instances (As, Sb, K) with considerable violence, yet its affinity for these elements is not as great as is the case with chlorine. For example, chlorine will displace bromine from its salts:

$$2AgBr + Cl_2 = 2AgCl + Br_2.$$

On the other hand, bromine liberates iodine from iodides and hydrogen iodide. Thus—

$$2KI + Br_2 = 2KBr + I_2.$$

Through its affinity for hydrogen, bromine reacts as a substituting element upon many organic compounds. Thus—

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} + Br_2 = \underset{\text{Mono-brom-camphor.}}{C_{10}H_{15}BrO} + \underset{\text{Hydrobromic Acid.}}{HBr.}$$

In the presence of water, bromine is an active oxidizing agent.

$$\underset{\text{Hydrogen Sulphide.}}{H_2S} + Br_2 = \underset{\text{Hydrobromic Acid.}}{2HBr} + S.$$

$$\underset{\text{Hydrogen Sulphide.}}{H_2S} + 4Br_2 + 4H_2O = \underset{\text{Sulphuric Acid.}}{H_2SO_4} + 8HBr.$$

$$\underset{\text{Ferrous Bromide.}}{\overset{\prime\prime}{Fe}Br_2} + Br = \underset{\text{Ferric Bromide.}}{\overset{\prime\prime\prime}{Fe}Br_3.}$$

Bromine bleaches, but in a less degree than chlorine. It bleaches litmus and indigo solutions and colors starch solution yellow.

Bromine, U.S.P.—This should contain not less than 97 per cent. of pure bromine, the remainder consisting of chlorine and water. The American bromine usually contains from 1.5 (Michigan) to about 6 (Ohio) per cent. of chlorine. German bromine assays about 99 per cent. For tests see U. S. Pharmacopœia.

Uses.—In the free state bromine is used in the manufacture of bromides used in medicine and photography, and of many bromine derivatives of the coal-tar compounds. Chemically it serves as an oxidizing agent. It is also extensively used as a disinfectant, either in solution or mixed with porous silica as infusorial earth.

BROMINE AND HYDROGEN

HYDROGEN BROMIDE. HYDROBROMIC ACID.

Formula, HBr. *Molecular Weight,* 80.93.

Preparation.—When equal volumes of hydrogen and bromine vapor are mixed, they do not explode by the application of a flame as in the case of hydrogen and chlorine, but when the mixture is passed over red-hot platinized asbestos, combination takes place and hydrogen bromide or hydrobromic acid gas results. The same compound is formed when a jet of hydrogen is burned in bromine vapor. A more practical method is to take one part of amorphous (red) phosphorus, mix it with two parts of water in a flask to which is fitted, with a good cork, a stoppered funnel tube containing ten parts of bromine. The apparatus may be arranged as in Fig. 96.

The stop-cock is opened so as to allow the bromine to run in drop by drop, when the following reactions take place:

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Bromine.}}{10Br_2} = \underset{\substack{\text{Phosphorus}\\\text{Pentabromide.}}}{4PBr_5}.$$

$$\underset{\substack{\text{Phosphorus}\\\text{Pentabromide.}}}{PBr_5} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Hydrogen}\\\text{Bromide.}}}{5HBr} + \underset{\substack{\text{Phosphoric}\\\text{Acid.}}}{H_3PO_4}.$$

The action is somewhat violent at first, and great care should be exercised during the operation to thoroughly agitate the mixture in order to bring the two elements in contact, and prevent the collection in one place of any appreciable quantity of bromine. The escape of free bromine is prevented by connecting the flask with a tube containing amorphous phosphorus mixed with pieces of glass. By this means the hydrogen bromide formed in the flask is augmented by that formed in the tube. After the first action ceases it is necessary to apply a gentle heat, when the gas comes off freely, and is best collected by downward displacement.

Hydrobromic acid may be prepared by heating together potassium bromide and phosphoric acid:

$$\underset{\substack{\text{Potassium}\\\text{Bromide.}}}{3KBr} + \underset{\substack{\text{Phosphoric}\\\text{Acid.}}}{H_3PO_4} = \underset{\substack{\text{Potassium}\\\text{Phosphate.}}}{K_3PO_4} + \underset{\substack{\text{Hydrobromic}\\\text{Acid.}}}{3HBr}.$$

It naturally occurs to one that a cheaper acid, like sulphuric, might be substituted; this, however, cannot be done in the case of the gas, but only in the preparation of the aqueous solution, since in the concentrated solution a reduction of the sulphuric acid takes place with liberation of sulphur dioxide and bromine as follows:

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Sulphuric Acid}}{2H_2SO_4} = \underset{\text{Acid Potassium Sulphate.}}{2KHSO_4} + \underset{\text{Hydrogen Bromide.}}{2HBr.}$$

$$2HBr + H_2SO_4 = \underset{\text{Sulphur Dioxide.}}{SO_2} + 2H_2O + Br_2.$$

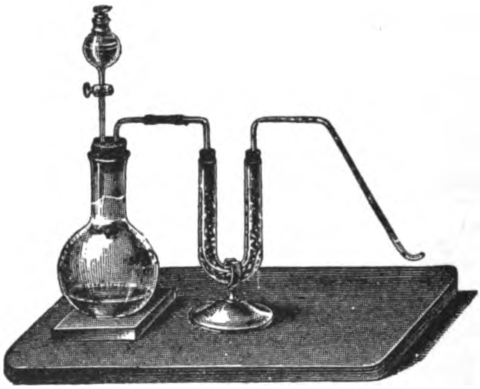
Hydrobromic acid gas is a by-product in the preparation of many organic bromides. Thus—

$$\underset{\text{Camphor.}}{C_{10}H_{16}O} + 2Br = \underset{\text{Mono-brom-camphor.}}{C_{10}H_{15}BrO} + HBr.$$

$$\underset{\text{Benzene.}}{C_6H_6} + 2Br_2 = \underset{\text{Dibrom-benzene.}}{C_6H_4Br_2} + 2HBr.$$

In the latter instance, the acid may be readily prepared, using the same form of apparatus as shown in Fig. 96, in which the bromine (135 mils) is slowly added to benzene (100 gm.) containing a few grams of reduced iron or powdered aluminum. While adding the first half of the bromine, the flask must be kept cool; thereafter the reaction proceeds quietly without precautions. The vapors are passed through the U-shaped tube, one arm of which should contain paraffin (for absorbing any benzene vapors), while the other is filled with naphthalin or red phosphorus mixed with broken glass (for absorbing free bromine).

FIG. 96.



Preparation of hydrobromic acid.

Properties.—Hydrogen bromide is a colorless, heavy gas, with a sharp, irritating odor and an acid taste and reaction. It condenses to a liquid at —73° and melts at —88.5°. The density of the gas is about 2.8 (air = 1), and it is very soluble in water, one volume of which dissolves about 600 volumes of the gas at 10°. The saturated aqueous solution (sp. gr., 1.78 at 0°) contains about 69 per cent. of hydrobromic acid, while at 15° (sp. gr., 1.51) it contains about 49 per cent. of the gas; the former concentrated solution fumes in the air, and when heated the gas is liberated; also if a very dilute solution is boiled, water distils over, until in both cases the remaining solution contains about 48 per cent. of the acid, which distils at 126° (sp. gr., 1.49 at 15°). Solutions of hydrobromic acid decompose on standing, bromine being liberated. Chlorine readily decomposes hydrogen bromide according to the following reaction:

$$2HBr + Cl_2 = 2HCl + Br_2.$$

Most metals (except Au and Pt) react with hydrogen bromide, forming bromides with evolution of hydrogen.

Acidum Hydrobromicum Dilutum, U.S.P.—The official acid should contain not less than 9.5 per cent. nor more than 10.5 per cent. of hydrobromic acid gas, and has a specific garvity of about 1.076 (25°). It may be prepared from the concentrated acid by dilution or according to any of the following convenient methods:

1. *By interaction between potassium bromide and tartaric acid.*

$$KBr + H_2C_4H_4O_6 = KHC_4H_4O_6 + HBr.$$

Add a solution of 15.3 gm. of potassium bromide in 30 mils of hot water to a solution of 18.6 gm. of tartaric acid in 40 mils of dilute alcohol; shake well, cool for several hours, filter and wash the precipitate (acid potassium tartrate) with diluted alcohol till 100 mils of filtrate have been obtained. Concentrate on a water-bath to about 60 mils and then dilute with water to measure 100 mils.

2. *By interaction between bromine and hydrogen sulphide.*

$$Br_2 + H_2S = 2HBr + S.$$

Through a mixture of 30 mils of bromine and 500 mils of water, hydrogen sulphide is passed, with frequent agitation, until the last traces of bromine have disappeared. The solution is then filtered, and distilled, rejecting the first portions till free from the odor of hydrogen sulphide, then collect the distillate until sulphuric begins to distil over. The product is diluted till of the specific gravity of 1.076 (25°), or assayed and then diluted accordingly.

3. *By adding diluted sulphuric acid to an aqueous solution of barium bromide until all the barium has been precipitated as sulphate, care must be exercised not to use an excess of sulphuric acid nor to leave any undecomposed barium bromide in the solution. This may then be distilled.*

$$BaBr_2 + H_2SO_4 = BaSO_4 + 2HBr.$$

Tests.—If to the acid or an aqueous solution of its salts a little chloroform be added, followed by chlorine water added drop by drop with constant agitation, the chloroform will dissolve the liberated bromine with an orange color. Silver nitrate yields a yellowish-white precipitate (AgBr), which is soluble in a large excess of ammonia water, solutions of the alkali cyanides, and thiosulphates, and insoluble in nitric acid. Mercury (*ous*) and lead salts yield insoluble bromides. Heat fuses and finally volatilizes the bromides, most of them with decomposition. All bromides are decomposed by chlorine, nitric, nitrous, and sulphuric acids.

The impurities in commercial diluted hydrobromic acid are usually unavoidable. Sulphuric acid, which might be present, is easily detected by solution of barium chloride. Barium also is sometimes present owing to the use of barium bromide in removing sulphates; it is detected in the usual manner by the addition of a solution of a soluble sulphate. If 25 mils of the diluted acid be evaporated and heated to 110°, not more than 0.0025 gm. of residue remains. When shaken with choroform no color should be imparted to the latter, showing the absence of free bromine.

Inasmuch as the percentage strength of hydrobromic acid is ascertained by titration with a standard tenth-normal silver nitrate, V.S., the presence of hydrochloric acid or chlorides would raise the apparent strength of this acid, hence the absence of these must first be established. This test is carried out by adding 8 mils of silver nitrate, V.S., to 0.5 mil of the acid diluted with 10 mils of water, followed by 6 mils of ammonium carbonate, T.S. After digesting for ten minutes, cooling and filtering, the filtrate should not become more than opalescent upon the addition of an excess of nitric acid.

Bromides.—The salts of hydrobromic acid are called bromides. These may be prepared by the following methods:

1. *By direct union of the elements:*

$$Zn + Br_2 = ZnBr_2\text{, Zinc Bromide.}$$
$$Fe + Br_2 = FeBr_2\text{, Ferrous Bromide.}$$
$$3FeBr_2 + Br_2 = Fe_3Br_8\text{, Ferroso-ferric Bromide.}$$

If the vapors of bromine are passed over moist iron filings, the crystalline salt ($FeBr_2 + 6H_2O$) results; if the iron be heated to redness, the anhydrous salt is obtained. Ferrous bromide may also be prepared by the gradual addition of 6 p. of bromine to 10 p. of water mixed with 3 p. of iron filings or reduced iron, filtering and evaporating to dryness with the addition of some hydrobromic acid.

Ferrous bromide ($FeBr_3$) is obtained by adding 3 mils of bromine to 25 gm. of the anhydrous ferrous bromide. Commercially, the ferroso-ferric bromide (Fe_3Br_8) is a very important salt, because of its employment in the preparation of the alkali bromides. This is formed during the distillation of bromine, in which the vapors are passed into hot iron turnings.

2. *The action of hydrobromic acid or bromine upon the oxides, hydroxides, or carbonates of the metals.*

$$\underset{\text{Potassium Hydroxide.}}{6KOH} + 3Br_2 = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + 3H_2O.$$

$$ZnO + 2HBr = ZnBr_2 + H_2O.$$

$$CaCO_3 + 2HBr = CaBr_2 + CO_2 + H_2O.$$

3. *By interaction between solutions of potassium bromide and the sulphate of the base desired;* the resulting less soluble side product, potassium sulphate, being nearly all removed by cooling or through the addition of alcohol. The filtrate is then concentrated to low bulk and granulated or evaporated to dryness on a water-bath.

$$\underset{\text{Potassium Bromide.}}{2KBr} + \underset{\text{Ammonium Sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Potassium Sulphate.}}{K_2SO_4} + \underset{\text{Ammonium Bromide.}}{2NH_4Br.}$$

Commercially, barium bromide is preferred in place of the alkali bromide because of the insolubility of the barium sulphate.

$$BaBr_2 + ZnSO_4 = ZnBr_2 + BaSO_4.$$

Uses.—Potassium, sodium, rubidium, ammonium, lithium, calcium, and strontium bromides are used medicinally. Silver bromide and the alkali bromides are extensively employed in photography.

All bromides are soluble in water excepting silver, mercury (*ous*) and lead. In alcohol, the alkali bromides are slightly, while calcium and mercury bromides are readily, soluble.

BROMINE AND CHLORINE

Bromine Monochloride.—When chlorine is passed into bromine at a low temperature (below 10°), large quantities are absorbed, and a reddish-yellow volatile liquid, bromine monochloride, BrCl, is formed. It is soluble in water and decomposes at or above 10°.

IODINE

Symbol, I. *Atomic Weight,* 126.92. *Valence,* I, *also,* 3, 5 *or* 7.

History.—In 1811, Courtois, a soap-boiler of Paris, noticed a peculiar corrosion of his copper kettle during the evaporation of kelp liquor, after crystallizing the sodium carbonate from it; subsequently he obtained violet vapors on the addition of sulphuric acid to some of the waste liquor.

This discovery was announced in 1812. Davy and Gay-Lussac both investigated the new element about a year later, and the latter gave it the name of iodine (*ἰώδης*) from the violet color of its vapor.

Occurrence.—Iodine occurs in small quantities, widely diffused in nature, chiefly in combination with sodium, potassium, calcium, and magnesium, in certain salt springs, in minute quantities in sea-water, from which the iodides are absorbed by sea-weeds and certain varieties of sponges, and in the sodium nitrate (Chili saltpeter) deposits of Chili and Peru. In certain rare minerals iodine occurs combined with silver, lead, mercury, or zinc. Traces are found in cod-liver oil, the blood, liver, thyroid gland (about 0.03 per cent.), and other internal organs.

Source.—The world's supply is now chiefly derived from Chili saltpeter (Caliche), whereas formerly all iodine was obtained from sea-weed ashes.

Isolation.—The sea-weeds found on the coasts of Scotland, Ireland, and some of the neighboring islands were gathered, and burned, the ash forming what has been known as *kelp.* The similar product from the coasts of Normandy and the Channel Islands is called *varec,* and that from the Spanish coasts is known as *barilla.* These three commercial products were long worked for their sodium carbonate; later, after the introduction of the Le Blanc Soda process, their potash salts were extracted until the discovery of the Stassfurt mines, when iodine became the chief product. The method of manufacture may be briefly outlined as follows:

Sea-weeds are burned to a fused mass of carbon and ash; this mass, which contains from 0.5 to 1.5 per cent. of alkali iodides, is lixiviated with water, the solution, after concentrating, was evaporated, when the less soluble alkali sulphates, chlorides, and carbonates crystallized out, leaving the very soluble iodides in the mother liquor. The iodine may be removed from the latter:

(1) By treating with sulphuric acid, whereby the remaining alkali carbonates are converted into sulphates and removed by crystallization. To the mother liquor, after a further addition of sulphuric acid, manganese dioxide is added, and the mass heated in stills, when the liberated iodine passes over and condenses in a series of earthenware receivers:

$$2NaI + MnO_2 + 2H_2SO_4 = Na_2SO_4 + MnSO_4 + 2H_2O + I_2.$$

(2) The mother liquor after acidifying with sulphuric acid is either treated with chlorine or heated with ferric chloride, whereby iodine is liberated. In the latter instance the reaction is as follows:

$$2NaI + 2FeCl_3 = 2FeCl_2 + 2NaCl + I_2.$$

The most important sources of iodine at the present time are nitre beds of Chili and Peru.

These deposits, called *caliche*, which consist chiefly of sodium nitrate, contain from 0.175 to 0.6 per cent. of iodine, present as sodium iodate ($NaIO_3$) with small amounts of the iodides of sodium and magnesium. The mother liquor remaining after the removal of the sodium nitrate contains about 22 per cent. of iodate, and yields from 2 to 5 gm. of iodine to the liter.

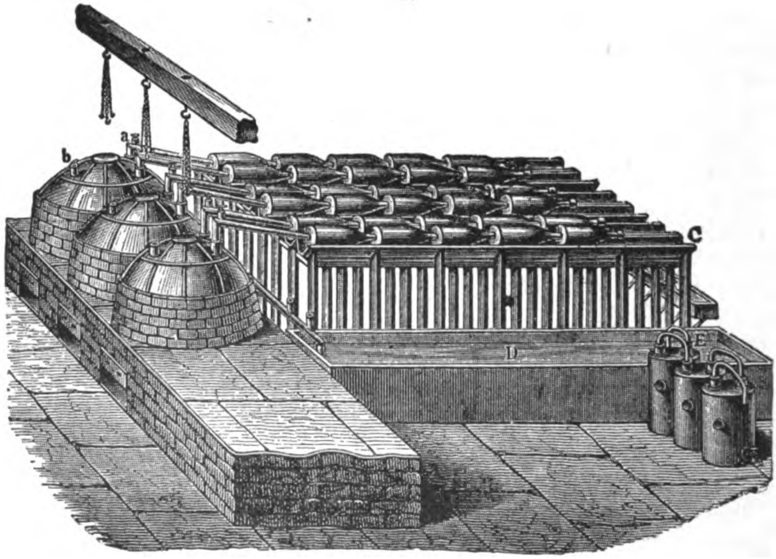
The iodine is precipitated from this mother liquor by means of a mixture of neutral and acid sodium sulphite.

$$\underset{\text{Sodium Iodate.}}{2NaIO_3} + \underset{\text{Sodium Sulphite.}}{3Na_2SO_3} + \underset{\text{Sodium Acid Sulphite.}}{2NaHSO_3} = \underset{\text{Sodium Sulphate.}}{5Na_2SO_4} + H_2O + I_2.$$

The iodine is collected on muslin strainers, dried, and purified by sublimation.

Physical Properties.—Iodine consists of "heavy, bluish-black, dry, and friable rhombic plates, of a metallic luster, a distinctive odor,

FIG. 97.



Sublimation of iodine.

a sharp and acrid taste, and a neutral reaction." It has a specific gravity of about 4.94 at 17°, melts at about 114°, and boils at about 184°, giving off a vapor which, when mixed with air, is violet-colored, but when pure is deep blue. At ordinary temperatures slow volatilization takes place, and if in a bottle minute crystals are deposited on the sides. Pure iodine is not hygroscopic; even when kept over water, not more than 0.05 per cent. of moisture is absorbed.

Iodine is slightly soluble in water, one part of the element requiring about 3000 parts of water to dissolve it, forming a yellowish solution, which, on exposure to light, decolorizes with formation of hydriodic acid. The solubility of iodine in water is much increased by the presence of an alkali iodide or hydriodic acid. The official **Liquor**

Iodi Compositus, U.S.P. (Lugol's Solution), is an aqueous solution containing 5 per cent. of iodine and 10 per cent. of potassium iodide. In strong alcohol iodine is soluble to the extent of one part in 12.5 of the solvent, forming a dark-brown liquid, which is stronger than the **Tincture Iodi,** U.S.P., which contains 7 parts of iodine, 5 parts of potassium iodide, and 5 parts of water, with alcohol to make 100 parts. Alcoholic solution of iodine readily undergoes decomposition upon standing, the loss in free iodine varying from 15 to 25 per cent. in one year's time or even less. The iodine is converted into hydriodic acid and ethyl iodide. This decomposition may be retarded by the presence of potassium iodide as directed in the U.S.P. With methyl alcohol the rate of decomposition is more rapid and the methyl iodide produced is very irritating. Iodine is freely soluble in ether, chloroform, carbon disulphide and benzene. Solutions in alcohol and ether are brown, while the others vary from red to violet. It is soluble in 80 parts of glycerin and in glacial acetic acid. The solubility is increased in water by a number of organic substances, notably tannic acid or drugs containing this principle; this is due to a combination with the tannin, as well as the formation of hydriodic acid.

Chemical Properties.—Iodine resembles chlorine and bromine chemically, although it is much less energetic. Its compounds with electro-positive elements are less stable, hence it is displaced from these by either chlorine or bromine; thus

$$2KI + Cl_2 = 2KCl + I_2;$$
$$2NaI + Br_2 = 2NaBr + I_2;$$

however, the reverse is true with the oxygen compounds, iodine displacing bromine or chlorine from bromates or chlorates,

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2;$$
$$2KBrO_3 + I_2 = 2KIO_3 + Br_2.$$

The affinity of iodine for hydrogen is relatively feeble, hence it bleaches vegetable colors in the presence of water but slowly; on the other hand, it combines more readily with chlorine, sulphur, phosphorus, and many of the metals, as As, Sb, Bi. When a small particle of iodine is laid on a small piece of phosphorus the combination is attended with so much heat as to inflame the latter. As in the case of bromine, sodium and iodine can be heated together without change, while with potassium the action is explosively rapid. Iodine, like chlorine and bromine, oxidizes under certain conditions metals from the "ous" to the "ic" state. Reducing agents are oxidized, as for example:

$$\underset{\text{Sulphur Dioxide.}}{SO_2} + 2H_2O + I_2 = \underset{\text{Sulphuric Acid.}}{H_2SO_4} + \underset{\text{Hydriodic Acid.}}{2HI.}$$

$$H_2S + I_2 = 2HI + S.$$

$$\underset{\text{Sodium Thiosulphate.}}{2Na_2S_2O_3} + I_2 = \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6} + \underset{\text{Sodium Iodide.}}{2NaI.}$$

This latter reaction takes place when tincture of iodine is decolorized with sodium tetrathionate.

When dissolved in the alkali hydroxides, iodine forms iodides and iodates.

$$\underset{}{3I_2} + \underset{\substack{\text{Sodium}\\\text{Hydroxide.}}}{6NaOH} = \underset{\substack{\text{Sodium}\\\text{Iodide.}}}{5NaI} + \underset{\substack{\text{Sodium}\\\text{Iodate.}}}{NaIO_3} + 3H_2O.$$

With ammonia water, iodine forms an iodide, but at the same time deposits a dark-brown powder, termed *nitrogen iodide* (NHI_2 and NI_3), which is violently explosive when dry.

Impurities and Tests.—Crude iodine contains from 10 to 20 per cent. of moisture, 0.7 to 1.2 per cent. of ash, 0.5 to 0.9 per cent. of chlorine, with small quantities of bromine and cyanogen. The resublimed iodine varies from 98 to 99.8 per cent. pure, with traces of chlorine and cyanogen. **Iodum,** U.S.P., should be of 99.5 per cent. purity. It may be further purified by pulverizing and mixing with one-tenth its weight of potassium iodide and subliming from porcelain vessels. This salt serves to retain the chlorine and bromine. Fixed impurities, in iodine as inorganic salts, may be recognized by volatilizing a small quantity of the sample, which should leave no residue. An excess of moisture is indicated by the iodine adhering to the sides of the bottle, and by its failing to form a perfectly clear, limpid solution with chloroform. Cyanogen, chlorine, or bromine may be present; these may be detected as directed in the U.S.P.

Free iodine in solution is readily detected by its color, which varies from a brown to a pale yellow, according to the quantity present. Upon adding a few drops of freshly made starch paste, a deep blue color is produced, which is decolorized by heating and reappears on cooling. A still more sensitive test is to agitate the solution with a little chloroform, which dissolves the slightest trace of liberated iodine, forming a faint but distinct violet-colored solution. These reactions are not produced with the compounds of iodine, but only after the cautious addition of chlorine water. Excess of this reagent combines with the liberated iodine (page 185), preventing thereby further identification.

Uses.—Iodine is used extensively in the manufacture of some of the coal-tar colors, in the preparation of iodides, in photography, and in medicine.

IODINE AND HYDROGEN

HYDROGEN IODIDE. HYDRIODIC ACID

Formula, HI. *Molecular Weight,* 127.93.

Preparation.—The compound of these two elements is still less stable than in the case of hydrogen bromide. Hence, if a mixture of the vapors of iodine and hydrogen be heated, only a portion combines (see page 137). Usually hydrogen iodide is prepared in the same manner as hydrogen bromide, by aid of amorphous phosphorus.

One part of amorphous phosphorus is mixed with fifteen parts of water in a suitable flask (Fig. 96), and twenty parts of powdered iodine are gradually added, keeping the flask cool, with ice if necessary, and allowing the action after each addition to cease before adding more. When all the iodine has been added, and action has finally ceased, gentle heat may be applied, and the gas, which is very heavy, collected by downward displacement. The same precautions of passing the gas over a mixture of amorphous phosphorus and broken glass may be observed here as with hydrogen bromide. Mercury is acted on by hydriodic acid gas, and, therefore, cannot be used for the collection. The reaction is as follows:

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Iodine.}}{6I_2} = \underset{\text{Phosphorus Tri-iodide.}}{4PI_3}.$$

$$\underset{\text{Phosphorus Tri-iodide.}}{4PI_3} + \underset{\text{Water.}}{12H_2O} = \underset{\text{Hydriodic Acid.}}{12HI} + \underset{\text{Phosphorous. Acid.}}{4H_3PO_3}.$$

Another method, used when a solution of the gas in water is desired, consists in passing hydrogen sulphide into water containing powdered iodine, stirring constantly until all of the iodine has been decolorized.

$$\underset{\text{Iodine.}}{2I_2} + \underset{\text{Hydrogen Sulphide.}}{2H_2S} = \underset{\text{Hydrogen Iodide.}}{4HI} + \underset{\text{Sulphur.}}{S_2}.$$

The small quantity of iodine in solution is first converted into hydrogen iodide, which in turn dissolves more iodine to be acted on by the hydrogen sulphide, sulphur being deposited as a side product. The solution must be boiled to remove the excess of hydrogen sulphide, and filtered to remove sulphur, or distilled, diluting until its specific gravity is 1.10 at 25°, if the U.S.P. acid is desired.

Hydrogen iodide may also be prepared by heating together phosphoric acid and potassium iodide.

$$3KI + H_3PO_4 = K_3PO_4 + 3HI.$$

The use of sulphuric instead of phosphoric acid in this process is precluded on account of the reduction of the sulphuric acid and liberation of iodine.

$$2KI + 2H_2SO_4 = 2KHSO_4 + 2HI.$$

$$2HI + H_2SO_4 = SO_2 + 2H_2O + I_2.$$

Properties.—Hydrogen iodide is a colorless, heavy gas, with a sharp, irritating odor, and an acid taste and reaction. At 0° and a pressure of four atmospheres it forms a colorless liquid, which boils at —34°. Its density is about 4.4 (air = 1). The gas is very soluble in water, one volume at 10° absorbing 425 volumes of the gas. An aqueous solution of the acid prepared by saturating water at 0° fumes freely in the air and has a density of 1.99 (15°). When heated, this acid gives off vapors of the gaseous acid until its strength reaches about 57 per cent. If the diluted acid be heated, water distils over until the solution reaches a concentration of 57.7 per cent., which boils at 127°. The composition of the distillate from this acid varies according to the pressure.

The gas commences to decompose at 180°, and if some of it be poured over the flame of a Bunsen burner, clouds of iodine vapor appear. It also readily decomposes when a red-hot platinum wire is plunged into a vessel of it, or more slowly when simply exposed to the air. This accounts for the difficulty of preparing the gas by the direct union of the elements. The aqueous solution of this acid rapidly decomposes on exposure to air; light has but little effect if air is excluded; it becomes dark brown in color in consequence of the separation of iodine through oxidation.

$$2HI + O = H_2O + I_2.$$

Acidum Hydriodicum Dilutum, U.S.P.—The official acid should contain not less than 9.5 per cent. and not more than 10.5 per cent. of the absolute acid, and has a specific gravity of about 1.100 (25°). This is prepared by interaction between potassium iodide and tartaric acid, the acid potassium tartrate, which is a by-product, being removed by the addition of alcohol.

$$KI + H_2C_4H_4O_6 = KHC_4H_4O_6 + HI.$$

To prevent browning of the solution, due to the separation of iodine, potassium hypophosphite is added; this also reacts with the tartaric acid with the liberation of hypophosphorous acid, which decolorizes the free iodine, forming hydriodic acid.

$$\underset{\text{Hypophosphorous Acid.}}{HPH_2O_2} + 2I_2 + 2H_2O = \underset{\text{Phosphoric Acid.}}{H_3PO_4} + 4HI.$$

Dilute hydriodic acid may also be prepared by passing a current of hydrogen sulphide through a mixture of finely pulverized iodine, 1 gm., and 100 mils of water, stirring at frequent intervals, until the color of iodine has disappeared. Then another portion of the latter is added and the procedure continued until 12 parts of iodine have been consumed. The mixture is then heated till free from hydrogen sulphide, filtered and made up to 100 mils.

$$I_2 + H_2S = 2HI + S.$$

Uses.—Hydriodic acid has some use in medicine. It is a very energetic reducing agent, hence is extensively employed in organic reactions. Its reducing properties are dependent upon the readiness with which it breaks up into nascent hydrogen and iodine:

$$2HI = H_2 + I_2.$$

$$\underset{\text{Ferric Chloride.}}{2\overset{\prime\prime\prime}{Fe}\overset{\prime}{Cl}_3} + 2HI = \underset{\text{Ferrous Chloride.}}{2\overset{\prime\prime}{Fe}\overset{\prime}{Cl}_2} + 2HCl + I_2.$$

$$\underset{\text{Auric Chloride.}}{\overset{\prime\prime\prime}{Au}Cl_3} + 2HI = \underset{\text{Aurous Chloride.}}{\overset{\prime}{Au}\overset{\prime}{Cl}} + 2HCl + I_2.$$

$$\underset{\text{Cupric Chloride.}}{2\overset{\prime\prime}{Cu}Cl_2} + 4KI = \underset{\text{Cuprous Iodide.}}{2\overset{\prime}{Cu}I} + 4KCl + I_2.$$

Iodides.—Nearly all the iodides are soluble in water, the important exceptions being silver, mercurous, mercuric, lead, and cuprous iodides. The iodides of bismuth, tin, and antimony require a little free acid (HI) to hold them in solution. Mercuric iodide (HgI_2) is soluble in an excess of an alkali iodide; this is also true of most all insoluble iodides. Heat fuses and higher temperature decomposes the iodides into iodine, the metal or its oxide.

These salts, like the bromides, may be prepared as follows:

(1) *By direct union of the elements, in presence of water.*

$$\underset{\text{Iron.}}{Fe} + I_2 = \underset{\text{Ferrous Iodide.}}{FeI_2}.$$

(2) *By the addition of iodine to the hydroxide of an alkali metal.*

$$3I_2 + \underset{\substack{\text{Potassium}\\\text{Hydroxide.}}}{6KOH} = \underset{\substack{\text{Potassium}\\\text{Iodide.}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{Iodate.}}}{KIO_3} + 3H_2O.$$

For the removal of the iodate, the mass is ignited with charcoal.

$$KIO_3 + 3C = KI + 3CO.$$

(3) *By interaction between an alkali carbonate or hydroxide and ferroso-ferric iodide.* The latter, known only in solution, is prepared by mixing reduced iron 1 part, iodine 4 parts, and water 10 parts; when the reaction is over, the solution is filtered and 2 parts of iodine added.

$$\underset{\substack{\text{Ferroso-}\\\text{Ferric Iodide.}}}{Fe_3I_8} + \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{4Na_2CO_3} = \underset{\substack{\text{Ferroso-}\\\text{Ferric Oxide.}}}{Fe_3O_4} + \underset{\substack{\text{Sodium}\\\text{Iodide.}}}{8NaI} + 4CO_2.$$

$$Fe_3I_8 + 8NH_4OH = Fe_3O_4 + 8NH_4I + 4H_2O.$$

(4) *By interaction between barium iodide and a soluble sulphate.*

$$BaI_2 + (NH_4)_2SO_4 = BaSO_4 + 2NH_4I.$$

(5) *The insoluble iodides are prepared by interaction between a soluble iodide and a solution of a soluble salt of the metal desired.*

$$\underset{\substack{\text{Sodium}\\\text{Iodide.}}}{2NaI} + \underset{\substack{\text{Mercurous}\\\text{Nitrate.}}}{2HgNO_3} = \underset{\substack{\text{Mercurous}\\\text{Iodide.}}}{2HgI} + \underset{\substack{\text{Sodium}\\\text{Nitrate.}}}{2NaNO_3}.$$

Double Iodides.—Many double iodides are known and are prepared by dissolving certain metallic iodides in solutions of alkali iodides, the double salts crystallizing out, thus:

$$AgI + KI = AgI.KI.$$
$$HgI_2 + KI = HgI_2.KI.$$

Tests.—The acid and its salts may be detected by the addition of a few drops of freshly prepared starch paste, followed by chlorine water, which, when added drop by drop with agitation, will liberate the iodine, and this forms the blue iodide of starch. This blue color disappears on heating and reappears on cooling. Excess of chlorine destroys the reaction, owing to the formation of colorless iodic acid:

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

A more sensitive test is the substitution of 1 or 2 mils of chloroform in place of the starch paste; this dissolves the slightest trace of iodine (from 0.05 mgm. KI) with a pink color. The chlorine water may be replaced by cupric or ferric sulphate solution. Hydriodic acid or solutions of its salts yield insoluble precipitates with solutions of lead, silver, mercury (*ous* and *ic*), and copper (*ous*). Before deciding finally on the presence of hydriodic acid and iodides, one must be sure that such salts as the sulphites and thiosulphates are either absent or are completely oxidized by the chlorine, for the blue color will not appear until all readily oxidizable substances have been oxidized. A few organic substances, notably tannin, interfere with the formation of the blue iodide of starch.

IODINE AND CHLORINE

These two elements unite in two proportions, forming iodine monochloride, ICl, and iodine trichloride, ICl_3. The former is prepared by passing dry chlorine over dry iodine until the latter is liquefied. It is a thick, reddish-brown liquid, which solidifies on standing, to well-defined crystals, which melt at 24.2°. It is decomposed by water, forming iodic acid, hydrochloric acid, and free iodine. This solution does not color solution of starch, owing to the absence of iodine ions.

Iodine trichloride is prepared by continuing the passing of chlorine over the iodine monochloride until a solid compound is obtained. This is a solid, crystalline compound, of a yellow color, which, when heated to 25° (33°), fuses and gives off chlorine, forming monochloride. It partly dissolves in water and is in part decomposed into iodic and hydrochloric acids and free iodine. This is a powerful antiseptic and disinfectant, a 1 to 1000 solution being sufficient to destroy bacteria of all kinds.

FLUORINE

Symbol, F. *Atomic Weight,* 19. *Valence,* I, *also* 3, 5 *or* 7.

Number of atoms in the molecule, 2; density, about 1.3 (air = 1).

History.—The art of etching glass by means of a mixture of fluorspar and sulphuric acid was known to Schwankhard, of Nuremberg, in 1670. Scheele (1771) was the first to note that this action was due to the formation of an acid, which he prepared by distilling fluorspar with sulphuric acid.

Moissan first isolated fluorine in any quantity in 1886, by the electrolysis of anhydrous hydrofluoric acid containing potassium hydrogen fluoride, which served as a conductor. In 1897, Moissan and Dewar, using liquid oxygen as a refrigerant, succeeded in liquefying fluorine at a temperature of about —187°.

Occurrence.—Fluorine occurs chiefly as calcium fluoride or fluorspar, CaF_2, and as sodium and aluminum fluoride or cryolite, $3NaF.AlF_3$. The former of these is widely distributed over the globe, the latter is found in deposits in Greenland. Fluorine has been found in minute amounts in sea-water, in many mineral waters, in the bones and teeth of man, and in milk.

Properties.—Fluorine is a pale greenish-yellow gas, intensely irritating, and of penetrating odor. The liquefied gas boils at —187° and possesses a light yellow color. When free from hydrogen fluoride, the dry or liquefied gas can be readily preserved in glass vessels. The density of the gas is 1.3 (air = 1). It is the most reactive of all the known elements; gold and platinum resist its action at moderate temperatures, while oxygen, nitrogen, chlorine, and argon are indifferent to it. Fluorine combines explosively with hydrogen even in the dark with a red flame; it decomposes the anhydrous alkali chlorides and hydrochloric acid gas, liberating chlorine. Water is decomposed by it, with formation of hydrogen fluoride and ozone. Cork chars and ignites in the gas (forming CF_4) and many organic substances, like benzene, alcohol, and terpentine, are inflamed on coming in contact with it. Its rapid action on many metals at ordinary temperatures is prevented by the formation of a coating of fluoride. Hydrogen, chlorine, bromine, sulphur, phosphorus, iodine, arsenic, antimony, silicon, boron, potassium, and sodium combine with it on contact with great energy, attended by heat and light. In its reactions toward the other halogen compounds, fluorine resembles chlorine, but is far more energetic, even displacing the latter from its compounds, thus—

$$\begin{array}{ccccccc} 2KCl & + & F_2 & = & 2KF & + & Cl_2. \\ CCl_4 & + & 2F_2 & = & CF_4 & + & 2Cl_2. \\ \text{Carbon} & & & & \text{Carbon} & & \\ \text{Tetrachloride.} & & & & \text{Tetrafluoride.} & & \end{array}$$

FLUORINE AND HYDROGEN

HYDROGEN FLUORIDE. HYDROFLUORIC ACID.

Formula, HF. *Molecular Weight,* 20.01.

Preparation.—The pure anhydrous acid is prepared by heating the acid potassium fluoride in a platinum retort, connected with a condenser and receiver of the same metal.

$$KaF.HF \quad = \quad HF \quad + \quad KaF.$$

The principal difficulties arise from moisture in the salt, and from danger of inhaling the vapor, which is extremely irritating and poisonous.

The diluted acid is more easily prepared from fluorspar and sulphuric acid in a leaden or platinum vessel. The vapor is conducted through a tube of the same metal into water contained in a lead, platinum, or gutta-percha vessel.

$$\begin{array}{ccccccc} CaF_2 & + & H_2SO_4 & = & CaSO_4 & + & 2HF. \\ \text{Calcium} & & \text{Sulphuric} & & \text{Calcium} & & \text{Hydrogen} \\ \text{Fluoride.} & & \text{Acid.} & & \text{Sulphate.} & & \text{Fluoride.} \end{array}$$

Properties.—The pure anhydrous acid is a colorless liquid which boils at 19.4°. Hydrogen fluoride forms a colorless, intensely corrosive gas which is readily soluble in water, and in the presence of moisture corrodes glass, porcelain, earthenware, and the metals, excepting platinum, gold, and lead; the non-metals are but slightly affected by the acid. Because of its exceedingly caustic action, the greatest care should be exercised in handling the gaseous acid or its solution. The concentrated solution (76.9 per cent.) has a specific gravity of 1.26 (at 0°), and this on heating gives off the gas until the specific gravity is reduced to 1.12 (20°), when it distils unchanged at 120°, and contains 36 per cent. of the anhydrous acid. The moist vapors or the aqueous acid rapidly attack glass, combining with the silica as follows:

$$\begin{array}{ccccccc} 4HF & + & SiO_2 & = & SiF_4 & + & 2H_2O. \\ \text{Hydrogen} & & \text{Silicic} & & \text{Silicon} & & \text{Water.} \\ \text{Fluoride.} & & \text{Oxide.} & & \text{Fluoride.} & & \end{array}$$

On account of this property, one of the most important uses of the acid is in etching glass. That portion of the glass to be preserved from its action is covered with a film of wax or paraffin, and after tracing the design or letters through the wax, the object is either immersed in the liquid or is exposed to the vapors of the acid over a heated leaden vessel containing a mixture of powdered fluorspar and sulphuric acid. In the former case the etching is deeper and transparent; in the latter it is superficial and matt. The divisions on thermometers, eudiometers, and other graduated apparatus are marked in this manner. The dilute commercial acid is transported in gutta-percha or paraffin (ceresin) bottles.

The commercial acids vary in strength from 38 to 55 per cent. of hydrogen fluoride, and contain from 2 to 10 per cent. of *hydrofluosilicic* acid (H_2SiF_6), with from traces to as much as 4 per cent. of sulphuric acid.

Salts and Tests.—The fluorides of the alkali metals are readily soluble in water; the fluorides of the alkaline earths are insoluble, as are those of copper, lead, zinc, and ferric iron. Calcium chloride solution yields with the acid or soluble fluorides an insoluble calcium fluoride. All fluorides when mixed with sulphuric acid etch glass. They are prepared by action of the acid on metals or their oxides.

Hydrofluosilicic Acid.—H_2SiF_6. This acid, which is only known in solution, results when the vapors of silicon fluoride are passed into water and the solution filtered.

$$\underset{\substack{\text{Silicon}\\\text{Tetrafluoride.}}}{3SiF_4} + 4H_2O = \underset{\substack{\text{Ortho-Silicic}\\\text{Acid.}}}{H_4SiO_4} + \underset{\substack{\text{Hydrofluosilicic}\\\text{Acid.}}}{2H_2SiF_6}.$$

When a concentrated solution is evaporated, silicon tetrafluoride escapes, leaving hydrogen fluoride in solution, while a dilute solution deposits silicic acid during evaporation, owing to the decomposition of the silicon tetrafluoride by the water. Solutions of hydrofluosilicic acid deport themselves like other acids, dissolving metals with evolution of hydrogen and neutralizing alkalies to form salts. The salts of this acid are all soluble with exception of the potassium salt, which is but slightly soluble, and the barium salt, which is insoluble. Hydrofluosilicic acid is used for hardening plaster of Paris casts. The ammonium salt of hydrofluoric as well as hydrofluosilicic acids is sometimes used to arrest mucoid and lactic fermentation.

THE HALOGEN GROUP

FLUORINE, CHLORINE, BROMINE, IODINE

The halogens constitute a distinctive group or family of elements, and present striking analogies in their physical and chemical properties. Also the same may be said of their various compounds with the other elements. Owing to the readiness with which they tend to form salts, analogous in physical properties to sea-salt, the name (ἅλς, ἁλός = sea salt, γεννάω = to produce) *halogens* has been applied to the entire group.

Physical Properties.—

	F.	Cl.	Br.	I.
Atomic weight	19.	35.46	79.92	126.92
Melting point	—233.0°	—102.0°	—7.3°	+114.0°
Boiling point	—187.0°	—33.6°	+59.0°	+184.0°
Density (at B. P. of liquid)...........	1.14	1.50	2.98	4.95 (Solid)

The values of the physical constants of this group rise in ratio to the increase of atomic weight.

The density and boiling points of their hydrides exhibit a like gradation.

	HF.	HCl.	HBr.	HI.
Molecular weight	20.01°	36.47	80.93	127.93
Density	10.0°	18.235	40.46	63.96
Boiling point	19.4°	—83.7°	—68.7°	—34.0°

Chemical Properties.—The chemical deportment of these elements admits like comparisons. Thus, the comparative affinities of the halogens for hydrogen decrease in accordance with their increase in molecular weight. For example, fluorine and hydrogen combine in the dark, chlorine and hydrogen on exposure to sunlight, while bromine requires a temperature of 190° with sunlight, and iodine combines through the agency of a catalyzer. This same rule applies to the relative affinities of these halogens for the electro-positive elements and the comparative stability of their compounds. Taking them in the order of increasing atomic weight, each element is capable of displacing any one of those following from its inorganic combination. Thus, fluorine displaces chlorine, bromine, and iodine. The facility with which this takes place increases with the atomic weight of the element. The stability and activity of the halogen acids present the same comparisons. Thus, hydrogen fluoride is the most stable and energetic in its chemical deportment, while hydrogen chloride requires a temperature much above 1500° C. for its decomposition; hydrogen bromide is less stable, and breaks up into its elements at about 800° C.; the least stable hydrogen iodide decomposes at gentle heat. The comparative intensities of their chemical affinities and the stability of their salts decrease in like ratio. Because of this relative instability of hydrobromic and hydriodic acids, they cannot be obtained pure by action of sulphuric acid on their corresponding alkali salts, bromine and iodine being liberated through the action of the sulphuric acid on their hydrides. For example:

$$2HI + H_2SO_4 = SO_2 + 2H_2O + I_2.$$

Hydrofluoric and hydrochloric acids, being stable, are prepared in this manner.

Since the degree of electrolytic dissociation is a relative measure of the "strength" of an acid, we find HF very much weaker than the other halogen acids, which are nearly alike in this respect. The salts of these resemble their respective acids, the chlorides being the most stable, while the iodides are the least stable. The fluorides differ in some respects, especially its salts of certain metals.

From the preceding we have seen that the affinity of the halogens for hydrogen diminishes with increasing atomic weight from F to I. With their affinities for oxygen this is reversed. Where fluorine fails to combine with oxygen, the chlorine and bromine compounds of oxygen are quite unstable; the iodine compounds are the most stable. This accounts for the fact that iodine will liberate chlorine and bromine from their higher oxygen compounds, the reverse of their deportment in the case of the hydrogen and metallic compounds of the halogens. We also find that the stability of the oxygen acids increases with the addition of oxygen. Thus, $HClO$, $HClO_2$, and $HBrO$ are very weak and unstable, while the acids $HClO_4$, $HBrO_3$, and HIO_3 are energetic and very stable.

CHAPTER IV

THE OXYGEN GROUP

OXYGEN, SULPHUR, SELENIUM, TELLURIUM

OXYGEN.

Symbol, O. *Atomic Weight,* 16. *Valence,* II.

Number of atoms in molecule, 2; *weight of one liter* (0° *and* 760 *mm.*), 1.429 *gm.; critical temperature,* –113°; *critical pressure,* 50.7 *atm.; boiling-point,* –182.9°; *density,* 1.10535 (*air* = 1) *and* 15.88 (*H* = 1).

History.—Oxygen was discovered by Priestley, of England, in 1771, but he did not publish his results until 1774, for he was long in doubt of its true nature. Scheele, the Swedish apothecary, likewise isolated this element independently and nearly simultaneously with Priestley. This latter investigator prepared oxygen by heating red oxide of mercury, while Scheele obtained his by heating manganese dioxide with sulphuric acid, also by heating nitrates and the oxides of silver and mercury. Both discoverers noted that this gas was capable of supporting combustion and respiration in an intensified degree. This gas was named by Lavoisier, oxygenium (ὀξύς = acid, and γεννάω = to produce), under the erroneous impression that all acids contained this element.

Occurrence.—Oxygen is the most widely diffused and abundant of all the elements. In combination, it constitutes approximately 47 per cent. of the crust of the earth, 86 per cent. of the water, and in the free state 20.9 to 21 per cent. by volume of the atmosphere. Immense quantities of this gas are given off daily by vegetation, which through the aid of sunlight decomposes the carbon dioxide present in the air with moisture into oxygen, retaining the carbon and hydrogen. In combination with carbon and hydrogen, oxygen forms the basis of nearly all the alkaloids in the vegetable kingdom.

Isolation.—(1) *By heating mercuric oxide (red precipitate):*

$$2HgO = 2Hg + O_2.$$

(2) *By heating a nitrate:*

$$2KNO_3 = 2KNO_2 + O_2.$$

(3) *By the electrolysis of water:*

$$2H_2O = 2H_2 + O_2.$$

Prepared industrially on large scale by this process.

(4) *By heating manganese dioxide and sulphuric acid:*

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Other oxides rich in oxygen, as barium dioxide, potassium persulphate, or potassium bichromate, may be used to replace the manganese dioxide.

$$2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO)_3 + 8H_2O + 3O_2.$$

(5) *Through interaction between certain salts containing oxygen, as potassium permanganate or the hypochlorites, and hydrogen peroxide:*

$$NaClO + H_2O_2 = NaCl + H_2O + O_2.$$

(6) The method most used on a small scale at the present time consists in heating a mixture of *four parts potassium chlorate and one part manganese dioxide.*

$$2KClO_3 = 2KCl + 3O_2.$$

One kilo of the chlorate yields 391 grams or 272 liters of oxygen, or 3.67 kilos of the salt are required for the production of 1 cubic meter of gas (0° and 760 mm.). The action of the manganese is catalytic, for the chlorate will yield oxygen when heated alone, evolution of the gas beginning at 370 to 380°. However, since the decomposition is exothermic (that is, heat is generated by the reaction), the evolution of gas is liable to become very violent, hence the addition of a non-fusible oxide (MnO_2) when the decomposition begins at about 240°.

The purpose of such a catalytic agent (see page 152) is to accelerate slowly occurring reactions; hence a steady current of gas is obtained at a much lower temperature, and without fusion of the chlorate and liability of explosion.

This method is usually carried out in a copper or iron retort, with arrangements for feeding in about one pound of the mixture at a time, without disconnecting.

Every new lot of manganese dioxide should be tested by heating a small quantity in a test-tube with some chlorate, in order to prove the absence of sulphides and impurities of an organic character, which, if present, would cause an explosion when heated.

Manganese dioxide (MnO_2), which promotes the decomposition of the chlorate, undergoes little or no alteration during the process, while it is capable of yielding oxygen on heating; yet the temperature of its decomposition is much higher than that of the chlorate. Lead peroxide, mercuric, cupric, and ferric oxides likewise share this property of manganese dioxide.

(7) *The alkali and alkaline earth peroxides.* For the commercial preparation of oxygen for technical uses, the sodium peroxide method is the most important. The peroxides which contain relatively high percentages of oxygen will, through heating or treating with water or dilute acids, give up oxygen, forming lower oxides or their salts. Thus, sodium peroxide (Na_2O_2), which is also to be had fused in cube form called "Oxone," will, upon adding to water, yield pure oxygen (100 grams furnishing about 13 liters).

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2.$$

Magnesium, calcium or barium peroxide (BaO_2) requires the addition of a dilute acid, hydrogen dioxide being the intermediate product which decomposes into water and oxygen.

$$MgO_2 + \underset{\text{Acetic Acid.}}{2CH_3COOH} = \underset{\text{Magnesium Acetate.}}{Mg(CH_3COO)_2} + H_2O + O.$$

The calcium peroxide contains from 13 to 15 per cent. of available oxygen, corresponding to about 10 liters of gas per 100 grams of salt. The magnesium peroxide contains 7 to 9 per cent. of available oxygen, yielding about 6 liters of gas per 100 grams.

A number of processes have been proposed for isolating oxygen on a larger scale and at a lower cost than is possible by the preceding. Among the more important of these are the following:

(8) *The Brin Process.*—This is based on the fact that barium oxide will, under certain conditions, take up oxygen gas from the atmosphere, forming a peroxide, and, when heated under reduced pressure, is decomposed into the oxide and oxygen.

$$\underset{\text{Barium Oxide.}}{BaO} + O \rightleftarrows \underset{\text{Barium Peroxide.}}{BaO_2}$$

Purified air is forced under pressure into retorts containing barium oxide heated to 700°, whereby the peroxide is produced. The air supply is then cut off and the pump is reversed so as to form a vacuum, whereby the peroxide is decomposed into its oxide and oxygen, which is removed. Each kilo of barium peroxide yields about 10 liters of oxygen.

(9) *From Liquid Air.*—Liquid air, which is readily prepared on a commercial scale, containing about 50 per cent. of oxygen, is allowed to evaporate at the ordinary atmospheric pressure. The nitrogen gas, which boils at a much lower temperature (—195.5°), escapes more rapidly than the oxygen (boiling at —182.9°), and leaves a residual gas very rich in oxygen. This oxygen, which still contains some nitrogen, is especially adapted for inhalation, owing to its freedom from other noxious gases.

Physical Properties.—Oxygen is a colorless, odorless, and tasteless gas. It is slightly soluble in water, 100 volumes of the liquid at 0° dissolving 4.9 volumes of the gas. The density of oxygen is 1.10535 (air = 1), and 15.88 (H = 1). One liter of the gas weighs 1.429 gm. at 0° and 760 mm. barometric pressure. The critical temperature of oxygen is —113° C. and critical pressure 50.7 atmospheres. Liquid oxygen is of a light-blue color, sp. gr. of 1.124, and boils at about —182.9° under a pressure of 1 atmosphere. At —252° it solidifies to an icy mass, melting at —227°; under a vacuum of 9 mm. it boils at —225°.

Chemical Properties.—Chemically, oxygen is very energetic, combining directly with all elements except the halogens, the rare atmospheric gases, as helium, argon, neon, etc., and the metals gold, platinum, and silver. In the restricted sense of the term, oxygen is not a combustible gas, but it supports the combustion of many elements and compounds. Since *combustion* in the ordinary sense is the result of chemical action accompanied by the production of heat and light, it then follows that oxygen cannot burn in the air, for there is no element present with which it will combine. A stream of oxygen issuing from a jet will, however, burn readily in an atmosphere of hydrogen, ammonia, or sulphur vapors, for it readily combines with either of these. Likewise such non-combustible gases as chlorine or ammonia can be made to burn in an atmosphere of hydrogen and oxygen respectively, the chlorine uniting with the hydrogen to form hydrochloric acid, while the ammonia is oxidized by the oxygen to nitrous and nitric acids. The experiment may be reversed. It therefore follows that the terms *combustible* and *non-combustible* are merely relative and dependent on conditions. Ordinarily the term combustible is restricted to such elements or substances which burn in the atmosphere (page 303).

Respiration is a process of combustion in which the inhaled oxygen combines with the hæmoglobin of the blood, oxidizing the carbon of the waste tissue, which is exhaled as carbon dioxide, while the other oxidation products are eliminated through the urine, etc.

With some elements, as potassium, sodium, and phosphorus, oxygen combines at ordinary temperature, while with others, as sulphur, carbon, and iron, an elevated temperature is necessary. When mixed with hydrogen, the two explode violently on the application of a flame, the product being water. The above phenomena embrace what is known as *oxidation,* and the products of the reactions are termed **oxides.** The various oxides may be divided into the following classes:

(1) *Oxides of the non-metals or acid-forming oxides* (see page 126).

$$\underset{\text{Sulphur Dioxide.}}{SO_2} + H_2O = \underset{\text{Sulphurous Acid.}}{H_2SO_3}.$$

$$\underset{\text{Sulphur Trioxide.}}{SO_3} + H_2O = \underset{\text{Sulphuric Acid.}}{H_2SO_4}.$$

(2) *Oxides of the alkali metals and alkaline earths, which form alkali hydroxides (bases) with water* (see page 130).

$$\underset{\text{Sodium Oxide.}}{Na_2O} + H_2O = \underset{\text{Sodium Hydroxide.}}{2NaOH}.$$

$$\underset{\text{Barium Oxide.}}{BaO} + H_2O = \underset{\text{Barium Hydroxide.}}{Ba(OH)_2}.$$

(3) *Oxides of the heavy metals, or insoluble oxides. Some of this class represent different stages of oxidation, as, for example:*

Pb_2O, Lead Suboxide.
PbO, Lead Oxide (Plumbous Oxide).
Pb_2O_3, Lead Sesquioxide.
PbO_2, Lead Peroxide (Plumbic Oxide).

Uses.—Except in the nascent state, oxygen has no bleaching action. In aging wines and liquors the gas has been found effective when forced into the liquid under a pressure of one or two atmospheres, to accomplish what usually requires years by the ordinary method of storage. It has also been found to assist in the removal of sulphur from illuminating gas when mixed with the latter previous to its passage over the lime. Also in the removal of silicon from pig iron, and the preparation of sulphur trioxide and sulphuric acid. Oxygen gas is extensively employed in connection with acetylene or hydrogen or illuminating gas for blowpipe welding or fusing of metals. Oxygen is extensively employed as an inhalant for stimulating the action of the heart in diseases of the lungs. For this purpose it is used either pure or admixed with some nitrous oxide.

Oxygen may be identified indirectly when present in mixtures of gases, through its absorption by an alkaline solution of pyrogallol (10 p. of pyro, 24 p. of potassium hydroxide, and 100 p. of water).

OZONE

ACTIVE (ALLOTROPIC) OXYGEN

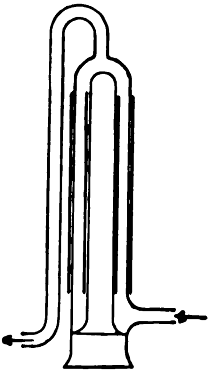
Formula, O_3. *Molecular Weight,* 48.

History.—The odor prevailing about a static electric machine when in action, and, to a slight extent, in the air after a lightning stroke, was long known, but first described by Van Marum in 1785, who noticed this same odor in the gas given off from the anode when acidulated water was subjected to electrolysis, and also from phosphorus when exposed to moist air. Schönbein, in 1840, gave it the name *Ozone,* from the Greek ὄζω, signifying "I smell."

Occurrence.—Ozone is found in minute and variable quantities in the atmosphere which is remote from large cities, and is especially noticeable after a thunder-storm. Various volatile oils and turpentine when exposed to light and air absorb oxygen with formation of peroxides, which, like ozone, oxidize and bleach energetically. This action was formerly ascribed to ozone.

Preparation.—(1) *Ozone is evolved at the positive pole in the electrolysis of water* acidified with sulphuric or chromic acids. (2) It is also formed by the *silent discharge of electricity through air or oxygen.* For this purpose a Siemens ozonizing tube * (Fig. 98) is employed. (3) *When phosphorus is allowed to slowly oxidize* in the air, or *oxygen is passed over pieces of moist phosphorus.* This is best accomplished by standing two or three sticks of phosphorus on end in a dish containing a shallow layer of water, so that they are about one-half immersed in the liquid. A stoppered bell-jar is then placed over the whole, and very soon ozone may be detected by the appropriate tests. (4) *By passing oxygen over manganese dioxide* (MnO_2) or *red lead* (Pb_3O_4), *heated not above* 400°. When prepared by means of the Siemens tube, the quantity of ozone rarely exceeds 6 per cent.; however, it may be obtained nearly pure (86 per cent.) by cooling this mixture by means of boiling liquid oxygen, whereby the ozone condenses to an indigo-blue fluid which may be separated from the oxygen through the lower boiling-point of the latter.

FIG. 98.



Siemens ozonizing tube.

Properties.—Ozone is a colorless gas with a peculiar odor, such as is noticeable about moist phosphorus. Liquid ozone boils at —119° (760 mm.). It reverts very gradually into ordinary oxygen, which change is hastened upon heating. Ozone dissolves readily in volatile and fixed oils (cod-liver oil dissolving 200 volumes), and at 12° water is gradually converted into oxygen and hydrogen dioxide ($H_2O + O_3 = O_2 + H_2O_2$). Characteristic of ozone are its active oxidizing properties in the presence of moisture, one-third of the (nascent) oxygen entering into the reaction while a molecule of inactive oxygen remains. It bleaches organic colors, such as indigo or litmus; it oxidizes all metals, excepting gold and platinum; phosphorus, sulphur, and arsenic are converted into their respective acids; ammonia is oxidized to ammonium nitrate or nitric acid. Silver is blackened through the formation of black silver peroxide; white lead hydroxide is converted into brown lead peroxide; black lead sulphide is oxidized into white lead sulphate, and iodine is precipitated from a solution of potassium iodide.

Detection.—(*a*) Paper moistened with potassium iodide solution and starch paste turns blue when exposed to an atmosphere of ozone, the

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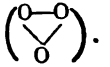
[*] This consists of a glass tube covered with tin-foil, which is placed inside of a larger one covered on the outside with tin-foil (right inverted tube of illustration). The outer and inner coatings are connected with the poles of an induction coil while a current of air or oxygen passes through.

reaction being $2KI + H_2O + O_3 = O_2 + 2KOH + I_2$. Other oxidizing agents, as chlorine, bromine, nitrogen dioxide, and hydrogen dioxide, also produce this reaction. (*b*) Paper moistened with a dilute solution of lead nitrate, then exposed to H_2S, will be oxidized by ozone to white lead sulphate. (*c*) Paper moistened with a solution of tetra-methyl-diamido-diphenyl-methane in acetic acid gives a violet with ozone; yellow with nitrogen dioxide, deep blue with chlorine or bromine, and no color with hydrogen dioxide.

Composition.—The density of ozone is 24 ($O = 16$), one-half more than oxygen; its molecular weight is 48; then if the atomic weight of oxygen is 16, it follows that the molecule of ozone contains 3 atoms of oxygen . Two volumes of ozone will yield three volumes of oxygen, and only one (nascent) atom of the three serves as the oxidizing agent. The two atoms of the molecule of ordinary oxygen are firmly linked; but with the introduction of a third atom, as in ozone, a very unstable condition results.

Uses.—Ozone is employed in industrial bleaching processes; for the destruction of fusel oil in alcohol; for the cleansing of wine and beer casks; for ozonizing air, and for the sterilization of water.

OXYGEN AND HYDROGEN

These elements combine in two proportions:

Hydrogen Monoxide, or Water, H_2O.
Hydrogen Dioxide, H_2O_2.

WATER

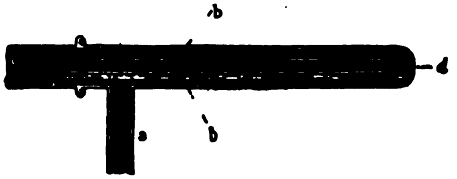
Formula, H_2O. $H—O—H$. *Molecular Weight*, 18.016.

History.—The observation by Cavendish (1781), that water was the product of the combustion of hydrogen, broke down the ancient belief in the elementary nature of water. This experiment of Cavendish was confirmed by Lavoisier, in 1783, who decomposed water into its elements and demonstrated that it was composed of one part, by weight, of hydrogen, and eight parts, by weight, of oxygen. Gay-Lussac (1805) proved the volume composition of water to consist of two volumes of hydrogen and one volume of oxygen.

Occurrence.—In addition to the abundant natural occurrence, as we are accustomed to see it, water is very widely distributed in such a way as to escape casual observation. It is present in green plants to the extent of from 75 to 90 per cent., in fruits from 80 to 95 per cent., in the animal body from 75 to 80 per cent., while the soil averages from 5 to 20 per cent. of moisture. Considerable but variable quantities exist in the atmosphere. The surface of all solids is covered with a layer of moisture, the amount of which varies according to the temperature of the body and the percentage of moisture in the air. For this reason, in the accurate determination of weight, bodies are first dried by heat and then cooled in desiccators before weighing. As water of crystallization and hydration, water enters very extensively into the composition of chemicals.

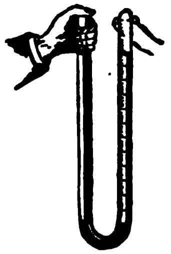
Formation.—The simplest method of forming this compound from its elements, hydrogen and oxygen, and proving the product to be water, is to burn a jet of hydrogen in air, and hold over the flame a cool bell-jar, which will immediately become coated with a film of moisture. When a mixture of the two gases is brought in contact with a flame, a violent explosion results. If, however, they are brought together at the moment of their combination, so as to prevent explosion, the mixture will burn with a very intense heat (2100 to 2500°). The apparatus by which this is accomplished is illustrated in Fig. 99, and is known as the oxyhydrogen blowpipe. The hydrogen or coal gas is introduced through the tube *a* and ignited at *d;* oxygen is then introduced through *c*. When the jet is directed against a piece of freshly burned lime, we have the oxyhydrogen lamp, the incandescent lime of which gives an intense light. This is an intensely exothermic reaction, 33,950 calories being developed in the formation of water from its elements. The combination of one gram of hydrogen with 7.94 gm. of oxygen generates sufficient heat to raise 33,950 grams of water from 0° to 1°. The mixture of oxygen and hydrogen is known as " detonating gas," for when ignited by means of a spark or spongy platinum, combination takes place with explosive violence. Water is also the product of many chemical reactions.

FIG. 99.



Oxyhydrogen blowpipe.

FIG. 100



Ure's eudiometer.

Composition.—Analytically, the composition of water may be demonstrated through the electrolysis of water (acidulated with sulphuric acid), which, when carried out in the Hoffman eudiometer (Fig. 92), yields *two* volumes of hydrogen, which collects in the arm containing the negative electrode, and *one* volume of oxygen in the other with the positive electrode.

Synthetically, the composition of water may be proven either by volume or weight. Volumetrically, by introducing exactly 1 volume of oxygen and 2 volumes of hydrogen over a column of mercury contained in a eudiometer tube (Fig. 100). After exploding this mixture by means of an electric spark, all the gas will have disappeared and the tube will be filled with mercury, excepting a very small quantity of water which has been formed. Should the two gases introduced be in proportions other than the above, any excess of one or the other will remain after the explosion. If the arm of the eudiometer containing the water be heated above 100 degrees, the latter will be converted into steam, which will measure two-thirds of the volume of the two gases employed. That is, 2 volumes of hydrogen and 1 volume of oxygen yield 2 volumes of steam. Gravimetrically, the quantitative synthesis of water is carried out by conducting pure dry hydrogen over a weighed quantity of heated copper oxide, the resulting water being collected and weighed. The weight of the copper oxide after the reduction is also noted. The loss in weight sustained by the copper oxide represents the oxygen consumed, and this subtracted from the water formed is the hydrogen. For example: 10 grams of copper oxide lost 2.011 grams of oxygen, which in turn yielded 2.2644 grams of water. The hydrogen consumed would be equivalent to 2.2644 — 2.011 = 0.2534 gram. Then the ratio of hydrogen to oxygen would be 0.2534 to 2.011, or 1 to 7.93, which represents the combining weights of these two gases. Since the vapor density of water is 9.008 (O = 16), its molecular weight must be 18.016 (2 × 9.008), and of this 2.016 parts by weight, or two atoms, are hydrogen, and 16 parts by weight, or one atom of oxygen.

Properties.—Pure water is an odorless and tasteless liquid. In small quantities it is colorless, but in deep layers it has a bluish-green color; it is but slightly compressible and a poor conductor of heat and electricity. When cooled, water contracts, reaching its greatest density or smallest volume at +4°. The metric gram represents the weight of 1 mil of water at this temperature. This temperature has also been selected as one of the standards for specific gravity; that is, a *number* expressing the weight of any volume of substance divided by the weight of an equal volume of water at the same temperature. When the standard is 4°, then specific gravity and density are the same. Density is the *mass of a unit volume* of a substance, hence is an *absolute* quantity, while specific gravity, which may be taken at 4°, 15.6°, 20°, or 25°, becomes merely a *relative* figure. One mil of water at 0° weighs 0.999878 gm., hence its density is 0.999878. Upon further cooling, water expands, and upon solidifying this expansion amounts to about 9 per cent. of its volume. One mil of ice at 0° weighs 0.91752 gm., hence its density is 0.91752, which causes it to float in water. While the freezing point of water may vary under certain conditions—for instance, under pressure—the melting point remains constant at 0°. When water crystallizes (hexagonal system), heat is set free, while, on the other hand, when ice is fused, heat is absorbed; this is true of all fluids and solids when they pass from one state of aggregation into another. If 1 gm. of ice at 0° is dissolved in 1 gm. of water at 80° (79.25°), the temperature of the resulting two grams of water is 0°, the 80 heat units (calories) have been consumed in melting the ice. The one gram of water at 0° contains 80 calories more than one gram of ice at 0°. This heat which disappears without raising the temperature of the body is called *latent heat.* Then with ice or water this heat consumption or liberation amounts to 80 (79.25) calories (see p. 48). That is, in order to fuse 1 kilo of ice, a quantity of heat will be required which is capable of raising 80 (79.25) kilos of water through one degree centigrade. At all temperatures water is constantly undergoing evaporation, increasing in rapidity with the temperature and diminishing with the increase of pressure and tension of the aqueous vapor of the atmosphere above.

The boiling point of water, like that of all other liquids, bears a constant relation to the pressure.* Under one atmosphere (the ordinary pressure, 760 mm.) the boiling point is constant; the application of more heat only causes the liquid to boil faster, but does not increase its temperature. When, however, the liquid is confined under a pressure of two atmospheres, the temperature will rise on the application of heat to 120.6°, when boiling will commence.† One volume of water at 100° will yield 1696 volumes of steam, the heat of vaporization being 536.5 calories. That is, to convert one gram of water at 100° into steam at 100°, 536.5 calories are consumed.

Water is a neutral, indifferent substance which is decomposed by various metals. Potassium, sodium, and calcium decompose it at ordinary temperature with liberation of hydrogen; thus,

$$K_2 + 2H_2O = 2KOH + H_2.$$

Other metals, as iron, copper, zinc, lead, nickel, etc., decompose water only at high temperature.

$$3Fe + 4H_2O \rightleftarrows \underset{\text{Ferroso-ferric Oxide.}}{Fe_3O_4} + 4H_2.$$

This is a reversible reaction, the oxide being reduced to metallic iron by the hydrogen at a still higher temperature.

The halogens will, under certain conditions, decompose water with liberation of oxygen, which in turn acts as an oxidizer, while the hydrogen forms a haloid acid.

$$2Cl_2 + 2H_2O = 4HCl + C_2.$$

$$I_2 + \underset{\text{Sulphurous Acid.}}{H_2SO_3} + H_2O = 2HI + \underset{\text{Sulphuric Acid.}}{H_2SO_4.}$$

Water combines with many bodies with considerable energy. Of these the most striking are certain electro-positive oxides, as potas-

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* The following table gives the temperature at which water boils under an increase of pressure:

Pressure in atmospheres.	Boiling point.	Pressure in atmospheres.	Boiling point.
1	100°	6	159°
2	120.6°	8	170.8°
3	133.9°	10	180.8°
4	144°	25	224.7°

† Below the ordinary boiling point of water the pressure is best expressed in millimeters of mercury, as follows:

Pressure in millimeters of mercury.	Boiling point.	Pressure in millimeters of mercury.	Boiling point.
760.0	100°	17.36	20°
525.5	90°	12.67	15°
354.9	80°	9.138	10°
233.3	70°	6.506	5°
148.9	60°	4.568	0°
91.97	50°	2.151	—10°
54.9	40°	0.944	—20°
31.51	30°		

sium oxide, K_2O, and calcium oxide, CaO, which form bases (hydroxides) as follows:

$$K_2O + H_2O = 2KOH.$$
$$CaO + H_2O = Ca(OH)_2.$$

With the oxides of certain electro-negative elements it combines energetically to form acids, as follows:

$$SO_3 + H_2O = H_2SO_4.$$
$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

The above reactions are all strongly exothermic.

Water is a very stable compound, withstanding a temperature of 1000° ; above this point, dissociation takes place very gradually. At 2500° it is dissociated or decomposed into its elements, which re-combine when the temperature is lowered.

Being readily obtainable in pure state, water is employed as the standard in specific gravity, specific heat, temperatures, and in the metric weights and measures. Because of its neutral character, water serves as a universal solvent.

Water of Crystallization or *Water of Hydration.*—Many chemicals in crystallizing from a state of solution assume molecular compounds with the water as water of crystallization. The quantity of such water taken up by a salt at a given temperature is always the same; but at different temperatures a salt may unite with different quantities of water to form crystals belonging to different systems.

Thus sodium carbonate forms at ordinary temperature monoclinic crystals, $Na_2CO_3 + 10H_2O$, between 30° and 50°, rhombic prisms, $Na_2CO_3 + 7H_2O$, and when crystallized from a saturated solution above 35°, $Na_2CO_3 + H_2O$. Common salt crystallizes at $-7°$ as $NaCl + 2H_2O$, at $-25°$ as $NaCl + 10H_2O$.

In many instances the color of the salt is determined by the presence of water of crystallization, thus anhydrous copper sulphate is white, while the crystals are blue; cobaltous chloride with two molecules of crystal water is blue, while the salt, which contains six molecules of water, is red. Water of crystallization may usually be removed at from 100 to 105°.

Water of Constitution.—Water which forms an integral part of the molecule and can usually be exchanged by another salt or group. Thus $MgSO_4 + 7H_2O$, when heated to 150°, loses six molecules of water, the remaining one escaping at above 200°, hence must be differently combined. This one molecule of water may be replaced by potassium or ammonium sulphate, giving rise to isomorphous double salts.

$$FeSO_4 + 7H_2O. = FeSO_4.(NH_4)_2SO_4 + 6H_2O.$$
$$MgSO_4 + 7H_2O. = MgSO_4.K_2SO_4 + 6H_2O.$$

Efflorescence.—Many crystalline salts when exposed to the air gradually lose their water of crystallization, disintegrating to a powder. Notably among this class are sodium carbonate, sodium sulphate, copper sulphate, and ferrous sulphate.

Hygroscopic salts are such as attract moisture from the air, and when they dissolve therein, forming solutions, they are said to *deliquesce.* For example, zinc chloride, calcium chloride, caustic soda, or potash, potassium acetate.

Distilled Water.—The various gaseous, saline, and other impurities present in natural waters preclude their employment in the preparation of solutions of many chemicals which are used as reagents in analysis and for medicinal purposes. For the removal of these we resort to distillation, using either a glass or block-tin condenser, and reject the first portions (10 per cent.) which distil over, and then collect about 80 per cent. of the whole. The small portion of water remaining in the still contains the solid impurities and should be washed out before introducing another portion.

Distilled water should be free from odor, taste, and perfectly neutral in reaction. It should give no reaction for inorganic acid radicles, salts, ammonia, or organic substances, and, when recently prepared, leave no residue upon evaporation. When kept for any time in glass containers variable quantities of soluble matter (silicates) are taken up. This may amount to as much as 0.060 gram per liter, depending upon the kind of glass of the container and the time of standing.* Distilled water exerts a slight solvent action upon metals, hence contact with lead or copper or their alloys should be avoided.

Aqua Destillata, U.S.P.—From 1000 volumes of water distilled, the first 100 volumes and the last 150 volumes are rejected. When evaporated on a water-bath and dried at 100° to constant weight, distilled water should not yield more than 0.001 per cent. of residue. This allows for soluble matter taken up from the container.

Aqua Destillata Sterilisata, U.S.P.—Distilled water sterilized by boiling for thirty minutes, keeping the neck of the flask closed with a pledget of cotton.

Natural Waters.—These include all such waters as occur naturally upon the surface of the earth which are more or less impure from the presence of dissolved gases and various inorganic substances taken up from the rocks and soil. These waters may be classed as rain, spring, mineral, and sea waters.

Aqua, U.S.P.—The percentage of solid matter remaining after evaporating 100 mils on a water-bath must not exceed 0.03 gm., with no evolution of ammonium salts nor charring when ignited. Limit tests are demanded for lead, copper, chlorides, nitrates, nitrites, and ammonium compounds, the presence of which above the standard limits is indicative of sewage contamination.

(1) **Rain Water.**—This is the purest form of natural water, provided it can be collected free from contamination. Ordinarily when collected in the vicinity of cities it contains such gases as carbon dioxide, ammonia, sulphur dioxide, and nitric acid, with small quantities of foreign suspended matter which are present in the atmosphere and are carried down with the rain drops. Generally, one gallon of rain water will contain about 4 cu. in. of nitrogen, 2 cu. in. of oxygen, and 1 cu. in. of carbon dioxide.

(2) **Spring Water.**—The water supply of cities is usually taken

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* When kept for one month in a green glass bottle, 1000 mils of distilled water took up 14 milligrams of soluble silicates; from a brown glass bottle 58 milligrams, and when boiled for two hours in Bohemian glass, one liter of water took up 20 milligrams of soluble matter. This naturally varies considerably according to the composition of the glass.

from lakes or rivers which are supplied from smaller streams and springs. The water from such sources, having been in contact with the earth, holds in solution variable quantities of inorganic compounds, the nature and quantity of which depends upon the rock formation of the region. Usually these waters contain chiefly the carbonates and sulphates of calcium and magnesium, with smaller amounts of the alkalies, iron, silica, and organic matter. Spring and well waters, which contain more solids than lakes and rivers, usually range from 4 to 180 parts of total solids per 100,000. When the total solids run above 100 parts they are classed as mineral waters, provided these possess medicinal value. Water taken from rivers is usually very impure because of sewage contamination, hence such must first undergo treatment before using. Water intended for domestic purposes is designated as *potable,* and should be pure from a sanitary standpoint. For drinking purposes, the presence of dissolved carbon dioxide and other gases with inorganic salts is essential, since these impart the sparkle and agreeable taste—without these, water is insipid.

All potable waters must be free from sewage and surface drainage which carries considerable organic matter possibly laden with disease germs. Organic matter (indicated by the blackening through heating of the residue after evaporation) is present in all varieties of potable water; however, the presence of this in greater or lesser amounts does not necessarily condemn water for drinking purposes. While the presence of organic matter is essential to the development of microorganisms, yet this does not necessarily indicate that a water is harmful until a bacteriological examination has determined whether such organisms are pathogenic or not.

Waters taken from shallow springs or wells which receive surface drainage, or such as are in proximity to barns or cesspools, as well as the water of rivers or lakes which receive the drainage of cities, are always to be regarded with suspicion. Sewage contamination is indicated by the presence of nitrites, nitrates, larger quantities of chlorides, free and albuminoid ammonia with organic matter.

Water of questionable purity may be rendered innocuous when treated with chlorinated lime, which serves to destroy all pathogenic bacteria. For convenience, the preparation is made into tablet form, each tablet containing 0.015 gm. calcium hypochlorite (Calx Chlorinata) (3.5 mgms. available Cl) and 0.08 gm. of sodium chloride; using one to each liter of water will render it fit for drinking in 20 minutes' time. The *Bacillus coli* are destroyed by this treatment in about 12 minutes.

Hard and Soft Waters.—One of the chief factors which determines the value of water for domestic and manufacturing purposes is its hardness. This is due to the presence of calcium and magnesium salts, which form insoluble precipitates with soap, whereby the water fails to lather and cleanse until these salts have been completely precipitated. When employed for feeding boilers, hard waters form a more or less coherent deposit called *boiler scale,* which causes clogging and frequent burning out of the tubes. This is composed chiefly of carbonate and sulphate of calcium with some iron oxide and silica.

Temporary hardness is caused by the presence of the bicarbonates of calcium and magnesium, which may be removed by boiling, whereby the free carbonic acid, which has held the insoluble carbonates in solution, passes off and precipitation ensues. $Ca(HCO_3)_2 + \text{heat} = CaCO_3 + H_2O + CO_2$. This temporary hardness may also be removed through the addition of alkali carbonates or hydroxides, thus:

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$
$$Ca(HCO_3)_2 + Na_2CO_3 = CaCO_3 + 2NaHCO_3.$$

Permanent Hardness.—After water has lost its temporary hardness through boiling, it may still remain more or less hard. This is due to the presence of sulphates and chlorides of calcium and magnesium, one or both. These may be removed through the addition of soluble carbonates which precipitate the calcium or magnesium as carbonates. The soluble alkali sulphate which remains in solution exerts a deleterious action when the water is used in boilers.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

Water is said to have one degree of hardness when it contains one part of calcium carbonate or its equivalent in one hundred thousand. The degree of hardness is determined by agitating the sample of water with a standard solution of soap until a permanent lather is produced. The standard solution of soap is prepared by titration with calcium chloride solution of known strength. Each degree of hardness indicates the destruction and waste of twelve parts of the best hard soap by one hundred thousand parts of water.

(3) **Mineral Waters** may be considered a class of spring waters, which have taken up various saline substances or gases, or both, from the strata through which they have passed. Their value for medicinal purposes depends upon the nature and quantity of the mineral matter present. Such waters are often designated by the character of their most important medicinal constituent. Therefore we have the following varieties:

Carbonated waters, or those which contain carbon dioxide in considerable quantity, often holding in solution calcium and magnesium carbonates. Such waters often effervesce on coming to the surface. The Waukesha water, from Waukesha, Wisconsin, the Apollinaris, and the Marien Spring are foreign examples of this class.

Sulphur waters contain hydrogen sulphide, and deposit sulphur on exposure to the atmosphere. Sometimes both sulphuretted hydrogen and carbon dioxide are present in the same water. Richfield Springs, New York, and White Sulphur Springs, West Virginia, belong to this class.

Alkaline waters usually contain considerable quantities of sodium bicarbonate with the sodium and magnesium sulphates. The Apollinaris water of Neuenahr and Ems (Prussia), Vichy (France), Saratoga Vichy, the Capon Springs (West Virginia), are examples of this class.

Lithia waters usually do not contain any notable quantity of mineral substance, but include small quantities of lithium carbonate or chloride. The Vichy water from Vichy (France), the Gettysburg, and the Aix-la-Chapelle are examples.

Saline waters contain relatively large proportions of magnesium and sodium sulphates with sodium chloride. The waters of Saratoga Springs (New York), Blue Lick Springs (Kentucky), Kissingen (Bavaria), Wiesbaden (Prussia), are examples of general saline waters. Those of Carlsbad and Franzensbad (Bohemia), Hunyadi Janos and Apenta (Hungary), and French Lick Springs (Indiana) are natural purgative waters which contain considerable quantities of the sulphates of magnesium and sodium.

Siliceous waters contain small quantities of alkaline silicates, and are represented by the hot springs of the Yellowstone Park and Iceland.

Chalybeate waters have iron as a constituent held in solution by carbon dioxide, and consequently deposit iron as a hydroxide or oxide on exposure to the atmosphere. The waters of Pyrmont and Schwalbach (Germany), Spa (Belgium), Alexisbad (Sweden), and numerous American springs belong to this class.

A number of saline waters are so rich in certain chemical compounds as to constitute an important source of these substances, notable examples being the salt-wells of Pennsylvania, Ohio, Michigan, and West Virginia, whose waters furnish sodium chloride with small quantities of bromides.

(4) **Sea-water.**—This averages 3 to 4 per cent. of inorganic salts. Sodium chloride constitutes 2.6 per cent., and the remainder consists chiefly of magnesium chloride and sulphate and calcium sulphate with traces of bromides and iodides. The specific gravity of sea-water is about 1.025 at 15°. The Dead Sea contains about 22.8 per cent., and Great Salt Lake, Utah, about 32 per cent. of solids.

HYDROGEN DIOXIDE

HYDROGEN PEROXIDE

Formula, H_2O_2. H—O—O—H. *Molecular Weight*, 34.02.

Occurrence.—Hydrogen peroxide was first prepared by Thénard in 1818, naming it oxygenated water.

It occurs as traces in the air, rain, and snow. Also when slow oxidation processes take place in the presence of water, as well as its electrolysis.

Preparation.—Through the action of acids on peroxides in the presence of water (BaO_2, CaO_2, MgO_2, K_2O_2, Na_2O_2),

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2$$
$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$
$$BaO_2 + H_3PO_4 = BaHPO_4 + H_2O_2.$$
$$BaO_2 + CO_2 + H_2O = BaCO_3 + H_2O_2.$$

Since the medicinal hydrogen peroxide solution must be as free as possible from soluble salts, especially barium, only such acids as sulphuric and phosphoric (usually both), which form insoluble barium compounds, are used. For technical purposes, as a bleaching or oxidizing agent, hydrofluoric acid is occasionally used in place of sulphuric and phosphoric acids. Such peroxides should never be employed medicinally.

Sodium perborate ($NaBO_3$), when dissolved in water, forms the unstable metaborate ($NaBO_2$), which with the carbon dioxide of the water is converted into borax, sodium carbonate and hydrogen dioxide.

$$NaBO_3 + H_2O = NaBO_2 + H_2O_2.$$
$$4NaBO_2 + CO_2 = Na_2B_4O_7 + Na_2CO_3.$$

By using 17 gm. of perborate with 6 gm. of citric acid, per 100 mils of water, a 10-volume hydrogen dioxide is obtained; a commercial hydrogen peroxide is prepared through the electrolysis of water acidulated with sulphuric acid.

For preparing the medicinal solution of hydrogen peroxide, barium dioxide is first washed to remove soluble saline matter, then hydrated ($BaO_2 + H_2O = BaO(OH)_2$) by slowly adding to it about double its weight of distilled water (ice cold) and allowing to stand; after hydration has taken place, phosphoric or sulphuric acid, or preferably both, diluted with water is gradually added with stirring, keeping cold by ice, until the mixture finally assumes a slightly acid reaction, when after permitting the subsidence of the barium sulphate it is filtered. Care must be exercised to remove all traces of barium from the solution. After this the solution is diluted until of proper concentration.

Physical Properties.—Prepared by the above methods, hydrogen dioxide is in dilute aqueous solution which may be concentrated by evaporation (between 50° and 60°) or distilling *in vacuo* till one volume contains about 50 volumes of oxygen (available). Further concentration must be made *in vacuo* (7 mm. or less), collecting the latter portions of the distillate. The anhydrous peroxide forms a thick, colorless fluid of about sp. gr. 1.437 (20°), which boils at 69° (26 mm.), and crystallizes at low temperature, fusing at —2°. It is soluble in ether and may thus be extracted from its aqueous solution.

Chemical Properties.—Concentrated solutions (30 volumes of hydrogen peroxide), free from acids, are quite stable when kept in clean containers which do not give up alkali. However, when once opened and exposed to the air containing even small quantities of ammonia, decomposition begins. This will increase rapidly with rise of temperature, and near 100° decomposition usually takes place ($2H_2O_2 = 2H_2O + O_2$) with explosive violence. Explosion of concentrated solutions may also be induced through the presence of solid matter in powder form or the introduction of finely divided metals (Pt, Fe, MnO_2, C). Such solutions are very caustic, hence should not be brought into contact with the skin. The dilute (3 per cent. or 10 volume) solutions are quite stable if kept of a slight acid reaction, to overcome the alkalinity of glass containers. Through the addition of certain organic substances, preferably aromatic amines (as acetanilid) in the proportion of 1 part to 2500 of the peroxide, the latter will generally not lose more than 10 per cent. in volume in one year, after which decomposition proceeds quite rapidly. When once alkaline, hydrogen peroxide decomposes very rapidly. The presence of suspended barium sulphate, ferric oxide, alumina, ammonium salts, particles of glass, cork dust, silica, etc., causes rapid decomposition of these solutions. Hydrogen dioxide is a powerful oxidizing (also reducing) agent, through its decomposition into nascent oxygen. It bleaches organic pigments, hair, feathers, bone, etc., the solution being made slightly alkaline for this purpose.

Oxidizing Reactions.—Hydrogen dioxide oxidizes:

(1) Sulphides to sulphates,

$$PbS + 4H_2O_2 = PbSO_4 + 4H_2O.$$
$$H_2S + 4H_2O_2 = H_2SO_4 + 4H_2O.$$

(2) "Ous" acids and salts to "ic" state,

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O.$$
$$H_3PO_3 + H_2O_2 = H_3PO_4 + H_2O.$$
$$2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O.$$

(3) Arsenic, arsenous oxide, aluminum, iron, magnesium, lead, etc., to their highest oxides,

$$Mg + 2H_2O_2 = MgO(OH)_2 + H_2O \quad (MgO_2 + 2H_2O).$$

(4) The hydroxides of barium, calcium, and strontium are converted into their peroxides,

$$Ba(OH)_2 + H_2O_2 = BaO_2 + 2H_2O.$$

(5) Hypochlorous and hypobromous acids and their salts yield their respective halogen acids or salts,

$$HClO + H_2O_2 = HCl + H_2O + O_2.$$
$$Ca(OCl)_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

(6) The halogens are converted into their binary acids,

$$Cl_2 + H_2O_2 = 2HCl + O_2.$$

Reducing Reactions.—

(7) Potassium ferr*o*-cyanide $[K_4\overset{''}{Fe}(CN)_6]$, in *acid* solution, is oxidized to the ferr*i*-cyanide $[K_3\overset{'''}{Fe}(CN)_6]$. $2K_4\overset{''}{Fe}(CN)_6 + 2HCl + H_2O_2 = 2K_3\overset{'''}{Fe}(CN)_6 + 2KCl + 2H_2O$. In *alkaline* solution, reduction takes place.

$$2K_3Fe(CN)_6 + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + O_2.$$

(8) Silver oxide is reduced to metallic silver,

$$Ag_2O + H_2O_2 = H_2O + Ag_2 + O_2.$$

(9) Brown lead peroxide is reduced to yellow-oxide,

$$PbO_2 + H_2O_2 = PbO + H_2O + O_2.$$

(10) In acidulated solution, potassium permanganate is reduced and decolorized,

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$

(11) Iodides are decomposed slowly by strong solutions of H_2O_2. In presence of ferrous salts, traces of H_2O_2 liberate iodine at once (see Tests, page 206).

$$2KI + H_2O_2 = 2KOH + I_2.$$

Liquor Hydrogenii Dioxidi, U.S.P.—This is an aqueous solution of hydrogen dioxide, containing not less than 3 per cent. by weight of the dioxide, which corresponds to ten volumes of available oxygen. It is colorless and odorless; it has a slightly acidulous taste, and produces a peculiar sensation and soapy froth in the mouth. When 20 mils are evaporated to dryness, not more than 0.03 gram of residue should be obtained. Not more than 2 mils of N/10 potassium hydroxide V.S. are required to neutralize 25 mils of the solution. The Pharmacopœia permits the presence of 1 part of an organic preservative in 2500 of the solution. It is best kept loosely corked with paraffined stoppers in a cool place. The assay process is based on reaction 10.

Uses.—On account of its oxidizing action, hydrogen dioxide is useful as a bleaching agent for cotton, wool, silk, ivory, hair, oils, etc. It is also useful for the sterilization and preservation of foods. In photography it serves to remove the last traces of thio-sulphate from prints. In medicine, hydrogen peroxide is used as an antiseptic and disinfectant, hence must be free from barium, arsenic, fluorides, and poisonous metals, also excessive amounts of mineral acids. As a bleaching agent, hydrogen peroxide is far preferable to chlorine or other bleaches, because of its freedom from odor and a less destructive action on tissues and fibres.

Tests.—(1) Upon adding hydrogen peroxide to a dilute solution of potassium iodide containing starch, T.S., and a few drops of ferrous sulphate, T.S., a blue color will appear. The ferrous salt is oxidized to the "ic," which in turn liberates iodine from the potassium salt, to form starch iodide.

(2) If a few drops of chromic anhydride (CrO_3) solution, or potassium dichromate with sulphuric acid, are added to hydrogen dioxide, a blue color (of perchromic acid) is produced, which dissolves with a blue color upon shaking with ether.

(3) The colorless solution of titanium dioxide (TiO_2) in sulphuric acid diluted with water, is colored lemon yellow (TiO_3) through the addition of a trace of hydrogen dioxide.

OXYGEN AND CHLORINE

Three oxides and four acids of chlorine are known, as follows:

OXIDES	ACIDS
Chlorine Monoxide, Cl_2O.	Hypochlorous Acid, $HClO$.*
Chlorine Dioxide or Peroxide, ClO_2.	(Chlorous Acid, $HClO_2$.)†
	Chloric Acid, $HClO_3$.
Chlorine Heptoxide, Cl_2O_7.	Perchloric Acid, $HClO_4$.

Chlorine and oxygen do not unite directly, and the above oxides are all made by indirect methods. The oxides and oxy-acids of chlorine

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* Known only in solution. † Represented by salts.

are unstable bodies; some of the former explode with decomposition when heated or subjected to percussion. The higher oxy-acids, especially $HClO_4$, are the most stable. All are active oxidizing agents.

CHLORINE MONOXIDE, Cl_2O (Cl–O–Cl).

Preparation.—Chlorine monoxide (hypochlorous oxide) is prepared by passing dry chlorine over dry precipitated mercuric oxide cooled by ice, brown oxychloride of mercury being formed at the same time.

$$2HgO + 2Cl_2 = HgO.HgCl_2 + Cl_2O.$$

The gas as formed is passed into a tube cooled by a freezing mixture, where it forms a reddish-brown liquid.

Properties.—Chlorine monoxide is a yellow gas, having an odor resembling chlorine, but not so suffocating. It is very soluble in water, 200 volumes of the gas dissolving in one volume of water at 0°, forming hypochlorous acid. When condensed to an orange-colored liquid it boils at +5°. The gas or liquid is very unstable and explodes through warming or jarring; it detonates on contact with sulphur, phosphorus, or organic substances, $2Cl_2O = O_2 + 2Cl_2$.

It is therefore an active oxidizing and bleaching agent. Hydrochloric acid is decomposed into chlorine ($2HCl + Cl_2O = 2Cl_2 + H_2O$), and with calcium chloride or alkali hydroxides hypochlorites are formed.

$$CaCl_2 + 2Cl_2O = Ca(ClO)_2 + 2Cl_2.$$
$$2KOH + Cl_2O = 2KClO + H_2O.$$

HYPOCHLOROUS ACID, HClO

Preparation.—This acid, known only in aqueous solution or its salts, is formed—

(1) *By passing chlorine monoxide into water:*

$$Cl_2O + H_2O = 2HClO.$$

(2) *On agitating chlorine gas with mercuric oxide and water:*

$$HgO + 2Cl_2 + H_2O = HgCl_2 + 2HClO.$$

The solution is then distilled *in vacuo*, or, upon shaking 15 gm. of precipitated mercuric oxide (previously heated to 300°), mixed with a little water, with one liter of chlorine, the mercury is precipitated as oxychloride ($HgO.HgCl_2$). The mixture is then filtered.

(3) *By conducting chlorine into a suspended mixture of chalk in water:*

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + CO_2 + 2HClO.$$

(4) *a—Distilling solutions of bleaching lime with very dilute acids*, just sufficient being used to liberate the hypochlorous acid and not hydrochloric acid from the calcium chloride, thus: $CaCl_2 + 2HNO_3 = 2HCl + Ca(NO_3)_2$. The free hydrochloric acid will decompose the hypochlorous acid with liberation of chlorine,

$$HClO + HCl = H_2O + Cl_2.$$
$$\underbrace{2Ca(OCl).Cl} + 2HNO_3 = CaCl_2 + Ca(NO_3)_2 + 2HClO.$$

b—Passing a current of carbon dioxide through a solution of bleaching powder in water and filtering:

$$2Ca(OCl).Cl + CO_2 + H_2O = CaCl_2 + CaCO_3 + 2HClO.$$

Properties.—The dilute acid is colorless, but when more concentrated (5 per cent.) it has a yellow color, such solutions being very caustic. When very dilute it can be distilled without decomposition. The concentrated solution is easily decomposed by sunlight or heat into chlorine, chloric acid, oxygen, and water. The acid, as well as its salts, possesses a strong oxidizing and bleaching action through the liberation of nascent oxygen ($2HClO = 2HCl + O_2$). Charcoal, iodine, sulphur, phosphorus, arsenic, and antimony are rapidly oxidized to their respective acids when brought into contact with hypochlorous acid, and, if the latter be concentrated, with explosive violence. Iron filings are immediately oxidized, with evolution of chlorine. Copper and mercury under similar circumstances are converted into oxychlorides.

Tests.—Hypochlorous acid or its salts when shaken with mercury yield a yellowish-red oxychloride ($HgO.HgCl_2$); all other oxygen acids ($HClO_2$, $HClO_3$, $HClO_4$) and their salts have no action on mercury. On the other hand, chlorine yields insoluble mercurous chloride in the presence of water.

Hypochlorites.—These are produced by passing chlorine into cold solutions (10 per cent. or under) of the alkali hydroxides or their carbonates. More concentrated or hot solutions of the former yield chlorates.

$$2KOH + Cl_2 = KCl + H_2O + KClO.$$
$$2K_2CO_3 + 2Cl_2 = 2KCl + 2KClO + 2CO_2.$$
$$6KOH + 3Cl_2 = KClO_3 + 5KCl + 3H_2O.$$

The well-known *bleach liquor* (sodium hypochlorite), which is extensively employed in various industries, is produced electrolytically (page 729). Chlorinated lime (page 377), as well as sodium hypochlorite solutions (liquid bleach), are produced in enormous quantities. being used as bleaching and disinfecting agents.

When treated with dilute acids, the hypochlorites yield hypochlorous acid, which in turn undergoes decomposition with liberation of chlorine.

$$(a)\ NaClO + HCl = NaCl + HClO.$$
$$(b)\ HClO + HCl = H_2O + Cl_2.$$

Hypochlorous acid or the hypochlorites react with hydrogen dioxide with liberation of oxygen:

$$HClO + H_2O_2 = HCl + H_2O + O_2.$$

CHLOROUS ACID, $HClO_2$

This is known only in the form of its salts, obtained by action of chlorine peroxide upon solutions of alkali hydroxides.

$$2KOH + 2ClO_2 = KClO_2 + KClO_3 + H_2O.$$

The chlorites are very unstable; when heated or triturated with sulphur or sulphides or other oxidizable substances ignition or explosion occurs.

CHLORINE DI- OR PEROXIDE, ClO_2

Preparation.—Chlorine dioxide or chlorine peroxide, ClO_2, is produced when potassium chlorate is added to concentrated sulphuric acid, but, owing to the heat generated through the reaction, explosion is liable to result from the sudden decomposition of the peroxide. It is usually prepared (mixed with some carbon dioxide) by warming a mixture of 40 gm. of potassium chlorate, 150 gm. of oxalic acid, and 20 mils of water to about 60°, passing the gas into water. This gas may be condensed by cooling into a red liquid which boils at +99°. This may be distilled (if free from organic matter) by heating at not over 30°.

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2KHSO_4 + H_2O + 2ClO_2.$$
$$2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2CO_2 + 2ClO_2.$$

Properties.—Chlorine peroxide is a heavy, greenish-yellow gas, with a strong, irritating odor similar to chlorine. It is stable in the dark, but gradually decomposed into its elements by light. The density of the gas is 2.389 (air = 1). The liquid or gaseous product is very explosive when heated (to 100°) or when brought into contact with organic matter, or shaken with mercury, or brought into contact with readily oxidizable substances, as phosphorus, sulphur, sugar, etc., $2ClO_2 = Cl_2 + 2O_2$. When dissolved in water it forms a yellow solution, which on adding an alkali yields a mixture of chlorite and chlorate:

$$2ClO_2 + 2KOH = KClO_2 + KClO_3 + H_2O.$$

CHLORIC ACID, $HClO_3$ ($ClO_2.OH$)

This acid is known only in solution and in combination with certain bases as chlorates.

Preparation.—Barium chlorate in solution is decomposed by an equivalent quantity of diluted sulphuric acid:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

The clear liquid is decanted from the precipitated barium sulphate and evaporated in a vacuum over sulphuric acid. The most concentrated solution obtainable by this method is 40 per cent. On further concentration it decomposes into perchloric acid, chlorine, and oxygen, according to the following:

$$8HClO_3 = 4HClO_4 + 2H_2O + 3O_2 + 2Cl_2.$$

Properties.—When of the above strength, chloric acid is a syrupy liquid, almost colorless, and of a faint odor resembling nitric acid. It has a powerful acid reaction, and in other chemical properties resembles nitric acid. It decomposes organic matter with evolution of heat and light. Sulphur and phosphorus are inflamed on coming in contact with it. Such metals as Zn, Cd, Cu, Fe, etc., dissolve readily in this acid, which usually undergoes reduction through the liberated hydrogen. With silver the reaction proceeds as follows:

$$3Ag_2 + 6HClO_3 = 5AgClO_3 + AgCl + 3H_2O.$$

The dilute solution of chloric acid is fairly stable; prolonged exposure to light generates perchloric acid.

Chlorates.—Chloric acid is monobasic, and its salts are called chlorates. The potassium salt is official under the title **Potassii**

Chloras. Potassium chlorate, which is soluble in 16 parts of water, is one of the least soluble of the potassium salts, while sodium chlorate requires only 1 part of water to effect solution.

Chlorates are formed by heating solutions of the hypochlorites, or with less loss by saturating them with chlorine while being heated. The excess of chlorine liberates hypochlorous acid, which, reacting with the hypochlorite, forms a chlorate:

$$2KClO + 2Cl_2 + 2H_2O = 2KCl + 4HClO.$$
$$KClO + 2HClO = KClO_3 + 2HCl.$$

The liberated hydrochloric acid again generates another portion of hypochlorous acid.

When a hot concentrated solution of a hydroxide is saturated with chlorine the result is a chloride and a chlorate, as follows:

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + H_2O.$$

When, however, a cold dilute solution of the alkali is used, a hypochlorite is formed instead of a chlorate, according to the following reaction:

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$

For preparation of chlorates upon commercial scale through the electrolysis of aqueous solutions of chlorides, see potassium chlorate.

The chlorates fuse on the application of heat, and then give off oxygen. When fused they energetically decompose such organic substances as are brought in contact with them. The dry chlorate should not be triturated with organic matter or sulphur. Such dry mixtures explode violently by percussion or rubbing, and burn brilliantly on the application of flame. When a chlorate is treated with concentrated sulphuric acid, chlorine peroxide is formed. When heated with an excess of hydrochloric acid, chlorates yield chlorine, $KClO_3 + 6HCl = KCl + 3H_2O + 3Cl_2$. If the quantity of hydrochloric acid employed is relatively small, some peroxide is generated, $2KClO_3 + 4HCl = 2KCl + 2H_2O + 2ClO_2 + Cl_2$. Unlike chlorides, chlorates do not yield precipitates with silver nitrate solution.

Uses.—In addition to their use in medicine, the chlorates are largely employed as oxidizing agents in dyeing and calico-printing and in the manufacture of colored fires. In the preparation of fireworks potassium chlorate and some organic substance, as sugar, starch, shellac, or wheat bran, are separately pulverized and then intimately mixed, avoiding friction or anything that might cause ignition or explosion. To this mixture is then added pulverized barium nitrate for green, strontium nitrate for red, sodium nitrate for yellow, and copper oxide for blue. Sulphur is sometimes an ingredient of these mixtures, but it greatly increases the risk of spontaneous combustion or explosion.

PERCHLORIC ACID, $HClO_4$ ($ClO_3.OH$)

Preparation.—Perchloric acid is produced in the decomposition of chloric acid, but this is not used as a method of preparing it. The process consists in first preparing potassium perchlorate by heating the chlorate. The latter salt when heated to 350° gives off a part of its oxygen and becomes a pasty mass of perchlorate and chloride.

$$2KClO_3 = KClO_4 + KCl + O_2.$$

The pasty mass is cooled, powdered, and treated with cold water to remove the potassium chloride. The undissolved residue is then digested with warm hydrochloric acid to decompose any remaining chlorate into chloride, which is then washed out with cold water. The residue which now remains consists of nearly pure perchlorate. On heating the perchlorate in a retort with four times its weight of concentrated sulphuric acid to 110°, pure perchloric acid distils over. A second distillation is necessary in order to get a pure acid, since in the decomposition of the first some of the sulphuric acid is liable to be carried over mechanically. It is advisable to carry out the distillation *in vacuo*.

Properties.—Perchloric acid is a colorless volatile liquid, which fumes copiously on coming in contact with moist air and is prone to violent decomposition. Its specific gravity is 1.764 at 22°. It dissolves in water with a hissing noise, and, when brought in contact with organic matter, causes the latter to ignite. The concentrated acid on standing, even in the dark, rapidly decomposes, becoming dark yellow to brown in color, and finally explodes with violence. Perchloric acid forms several hydrates through the addition of the calculated quantity of water. The pure acid produces painful, slow-healing burns. When dropped on paper, wood, or charcoal it inflames with explosive violence. The diluted acid, which is stable, has a sour taste, and reddens litmus paper without bleaching it. Iron and zinc dissolve in the diluted acid, causing evolution of hydrogen.

Perchlorates.—These are nearly all quite soluble in water, and some of them are deliquescent. The potassium salt is one of the most insoluble, requiring fifty-eight parts of water to dissolve it.

Perchlorates are distinguished from the chlorates by decomposing into chlorides at a higher temperature, by remaining undecomposed on the addition of hydrochloric acid, and by not yielding ClO_2 on the addition of concentrated sulphuric acid. From chlorides they are distinguished by giving no precipitate with silver nitrate, and from both nitrates and chlorates by not decolorizing indigo solution on the addition of hydrochloric acid.

OXYGEN AND BROMINE

Unlike chlorine, bromine appears to form no stable compounds with oxygen; the following acids, however, show a similarity between the oxygen compounds of these two halogen elements:

Hypobromous Acid,	$HBrO$.
Bromous Acid,	$HBrO_2$.
Bromic Acid,	$HBrO_3$.
Perbromic Acid	$HBrO_4$.

HYPOBROMOUS ACID, $HBrO$

Preparation.—This compound is prepared by agitating a mixture of mercuric oxide, water, and bromine, whereby hypobromous acid, mercuric hypobromite and oxybromide are formed. The filtered liquid is distilled *in vacuo* at 40° with pressure of 50 mm.

Properties.—This dilute aqueous acid has a yellow color, and is an active oxidizing and bleaching agent. Solutions of the hypobromites are more unstable than those of the hypochlorites, passing gradually into bromides and bromates.

Sodium hypobromite solution, which is employed in the determination of urea in urine, is prepared by dissolving 10 gm. of sodium hydroxide in 25 mils of water and, when cold, adding 2.5 mils of bromine. The solution should be made fresh when needed.

BROMIC ACID, $HBrO_3$

Preparation.—Bromic acid is prepared by first obtaining a bromate from bromine and barium hydroxide:

$$6Br_2 + 6Ba(OH)_2 = 5BaBr_2 + Ba(BrO_3)_2 + 6H_2O.$$

The bromate, being less soluble than the bromide, is easily separated from it by crystallization. Of this powdered barium bromate, 200 p. are mixed with water and 50 p. of sulphuric acid added with stirring; when the precipitated barium sulphate has settled, the clear liquid is decanted off and the excess of sulphuric acid removed by adding just sufficient baryta water. The barium sulphate is removed by filtration and the aqueous solution is concentrated *in vacuo* till it reaches 50.6 per cent. ($HBrO_3.7H_2O$). When heated to 100° it decomposes into bromine and oxygen. In properties it resembles chloric acid.

The bromates are moderately soluble in water, and are decomposed on heating. Barium and mercury bromates are only slightly soluble. Some (K, Na, Ag, Hg) give off their oxygen with formation of bromides, while others (Mg, Al, Zn) evolve both bromine and oxygen, leaving an oxide of the metal.

OXYGEN AND IODINE

Two oxides and three acids of these elements are known, as follows:

OXIDES	ACIDS
Iodine Tetroxide, I_2O_4.	Hypo-iodous Acid, HIO.
Iodine Pentoxide, I_2O_5.	Iodic Acid, HIO_3.
	Periodic Acid, HIO_4.

HYPO-IODOUS ACID, HIO

Dilute solutions of this may be prepared by agitating finely powdered iodine with freshly precipitated mercuric oxide and filtering.

$$HgO + 2I_2 + H_2O = HgI_2 + 2HIO.$$

Hypo-iodous acid is very unstable. The salts in solution change to MeI and $MeIO_3$.

IODINE TETROXIDE, I_2O_4

Obtained by triturating 1 part of pulv. iodine and 12 parts of nitric acid (sp. gr. 1.5) until a voluminous yellow powder remains. This is dried in a desiccator over soda-lime. Iodine tetroxide is an amorphous, pale-yellow powder, stable to light and air. In contact with water iodic acid gradually forms.

$$5I_2O_4 + 4H_2O = 8HIO_3 + I_2.$$

IODINE PENTOXIDE, I_2O_5 (Iodic Anhydride)

Preparation.—Obtained by heating iodic acid to 180°

$$2HIO_3 = H_2O + I_2O_5.$$

When dissolved in water, iodic anhydride yields iodic acid. It forms a white crystalline substance which decomposes into its elements at 300°. Iodic anhydride is a powerful oxidizing agent, readily oxidizing sulphur and carbon to their dioxides and powdered oxidizable metals to their oxides, explosion frequently taking place if the mixture be heated.

IODIC ACID, HIO_3

Preparation.—The simplest method of preparation is by heating 1 p. of powd. iodine with 10 p. of fuming nitric acid until the oxides of nitrogen and water have been expelled. This should be redissolved in water and again evaporated to dryness (100 to 130°) till free from HNO_3.

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

It may also be prepared from barium iodate and sulphuric acid. The iodate is made by dissolving powdered iodine in hot concentrated solution of potassium chlorate, and adding a few drops of nitric acid. After the evolution of chlorine has ceased and the solution has become cool, crystals of potassium iodate separate, $KClO_3 + I = KIO_3 + Cl$. On dissolving this salt in water and adding barium chloride, barium iodate separates as a white solid. This is then decomposed by the careful addition of sulphuric acid, the barium sulphate filtered off and the filtrate concentrated at 100° for crystallization.

Iodic acid is also formed when chlorine is passed into water in which finely powdered iodine is suspended:

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

The hydrochloric acid is removed by moist, freshly precipitated silver oxide.

Properties.—Iodic acid occurs in the form of colorless, rhombic crystals, very soluble in water, and slightly soluble in alcohol. On heating to 180° the acid decomposes into iodine pentoxide and water. Exposure to sunlight causes decomposition into its elements. Because of its powerful oxidizing action, organic matter, phosphorus, and sulphur inflame on coming into contact with the acid. Sulphurous oxide, sulphuretted hydrogen, and hydriodic acid are oxidized with liberation of iodine: $HIO_3 + 5HI = 3H_2O + 3I_2$. $2HIO_3 + 5SO_2 + 5H_2O = I_2 + H_2O + 5H_2SO_4$. $2HIO_3 + 2H_2S = 3H_2O + S_2 + I_2$.

The iodates are usually prepared from barium iodate by interaction with the sulphate of the desired electro-positive element, removing the insoluble barium sulphate by filtration. Barium iodate may be prepared by passing a current of chlorine into a solution of barium chloride containing suspended iodine, or as detailed under iodic acid. The iodates are detected by adding to the solution a small quantity of sulphurous acid or a sulphite, to liberate iodine, and then a dilute solution of starch, with which the latter forms a blue color. Solutions of alkali iodides and iodates when acidulated react with the liberation of iodine.

$$5KI + KIO_3 + 6HCl = 6KCl + 3H_2O + 3I_2.$$

PERIODIC ACID, $HIO_4.2H_2O$ or H_5IO_6

Preparation.—This acid, which is the final oxidation-product of iodine, is known only in the free state with two molecules of water. It is obtained most readily by acting on perchloric acid with iodine.

$$HClO_4 + I + 2H_2O = HIO_4.2H_2O + Cl.$$

Properties.—This compound consists of colorless, transparent crystals, which are deliquescent and readily soluble in water. They melt at 133°, and on the further increase in temperature (140°) are decomposed into iodine pentoxide, water, and oxygen, $2(HIO_4.2H_2O) = I_2O_5 + 5H_2O$.

THE OXYGEN GROUP

OXYGEN, SULPHUR, SELENIUM, TELLURIUM

These (like the halogens) constitute a natural group of elements which (particularly the latter three) present a gradation in their physical and chemical properties corresponding to their atomic weights. While the valency of oxygen is invariably 2, the others vary as 2, 4, and 6. With rising atomic weights, these elements decrease in electro-negative intensity, tellurium exhibiting the physical properties of a metal.

The general formula RH_2 represents the hydrogen compounds of these elements. The readiness with which they are decomposed by heat increases from oxygen to tellurium, a temperature of about 2500° being necessary to decompose water, while a gentle heat will decompose hydrogen telluride. The oxides are represented by the formulæ RO_2 and RO_3, while the acids are H_2RO_3 and H_2RO_4. The relative strength (reactive ability or avidity) of the acid decreases from sulphuric to telluric acid, the latter possessing very feeble acid properties. The following table will serve to illustrate the marked similarities of some of the principal compounds of this group:

	O	S	Se	Te
Hydrides	H_2O	H_2S	H_2Se	H_2Te
Oxides		SO_2 SO_3	SeO_2	TeO_2 TeO_3
Chlorides	Cl_2O ClO_2	S_2Cl_2 SCl_2	$SeCl_2$ $SeCl_4$	$TeCl_2$ $TeCl_4$
Acids		H_2SO_3 H_2SO_4	H_2SeO_3 H_2SeO_4	H_2TeO_3 H_2TeO_4

The gradations of the physical properties may be noted in the following table:

	O	S	Se	Te
Atomic Weight	16.00	32.07	79.2	127.5
Specific Gravity	1.12(−181°)	1.95-2.07	4.2-4.8	6.2
Fusing-Point	— 227.0°	115°	217°	455°
Boiling-Point	—182.9°	445°	680°	1390°
Color	light blue	yellow	red	black

SULPHUR

Symbol, S. *Atomic Weight,* 32.07. *Valence,* II, *also* IV *or* VI.

Sulphur was known to the ancients.

Occurrence.—It occurs in the free state, mixed with earthy matter, in the vicinity of extinct as well as active volcanoes. Its existence in the free state is supposed to be due to the sulphur dioxide and hydrogen sulphide in volcanic gases, which, reacting on each other, form sulphur, as follows:

$$SO_2 + 2H_2S = 2H_2O + S_3.$$
$$H_2S + O = H_2O + S.$$
$$H_2S + 3O = H_2O + SO_2.$$

Sulphur combined as sulphides and sulphates is very widely distributed. Some of these metallic sulphides are known as *blendes* or *glances*. As examples of the many native sulphides are *zinc blende,* ZnS; *galenite,* PbS; *pyrite,* FeS_2; *cinnabar,* HgS; *stibnite,* Sb_2S_3; *realgar,* As_2S_2. Combined with oxygen we find such native sulphates as *heavy spar,* $BaSO_4$; *gypsum,* $CaSO_4.2H_2O$; *kieserite,* $MgSO_4$, etc. Sulphur exists also in the vegetable and animal kingdoms, combined in various organic compounds, and in some mineral waters, as hydrogen sulphide.

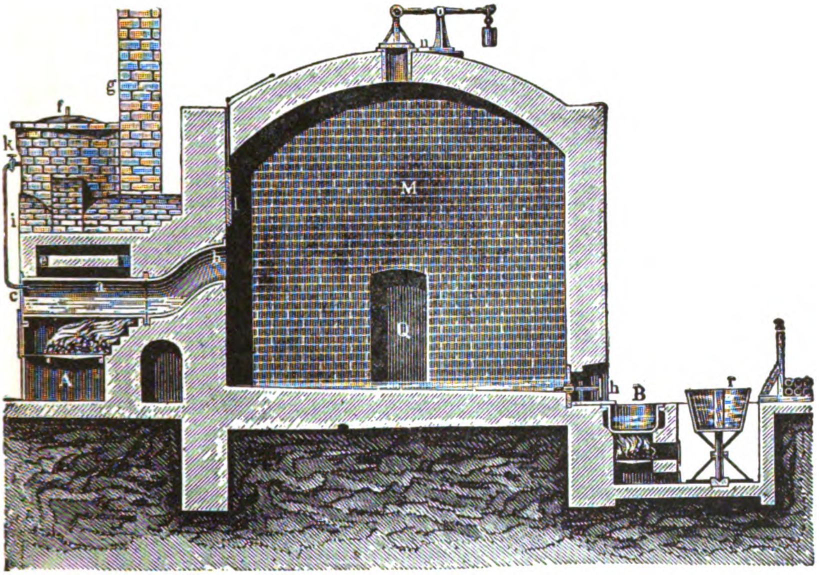
Sources.—The principal source of sulphur has in the past been the volcanic districts in the island of Sicily and other volcanic regions that border the Mediterranean.

Very large deposits of arsenic-free sulphur occur in Utah, Louisiana, and Texas. Our chief supply is from the deposits in Louisiana, which occur at a depth of about 400 feet. Water at high temperature is forced under pressure through driven tubes into the deposits; the sulphur, having been liquefied, is forced to the surface through an inside tube. This sulphur, which is nearly pure, is free from arsenic and selenium. For the production of sulphur dioxide, such as is used in the manufacture of sulphuric acid, immense quantities of iron (FeS_2) and copper ($Cu_2S.Fe_2S_3$) pyrites are consumed.

In addition to the above sources, sulphur is found in Iceland, Mexico, Central America, and the Hawaiian Islands. Volcanoes in all these places either are or have been the cause of the deposit.

Extraction and Purification.—In Sicily the sulphur earth and masses of ore (over 12 per cent.) are piled, with a small amount of fuel, in heaps over depressions in the earth. The heaps are then ignited; the sulphur melts, runs down, and is collected from the hollow beneath. About one-third of the sulphur is lost, being consumed in heating. Steam under high pressure is also employed for melting the sulphur from ores.

FIG. 101.



Sublimation of sulphur.

The crude sulphur contains 3 to 5 per cent. of impurities. To remove these the process of sublimation is resorted to. A furnace similar to that in Fig. 101 is employed. The crude sulphur is melted in the vessel K, with the waste heat from the furnace; it is then run in small quantities at a time into the retort *a*, from which it sublimes into the larger chamber M. At first, while the chamber is cool, the sulphur is deposited in fine powder, but as the whole becomes heated it melts and is run off at the bottom into moulds, and becomes the roll sulphur or brimstone of commerce.

Physical Properties.—Sulphur is a lemon-yellow, hard, brittle, crystalline solid, odorless, and almost without taste. It is negatively electrified by friction, is insoluble in water, almost insoluble in alcohol, ether, and volatile oils, but easily soluble in fixed oils, carbon disulphide (46 p. in 100 p.), sulphur monochloride, benzene, turpentine, etc. The specific gravity of native sulphur is 2.05. On the application of heat it melts at 115°, and remains liquid until cooled to 111°. The liquid is straw-yellow at first, but becomes dark red and viscid on gradually raising the temperature to 160°, when it is too thick to pour, and becomes almost black in color. A further increase of temperature causes the sulphur to become thin in consistence, but it remains dark in color, and at 444.7° it boils under ordinary pressure. The density of sulphur vapor below its boiling-point indicates a molecular formula of S_8, above 860° of S_2.

SULPHUR EXISTS IN THREE ALLOTROPIC MODIFICATIONS:

(a) *Octahedral or Rhombic Sulphur* ($S\alpha$). This is the form in which it occurs in nature, as well as that form in which it crystallizes from carbon disulphide. It melts at 112.8°.

(b) *Prismatic or Monoclinic Sulphur* ($S\beta$). This is a labile form which crystallizes upon cooling fused sulphur. On heating sulphur in a Hessian crucible until melted, allowing to cool until a crust forms on the surface, then quickly pouring out the liquid portion, the crucible will be lined with long, brilliant, transparent crystals, having the form of monoclinic prisms; these become opaque after twenty-four hours at ordinary temperature, and are then found to be made up of minute rhombic crystals. Monoclinic sulphur has a specific gravity of 1.96, melts at 119°, and is soluble in carbon disulphide. This form can exist only between 96° and 119°; below 96° it is rhombic and above 119° the pale mobile liquid is obtained.

(c) *Plastic or Amorphous Sulphur* ($S\gamma$). This may be prepared by carefully heating sulphur to 330°, and then pouring in a thin stream into water. The product in this case is an amber-colored, elastic mass, which may be drawn out into threads or kneaded between the fingers. This is called the plastic variety. It gradually becomes hard and brittle. It has a specific gravity of 1.920, and is insoluble in carbon disulphide. Once this insoluble variety has been formed it reverts only very slowly to the soluble, years being required for the conversion at ordinary temperature; at 100° the conversion is completed in one hour.

COMMERCIAL FORMS OF SULPHUR:

(a) *Brimstone, or Roll Sulphur.* This is the crude moulded sulphur, which is used for technical purposes only.

(b) **Sulphur Sublimatum** (U.S.P.) (Flowers of Sulphur). This is the commercial sublimed sulphur, which should contain, when dry, not less than 99.5 per cent. of S. It consists of a mixture of the rhombic and amorphous varieties.

(c) **Sulphur Lotum** (U.S.P.). Commercial sublimed sulphur is of acid reaction from adhering sulphurous acid. For the removal of this it is washed with water containing a little aqua ammonia. This must contain when dry 99.5 per cent. of S.

(d) Sulphur Præcipitatum (U.S.P) (*Milk of Sulphur*). If sulphur, slaked lime, and water are boiled together, soluble polysulphides of calcium are formed, and, after decanting the clear solution, it is precipitated by the addition of hydrochloric acid.

$$6S_2 + 3Ca(OH)_2 = 2CaS_5 + CaS_2O_3 + 3H_2O.$$
$$2CaS_5 + CaS_2O_3 + 6HCl = 3CaCl_2 + 6S_2 + 3H_2O.$$

This must also be of 99.5 per cent. purity.

Chemical Properties.—Sulphur burns with a pale bluish flame, forming sulphur dioxide. Nearly all metals unite with it to form sulphides, mercury requiring trituration only, while copper and iron burn readily in sulphur vapor. Sulphur combines directly with many other non-metals, as hydrogen, chlorine, bromine, iodine, and phosphorus. When heated with oxidizing agents sulphur is converted into sulphuric acid. Caustic alkalies dissolve it to form a mixture of alkali sulphides and thiosulphate.

Uses.—Immense quantities of sulphur are used in the manufacture of sulphuric acid, sulphur dioxide for bleaching purposes and in vulcanizing rubber. Sulphur is employed to some extent internally.

SULPHUR AND HYDROGEN

HYDROGEN SULPHIDE

SULPHURETTED HYDROGEN. HYDROSULPHURIC ACID

Formula, H_2S. *Molecular Weight,* 34.09.

Occurrence.—It occurs in nature when organic bodies containing sulphur putrefy; hence the odor of rotten eggs, drains and closets, also found in volcanic gases, and in many mineral waters. The sulphur waters in Virginia are the most important in the United States.

Preparation.—Hydrogen sulphide is formed when a stream of hydrogen is passed over sulphur heated to the boiling point.

It is generally prepared through the action of sulphuric or hydrochloric acid on metallic sulphides in the presence of water. An apparatus similar to that illustrated in Fig. 102 answers the purpose satisfactorily. In the generator, A, is placed some ferrous sulphide covered with water, and to it is added sulphuric or hydrochloric acid in small portions at a time just sufficient to keep up the evolution of gas, when the following reaction takes place:

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

The gas is readily evolved without the application of heat, and may either be used directly or, preferably, passed through a little water in the wash-bottle at C. Excess of sulphuric acid causes the evolution of gas to cease through the precipitation of anhydrous ferrous sulphate over the iron sulphide, preventing further action. With hydrochloric acid this does not occur. The use of a wash-bottle is advisable, as it retains portions of the acid or salt that may be carried over mechanically through the violence of the reaction.

Ferrous sulphide frequently contains metallic iron, in which case the gas will contain some free hydrogen. This is rarely an objection, but, if it should be, then a pure gas may be obtained by treating antimonous sulphide with hydrochloric acid:

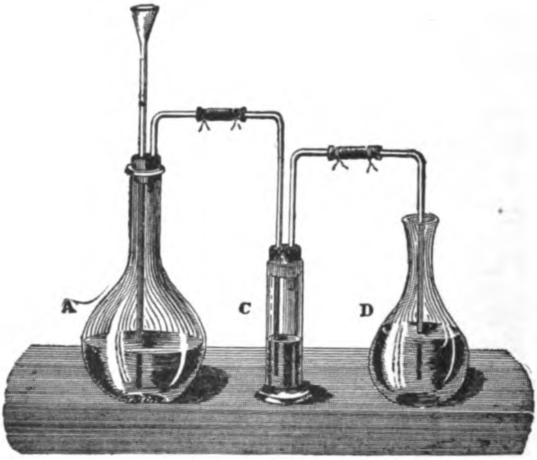
$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Hydrogen Sulphide, T.S. (U.S.P.), is a saturated aqueous solution of the gas. To remove any traces of arsenic (arsine gas) liable to be present in the gas prepared from ferrous sulphide, it is first thoroughly dried and then passed over pulverized iodine, which serves to retain the arsenic.

Physical Properties.—Hydrogen sulphide is a colorless gas (sp. gr. 1.18, air = 1) with a disagreeable odor and a sweetish taste. One volume of water dissolves 4.4 volumes of the gas at 0°, and 3.2 volumes at 15°.

The solution reddens litmus, and rapidly undergoes change on exposure to air, water and sulphur being the result, the latter separating. Under a pressure of 17 atmospheres the gas condenses to a liquid, of the specific gravity of 0.9, which boils at —62° and solidifies at —83°. One liter of H_2S weighs 1.539 gm. (0° and 760 mm.).

FIG. 102.



Preparation of hydrogen sulphide.

Chemical Properties.—Hydrogen sulphide is a very inflammable gas, burning with a pale blue flame. The products of its combustion are water and sulphur dioxide, or sulphur if the combustion is rapid.

The gas is decomposed by many oxidizing agents; chlorine, bromine, and iodine unite with its hydrogen, sulphur precipitating. In the case of iodine the reaction is possible only in the presence of water.

$$H_2S + Cl_2 = 2HCl + S.$$

Sulphuretted hydrogen, owing to the readiness with which it parts with its sulphur, acts as an active reducing agent. Thus—

$$\underset{\text{Ferric Chloride.}}{\overset{\text{III I}}{2FeCl_3}} + \overset{\text{II}}{H_2S} = \underset{\text{Ferrous Chloride.}}{\overset{\text{II I}}{2FeCl_2}} + 2HCl + \overset{\text{II}}{S}.$$

$$\underset{\text{Arsenic Oxide.}}{\overset{\text{V II}}{As_2O_5}} + \overset{\text{II}}{2H_2S} = \underset{\text{Arsenous Oxide.}}{\overset{\text{III II}}{As_2O_3}} + 2H_2O + \overset{\text{II}}{S_2}.$$

$$\underset{\text{Chromium Trioxide.}}{\overset{\text{VI II}}{2CrO_3}} + \overset{\text{II}}{3H_2S} = \underset{\text{Chromium Sesquioxide.}}{\overset{\text{III II}}{Cr_2O_3}} + 3H_2O + \overset{\text{II}}{S_3}.$$

In aqueous solution hydrogen sulphide undergoes slow oxidation from contact with air and light, sulphur being liberated. Boiled (air-free) water should be used for its solution, which should be kept in well-closed containers away from the light.

Hydrogen sulphide combines with many metals, decomposing their oxides, hydroxides, or carbonates. Paper moistened with lead acetate solution is blackened by this gas, lead sulphide being formed, hence this reagent is usually employed to detect its presence.

Uses.—The solution has also been used medicinally; it is given internally in about 15-mil doses. Hydrogen sulphide is employed industrially for the removal of metals from acids and salts. Also used extensively in analysis for the precipitation of basic ions, as sulphides from acid solutions, *e.g.*, Au, Pt, As, Sb, Sn, Ag, Hg, Pt, Bi, Cu and Cd. Another group of cations is precipitated as sulphide by means of ammonium sulphide, *e.g.*, Ni, Co, Fe, Mn, etc.

Hydrosulphides.—These correspond to the hydroxides in which the oxygen has been replaced by sulphur. The alkali hydrosulphides are prepared by passing hydrogen sulphide into solutions of the hydroxides:

$$MeOH + H_2S = MeSH + H_2O.$$

Sulphides.—These are binary compounds and may be viewed as salts of hydrosulphuric acid. Many sulphides occur native (as pyrite, FeS_2; galenite, PbS.; stibnite, Sb_2S_3). Other sulphides may be prepared as follows:

(1) *By fusion of the metals with sulphur:*

$$Fe_2 + S_2 = 2FeS, \text{ or } Cu_2 + S_2 = 2CuS.$$

(2) *By action of H_2S upon metals by aid of heat, excepting Hg and Ag, which react in the cold:*

$$Ag_2 + H_2S = Ag_2S + H_2.$$

(3) *Action of H_2S on metallic oxides or hydroxides.*

$$PbO + H_2S = PbS + H_2O, \text{ or } 4CaO + 3S_2 = 4CaS + 2SO_2.$$

$$4Fe(OH)_3 + 6H_2S = 4FeS + S_2 + 12H_2O.$$

Also salts:

$$CuSO_4 + H_2S = H_2SO_4 + CuS.$$

The alkali sulphides result upon adding an equal quantity of alkali hydroxide to the hydrosulphide ($MeSH + MeOH = Me_2S + H_2O$). The various alkali *polysulphides* (Me_2S_2 to Me_2S_5) are prepared by boiling the normal sulphide with the calculated quantity of sulphur. If the hydroxide of an alkaline earth (Ca, Ba, Sr) be boiled with an excess of sulphur, polysulphides, thiosulphates, and sulphates result.

(4) *By the reduction of sulphates with charcoal:*

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

(5) *By the action of H_2S upon solutions of the metals, usually their chlorides:*

(*a*) Sulphides insoluble in dilute acids—HgS, PbS, Bi_2S_3, CuS, CdS, Sb_2S_3, As_2S_3, SnS, AuS, PtS_2.

(*b*) Sulphides soluble in dilute acids, but insoluble in alkaline sulphides, precipitated by NH_4HS—FeS, NiS, CoS, MnS, ZnS.

(*c*) Soluble sulphides, K_2S, Na_2S, CaS, BaS, SrS.

Many of the above insoluble sulphides are distinguished from one another by their characteristic colors.

Potassa Sulphurata or Liver of Sulphur, U.S.P.—A mixture of the polysulphides and thiosulphate of potassium containing not less than 12.8 per cent. of sulphur. It is prepared by fusing together sulphur and potassium carbonate.

Properties.—In the presence of moisture, oxygen unites with sulphides, forming sulphates. $CuS + O_4 = CuSO_4$. This property is made use of in many industrial operations, as the weathering of sulphides, $2FeS + 3O = Fe_2O_3 + S_2$; black ferrous sulphide is converted into red ferric oxide. The former is obtained in the removal of sulphur compounds from illuminating gas, by means of ferric oxide. This reaction enables the gas manufacturer to renew the ferric oxide many times. This same air oxidation of sulphides takes place in making aluminum sulphate from alum shales, or calcium thiosulphate from waste lime sulphides ($2CaS_5 + 3O_2 = 2CaS_2O_3 + 3S_2$). When roasted, sulphides are converted into the oxides of the bases and sulphur dioxide ($2ZnS + 3O_2 = 2ZnO + 2SO_2$); if the oxide of the metal is decomposable by heat, then the metal remains ($HgS + O_2 = Hg + SO_2$). Chlorine decomposes all sulphides, forming chlorides and sulphur chloride; in the presence of water, sulphur separates. The sulphides of the alkalies and alkaline earths are soluble in water, while the sulphides of the metals are insoluble.

HYDROGEN POLYSULPHIDE

The polysulphides may be prepared by the action of acids on polysulphides of the alkalies or alkaline earths.

These unstable compounds are prepared by boiling together 1 part of slaked lime, 6 parts of water, and 2 parts of sublimed sulphur, and pouring the clear solution into cold concentrated hydrochloric acid. The heavy, yellowish, oily compound separates and sinks to the bottom. It possesses an odor similar to that of hydrogen sulphide, and an acrid, unpleasant taste. It readily decomposes into hydrogen sulphide and sulphur. The exact composition has not been determined; when distilled it yields H_2S_2 (hydrogen disulphide, sp. gr. 1.37) and H_2S_3 (hydrogen trisulphide, sp. gr. 1.5).

COMPOUNDS OF SULPHUR AND THE HALOGENS

SULPHUR AND CHLORINE

These elements combine directly to form three distinct compounds.

Sulphur Monochloride, S_2Cl_2, is formed by passing dry chlorine over molten sulphur. A reddish-yellow liquid is formed, which may be rectified by distillation. It has a specific gravity of 1.70 and boils at 139°. It decomposes in contact with water:

$$2S_2Cl_2 + 2H_2O = SO_2 + 3S + 4HCl.$$

Sulphur monochloride is a solvent of sulphur to the extent of 66 per cent., forming a thick syrupy liquid which is used in vulcanizing rubber.

Sulphur Dichloride, SCl_2, is formed when dry chlorine is passed into the monochloride at 0°. The excess of chlorine is removed by passing carbon dioxide through the liquid. The dichloride is an unstable, dark-red liquid, slowly decomposing at ordinary temperatures into the monochloride and chlorine. The same decomposition takes place on the addition of water.

Sulphur Tetrachloride, SCl_4, a white powder prepared by passing chlorine into the dichloride at $-75°$. This is stable only below 0°.

SULPHUR AND BROMINE

Sulphur Monobromide, S_2Br_2, is the only compound of these two elements known at the present time. It is prepared by the direct union of the elements, the excess of bromine being removed by carbon dioxide. It is a heavy, red liquid, which is stable at ordinary temperatures but decomposes slowly at the boiling point, 200° to 210°, into sulphur and bromine.

SULPHUR AND IODINE

These two elements unite in two proportions.

Sulphur Moniodide, S_2I_2, is formed when the two elements are heated together under water, or without water, in a loosely stoppered flask. They are first thoroughly mixed and then gently heated until the mass becomes of a uniform, dark color, when the temperature is increased to the point necessary to fuse them. It is insoluble in water, soluble in sixty parts of glycerin, and very soluble in carbon disulphide. Alcohol and ether remove the iodine, leaving the sulphur. It is gradually decomposed on exposure to the air, with loss of iodine. On the application of heat it melts at 60°, and at a higher temperature sublimes with partial decomposition, without leaving any residue. Prolonged boiling with water removes the iodine, which escapes with the steam, leaving the sulphur.

Sulphur hexiodide, SI_6, is obtained by evaporating a solution of the two elements in carbon disulphide, when crystals similar to those of iodine separate.

SULPHUR AND OXYGEN

The following compounds of these two elements are known:

Sulphur Sesquioxide (Disulphur Trioxide), S_2O_3.
Sulphur Dioxide (Sulphurous Anhydride), SO_2.
Sulphur Trioxide (Sulphuric Anhydride), SO_3.
Sulphur Heptoxide (Persulphuric Anhydride), S_2O_7.

Two of these, SO_2 and SO_3, unite with water to form corresponding acids.

$SO_2 + H_2O = H_2SO_3$, Sulphurous Acid.
$SO_3 + H_2O = H_2SO_4$, Sulphuric Acid.

There are also the following acids, which are known only in the form of their salts: $H_2S_2O_4$, Hyposulphurous Acid. $H_2S_2O_3$, Thiosulphuric Acid.

POLYTHIONIC ACIDS

$H_2S_2O_6$, Dithionic Acid.
$H_2S_3O_6$, Trithionic Acid.
$H_2S_4O_6$, Tetrathionic Acid.
$H_2S_5O_6$, Pentathionic Acid.

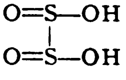
SULPHUR SESQUIOXIDE, S_2O_3

This compound is formed when sulphur is added, in small quantity at a time, to sulphur trioxide. It separates as a dark-blue liquid, which solidifies into bluish-green, crystalline crusts.

It readily decomposes when warmed into sulphur dioxide and sulphur:

$$2S_2O_3 = 3SO_2 + S.$$

HYPOSULPHUROUS ACID, $H_2S_2O_4$, or



$$\begin{array}{l} O{=}S{-}OH \\ \quad | \\ O{=}S{-}OH \end{array}$$

Hydrosulphurous Acid.

This compound should not be confounded with *thiosulphuric acid*, $H_2S_2O_3$, which is sometimes improperly called hyposulphurous acid.

Preparation.—When zinc is added to sulphurous acid the following reaction takes place:

$$3H_2SO_3 + Zn = H_2S_2O_4 + ZnSO_3 + 2H_2O.$$

Properties.—This is a yellow liquid with powerful reducing properties. On exposure to air it is rapidly decomposed, as follows:

$$2H_2S_2O_4 = 3SO_2 + 2H_2O + S.$$

It is a more powerful bleaching agent than sulphurous acid, bleaching indigo, also iodine to HI, also precipitates a number of the metals (Hg, Ag, Cu) from solutions of their salts, for example:

$$\underset{\text{Mercuric Chloride.}}{HgCl_2} + \underset{\text{Hyposulphurous Acid.}}{H_2S_2O_4} = \underset{\text{Mercury.}}{Hg} + 2HCl + \underset{\text{Sulphur Dioxide.}}{2SO_2}.$$

This serves to distinguish it from sulphurous acid. Salts of this acid have been formed which are true hyposulphites. When sodium bisulphite is treated with zinc, the mixture kept cool, and air excluded, the hyposulphite is formed according to the following reaction:

$$4NaHSO_3 + Zn = Na_2S_2O_4 + Na_2SO_3 + ZnSO_3 + H_2O.$$

Sodium hyposulphite is decomposed by acids, with formation of sulphur dioxide, sulphur, and a salt of sodium.

$$2Na_2S_2O_4 + 2H_2SO_4 = 3SO_2 + S + 2H_2O + 2Na_2SO_4.$$

SULPHUR DIOXIDE

SULPHUROUS OXIDE. SULPHUROUS ANHYDRIDE

Formula, SO_2, or $O = S = O$. *Molecular Weight*, 64.07.

History.—Sulphur dioxide, or sulphurous oxide, has been known from very early times, being produced by burning sulphur. It was used as a disinfectant by the Romans.

Occurrence.—It occurs native as a volcanic gas, and is found in small quantity in the air of large cities, on account of the presence of sulphur in coal.

Preparation.—(1) *When sulphur is burned in air or oxygen, direct union of the elements takes place, with the formation of sulphur dioxide:*

$$S_2 + 2O_2 = 2SO_2.$$

This process of burning is used in nearly all cases where the gas is made on a large scale, as in bleaching and the manufacture of sulphites and sulphuric acid.

(2) Sulphur dioxide is prepared industrially by roasting certain metal sulphides, especially those of iron and copper, in furnaces. This is preliminary to the extraction of metals; also, sulphur dioxide is thus prepared for the manufacture of sulphuric acid.

$$2FeS_2 + 7O = Fe_2O_3 + 2SO_2, \text{ or } Cu_2S + 2O_2 = 2CuO + SO_2.$$

(3) *Through the decomposition of sulphuric acid* (1 *part*) *by heating with copper* (⅓ *part*), *mercury, silver, zinc, sulphur, or carbon:*

$$2H_2SO_4 + Cu = CuSO_4 + 2H_2O + SO_2.$$
$$2H_2SO_4 + S = 2H_2O + 3SO_2.$$
$$2H_2SO_4 + C = 2H_2O + CO_2 + 2SO_2.$$

(4) *By heating sulphur with various metallic oxides, as Pb, Hg, Mn, Zn, etc.:*

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Manganese Dioxide.}}{MnO_2} = \underset{\text{Manganous Sulphide.}}{MnS} + \underset{\text{Sulphur Dioxide.}}{SO_2}.$$

$$2PbO + 2S = 2PbS + SO_2.$$

(5) *By decomposing sulphites with dilute acids:*

$$Na_2SO_3 + H_2SO_4 = Na_2SO_4 + H_2O + SO_2.$$

Physical Properties.—Sulphur dioxide is a colorless gas, having suffocating odor. One volume of water at 0° dissolves 79.8 volumes and at 25° 32.8 volumes of the gas. Boiling removes the gas from solution. Alcohol at 25° dissolves about 26.5 per cent. of the gas. At a temperature of —10°, or under a pressure of three atmospheres, the gas condenses to a colorless, mobile liquid, which boils at — 10°, and at — 76° becomes a crystalline solid, and has a sp. gr. of 1.433 at 0°. The density is 2.264 (air = 1), and one liter weighs 2.9261 grams. The critical temperature is +157.2° and the critical pressure is about 78 atmospheres.

The liquid is obtainable in iron cylinders. On the large scale, pressure affords the cheapest means of converting the gas into the liquid state, but for laboratory experiments it may be readily obtained in the liquid condition by passing it through a tube surrounded by a freezing mixture of salt and ice.

A low temperature may be produced by the vaporization of liquid sulphur dioxide, and this may be intensified by directing a current of air over its surface. Like liquid ammonia, it is employed in artificial refrigeration.

The gas is very stable under high temperatures until 1200° is attained, when decomposition into sulphur trioxide and sulphur takes place:

$$3SO_2 = 2SO_3 + S.$$

Chemical Properties.—Both gaseous and liquid sulphur dioxide, in the presence of water, possess active bleaching properties. The action in this case is a *reducing* one, because it removes oxygen, the opposite to that by which chlorine accomplishes the same purpose. In the presence of organic matter it appears to have the power of decomposing water, combining with the oxygen, while the hydrogen in the nascent state is free to combine with the oxygen of the coloring matter, forming colorless compounds:

$$SO_2 + 2H_2O = H_2SO_4 + H_2.$$

The coloring matter is not destroyed, as in the case of chlorine, but may be restored by neutralizing with an alkali, or by the action of a halogen, hence the importance of thorough washing to remove these sulphur compounds in the process of bleaching. It is especially valuable in the bleaching of wool and silk where chlorine would injure the fabric. The articles to be bleached are exposed in moist condition, in a closed compartment, to the vapors of burning sulphur, and afterwards thoroughly washed. Upon exposure to the air, the color gradually returns.

With solutions of the metallic hydroxides and carbonates, sulphur dioxide produces sulphites according to the following reactions:

$$2KOH + SO_2 = K_2SO_3 + H_2O.$$
$$K_2CO_3 + SO_2 = K_2SO_3 + CO_2.$$

Certain metallic peroxides serve as absorbents for SO_2 and are converted by the sulphur dioxide into sulphates, as follows:

$$PbO_2 + SO_2 = PbSO_4.$$

In presence of the halogens, water is reduced, forming the haloid acid and sulphuric acid:

$$I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI.$$

In the absence of water this reaction is reversed, as follows:

$$H_2SO_4 + 2HI = I_2 + SO_2 + 2H_2O.$$

Tests.—Sulphur dioxide is detected by paper which has been saturated with solutions of potassium iodate and starch. When this is brought in contact with the gas the starch is turned blue by the liberated iodine, as follows:

$$2KIO_3 + 5SO_2 + 4H_2O = 2KHSO_4 + 3H_2SO_4 + I_2.$$

If, however, the gas be in excess it will react with the free iodine, according to the reaction given above for the formation of hydriodic acid, and the color will be destroyed.

When brought into contact with paper moistened with mercurous nitrate solution, sulphurous oxide causes blackening through reduction to metallic mercury.

$$2HgNO_3 + SO_2 + 2H_2O = Hg_2 + 2HNO_3 + H_2SO_4.$$

Uses.—The gas is used extensively in bleaching straw and wood pulps, disinfecting, in the manufacture of glue and gelatin, also sugar refining, and in the manufacture of sulphurous acid and the sulphites. The fumes of sulphur dioxide are employed in fumigating, while its aqueous solution or acid salt is an antizymotic arresting fermentation (or putrefaction) by destroying their organic growth. The chief extensive industrial use of sulphur dioxide is in the manufacture of sulphuric acid.

Sulphuryl chloride, SO_2Cl_2, obtained by the union of sulphur dioxide and chlorine. It forms a colorless, fuming liquid of penetrating odor, boiling at 69.1°. The addition of a little water converts it into chlorosulphonic acid and hydrochloric acid, $SO_2Cl_2 + H_2O = SO_3HCl + HCl$. Excess of water as follows: $SO_2Cl_2 + 2H_2O = H_2SO_4 + 2HCl$.

SULPHUROUS ACID

Formula, H_2SO_3, *or* $SO(OH)_2$. *Molecular Weight,* 82.09.

This acid is not known in the free state, but we assume its presence in solution, because of its acid properties, forming salts with bases and that it evolves hydrogen gas with some metals (Mg, Zn), as well as conducting the electric current.

Preparation.—It is prepared by saturating distilled water with sulphur dioxide; such solutions contain usually from 6 to 7 per cent. of the anhydride. The U.S.P. recognizes sulphurous acid as a reagent, which must not contain more than 0.00002 per cent. of As_2O_3.

Properties.—Sulphurous acid is a colorless liquid, of a sulphurous odor, and an acid, sulphurous, and somewhat astringent taste. It has a specific gravity of about 1.028 at 25°, and contains 6 per cent. of the gas by weight. It reddens litmus paper strongly, and then bleaches it. On the application of heat, all the gas is given off. Upon standing, especially in sunlight, sulphurous acid absorbs oxygen and rapidly passes over into sulphuric acid. The extent to which this decomposition has taken place may be determined by adding a few drops of hydrochloric acid, followed by barium chloride T.S. Not more than a turbidity should be produced.

Since sulphurous acid readily absorbs oxygen, being oxidized into sulphuric acid, it becomes an active de-oxidizing or reducing agent. Thus solutions of gold and silver are reduced to the metallic state. Iodine is reduced to hydriodic acid, and mercuric chloride to mercurous chloride, potassium permanganate to manganous and potassium sulphate with loss of color.

$$H_2SO_3 + H_2O + I_2 = 2HI + H_2SO_4.$$
$$2HgCl_2 + H_2SO_3 + H_2O = 2HCl + H_2SO_4 + 2HgCl.$$
$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

Sulphites.—Sulphurous acid is dibasic—that is, has two hydrogen atoms replaceable by bases. This gives rise to two series of salts, the *acid* or *bi*-sulphites, in which only one hydrogen atom is replaced, as follows:

$$KOH + H_2SO_3 = KHSO_3 + H_2O,$$

and the *normal* sulphites, in which both hydrogen atoms are replaced, as follows:

$$2KOH + H_2SO_3 = K_2SO_3 + 2H_2O.$$

The sulphites are usually prepared by passing the gas into a solution of a hydroxide or carbonate; the amount of gas used determines whether an acid or normal sulphite is formed. Since sulphurous acid is a weak acid, it cannot saturate strong electro-negative bases, hence the normal sulphites possess a weak alkaline and acid sulphites a weak acid reaction. Except the sulphites of the alkali metals, all sulphites are more or less insoluble in water.

Heat decomposes the sulphites of the alkaline earths and metals into oxides and sulphur dioxide, as:

$$CaSO_3 = CaO + SO_2;$$

the alkali sulphites into sulphates and sulphides, as:

$$4K_2SO_3 = 3K_2SO_4 + K_2S.$$

Sulphites are also decomposed by the addition of hydrochloric or sulphuric acid, evolving sulphur dioxide, and forming a chloride or sulphate of the base. Because of its greater stability and uniformity, exsiccated sodium sulphite is official as **Sodii Sulphis Exsiccatus,** which contains not less than 90 per cent. of Na_2SO_3. This salt is extensively employed in the manufacture of paper, not only for its bleaching action, but also as an *antichlor* for neutralizing the effect of chlorine when used: $Na_2SO_3 + H_2O + Cl_2 = Na_2SO_4 + 2HCl$. In solution sulphites gradually oxidize to sulphates.

Detection.—Sulphurous acid, the sulphites, as well as the bisulphites, are easily detected by the addition of zinc and hydrochloric acid to their solution, when hydrogen sulphide will be evolved:

$$3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + 3H_2O + H_2S.$$

The use of an acid is necessary in this reaction, since in its absence a hyposulphurous acid salt is produced (page 221).

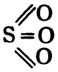
Upon adding an acid to the solution of a sulphite, sulphur dioxide is liberated, which may be detected, as directed on page 224.

The salts of silver, mercury, and lead added to sulphurous acid or a sulphite produce a precipitate which blackens on heating, owing to formation of sulphide.

The sulphites and bisulphites are largely used in bleaching, disinfecting and as antiferments, and in addition are employed more or less in medicine.

SULPHUR TRIOXIDE

SULPHURIC OXIDE. SULPHURIC ANHYDRIDE

Formula, SO_3, or 
$$S\begin{smallmatrix}\diagup\!\!\diagup O\\ =O\\ \diagdown\!\!\diagdown O\end{smallmatrix}$$
Molecular Weight, 80.07.

Preparation.—Formerly sulphur trioxide was prepared by distilling the fuming Nordhausen sulphuric acid. In 1875 Clemens Winkler prepared it by direct union of two volumes of sulphur dioxide with one volume of oxygen, by passing them over platinized asbestos or clay (finely divided platinum) heated to about 400° (page 230).

$$2SO_2 + O_2 = 2SO_3.$$

The white fuming compound is conducted into a well-cooled receiver, where it condenses in long needles. Finely divided ignited oxides of certain metals, as Fe_2O_3, Cr_2O_3, MnO_2, etc., also possess this property, though in lesser degree than platinum. These are termed "contact" substances, since they bring about chemical union of these two gases (page 152).

Sulphuric anhydride may be prepared by heating anhydrous sulphates, *e.g.*, ferric sulphate:

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

Also on heating the fuming ("oleum") sulphuric acid:

$$H_2S_2O_7 = H_2SO_4 + SO_3.$$

On heating concentrated sulphuric acid with phosphorus pentoxide, water is extracted and sulphuric oxide formed:

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3.$$

Physical Properties.—Sulphur trioxide consists of long, transparent prisms. When perfectly anhydrous it fuses at 17.7°, and boils at 46°. On standing for some time at ordinary temperatures, long crystalline fibres slowly form, which fuse at 40°.

The pure trioxide at 20° is a colorless, mobile fluid which has a specific gravity of 1.97.

Chemical Properties.—Sulphur trioxide possesses a great affinity for water, and fumes on exposure to air. When thrown on water it dissolves with a hissing noise, generating considerable heat.

$$SO_3 + H_2O = H_2SO_4.$$

When mixed with metallic oxides, *e.g.*, barium oxide, sulphates result.

$$BaO + SO_3 = BaSO_4.$$

The evolution of heat is so great in this reaction that the mass becomes red-hot. At red heat, sulphuric oxide vapors are decomposed into sulphur dioxide and oxygen. Because of its great affinity for moisture, it chars many organic substances. Sulphur trioxide is manufactured on a large scale, and comes into commerce in iron drums.

Uses.—It is used in the preparation of artificial alizarin, and in dissolving indigo, and the manufacture of sulphuric acid.

SULPHURIC ACID

HYDROGEN SULPHATE

Formula, H_2SO_4, $SO_2(OH)_2$. *Molecular Weight,* 98.09.

History.—A weak sulphuric acid was known from very early times; pyrosulphuric acid was prepared by the Arabians through the dry distillation of burnt alum. The Benedictine monk, Basilius Valentinus, of Erfurt, introduced (about 1450) fuming acid prepared by the dry distillation of weathered ferrous sulphate (basic ferric sulphate). Later, Valentinus prepared sulphuric acid by burning a mixture of sulphur and saltpetre. About 1613, Angelus Sala modified this process by burning sulphur in the presence of an abundant supply of air with steam. The preparation of sulphuric acid from sulphur, on the technical scale, was first attempted about the middle of the eighteenth century. A crude form of the present "chamber" process is said to have been introduced into England, from the Continent, in the eary part of the last century, by Cornelius Drebbel. This method consisted in burning sulphur and nitre together in large glass globes, the bottoms of which were covered with water. This glass vessel was replaced by the present lead chamber at the suggestion of Dr. Roebuck, in 1746. The Gay-Lussac tower has been in use since 1842, and the Glover tower since 1859. The "Contact Process" for the manufacture of sulphuric acid is the outcome of the investigations of Clemens Winkler (1875), and Squire and Messel, on the technical production of sulphuric anhydride.

Occurrence.—In combination it occurs native as the sulphates of calcium, barium, magnesium, and sodium originating in the vicinity of volcanoes.

Preparation.—There are two methods in use for the preparation of sulphuric acid; both of these depend upon the fundamental reaction represented by $SO_2 + O + H_2O = H_2SO_4$; that is, the oxidation of SO_2 to SO_3, which dissolves in water, forming the acid. In one process (*lead chamber*), SO_2 is oxidized by means of the vapors of nitric acid, while in the other (*contact process*) the SO_2 is oxidized by means of air (O) through the agency of catalytic substances.

Lead Chamber Process.—In this, the formation of sulphuric acid is based on the oxidation of sulphur dioxide in the presence of water. This takes place slowly with atmospheric oxygen, but rapidly in the presence of the oxides of nitrogen, which after deoxidation readily abstract oxygen from the air introduced during the process.

The reactions that take place are complex, but in general may be simplified as follows: nitric oxide, 2NO, with air forms nitrogen tetroxide, NO_2, in the chamber, which with the steam yields nitrous acid: $2NO + 2NO_2 + 2H_2O = 4HNO_2$, or $N_2O_3 + H_2O = 2HNO_2$. This with the oxygen of the air and SO_2 yields sulphuric acid and NO, which in turn repeats the same cycle. The oxides of nitrogen act as carriers of the oxygen of the air to the SO_2.

This reaction may be accomplished on a small scale by conducting into a large glass globe sulphur dioxide, nitric oxide, steam, and air. The process will apparently go on indefinitely, since the nitric oxide is converted into tetroxide by the oxygen of the air; but the nitrogen of the air introduced gradually accumulates and so dilutes the oxygen mixture as to prevent further action until it is removed.

When the steam is not simultaneously admitted with the other gases there are deposited "lead chamber crystals," nitrosyl-sulphuric acid:

$$2SO_2 + N_2O_3 + O_2 + H_2O = 2[SO_2.OH(ONO)],$$

which dissolve on the admission of steam, forming sulphuric acid and oxides of nitrogen:

$$2[SO_2.OH(ONO)] + H_2O = 2H_2SO_4 + NO + NO_2.$$

On the large scale the lead chamber process is carried out by the most economical methods, and therefore by the use of the cheapest materials. In England the sulphur dioxide is prepared by roasting iron or copper pyrites ($4FeS_2 + 11O_2 = 8SO_2 + 2Fe_2O_3$); in the United States from pyrites and by burning sulphur. The oxides of nitrogen are prepared by the action of sulphuric acid on Chili saltpetre.

A view of the lead chambers with the two towers is shown in Fig. 103.

The details of the process are, briefly, as follows: Sulphur dioxide, generated by one of the methods above stated, is passed into the Glover tower, C, where it is cooled and mixed with dilute sulphuric acid, which trickles down over the pieces of bricks into the tower from M; at the same time from an adjoining cistern there runs down, and mixes with this, concentrated sulphuric acid containing oxides of nitrogen in solution.

The effect of this mixing with dilute acid is to liberate the oxides of nitrogen from the concentrated acid, which, with the sulphur dioxide, oxygen, nitric acid, and steam, are passed into chamber A, where the following reactions take place:

(1) $2SO_2 + 2HNO_3 + H_2O = 2H_2SO_4 + NO_2 + NO.$
(2) $2SO_2 + NO_2 + NO + O_2 + H_2O = 2SO_4H(NO).$
(3) $2SO_4H(NO) + 2H_2O = 2SO_4H_2 + 2HNO_2.$
(4) $2HNO_2 = NO + NO_2 + H_2O.$

From the first chamber the uncombined gases pass into a second chamber, where further combination and condensation take place, and in a third chamber the condensation is completed, so that only oxides of nitrogen and nitrogen gas escape into the Gay-Lussac tower, K. In this latter tower the oxides are dissolved by concentrated sulphuric acid from M trickling down over pieces of coke.

When this concentrated acid reaches the bottom, saturated with oxides of nitrogen, it is transferred by suitable pipes to the top of the Glover tower, to run down and mix with fresh quantities of dilute acid and sulphur dioxide. The concentrated acid for the Gay-Lussac tower is taken from the bottom of the Glover tower, as the mixed dilute and strong acids in meeting with the hot gases have been deprived of nearly all water.

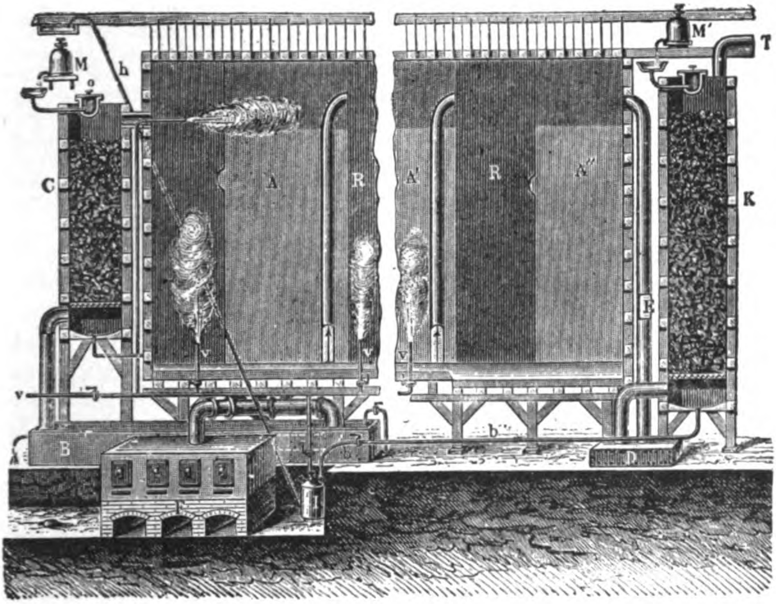
The circulation of gases through the system of towers and chambers is maintained by the draught of a tall chimney.

It will be seen that the same sulphuric acid is repeatedly used and nearly all the oxides of nitrogen are saved, so that the process consists in generating a continuous supply of sulphur dioxide with a small quantity of nitric acid to make up the loss which is unavoidable. The principal supply of oxygen comes from the atmosphere. The oxides of nitrogen serve as the oxygen carriers.

The furnace in which the sulphur or pyrites is burned is so arranged as to furnish the necessary heat for the decomposition of the nitrate.

The acid in the bottom of the lead chamber is drawn off when it attains a concentration of about 63 per cent. of absolute sulphuric acid. This crude acid is used directly in the manufacture of fertilizers ("superphosphate"). If allowed to become more concentrated than this it begins to absorb nitrous fumes. It is then concentrated in leaden pans until it reaches the specific gravity of 1.75, containing 78 per cent. of the acid, when it commences to attack the lead, and is, therefore, transferred to vessels of iron, glass, or, best of all, platinum, to be finally concentrated or distilled. Those manufacturers who are still provided with platinum stills concentrate the acid to about 98 per cent. The weak pure acid is now usually concentrated in hot towers packed with quartz over which the acid trickles while heated with a non-luminous oil flame.

FIG. 103.



Preparation of sulphuric acid.

The crude lead chamber acid of 63 per cent. is now concentrated for transport to 78 per cent. in the heated Glover towers. The usual impurities occurring in chamber acid are nitrosylsulphuric, lead, copper, iron, alumina, arsenic, ammonium sulphate, and sometimes selenium. Most of these are either deposited from the acid or removed by distillation except arsenic. Arsenic-free sulphuric acid is prepared from arsenic-free (Louisiana) sulphur and usually by the contact-process.

Contact Process.—As already noted, sulphur dioxide unites directly with oxygen to form sulphur trioxide through the catalytic action of platinized asbestos or other suitable contact substances when heated. This reaction is the basis of the "contact" process as carried out on an immense scale industrially. The successive operations involved are (1) the preparation of a mixture of sulphur dioxide and air (O); (2) the purification of this mixture; (3) the formation of sulphur trioxide; (4) the absorption of SO_3 in sulphuric acid and water. The sulphur dioxide, prepared by roasting pyrites or burning sulphur, is mixed with air in the proportion to secure 2 volumes of SO_2 to 3 volumes of O (15 vols. of air). This roast gas mixture is freed from dust, selenium, antimony, and arsenic vapors (which tend to destroy the catalytic properties of the contact mass of platinum) either by means of a jet of steam or by partially cooling and filtering through asbestos wool. The dried vapors are then passed upwards through vertical wrought-iron tubes kept at about 400°, which contain either platinized asbestos, platinized magnesium sulphate alone, or mixed with metallic oxides,* supported upon perforated diaphragms. Or according to the Schroeder process, magnesium sulphate moistened with platinic chloride, and heated in the presence of SO_2, serves as the contact mass. The mixed gases, heated to about 350°, pass through this. Through contact, sulphur trioxide is formed, which is passed into concentrated sulphuric acid (98 to 98.5 per cent.) for absorption, water being added from time to time to keep the concentration of the acid down to this point. The commercial "oleum" made by saturating concentrated sulphuric acid with SO_3 is generally made to contain 20 per cent. of SO_3, as this remains fluid at winter temperature. An oleum containing 30 per cent. SO_3 is also supplied. Foreign markets supply oleums of 20, 30, 60, 75 and 100 per cent. SO_3. The stronger oleums are solid at ordinary temperature.

Physical Properties.—When pure, sulphuric acid is a colorless, oily, inodorous, corrosive liquid of the specific gravity of 1.828 (25°) when of 93 per cent. strength, and of the specific gravity of 1.837 (25°) when of 98 per cent. strength. The acid prepared by the "contact" process is not distilled and is purer than the lead-chamber acid; its specific gravity ranges from 1.85 to 1.90. When the concentrated acid is sufficiently cooled, crystals of anhydrous acid separate, which fuse at 10.5°. When heated, the anhydrous acid begins to fume at 40°, SO_3 escaping; this continues until the temperature reaches 338°, when an acid of 98.5 per cent. distils over unchanged.

Chemical Properties.—Sulphuric acid has a strong affinity for water, hence is employed for drying gases and in desiccators. When mixed with water great heat is developed. In diluting, the acid should always be poured into the water slowly and with constant stirring; when the reverse is attempted the acid is liable to be thrown out by the violent ebullition resulting from the sudden rise in temperature. The mixing is accompanied by diminution of volume, the maximum contraction amounting to 8 per cent. when one molecule of the acid is mixed with

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* The various metals which serve as catalytic contact agents when in a finely subdivided state may be classed as follows:

1. Metals of the platinum group.
2. Highest oxides of Fe, Cr, Ni, Co, Mn, Ur, Cu, Mo, V, W.
3. Oxides of Al, Be, Ce, Di, La, Th, Ti, Si.
4. Mixtures of class 1 with one or more of 2 and 3.
5. Mixtures of classes 2 and 3.

Metals of classes 2, 3, and 5 are only efficient at high temperature (about 700°), while 1 and 4 react at a lower temperature (200°).

two of water, the hydrate $H_2SO_4 + 2H_2O$ being formed. On account of this affinity for water, organic substances are rapidly decomposed, hydrogen and oxygen in the proportion to form water being removed, and carbon, in many compounds, separating. An example of this occurs when sulphuric acid is added to sugar. The concentrated acid does not so readily attack metals as that which is more diluted. In some cases the metal becomes coated with a layer of sulphate, which prevents further action. This is notably the case with zinc and iron. Copper, mercury, antimony, bismuth, lead, and silver are dissolved on heating with the acid, a reduction of the latter taking place with an evolution of sulphur dioxide at the same time. Gold, platinum, and some other of the noble metals are not appreciably affected even by boiling with the acid. When sulphuric acid vapors are passed over red-hot porous bodies or heated to 450°, it is decomposed into SO_2, H_2O, and O.

Lead-chamber sulphuric acid, when prepared without distillation, is dark in color and contains chiefly lead, iron and copper sulphates, arsenic and frequently oxides of nitrogen. Such an acid is employed in various technical operations. Chemicals prepared by the use of this acid will naturally contain some of the chief impurities of the sulphuric acid. The standard commercial **Concentrated Sulphuric Acid** or "Oil of Vitriol" contains about 93.2 per cent. of H_2SO_4.

There is a commercial concentrated acid of 98 per cent. strength which is used in the manufacture of explosives and for special purposes.

The *Chemically Pure* (C.P.) concentrated acid contains from 95 to 96 per cent. of H_2SO_4. The impurities present may be Fe, Cu, Pb, As, NO_2, but in very minute amounts. Acids containing more than 20 per cent. of free SO_3 are stored in wrought-iron vessels, which better resist the action of the acid; such acids contain less than 0.008 per cent. of iron. **Acidum Sulphuricum,** U.S.P., which contains not less than 93 nor more than 95 per cent. of H_2SO_4, and of gravity of about 1.83 (25°), is practically a chemically pure acid. **Acidum Sulphuricum Dilutum,** U.S.P., contains not less than 9.5 nor more than 10.5 per cent. of H_2SO_4.

Uses.—Sulphuric acid is consumed in all branches of chemical industry, among which are the manufacture of the inorganic acids, fertilizers, and parchment (by immersion of paper into a cold mixture of sulphuric acid 2 p. and water 1 p., followed by washing). Owing to its intense affinity for moisture, sulphuric acid is employed as a desiccant in drying gases and in exsiccators for drying solids. The fuming acid is employed in large quantities in the manufacture of the aniline colors, synthetic medicinals, explosives, and in the refining of mineral oils, etc.

Tests and Impurities.—Concentrated sulphuric acid when heated with mercury or charcoal evolves fumes of sulphur dioxide. Sulphuric acid and sulphates in aqueous solution are detected by giving a white precipitate with barium chloride, insoluble in hot concentrated acids; also by the white precipitate which they form with salts of lead, insoluble in dilute acids, but soluble in hot concentrated acids. Sulphates may also be detected by heating with powdered charcoal, which removes the oxygen, and moistening the fused mass of alkali sulphide on a silver coin with a drop of diluted hydrochloric acid, when a dark stain of silver sulphide will be produced. This is known as the *Hepar* reaction.

The chief impurities in the "lead-chamber" acid are lead, iron, copper, arsenic, selenium, and the oxides of nitrogen. For the detection of these see U.S.P. The presence of organic matter is recognized by the dark color it imparts to the acid.

Sulphates.—Sulphuric acid forms two series of salts, the *neutral* or *normal* sulphates, in which both hydrogen atoms of the acid are replaced by a base, as Na_2SO_4, and the *acid* sulphates, in which only one hydrogen atom is replaced by a base, as $NaHSO_4$. Potassium acid sulphate is employed in metallurgic fusions because when heated it yields sulphur trioxide, $4KHSO_4 = 2K_2SO_4 + 2SO_3 + 2H_2O$. Most sulphates are soluble in water, the important exceptions being those of barium, strontium, calcium, and lead. The sulphates of the alkalies, alkaline earths, and lead are not affected by heat, magnesium sulphate is only partly decomposed, the other metallic sulphates are decomposed at high temperature, generally yielding an oxide or the metal and sulphur dioxide.

$$\begin{aligned} CuSO_4 &= CuO + SO_2 + O. \\ HgSO_4 &= Hg + SO_2 + O_2. \\ 2FeSO_4 &= Fe_2O_3 + SO_2 + SO_3. \end{aligned}$$

Sulphates of the formula $Me_2(SO_4)_3$ yield SO_3.

$$Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3.$$

When heated to redness with charcoal, the sulphates yield sulphides.

$$\begin{aligned} CaSO_4 + C_4 &= CaS + 4CO. \\ Na_2SO_4 + C_4 &= Na_2S + 4CO. \end{aligned}$$

FUMING SULPHURIC ACID—PYROSULPHURIC ACID—DISULPHURIC OR NORDHAUSEN SULPHURIC ACID,

$$H_2SO_4 + SO_3.$$

This is the oldest of sulphuric acids (the original oil of vitriol), and was first manufactured in the vicinity of Nordhausen, Germany, but later the industry was transferred to Bohemia.

The original operation was commenced by roasting pyrites, in which ferrous sulphate and basic ferric sulphate, $Fe_2S_2O_9$, were formed. On lixiviating the mass a solution of the sulphates was obtained, which, on evaporation and ignition, gave a residue of the basic sulphate. The presence of the ferrous salt was avoided as far as possible on account of the formation of sulphur dioxide ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$). On submitting the basic salt to distillation the following reaction takes place:

$$Fe_2S_2O_9 = Fe_2O_3 + 2SO_3.$$

The residue was called *caput mortuum* or colcothar, which was used as a pigment and in polishing. This method of preparation of "oleum" has long since been displaced by the contact or catalytic process as outlined above. Fuming sulphuric acid or oleum is a thick, oily liquid, which fumes strongly in the air.

Fuming Sulphuric Acid ($H_2SO_4 + SO_3$), employed as U.S.P. reagent, contains from 14 to 16 per cent. of free sulphur trioxide, corresponding to 84.2 to 84.6 per cent. of total sulphuric anhydride with a specific gravity of from 1.869 to 1.875 at 25° C.

SULPHUR HEPTOXIDE, S_2O_7

PERSULPHURIC ANHYDRIDE

This is the highest oxide of sulphur and is obtained by the silent discharge of high tension on a mixture of sulphur dioxide and oxygen ($4SO_2 + 3O_2 = 2S_2O_7$). The compound, which forms oily drops, is quite unstable. When added to water, sulphuric acid and oxygen are produced; if added to dilute sulphuric acid, persulphuric acid results.

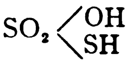
PERSULPHURIC ACID, $H_2S_2O_8$.

This acid is known only in form of its salts.

Potassium and ammonium persulphates may be prepared by electrolyzing solutions of potassium or ammonium sulphates in 40 per cent. sulphuric acid. Lead may be employed as the cathode and platinum as the anode. The HSO_4 ions are discharged from the anode, these unite to form $H_2S_2O_8$, which with the K ions form the slightly soluble potassium salt.

The most striking property of the persulphates is their powerful oxidizing action, whether used in neutral, acid, or alkaline solution. From chlorides and iodides the halogen is liberated, while a neutral sulphate is formed; ferrocyanides are oxidized to ferricyanides, manganates in alkaline solution to permanganates, and many of the metals are dissolved with the formation of sulphates. Many organic substances are also oxidized by acid or alkaline persulphate solutions. Indigo, litmus, and turmeric are easily bleached by it; permanganate solution is not decolorized. **Caro's acid** or sulpho-mono-peracid, H_2SO_5, is obtained by the action of 100 per cent. hydrogen peroxide on sulphur trioxide, $SO_3 + H_2O_2 = H_2SO_5$. A solution of Caro's acid in sulphuric acid may be prepared by mixing hydrogen peroxide with an excess of concentrated sulphuric acid.

THIOSULPHURIC ACID, $H_2S_2O_3$.



$$SO_2\begin{cases}OH\\SH\end{cases}$$

This acid is not known in the free state, but only in combination with bases, of which sodium thiosulphate, $Na_2S_2O_3.5H_2O$, is the most important. Upon attempting to liberate the acid it decomposes into sulphurous oxide and sulphur:

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3.$$
$$H_2S_2O_3 = H_2O + SO_2 + S.$$

The salt is improperly called hyposulphite of sodium, and consequently the acid is also miscalled hyposulphurous acid, a name which belongs to the compound $H_2S_2O_4$.

Thiosulphates.—The sodium salt, which is the only one used, may be prepared by boiling together sulphur and sodium sulphite:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

By boiling a concentrated solution of sodium hydroxide with sulphur, sodium thiosulphate and pentasulphide are formed.

$$6NaOH + 6S_2 = Na_2S_2O_3 + 2Na_2S_5 + 3H_2O.$$

It is also formed when sulphur dioxide is passed into a solution of sodium sulphide (obtained by heating the sulphate with carbon), the reaction taking place in two stages according to the following:

$$3SO_2 + 2Na_2S = 2Na_2SO_3 + 3S.$$
$$Na_2SO_3 + S = Na_2S_2O_3.$$

When sodium polysulphide (soda waste of alkali works), which contains much calcium sulphide, is exposed to the air, it absorbs oxygen and is converted into a thiosulphate:

$$2CaS + 2O_2 + H_2O = CaS_2O_3 + Ca(OH)_2.$$

In case the calcium salt is formed it may be converted into the sodium salt by the addition of sodium carbonate. The lime used in purifying illuminating gas, and known as *gas lime,* contains calcium pentasulphide and thiosulphate. This is exposed to the air, whereby the sulphide is converted into thiosulphate, the mass is lixiviated with water, and the solution, by interaction with sodium carbonate, gives calcium carbonate and sodium thiosulphate, as follows:

$$CaS_2O_3 + Na_2CO_3 = CaCO_3 + Na_2S_2O_3.$$

This and the waste lime and alkali sulphides from the manufacture of sodium carbonate are the sources of the commercial salt.

Properties.—Sodii Thiosulphas, U.S.P., $Na_2S_2O_3 + 5H_2O$, occurs in large, colorless, transparent, monoclinic prisms or plates, efflorescent in dry air, odorless, having a cooling, somewhat bitter, and sulphurous taste.

The aqueous solution dissolves the halogen salts of silver.

$$\underset{\text{Silver Chloride.}}{AgCl} + \underset{\text{Sodium Thiosulphate.}}{Na_2S_2O_3} = \underset{\text{Sodium-silver Thiosulphate.}}{NaAgS_2O_3} + NaCl.$$

This reaction takes place in "fixing" dry photographic plates after development.

Solutions of iodine are discolored by this salt according to the following equation:

$$I_2 + 2Na_2S_2O_3 = 2NaI + \underset{\text{Sodium Tetrathionate.}}{Na_2S_4O_6}.$$

Sodium Thiosulphate, V.S. (U.S.P.), is employed in volumetric analysis in the determination of halogens, bichromates, arsenates, and ferric salts.

Upon adding an acid to the aqueous solution of a thiosulphate, sulphur dioxide escapes (recognized by its odor, and blackening paper moistened with mercurous nitrate, T.S.), and a white precipitate of sulphur forms (distinction from a sulphite).

POLYTHIONIC ACIDS

These acids, of minor importance, may be grouped under the general formula $H_2S_nO_6$, in which n indicates the number of sulphur atoms as well as determining the names of the acids.

DITHIONIC OR HYPOSULPHURIC ACID, $H_2S_2O_6$

Preparation.—When sulphur dioxide is passed into iced water in which manganese dioxide is suspended, the following reaction takes place: $MnO_2 + 2SO_2 = MnS_2O_6$. On treatment with barium hydroxide, manganese oxide with barium sulphate are precipitated, leaving barium dithionate in solution. This upon treatment with dilute sulphuric acid yields barium sulphate and free dithionic acid.

Dithionic acid is only known in aqueous solution; upon concentrating. it is decomposed into sulphuric acid and sulphuric dioxide.

The dithionates do not precipitate sulphur on the addition of hydrochloric acid and heating; this distinguishes them from the thiosulphates.

TRITHIONIC ACID, $H_2S_3O_6$

Preparation.—When sublimed sulphur and a strong solution of acid potassium sulphite are digested at a temperature of from 50° to 60°, the potassium salt of trithionic acid is formed, as follows: $6KHSO_3 + S_2 = 2K_2S_3O_6 + K_2S_2O_3 + 3H_2O$.

When a concentrated solution of potassium thiosulphate is saturated with sulphur dioxide, potassium trithionate is formed: $2K_2S_2O_3 + 3SO_2 = 2K_2S_3O_6 + S$.

When the potassium salt is treated with hydrofluosilicic acid the free acid is produced: $K_2S_3O_6 + SiF_4.2HF = H_2S_3O_6 + SiF_4.2KF$.

This diluted acid allows of only moderate concentration in a vacuum, for it readily decomposes into sulphur, sulphur dioxide, and sulphuric acid.

TETRATHIONIC ACID, $H_2S_4O_6$

Preparation.—The sodium salt of this acid is formed when iodine is added to an aqueous solution of sodium thiosulphate: $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$.

The free acid may be prepared by carefully decomposing barium tetrathionate with diluted sulphuric acid. The diluted acid may be boiled, but on concentrating decomposition takes place, as follows: $H_2S_4O_6 = H_2SO_4 + SO_2 + S_2$.

PENTATHIONIC ACID, $H_2S_5O_6$

When hydrogen sulphide is passed into a solution of sulphur dioxide, pentathionic acid results, with separation of sulphur: $5H_2S + 5SO_2 = H_2S_5O_6 + 4H_2O + 5S$. The solution is milky, and is best cleared by digesting with metallic copper. Any copper which is dissolved is precipitated by hydrogen sulphide. When heated, the acid decomposes: $H_2S_5O_6 = H_2SO_4 + SO_2 + 3S$.

SELENIUM

Symbol, Se. *Atomic Weight*, 79.2. *Valence*, II, IV, VI.

History.—Selenium was discovered in 1817 by Berzelius, in the deposits from sulphuric acid chambers, and named from σελήνη, the moon, because of its similarity to tellurium (τελλυς, earth).

Occurrence.—It is widely distributed in small quantities associated with sulphur, in the native sulphides of iron, copper, silver, etc., more rarely in *selenides*.

Isolation.—This element is most conveniently prepared from lead-chamber deposits where pyrites are roasted for the production of sulphur dioxide. The crude material is mixed with sufficient sulphuric acid to make a paste, heated to the boiling point, and treated with nitric acid from time to time, until no more red fumes are given off. The solution, which now contains selenous and selenic acids, is diluted with water, filtered, hydrochloric acid added, then concentrated, whereby the selenic acid is reduced to selenous acid ($H_2SeO_4 + 2HCl = H_2SeO_3 +$

$H_2O + Cl_2$). This solution is then saturated with sulphur dioxide, when selenium separates as a red powder:

$$H_2SeO_4 + 3SO_2 + 2H_2O = 3H_2SO_4 + Se.$$

Selenium may also be prepared by digesting the lead-chamber deposit on a water-bath with a concentrated solution of potassium cyanide:

$$KCN + Se = KSeCN.$$

From this solution of potassium selenocyanide the selenium is deposited, in red flakes, on the addition of hydrochloric acid, which change to a black mass upon heating the solution.

Properties.—Like sulphur, selenium exists in different allotropic modifications.

The *amorphous* selenium, obtained by reduction of the dioxide by means of sulphur dioxide, forms a reddish-brown powder soluble in carbon disulphide, which changes at 100° to dark-gray crystalline selenium.

The *red crystalline* variety is deposited in monoclinic crystals from the solution of the amorphous variety in carbon disulphide. It fuses at 170 to 180°.

The *gray, metallic-like crystalline* variety is obtained by fusing the amorphous selenium and slowly cooling. It is insoluble in carbon disulphide, has a gravity of 4.8, fuses at 217°, and boils at 690°. Amorphous selenium is a poor heat and electric conductor, while the crystalline variety is a good conductor, the conductivity increasing when exposed to light. It is thus possible to make and break an electric circuit by means of a beam of light. Based on the use of an arc light influenced by sounds, a wireless telephone has been invented. Photographic transmission may also be sent over long distances through the use of selenium. This element is also used for producing a red color on porcelain and glass.

When heated in the air, selenium burns with a bright blue flame, yielding selenium dioxide, SeO_2, which condenses to needle-like crystals. The vapor has a disagreeable odor, due possibly to the presence of another compound, since pure SeO_2 is inodorous. Selenium dissolves in strong sulphuric acid with a green color, forming the dioxide:

$$Se + 2H_2SO_4 = 2SO_2 + SeO_2 + 2H_2O.$$

Dissolved in water, SeO_2 forms *selenous acid,* H_2SeO_3. This, like the anhydride (SeO_2), is very easily reduced (the former by simple contact with dust) to the red amorphous selenium. Acid and neutral *selenites* are known. Through the oxidation of selenous acid or selenites, *selenic acid,* H_2SeO_4, is obtained. This combines with water to form crystals ($H_2SeO_4 + H_2O$) which fuse at 25°. The anhydrous acid is crystalline and fuses at 58°. Selenic acid (95 per cent.) resembles sulphuric acid in its general properties; it is a powerful oxidizing agent and dissolves gold, being reduced to selenous acid at the same time.

Like sulphur, selenium combines with metals, forming *selenides,* which, with acids, yield *hydrogen selenide,* SeH_2, a colorless, poisonous, and disagreeable-smelling gas, which precipitates the heavy metals from their solutions as selenides. *Selenium monochloride,* Se_2Cl_2, a brown oily liquid, *selenium tetrachloride,* $SeCl_4$, a yellow solid mass, and *selenium oxychloride,* $SeOCl_2$, are known, with corresponding bromides and iodides.

The compounds of selenium are best detected by the red precipitate of the element which occurs on the addition of sulphurous acid or sulphur dioxide to their solutions. Selenous acid is used by the U.S.P. as a test for morphine.

TELLURIUM

Symbol, Te. *Atomic Weight,* 127.5. *Valence,* II.

History.—Tellurium was discovered in 1782 by Müller von Reichenstein, and more fully investigated by Klaproth and Berzelius. It was named tellurium by Klaproth, from *τελλυς*, the earth.

Occurrence.—This element occurs sparingly in the free state, and as tellurides of gold, silver, lead, bismuth, and mercury in California, Colorado, Transylvania, Brazil, and Hungary.

Properties.—Tellurium separates as an amorphous black powder upon treating solutions of tellurous acid with sulphur dioxide. When fused, it forms a silver-white crystalline mass of a brittle texture, and has a specific gravity of 6.7. It melts at 450°, and boils below 1390°, yielding yellow vapors. It is insoluble in carbon disulphide, but dissolves in concentrated sulphuric acid, imparting a deep-red color to the solution, from which it is precipitated on the addition of water.

On heating in the air, it burns with a blue flame, yielding white fumes of tellurium dioxide, TeO_2, which may be obtained in small octahedra. *Tellurous acid,* H_2TeO_3, is obtained by oxidizing tellurium with nitric acid and pouring into water. The resulting white precipitate decomposes, when heated, into the dioxide and water. Neutral and acid tellurates are known. *Telluric acid,* H_2TeO_4, obtained by oxidation of tellurous acid or the dioxide, with nitric or chromic acid, forms a crystalline hydrate, which on heating to 160° yields the yellow *trioxide,* TeO_3, which on further heating decomposes into the dioxide and oxygen. These two acids act as weak bases, forming salts with strong acids. *Tellurides,* $Me''Te$, are known, which with acids yield *hydrogen telluride,* H_2Te, a colorless, poisonous gas of offensive odor.

Tellurium compounds are recognized by fusing with potassium carbonate, by which potassium telluride is formed, which dissolves in water with a red color, and, on the addition of hydrochloric acid, yields the disagreeably smelling compound, hydrogen telluride (H_2Te). When fused with potassium cyanide, tellurium yields K_2Te, potassium telluride, which decomposes in the air with separation of tellurium.

CHAPTER V

THE NITROGEN GROUP

The members of this group, consisting of N, P, As, Sb, and Bi,* present similar graded differences in their physical and chemical properties as shown in the halogen and oxygen groups. The members of group V are usually triads and pentads. It will be noted that the hydrides are all gases, and decrease in their basicity, as well as their stability towards heat, from nitrogen to antimony. The oxides show a similar gradation with increase in atomic weight; thus the oxides which possess strongly acid properties, as those of N and P, acquire a more basic nature as we pass to the oxides of As, Sb, and Bi. Based on the regular variations in their chemical properties, the non-metallic characters gradually give way to the metallic with increase in atomic weight. In connection with nitrogen, the inert atmospheric gases will be taken up.

	N	*P*	*As*	*Sb*
Atomic Weights	14.01	31.04	74.96	120.2
Specific Gravity	0.967 (air = 1)	1.83	5.7	6.7
Hydrides	NH_3	PH_3	AsH_3	SbH_3
Oxides	N_2O			
	NO			
	N_2O_3	$P_2O_3 (P_4O_6)$	As_2O_3	Sb_2O_3
	NO_2	P_2O_4		Sb_2O_4
	N_2O_5	P_2O_5	As_2O_5	Sb_2O_5
Acids. "ous"	HNO_2	H_3PO_3	(H_3AsO_3)†	H_3SbO_3
meta "		H_3PO_2 hypo.	$(HAsO_2)$‡	$HSbO_2$
ortho "ic"..........	HNO_3	H_3PO_4	H_3AsO_4	H_3SbO_4
meta "		HPO_3	$HAsO_3$	$HSbO_3$
pyro "		$H_4P_2O_7$	$H_4As_2O_7$	$H_4Sb_2O_7$

NITROGEN

Symbol, N. *Atomic Weight,* 14.01. *Valence,* III *and* V.

Number of atoms in molecule, 2; *weight of one liter,* 1.2507 (0° *and* 760 *mm.*); *critical temperature,* -146°; *critical pressure,* 35 *atm.; boiling-point,* -195.7°.

History.—Dr. Rutherford (Edinburgh) is usually credited with the discovery of nitrogen, since he was the first to publish, in 1772, the observation that after absorbing the carbon dioxide produced by respiration in an enclosed volume of air, the remaining gas would support neither combustion nor respiration. Priestley found that one-fifth of a measured volume of air was converted into "fixed air" (CO_2) by means of glowing charcoal, the remaining gas (N) being called "phlogisticated air." Scheele showed (1777) that air consisted of a mixture of two gases. Lavoisier was the first to recognize the true nature of air, showing that the one gas supported respiration and combustion and that the other was inert. He suggested the name *azote* (Az), now accepted by the French, which means *not supporting life,*

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* Because the physical and chemical properties of bismuth are those of a metal, it is considered under the metals.

† Known only in solution.

‡ Known only in salts.

while the name nitrogen was proposed by Chaptal, from νιτρον, nitre, and γενναω, I produce, since it was found to be a constituent of saltpetre.

Occurrence.—In the free state nitrogen constitutes about four-fifths of the atmosphere. In combination with sodium and oxygen, it occurs in enormous quantities as Chili saltpetre. With hydrogen, nitrogen is combined as gaseous ammonia, which is produced in the distillation of coal. Animal and vegetable substances always contain nitrogen, which is given off as ammonia when they decay.

Isolation.—Nitrogen may be prepared by removing the oxygen from the air. Until 1894 the nitrogen thus prepared was considered pure, when Ramsey and Rayleigh demonstrated the presence of about one per cent. of argon. Other elementary gases have since been discovered in minute amounts in the atmosphere. The isolation of nitrogen may be accomplished in several ways:

(1) *By burning phosphorus in a confined space of air.* The phosphorus combines with the oxygen, forming phosphorus pentoxide (P_2O_5), which dissolves in water, forming phosphoric acid, while nitrogen remains.

(2) *Passing air over red-hot copper filings.* The copper unites with the oxygen to form copper oxide, while the nitrogen remains.

(3) *By shaking air in a vessel with a solution of pyrogallol and sodium hydroxide in water*, or a solution of cuprous chloride in hydrochloric acid, the oxygen is dissolved, leaving the nitrogen.

(4) By the fractional distillation of liquid air; the nitrogen, boiling at —195.7°. distils over, leaving practically pure oxygen (boiling at —182.9°).

Chemically, nitrogen may be prepared:

(1) *By heating ammonium nitrite, or boiling concentrated solutions of sodium nitrite (1 part) and ammonium sulphate (1 to 2 parts). Passing the gas through dilute sulphuric acid, which retains any ammonia carried over.*

$$NH_4NO_2 = N_2 + 2H_2O.$$

$$(NH_4)_2SO_4 + 2NaNO_2 = Na_2SO_4 + 4H_2O + 2N_2.$$

(2) *By heating ammonium dichromate or a mixture of potassium dichromate and ammonium chloride:*

$$K_2Cr_2O_7 + 2NH_4Cl = Cr_2O_3 + 2KCl + 4H_2O + N_2.$$

Physical Properties.—Nitrogen is a colorless, tasteless, and inodorous gas. Its density is 0.96737 (air = 1.000); that of atmospheric nitrogen (including argon) is 0.97209. The density of N compared to H = 1 is 13.93. One liter of N weighs 1.2507 gram, while one liter of atmospheric N weighs 1.25718 gm., at 0° and 760 mm. This difference in density caused Rayleigh in 1893 to suspect the presence of an unknown gas (argon).

Under a pressure of 35 atmospheres and a temperature of —146° nitrogen liquefies. In this liquid state it has a specific gravity of 0.804 (water = 1), boils at —195.7°, and solidifies at —214°. One liter of water at 20° dissolves 2.35 mils (0.00293 gm.) of nitrogen.

Chemical Properties.—Nitrogen is neither combustible nor a supporter of combustion. In the free state it is remarkably inactive toward all other elements; but its compounds, which are almost always formed by indirect means, are in nearly all cases very active; many of them, the alkaloids and cyanides, for example, being especially active physiologically. At red heat, nitrogen forms nitrides with Li, B, Si, Ba, Sr, Ca, Mg (Mg_3N_2), Cr, and certain rare elements. Under the influence of the induction-spark, nitrogen unites with oxygen to form nitrogen peroxide, with hydrogen to form ammonia. In moist air, electric discharges produce ammonium nitrite and nitrate. Nitrogen combines with certain metallic carbides, yielding cyanamides, which are useful in the manufacture of cyanids and fertilizers. Nitrogen is absorbed by certain leguminous microörganisms.

Uses.—Nitrogen is useful in carrying out such chemical operations as require the exclusion of oxygen. Industrially in the manufacture of calcium cyanamide, ammonia, and nitric acid.

Utilization of Atmospheric Nitrogen.—This has been one of the most important problems confronting the industrial chemist, owing to the rapid depletion of the Chilean nitre fields and the enormous demand for artificial nitrogenous fertilizers in agriculture and nitrates and ammonium salts in chemical industry. Plant life does not absorb nitrogen from the atmosphere direct nor from the ammoniacal compounds present in the soil. This is accomplished indirectly by the plant through the presence of certain varieties of bacteria present in the soil and accumulations of these (as nodules) upon the roots of plants. The functions of these organisms are to fix atmospheric nitrogen, to transform nitrogenous organic albuminoids into ammonium compounds, nitrites, and nitrates, which are then readily assimilated. Cultures of these bacteria have been prepared and marketed ready for inoculating exhausted soil. Industrially, various processes have been devised for the preparation of nitrates (see page 255) and ammonia (see page 246). One important discovery in this line deserves mention because of its use as a fertilizer and in a process for the preparation of ammonia and cyanides. It has been found that calcium carbide (page 383), when heated to about 2000° in an electric furnace, absorbs atmospheric nitrogen from a current of air yielding calcium cyanamide (nitro-lime), ($CaC_2 + N_2 = NC.NCa + C$). This contains about 20 per cent. of N, and when mixed with soil, the soil bacteria decompose it into ammonia and calcium carbonate. Calcium cyanamide when fused with caustic alkalies yields their cyanides; it may also be decomposed with steam with liberation of ammonia, thus—$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3$.

THE ATMOSPHERE

History.—The air was regarded as an element till the latter part of the eighteenth century. The discovery of oxygen by Priestley (1774), following the observation of Rutherford on the presence of nitrogen, led Lavoisier to demonstrate the compound nature of the atmosphere. In 1781 Cavendish proved that air consisted of a mixture of oxygen and nitrogen in constant proportions.

Before Lavoisier's time, all combustible or oxidizable substances were assumed to contain an inflammable principle called phlogiston. Also, all metals when heated gave up phlogiston and were converted into metallic calxes (oxides), and these, when heated with substances rich in phlogiston (as carbon or hydrogen), were regenerated into their metals. According to this theory, there was no occasion to consider the air as being concerned in the process of combustion, hence no one doubted its assumed elementary nature. But as soon as it was proven that combustion and ignition withdrew something from the air, the substance *increasing* thereby in weight instead of giving off phlogiston, as was formerly assumed, the phlogistic theory became untenable. In the discovery of oxygen, Lavoisier at once recognized that this gas was the necessary principle of combustion and oxidation. Further, he proved the non-elementary nature of the air and that it contained another gas in addition to oxygen, which did not support combustion—namely, nitrogen.

Distribution.—Air is distributed over the surface of the earth and to an unknown height above it. It is estimated to extend to a height of from 58 to 70 km. On account of its being an elastic body, it will be denser at the sea-level, and at a height of 70 km. a gas of extreme tenuity. At a height of 14 km. the atmospheric pressure is not over 110 mm. and the temperature about —53°.

The temperature of space beyond our atmosphere is estimated to be below —100°.

Properties.—Pure dry air is 14.39 times heavier than hydrogen and 773.22 times lighter than water; one liter at 0° and 760 millimeters pressure weighs 1.2934 gm. The pressure of the atmosphere at the sea-level is very nearly fifteen pounds on every square inch of surface, equal to a column of mercury at 0°, 760 millimeters in height. Since 1 mil of mercury weighs 13.6 gm., the atmospheric pressure on each square centimeter of surface would be 1033.5 gm. This pressure rapidly diminishes as we ascend from the sea-level. The critical temperature of air is —140° and the critical pressure 39 atmospheres. When liquid air is evaporated at about —192° the nitrogen, which boils at —195.7°, passes off, leaving oxygen behind.

Composition.—The quantitative composition of pure atmospheric air is practically constant, irrespective of locality and elevation. According to locality, there are always present variable quantities of water vapor, carbon dioxide, ozone, traces of ammonia, nitrous, nitric, and sulphurous acids, and particles of floating matter—as dust and microörganisms—which are found more abundantly in densely populated districts. The average composition of pure dry air is as follows:

Nitrogen	78.06 p. by volume	75.5 p. by weight.
Oxygen	21.00 p. by volume	23.2 p. by weight.
Argon	0.94 p. by volume	1.3 p. by weight.

Helium, Neon, Krypton, Xenon, and Hydrogen, traces.

The nitrogen, because of its inert character, serves as a diluent for the active life-sustaining oxygen. The oxygen supports life, combustion, and oxidation, and although it is constantly diminishing in consequence, yet its proportion in the air remains quite constant. This is due to the absorption of its combustion-product, carbon dioxide, by the leaves of plants, which in turn liberate pure oxygen. The proportion of carbon dioxide is variable, since it is a product of combustion, respiration, fermentation, and decay. In cities it is found often as high as 0.11 per cent. In the air it averages 0.04 volume per cent.; in rooms it should not rise over 0.1 volume per cent. The amount of aqueous vapor is still more variable, and is affected by local causes, as temperature and altitude.

The Air a Mechanical Mixture.—The following are some of the characters which prove it to be a mixture:

(1) The physical and chemical properties of a mixture of seventy-nine volumes of nitrogen and twenty-one volumes of oxygen are exactly the same as air. When the two gases are mixed there is no evidence of chemical action.

(2) The proportion in which the two elements exist in air bears no relation to their atomic weights or multiples thereof.

(3) When air is drawn through a thin layer of caoutchouc or any porous medium which permits diffusion, the nitrogen passes through more rapidly than the oxygen. If air were a chemical compound this would not take place.

(4) On agitating air with water until the latter is saturated, the composition of the dissolved gas is found to be 35 volumes of oxygen to 65 volumes of nitrogen on account of the solubility of oxygen in water being greater than that of nitrogen.

(5) The oxygen may be removed by solvents (alkaline solution of pyrogallol) or deoxidizing agents, as phosphorus, leaving the nitrogen.

Analysis.—Moisture is determined by passing known quantities of air over calcium chloride and noting the increase in weight of the latter. Carbon dioxide is determined in the same manner, using potassium hydroxide. Oxygen is determined by taking a definite volume of pure dry air in a eudiometer tube over mercury and introducing a piece of phosphorus or an alkaline solution of pyrogallol for its absorption, or by adding a measured volume of pure hydrogen, and exploding the mixture by means of an electric spark. In the latter instance, after cooling there will be a contraction equal to the volume of hydrogen and oxygen which have combined, the resulting volume of water being so small as to be disregarded unless great accuracy is desired. Nitrogen may be removed from air by passing it over red-hot metallic magnesium, whereby magnesium nitride is formed (Mg_3N_2).

LIQUID AIR

In order to liquefy a gas it is cooled to a temperature below its critical point and subjected to pressure. Since the boiling-points of some gases are very low, they are subjected to pressure, which raises their boiling-points. It therefore follows that if a gas be compressed it requires less cooling to liquefy it, since the boiling-point of the resulting liquid is higher. Gases are then liquefied by means of pressure while cooling below their critical temperatures. Formerly a gas to be liquefied was cooled by the rapid evaporation, under reduced pressure, of another liquefied gas. This newly liquefied gas was then employed in the same manner for cooling and condensing a third gas of still lower boiling-point. Modern liquefaction, as carried out in the Linde machine, is based on the cooling produced by the expansion of a compressed gas. That is, a gas under pressure is passed through a small orifice and in escaping and expanding produces a lowering in temperature proportional to the difference between the pressures inside and outside the orifice. Linde utilized the cold produced through the expansion of each portion of compressed gas to cool the next portion to be expanded, continuing this process until liquefaction ensued.

Liquefied air and gases are collected and preserved in the Dewar vacuum flasks. These are double-walled glass or metal vessels, the space between the walls being completely evacuated of air. Very little heat is radiated through this vacuum, hence liquefied gases may be preserved for a considerable time. A modern utilization of this principle is embodied in the "thermos" flasks. Liquid air is more or less turbid from the presence of solid particles of carbon dioxide; after filtration it forms a clear mobile liquid of bluish tint, boiling at —192°, the boiling-point gradually rising to about —182° as the nitrogen evaporates. Since nitrogen boils about 10° lower than oxygen, this gas passes off rapidly, leaving a blue liquid of pure oxygen.

The chief commercial use of liquid air is the production of pure oxygen for inhalation. Rubber, eggs, meat, flowers, etc., become brittle and pulverizable when immersed in liquid air. When applied to the skin with cotton, local insensibility results, thereby enabling minor surgical operations to be carried out without pain.

Liquid air can be kept only in Dewar vacuum flasks; steel cylinders would be unable to resist the pressure, since above —140°, its critical temperature, liquid air is a gas.

With the aid of liquid air boiling *in vacuo* and compression, hydrogen was liquefied at —205° and 180 atmospheres. In the same manner, using liquid hydrogen as cooling medium, helium, the most refractory of all gases, was liquefied. Liquid air has greatly aided the discovery and study of the other rarer gases of the atmosphere.

THE ARGON GROUP

ARGON-HELIUM-NEON-KRYPTON, XENON, NITON

This remarkable group of inert gases, with the exception of helium, was unknown previous to 1892. Rayleigh (1894) found that one liter of nitrogen prepared from the air weighed 1.2572 gm., and one liter of nitrogen from its oxides weighed 1.2507 gm. In studying the cause of this difference in conjunction with Ramsay, they discovered the presence of another gas, which they named argon. In 1895 Ramsay, which searching for other sources of argon, discovered the elementary gas helium, which had already been identified (1868) in the solar spectrum. In their endeavor to classify these elements in the periodic system, the discoverers concluded that there must be other still undiscovered elements which would aid in filling the gaps. By the fractional evaporation of liquefied air and argon, neon, krypton, and xenon were isolated and identified as elementary gases. All of these gases are colorless, odorless, tasteless, and chemically inert; do not combine with any other element; their molecules are monatomic; they give characteristic spectra and show general similarities with gradations in physical characters, as may be noted in other groups of elements in the periodic system.

PHYSICAL CONSTANTS

	He	Ne	A	Kr	Xe	Nt.
Density (o = 16)	1.99	10.10	19.95	41.50	65.35	111.5
Weight of 1 liter in gm...	0.178	0.900	1.782	3.708	5.851	9.97
Atomicwt.(molecular wt.)	3.99	20.2	39.88	82.92	130.22	222.4
Critical temp. (absolute).	5.2°	60.0°	150.6°	210.5°	289.6°	377.5°
Critical pressure (atm.)..	2.75	29.	47.9	54.3	58.2	62.5
Boiling-point	−269°	−248	−186.9°	−151°	−109°	−62°

Argon (ἀργόν = *inert*). Symbol, A; atomic weight, 39.88; molecular weight, 39.88. Air is passed over potassium hydroxide and through sulphuric acid to remove the carbonic acid and moisture, then over a heated mixture of magnesium 3 p., sodium ¼ p., and freshly-ignited lime 5 p. At high temperature calcium is formed which absorbs the oxygen and nitrogen. Calcium carbide absorbs at 800° both oxygen and nitrogen from air: $2CaC_2 + O_2 = 2CaO + 2C_2$; $CaC_2 + N_2 = CaCN_2 + C$. This atmospheric argon still contains about 0.25 per cent. of other inert gases of this group. These may be removed by fractional distillation of the liquefied gas. One liter of argon weighs 1.786 gm.; it is 19.95 times heavier than H, and boils at —186.9°. The air contains 0.935 per cent. by volume of argon.

Helium (ἡλιος = *sun*). Symbol, He; atomic weight, 3.99; molecular weight, 3.99. This gas was discovered spectroscopically in the solar atmosphere as well as some stars by Norman Lockyer in 1867. Terrestrial helium was discovered by Sir William Ramsay in 1894 while searching for new sources of argon among such minerals as cleveite, monazite, and uranite (containing salts of Ur, Ytt, Th). Helium is also a disintegration-product of radium and radio-active substances. One liter weighs 0.1785 gm. The liquefied gas boils at —268.7°. The atmosphere contains about 4 p. of helium per million. This gas is used for filling low temperature gas thermometers.

In seeking a position in the periodic system for argon and helium, Ramsay concluded that there was a gap between these elements which would accommodate an element of an atomic weight of two or three units less than that of sodium. A vessel containing liquefied atmospheric argon was allowed to boil off gradually and the fractions collected. The first fraction consisted of a mixture of helium and a new gas of a density of 10.1, which he named neon. The next gas to distil over was argon, which left a residue consisting of krypton of a density of 41.5 and xenon of a density of 65.35. In repeating these fractionations, the gases were separated and identified by their characteristic spectra. Helium and neon are separated by cooling with liquid hydrogen, whereby neon congeals.

Neon (νέος = *new*). Symbol, Ne; atomic weight, 20.2; molecular weight, 20.2. This gas liquefies at about —243°. One part of neon is present in 81,000 parts of air.

Krypton (κρυπτος = *hidden*). Symbol, Kr; atomic weight, 82.92; molecular weight, 82.92. This element liquefies at —152°. Its spectrum is found in the aurora borealis. One part of krypton is present in twenty million parts of air.

Xenon (ξένος = *foreign*). Symbol, Xe; atomic weight, 130.2; molecular weight, 130.2. This gas liquefies at —109°. Is present 1 part in forty million parts of air.

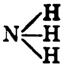
Niton. Symbol, Nt; atomic and molecular weights, 222.4. Niton is probably present in all radium minerals, but, owing to radio-active changes, only in minute amounts.

NITROGEN AND HYDROGEN

Among the simpler compounds of nitrogen and hydrogen are,

Ammonia, $\overset{'''}{N}H_3$. Hydrazin, $\overset{'''}{N}_2H_4$.
Hydrazoic Acid, $\overset{'''}{N}_3H$.

AMMONIA

Formula, NH_3.  *Molecular Weight*, 17.03.

History.—Ammonium chloride, or sal ammoniac, appears to have been known from the earliest times, and the aqueous solution of the gas was described by the alchemists under the name of "spirits of hartshorn." Priestley, in 1747, was the first to prepare gaseous ammonia, by heating together sal ammoniac and lime, and collecting the gas over mercury. He gave to this gas the name "alkaline air," which later became "volatile alkali."

Occurrence and Formation.—Ammonia, in combination with carbonic, nitric, and nitrous acids, exists in the air in minute quantities, being produced through electric discharges. Ammonia and its salts are formed in the dry distillation of many organic substances as well as the putrefaction of nitrogenous organic matter, such as fæces, urine, etc.

Formerly horns, hoofs, urine, and other animal products were distilled, and the ammonium carbonate thus produced neutralized with hydrochloric acid, the product after sublimation being known as sal ammoniac. Ammonium compounds occur in guano beds. Sal ammoniac was first obtained from Egypt, where it was obtained as a sublimate when burning dried camel's dung as a fuel. At the present time our supply is obtained from bituminous coal, which yields on distillation about 2 per cent. of ammonia. This occurs in the ammoniacal liquor formed during the manufacture of coke and illuminating gas. In addition to free ammonia, there are present in this ammoniacal gas-liquor the carbonate, sulphide, sulphate, and thiosulphate. The gas-liquor is usually distilled with lime, by which the ammonia is liberated and collected in a suitable receiver with some water. This distillate is neutralized with hydrochloric or sulphuric acid, and the resulting ammonium chloride or sulphate purified and used for preparing the other ammonium salts.

Formation.—(1) *Through the union of its elements by means of the silent electric discharge.*

(2) *Magnesium nitride, prepared by passing N over red-hot Mg, reacts with steam with liberation of ammonia:*

(a) $3Mg_2 + 2N_2 = 2Mg_3N_2$.

(b) $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$.

($4Zn + 9HNO_3 = 4Zn(NO_3)_2 + NH_3 + 3H_2O$.)

(3) *Reduction of nitrates or nitrites by nascent hydrogen in alkaline solution:*

$$NaNO_2 + 3H_2 = NaOH + H_2O + NH_3.$$

$$HNO_3 + 4H_2 = 3H_2O + NH_3.$$

$$8Al + 5KOH + 3KNO_3 + 2H_2O = \underset{\text{Potassium Aluminate.}}{8KAlO_2} + 3NH_3.$$

(4) *Ammonia gas can be prepared on a large scale by heating together calcium hydroxide and ammonium sulphate or chloride:*

$$(NH_4)_2SO_4 + Ca(OH)_2 = CaSO_4 + 2HN_3 + 2H_2O.$$

(5) *For laboratory purposes it is preferable to heat the solution of ammonia* (28 *per cent.*).

Industrial Preparation.—From atmospheric nitrogen:

(a) The Frank-Caro process decomposes calcium cyanamide (page 240) by means of superheated steam:

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

(b) The Haber process consists essentially in passing hydrogen and nitrogen gases in their combining proportions, heated to about 500° and at a pressure of 150 atmospheres, over a "catalyzer" (iron containing uranium). The ammonia produced is withdrawn by absorption or by cooling to liquefaction.

The efficiency yield in the transformation of lime nitrogen into ammonia gas is about 98 per cent., hence its successful utilization in the unlimited production of ammonia, anhydrous ammonia, and its salts.

(c) From Gas-Liquor: Coal, which contains about 1 per cent. of nitrogen, yields ammonia when used in making illuminating gas or the preparation of metallurgic coke. The gas-liquor from the scrubbers of the illuminating gas manufacture is distilled with caustic lime and the escaping ammonia vapors absorbed in vessels containing sulphuric acid. The resulting ammonium sulphate cake may then be again heated with slaked lime, whereby pure ammonia is liberated.

When required pure, the gas must be passed over calcium oxide (quicklime) to remove the moisture, and collected over mercury. As ordinarily needed it may be collected by "upward displacement"; that is, by holding an inverted vessel over the tube from which the gas is escaping, which gas, being lighter than air, rises and fills the vessel.

Physical Properties.—Ammonia is a colorless gas, of a pungent, suffocating odor and a caustic taste. It has a density of 0.5963 (air = 1); one liter weighs 0.7708 gram (0° and 760 mm.). The gas is liquefied by passing into a tube cooled to —40° by means of a mixture of ice and calcium chloride. It may also be liquefied by subjecting to a pressure of from six to seven atmospheres at 10°. This liquid is colorless and highly refractive, and may be solidified by cooling to —77°. At —33.5° it boils, and in vaporizing absorbs large quantities of heat. On account of this property it is used in ice machines and in the several varieties of cooling apparatus employed in breweries.

Ammonia is very soluble in water, one volume of the latter absorbing 1146 volumes (0.875 parts by weight) of the gas at 0°, and about 600 volumes at ordinary temperature, or one part by weight of water dissolves about 0.526 part by weight of ammonia. Water saturated at 15° contains 35 per cent. of ammonia and has a gravity of 0.881. Commercially, the 28 and 10 per cent. solutions are used, owing to the loss of ammonia gas and danger entailed in handling more concentrated solutions. When heated, all of the NH_3 is liberated from such aqueous solutions.

Chemical Properties.—Ammonia is not a combustible gas, although if it be mixed with a small quantity of oxygen combustion readily takes place on the application of a flame, with the formation of water, nitrogen, and nitric acid. It is decomposed at red heat or by the electric spark into nitrogen and hydrogen; when passed over heated sodium, potassium, or magnesium, the nitrogen combines with the metal, forming a nitride, and hydrogen escapes.

$$3Mg + 2NH_3 = Mg_3N_2 + 3H_2.$$

When treated with an excess of chlorine or iodine, at first a salt of ammonia is formed, which is in turn decomposed by the halogen, yielding very explosive compounds, as nitrogen chloride (NCl_3) or nitrogen iodide (NHI_2 or NI_3). Ammonia is alkaline to litmus paper, and combines with acids, forming the well-known ammonium salts. The formula NH_4 represents a hypothetical compound, *ammonium*, which has many properties in common with those of sodium and potassium, and will be treated of in connection with them (see page 361).

Uses.—Anhydrous liquid ammonia is prepared on a large scale by drying the gas over calcium oxide and then liquefying in steel cylinders under a pressure of 6.5 atmospheres at 10°. In this condition ammonia is used in refrigeration and ice machines, where it is forced through a small opening with a coil of pipe from which the gas is rapidly exhausted by a pump. The rapid expansion of the liquefied gas absorbs the heat, cooling the pipe below freezing point. The gas is then compressed and liquefied again by passing through coils cooled by cold water. It comes into commerce in large iron cylinders strong enough to withstand the pressure necessary to keep it in the liquid condition. At 0° liquid ammonia has a specific gravity of 0.623 and boils at —33.5°. Its critical temperature is + 131°. The aqueous solution of ammonia is used largely in medicine and in the manufacture of pharmaceutical preparations.

Detection.—Ammonia and its solution are easily detected by the odor; in small quantities by bringing over the suspected solution a piece of moistened red litmus paper, which will be turned blue. Still more delicate is the reaction with fumes of hydrochloric acid. A rod moistened with the acid is brought into contact with some of the gas or over some of the warmed ammonia solution, when immediately white fumes of ammonium chloride will form. When combined with acids, ammonia is detected by first liberating it from its combination by heating with an alkali, as potassium or sodium hydroxide, and then applying one of the above tests for the gas; or the solution is acidified with hydrochloric acid and solution of platinic chloride added, when a yellow precipitate of ammonium chloro-platinate, $(NH_4)_2PtCl_6$, will slowly separate in minute crystals. Einbrodt's reagent, consisting of a solution of mercuric chloride to which a minute quantity of an alkaline carbonate has been added, will detect the merest trace of ammonia or its compounds, if the latter are previously made alkaline, by forming a white precipitate or cloudiness. Nessler's reagent produces a brown precipitate with ammonium compounds, or if in very dilute solution a brown or yellow color. This reagent is made by adding to a solution of mercuric chloride a solution of potassium iodide until the precipitate at first formed is nearly all redissolved. Solution of potassium hydroxide is then added to strongly alkaline reaction and the liquid allowed to settle until it becomes clear, when it is decanted from any sediment (see U.S.P. Reagent, page 538).

Aqua Ammoniæ, U.S.P.—The solution of ammonia is official in two strengths, one *aqua ammoniæ,* containing not less than 9.5 nor more than 10.5 per cent., by weight, of the gas, and the other, *aqua ammoniæ fortior,* containing not less than 27 nor more than 29 per cent., by weight, of the gas. That of about 10 per cent. strength has the specific gravity of about 0.958 at 25°, and the stronger solution has the specific gravity of about 0.897 at 25°. The commercial "F.F.F." or "20°" water of ammonia contains about 14 per cent. of the gas.

Properties.—Solution of ammonia is a colorless, transparent liquid with the pungent alkaline odor and taste of the gas. On the application of heat the solution evolves ammonia gas at a temperature considerably below the boiling point of water. The gas may also be removed by passing air into the solution. In this case there is a great absorption of heat by the escaping gas.

Spirit of Ammonia (U.S.P. Reagent) is an alcoholic solution of ammonia containing about 10 per cent., by weight, of the gas. The gas is prepared by heating the stronger aqueous solution, and passing this into alcohol which has been distilled from sodium hydroxide. The specific gravity of the alcoholic solution is about 0.808 at 25°.

DIAMIDE, OR HYDRAZINE, $NH_2—NH_2$

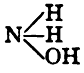
This compound of two unsaturated amidogen (NH_2) groups or radicles is prepared by interaction between sodium hypochlorite and ammonia whereby *chloramine* is produced: $NH_3 + NaOCl = NH_2Cl + NaOH$. If this be distilled at a low temperature in an atmosphere of ammonia, *in vacuo,* hydrazine hydrochloride forms, $NH_2Cl + NH_3 = NH_2.NH_2.HCl$.

Free hydrazine is obtained by distilling its hydrate or sulphate in a current of hydrogen under reduced pressure with barium oxide:

$$N_2H_4.H_2O + BaO = Ba(OH)_2 + N_2H_4.$$

Hydrazine is a colorless liquid which boils at 113.5°, solidifies at 0°, and dissolves in water with formation of a hydrate, $N_2H_4.2H_2O$. After evaporation of the water $N_2H_4.H_2O$ remains. Hydrazine is exceedingly alkaline and with acids forms two classes of salts, $N_2H_4.HCl$ and $N_2H_4.2HCl$. It is not explosive and is readily distinguished from ammonia by its reducing power.

HYDROXYLAMINE, NH_2OH.

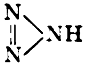


$$N\begin{cases}H\\H\\OH\end{cases}$$

This compound is prepared by the action of nascent hydrogen on nitrogen dioxide, nitric acid, or some nitrates. Thus through the action of dilute nitric acid on tin, the hydroxylamine being basic, combines with hydrochloric acid and remains in solution ($NH_2OH.HCl$), while the tin of the stannous chloride may be precipitated by means of hydrogen sulphide. On concentration of the filtrate, hydroxylamine hydrochloride crystallizes. Hydroxylamine is usually prepared by the electrolytic reduction of nitric acid in the presence of sulphuric acid. Hydroxalmine forms colorless crystals which fuse at 30°, boil at 70° at 60 mm.

pressure, and explode when heated to 90° under ordinary pressure. The hydrochloride which slowly decomposes on standing differs physically from ammonium chloride in being soluble in alcohol; its aqueous solution as well as that of the base is an active reducing agent, precipitating cuprous oxide from alkaline copper solution, reducing mercuric chloride solution to calomel, silver nitrate to silver, etc.

HYDRAZOIC ACID, OR AZOIMID, N_3H, or



Discovered by Curtius in 1890. It may be prepared by pouring an ice-cold solution of nitrous acid into the same of hydrazine.

$$H_2N.NH_2 + HNO_2 = N_3H + 2H_2O.$$

Also by boiling an alcoholic solution of hydrazine hydrate with amyl nitrite and sodium alcoholate and then distilling the sodium hydrazoid with diluted sulphuric acid, which yields a dilute solution of the gas.

$$NaNH_2 + N_2O = NaN_3 + H_2O.$$

Azoimid is a colorless, poisonous, caustic, strongly acid liquid which boils at 37° and possesses an intolerable odor. It, as well as its salts (excepting the alkali salts), readily explodes with violence.

NITROGEN AND CHLORINE

The halogen compounds of nitrogen are all extremely unstable and violent explosives. They are obtained through the action of an excess of the halogen upon ammonia or its derivatives.

NITROGEN CHLORIDE, NCl_3

Preparation.—This is prepared by the action of an *excess* of chlorine upon ammonium chloride.

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

It is also formed when solution of ammonium chloride is submitted to the electric current; the chlorine which forms at the positive pole acts on the ammonium chloride.

Properties.—Nitrogen chloride is a yellow oil of the specific gravity 1.653. It possesses a disagreeable, pungent odor, and the vapor which always escapes on exposure to air attacks the eyes. It is one of the most violent explosives known. The explosion takes place on the slightest provocation, as exposure to direct sunlight or contact with many kinds of organic matter, as caoutchouc or turpentine. Its solution in ether or benzene can be handled with little danger. Decomposition takes place rapidly in the presence of solvents and sunlight.

Nitrosyl Chloride, NOCl, is produced through the interaction of 2 vols. of NO and 1 vol. of Cl; also in *aqua regia.* It is most conveniently prepared by heating nitrosulphonic acid with sodium chloride at 85°; $NO.HSO_4 + NaCl = NOCl + NaHSO_4$. Nitrosulphonic acid (lead chamber crystals) results through interaction between SO_2 and HNO_3 or N_2O_3 and sulphuric acid. Nitrosyl chloride is a red gas, condensed to a red liquid which boils at −5.6°, by cooling. With water it forms nitrous and hydrochloric acids, $NO.Cl + H.OH = NO.OH + HCl$.

NITROGEN IODIDE

Several compounds of nitrogen, iodine, and hydrogen are known, the composition depending upon the conditions of the experiment. All of these compounds are explosive. Nitrogen iodide usually represents a mixture of NI_3, $NH_3.NI_3$, $2NH_3.NI_3$, etc.

Preparation.—Nitrogen di-iodide (NHI_2) and tri-iodide (NI_3) are obtained by powdering a little iodine in a mortar and covering with solution of ammonia; after standing ten minutes the insoluble portion is collected on a filter. If washed, nitrogen tri-iodide only remains.

Properties.—While moist, nitrogen iodide is comparatively safe in small quantities, but so soon as it becomes dry it explodes on the slightest touch. Nitrogen iodide dissolves in dilute hydrochloric acid, decomposing into ammonia and iodine monochloride, $NH_2I + HCl = NH_3 + ICl$.

Hydrogen sulphide and sulphurous acid convert it into ammonia and hydrogen iodide.

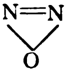
NITROGEN AND OXYGEN

Nitrogen combines with oxygen in five different proportions, three of which are acid anhydrides.

OXIDES	ACIDS
Nitrogen Monoxide, N_2O.	Hyponitrous Acid, $(HNO)_2$.
Nitric Oxide, NO (N_2O_2).	
Nitrogen Trioxide, N_2O_3.	Nitrous Acid, HNO_2.
Nitrogen Tetroxide, NO_2 (N_2O_4).	
Nitrogen Pentoxide, N_2O_5.	Nitric Acid, HNO_3.

NITROUS OXIDE—HYPONITROUS OXIDE
NITROGEN MONOXIDE

Formula, N_2O.



Molecular Weight, 44.02.

History.—Nitrogen monoxide, which is also known as nitrous oxide and laughing gas, was discovered by Priestley in 1772.

Preparation.—The usual method of preparing the gas is by heating ammonium nitrate to somewhat below 250°, when it is decomposed into water and nitrogen monoxide. Since the reaction becomes violent if the temperature is too high, it is usually preferred to heat a mixture of sodium nitrate and ammonium sulphate to 230°, $2NaNO_3 + (NH_4)_2SO_4 = Na_2SO_4 + 2N_2O + 2H_2O$.

$$NH_4NO_3 \quad = \quad N_2O \quad + \quad 2H_2O.$$

The most probable impurity in ammonium nitrate is ammonium chloride, which would cause the presence of chlorine in the gas. It is, therefore, best to pass the gas through three wash-bottles, one of ferrous sulphate solution, to remove the other oxides of nitrogen formed through secondary decomposition, one of sodium hydroxide solution to remove chlorine, and, finally, one of pure water.

Physical Properties.—Nitrogen monoxide is a colorless gas of a faint, peculiar odor and a sweetish taste, with a specific gravity of 1.53 (air = 1). It is about twenty-two times heavier than hydrogen. One liter of nitrous oxide weighs 1.97 gm. (0° and 760 mm.). Under ordinary atmospheric pressure it liquefies at —88°, and at —102° becomes solid. It may also be liquefied at 0° by a pressure of thirty atmospheres. Liquid nitrogen monoxide is colorless and very mobile, and has a specific gravity of 0.9367 at 0°; it boils under ordinary pressure at —89.8°. This liquid when evaporated *in vacuo* produces a lowering in temperature to —140°. A drop of the liquid, when brought in contact with the skin, will cause a blister, and water poured on the liquid is immediately frozen, producing at the same time an explosive evolution of the gas.

Chemical Properties.—Gaseous nitrogen monoxide supports the combustion of many substances almost as actively as oxygen. Mixed with hydrogen it explodes when ignited.

$$N_2O + H_2 = N_2 + H_2O.$$

Uses.—The gas is extensively used in inhalation in minor surgery and dentistry, where a short anæsthesia is desired. For this purpose the gas must be perfectly pure. When mixed with air or oxygen the gas produces a condition of partial insensibility in which the patient often becomes hysterical, laughing immoderately, hence the name *laughing gas.*

It is manufactured on a large scale, and pumped into strong steel cylinders under a pressure of sixty-five atmospheres, and at a temperature of 5° to 10°.

Test.—Hyponitrous oxide resembles oxygen in its various reactions, but does not redden nitrogen dioxide when mixed with it. It is much more soluble in water than oxygen.

HYPONITROUS ACID

Formula, $H_2N_2O_2$, *or* $HO—N=N—OH$. *Molecular Weight,* 62.036.

This acid is known only in dilute solution or in combination with certain bases. It is usually obtained by the reduction of nitric or nitrous acid or their salts. When an aqueous solution of potassium nitrate is treated with nascent hydrogen in form of sodium amalgam in the proportion of four atoms of sodium to one molecule of the nitrate, potassium hyponitrite is formed:

$$2KNO_3 + 4H_2 = K_2N_2O_2 + 4H_2O.$$

On carefully neutralizing with acetic acid, and adding silver nitrate, a yellow precipitate of silver hyponitrite, $Ag_2N_2O_2$, separates. This upon treating with hydrochloric acid in ether yields silver chloride and hyponitrous acid solution, which upon evaporation deposits crystals of $H_2N_2O_2$. Like all compounds of the group N : N, they are explosive. All the salts are quite unstable. The aqueous solution of this acid, which slowly decomposes into $N_2O + H_2O$, liberates iodine slowly from potassium iodide and decolorizes permanganate solutions undergoing oxidation to nitric acid.

NITRIC OXIDE

Formula, NO, *or* $— N = O$. *Molecular Weight,* 30.01.

Preparation.—Nitric oxide is a product of the decomposition of nitric acid or nitrates, and may be prepared as follows:

(1) *Through the action of certain metals (Cu, Hg, Ag, etc.) upon diluted nitric acid:*

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

$$\left(\begin{array}{l} Cu + 2HNO_3 = Cu(NO_3)_2 + H_2 \\ \qquad\qquad 2HNO_3 + 3H_2 = 4H_2O + 2NO \end{array}\right)$$

(2) *By the action of a ferrous salt upon nitric acid or a nitrate in the presence of sulphuric or hydrochloric acid:*

$$6FeSO_4 + 2KNO_3 + 5H_2SO_4 = 3Fe_2(SO_4)_3 + 2KHSO_4 + 4H_2O + 2NO.$$

$$6FeCl_2 + 2KNO_3 + 8HCl = 6FeCl_3 + 2KCl + 4H_2O + 2NO.$$

The proportions for the above reaction are 30 gm. of potassium nitrate, 240 gm. of ferrous sulphate, and 250 mils of a mixture of one volume concentrated sulphuric acid and three volumes of water. A colorless gas escapes, which, however, forms brown vapors of nitrogen peroxide (NO_2) as it comes in contact with the air; but as soon as all the air has been driven from the apparatus it passes off colorless and may then be collected over water.

(3) *By adding sulphuric acid slowly to a mixture of a saturated solution of sodium nitrate and copper turnings:*

$$8NaNO_3 + 4H_2SO_4 + 3Cu = 4Na_2SO_4 + 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Physical Properties.—Nitric oxide is a colorless gas, of specific gravity 1.0368 (air = 1); 1 liter weighs 1.3402 grams. Its critical temperature is —93.6°, and critical pressure 71 atmospheres, being liquefied at —154°. It dissolves readily in solutions of ferrous salts, forming a black-colored solution, from which it is expelled upon heating. It is upon the formation of this coloration that the test for nitric acid or nitrates is based. Nitric oxide also dissolves in nitric acid, forming a brown to green or blue color, as nitrogen trioxide is formed:

$$2HNO_3 + 4NO = 3N_2O_3 + H_2O.$$

It is distinguished from all other gases by the production of red fumes of nitrogen tetroxide when the colorless gas comes in contact with uncombined oxygen (air).

Chemical Properties.—Nitric oxide sustains the combustion of only such substances whose heat liberated is sufficiently high to cause it to break down into nitrogen and oxygen. Hence phosphorus and carbon disulphide burn brilliantly in this gas, the latter forming carbon dioxide and sulphur dioxide. The mixture of nitric oxide and carbon disulphide vapors, when burning, emits a blinding blue-white light, very rich in actinic rays.

NITROGEN TRIOXIDE, OR NITROUS ANHYDRIDE

Formula, N_2O_3, *or* $O = \overset{'''}{N} - O - \overset{'''}{N} = O$. *Molecular Weight*, 76.02.

Preparation.—Nitrogen trioxide, known only at low temperature, is formed through the union of nitrogen dioxide (4 vols.) with oxygen (1 vol.) at —18°, $4NO + O_2 = 2N_2O_3$. When a 50 per cent. nitric acid is reduced by heating with starch or arsenous oxide, orange-red fumes are evolved according to the equation:

$$4HNO_3 + \underset{\text{Arsenic Trioxide.}}{2As_2O_3} + 4H_2O = \underset{\text{Arsenic Acid.}}{4H_3AsO_4} + 2N_2O_3.$$

On passing these vapors into a vessel surrounded by a freezing mixture, they form a green liquid. Pure trioxide at —10° is an indigo-blue liquid. At higher temperature the liquid begins to decompose: $N_2O_3 \rightleftarrows NO + NO_2$, which recombine to nitrogen trioxide when cooled. With a small quantity of water at 0°, nitrogen trioxide forms nitrous acid:

$$N_2O_3 + H_2O = 2HNO_2.$$

With a large quantity of water decomposition takes place with formation of nitric acid and nitric oxide ($3N_2O_3 + H_2O = 2HNO_3 + 4NO$).

NITROUS ACID

Formula, HNO_2, *or* $O = N - OH$. *Molecular Weight*, 47.02.

Preparation.—Nitrous acid is not known in the free state, except in dilute solution at lower temperature. It is formed by adding liquid nitrogen trioxide to ice water ($N_2O_3 + H_2O = 2HNO_2$), but, owing to its instability, it breaks up into nitric acid and nitric oxide ($3HNO_2 = HNO_3 + 2NO + H_2O$).

Nitrites.—The nitrites, or salts of nitrous acid, are quite stable and are the product of the oxidation (decomposition) of nitrogenous organic matter in the presence of the alkalies of the soil; owing, however, to their ready oxidation to nitrates, they occur in the soil in this latter form. The nitrites may be obtained by heating nitrates or fusing them with lead ($KNO_3 + Pb = PbO + KNO_2$), or by interaction between silver or sodium nitrite and a salt of the respective metal ($AgNO_2 + NH_4Cl = NH_4NO_2 + AgCl$). Commercially, nitrites may be made by passing nitric oxide and tetroxide gases, as produced in the electric furnace process in making nitric acid from the atmosphere, into a hot solution of sodium hydroxide.

$$2NaOH + NO + NO_2 = 2NaNO_2 + H_2O.$$

When heated, all nitrites are decomposed into oxides; however, with sodium and potassium nitrite white heat is necessary. The nitrites of silver, mercury, gold, and platinum, whose oxides are decomposed by heat, yield free metals upon ignition.

Upon the addition of acids, nitrites are decomposed with liberation of nitrous acid, which, if the salt is dry, escapes in the form of dense reddish vapors (N_2O_3). Nitrites when added to acidulated solutions of iodides liberate iodine; sulphurous acid is oxidized to sulphuric; ferrous sulphate to ferric sulphate, and potassium ferrocyanide to ferricyanide. When added to acid solutions of potassium permanganate, the latter is decolorized (reduced) with oxidation of the HNO_2 to HNO_3. $2KMNO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$. All nitrites are soluble except the silver salt.

NITROGEN TETROXIDE, $N_2O_4(NO_2—O—NO)$.

NITROGEN PEROXIDE, NO_2.

Molecular Weight, 46.01, *or* 92.02.

Preparation.—Nitrogen tetroxide is prepared:

(*a*) *Through the union of nitric oxide and oxygen:*

$$2NO + O_2 = N_2O_4\ (2NO_2).$$

(2) *Heating lead nitrate:*

$$2Pb(NO_3)_2 = 2PbO + O_2 + 2N_2O_4(2NO_2).$$

The gas may be liquefied by passing into a U-tube cooled by ice and salt.

Properties.—Nitrogen tetroxide, which is stable only below 0°, is a dark-brown gas which is readily cooled to a light yellow fluid. At —20° it becomes a colorless crystalline solid which fuses at —12°. Above 0° the liquid takes on a yellow color, which becomes darker with rise in temperature until at 150° the gas assumes a dark red. This change is due to a gradual dissociation of the tetroxide molecule, which exists at low temperature as N_2O_4, to the simple form which at 150° has the composition of NO_2 and at 500° is colorless, being dissociated into NO and O.

$$\underset{\text{Colorless}}{2NO} + O_2 \rightleftarrows \underset{\text{Brown}}{2NO_2} \rightleftarrows \underset{\text{Colorless}}{N_2O_4}.$$

With a little cold water, nitrogen tetroxide forms nitrogen trioxide and nitric acid ($2N_2O_4 + H_2O = N_2O_3 + 2HNO_3$); with an excess of water or with aqueous solutions of alkalies, nitric and nitrous acid or their salts are produced, demonstrating that nitrogen tetroxide is a mixture of the anhydrides of nitrous and nitric acids.

$$NO_2—O—NO \;+\; HOH \;=\; \underset{\text{Nitric Acid}}{NO_2.OH} \;+\; \underset{\text{Nitrous Acid}}{NO.OH.}$$

With hot water the nitrous acid decomposes to nitric acid and NO.

The liquefied gas is very corrosive and a powerful oxidizer, while the fumes are very irritating.

NITROGEN PENTOXIDE, OR NITRIC ANHYDRIDE

Formula, N_2O_5, *or* $O_2N—O—NO_2$. *Molecular Weight,* 108.02.

Preparation.—Nitric anhydride is produced:

(1) *By carefully heating phosphoric anhydride with nitric acid which have both been previously cooled by ice and salt before mixing.*

$$2HNO_3 \;+\; P_2O_5 \;=\; N_2O_5 \;+\; 2HPO_3.$$

(2) *By passing perfectly dry chlorine over silver nitrate:*

$$2(NO_2.OAg) \;+\; 2Cl \;=\; 2AgCl \;+\; NO_2.O.NO_2 \;+\; O.$$

Properties.—Nitrogen pentoxide is a white, colorless, crystalline solid. The crystals melt at 30° to a dark-yellow liquid, which boils with decomposition between 45° and 50° into nitrogen tetroxide and oxygen, $2N_2O_5 = 4NO_2 + O_2$.

When heat is applied suddenly this decomposition takes place with explosive violence. It dissolves in water with evolution of heat and forms nitric acid. When brought in contact with oxidizable substances, as phosphorus and sulphur, oxidation takes place with ignition; organic matter is also violently attacked.

$$N_2O_5 \;+\; H_2O \;=\; 2HNO_3.$$

NITRIC ACID

HYDROGEN NITRATE

Formula, HNO_3. $O_2\overset{V}{N}—OH$. *Molecular Weight,* 63.02.

History.—Nitric acid was prepared by Geber, in the eighth century, through distillation of saltpeter with alum or copper sulphate. The composition of the acid was first made known through the investigations of Lavoisier, in 1776, and Cavendish, in 1784.

Occurrence and Formation.—Nitric acid is not found in the free state in nature, but in combination with potassium, sodium, calcium, magnesium, and ammonium it is widely distributed. In warm, arid regions where there is only surface drainage, these salts occur as an efflorescence on the surface of the ground and walls through the putrefaction of organic matter. The largest known deposits are the sodium nitrate (*caliche*) beds in the rainless districts on the coasts of Chili. These deposits, containing from 20 to 25 per cent. of $NaNO_3$, owe their origin to the decay of nitrogenous vegetable matter through the agency of the soil microörganisms in the presence of alkalies. These were formed through the presence of vegetation on the western slopes of the Andes, and were gradually washed down, accumulating in deposits near the coast-line hills (page 350).

When air in a glass globe is submitted to a series of electric sparks, red fumes of nitrogen tetroxide (from NO_2) are formed, which, in the presence of water, are decomposed with the formation of nitric acid.

Preparation.—On the small scale nitric acid is prepared by heating in a glass retort equal parts of sodium or potassium nitrate and sulphuric acid:

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

The apparatus becomes filled with reddish-brown vapors, and the liquid which condenses has a yellowish color on account of the presence of nitrogen tetroxide. A very concentrated acid is prepared by placing the above distillate with 2 volumes of concentrated sulphuric acid in a retort connected with a well-cooled receiver, and applying a gentle heat. The distillate in this case is usually freed from color by warming gently and passing through it a current of air to remove the fumes of the lower oxides of nitrogen.

The commercial acid is obtained by distilling sodium nitrate and sulphuric acid in cast-iron or stoneware retorts. The sodium nitrate is much cheaper and for the same weight yields 20 per cent. more nitric acid than the potassium salt. If half the quantity of sulphuric acid is used, as in the above equation, then a higher degree of heat will be necessary to secure liberation of the nitric acid, owing to interaction between the sodium acid sulphate and sodium nitrate: $NaNO_3 + NaHSO_4 = Na_2SO_4 + HNO_3$; hence a decomposition of a portion of the nitric acid will take place, resulting in the formation of red *fuming* nitric acid:

$$2HNO_3 = 2NO_2 + H_2O + O.$$

The resulting sodium sulphate is more difficult to remove, for it remains as a hard, solid mass, while the acid sulphate is in a liquid condition at a moderate temperature and may be poured out. The condensation of the acid during distillation is so regulated that the various foreign gases which are given off with the HNO_3 vapors are collected separately. These gases consist of nitrogen trioxide, nitrosyl chloride, hydrochloric acid, chlorine, and sometimes iodine. The HCl is formed from sodium chloride present in the nitrate, which with the nitric acid forms nitrosyl chloride ($HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O$). All these pass over at the beginning of the distillation. To remove nitrous fumes, which impart a yellow to orange color to the acid, it is redistilled with a current of air passing upward through the condensing coil. For chemically pure acid, pure materials are used. Nitric acid is also produced (where water-power for the economical production of electric current is available) from the atmosphere by drawing air through a special form of furnace in which is contained one or more large and powerful arc flames produced by an alternating current of very high pressure (5000 volts) and temperature of about 3500°. The electrolyzed gas leaving the furnace contains about 2 per cent. of nitric oxide (NO), which, upon rapid cooling, unites with the oxygen of the air to form nitrogen peroxide (NO_2). This gaseous mixture is then passed into absorption towers filled with quartz, over which water trickles, the same water being used over again until an acid of 50 per cent. is obtained. The acid gases which escape absorption are conducted into chambers containing slaked lime, where they are fixed as calcium nitrate. The acid is also converted into this salt, which is then fused and transferred to iron drums. Calcium nitrate can be utilized for the preparation of the acid or its salts. Nitric acid is also produced through the oxidation of ammonia (cyanamide or synthetic). This is carried out by passing a mixture of ammonia with ten volumes of air (which furnishes the oxygen) through an electrically heated net of platinum wire or over pure iron activated with such metals as bismuth, copper, tungsten, etc., at a high velocity to minimize the decomposition of the oxides of nitrogen.

Physical Properties.—Nitric acid is a colorless, fuming, very corrosive liquid. When absolute (99.8 per cent.), it solidifies to a crystalline mass at —40° and has a specific gravity of 1.50 (25°), and commences to boil at 86°, but on account of partial decomposition into water, nitrogen tetroxide, and oxygen, the temperature rises, until at 121° a liquid containing 68 per cent. of the acid distils over unchanged, and has a specific gravity of about 1.402 at 25°. When a weaker acid is heated, water is first given off until the acid attains the strength of the above, when it distils unchanged. This is *Acidum Nitricum*, U.S.P. When exposed to light, nitric acid will acquire a yellow to orange color, due to a slight decomposition with formation of NO_2.

Chemical Properties.—Owing to its unstable character, nitric acid is a powerful oxidizing agent. Through its oxidizing action, nitric acid itself undergoes deoxidation to the lower nitrogen oxides (NO, N_2O_3, NO_2), while its hydrogen is oxidized to water. With metallic oxides it acts like other acids. If nitric acid be heated in a sealed tube to 260°, it breaks up completely into water, oxygen, and nitrogen tetroxide. In aqueous solution nitric acid ionizes into the monovalent ions NO'_3 and $H^{\cdot}$. Because of its energetic properties, it oxidizes and dissolves most all metals except gold and platinum.

The products of the action of nitric acid upon metals vary with the nature of the metal and the concentration of the acid employed. Some metals dissolve, forming nitrates, while others are converted into acids or insoluble oxides. To this latter class belong such metals as As, Sb, Sn, Mo.

$$(1)\ a.\quad 2Sb + 2HNO_3 = \underset{\text{Antimony Trioxide (insoluble).}}{Sb_2O_3} + 2NO + H_2O.$$

$$b.\quad 6Sb + 10HNO_3 + 4H_2O = \underset{\text{Antimonic Acid (insoluble).}}{6H_3SbO_4} + 10NO.$$

$$(2)\ a.\quad 2As + 2HNO_3 = As_2O_3 + 2NO + H_2O.$$

$$b.\quad As_2O_3 + 2HNO_3 + 2H_2O = \underset{\text{Arsenic Acid (soluble).}}{2H_3AsO_4} + N_2O_3.$$

$$(3)\ a.\quad 3Hg + 4HNO_3 = 3\underbrace{HgNO_3.2H_2O}_{\text{Mercurous Nitrate.}} + NO.$$

$$b.\quad 3Hg + 8HNO_3 = \underset{\text{Mercuric Nitrate.}}{3Hg(NO_3)_2} + 4H_2O + 2NO.$$

$$(4)\quad 6Sn + 8HNO_3 + 2H_2O = \underset{\text{Meta-stannic Acid.}}{6H_2SnO_3} + 8NO.$$

Other metals, as Zn, Cd, Fe, Sn, when reacting with very dilute nitric acid, produce, in addition to the nitrate of the metal, ammonium nitrate, due to the reducing action of the nascent hydrogen upon the acid.

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O.$$

Sulphur, phosphorus, iodine, and carbon are oxidized by nitric acid to oxides or acids. Many organic bodies, like turpentine, are inflamed at once on coming in contact with it, while other organic compounds are merely turned yellow. A number of substances, like cotton and benzene, undergo a process of *nitration* when brought in contact with the concentrated acid. In this operation the group NO_2 replaces hydrogen in the compound. With cotton or cellulose, gun cotton (cellulose nitrate) is formed; with glycerin, nitro-glycerin (glyceryl nitrate), and with benzene, nitro-benzene.

Fuming Nitric Acid, of an orange color, sometimes erroneously called nitrous acid, differs from the ordinary variety by containing nitrogen tetroxide in solution. It may be prepared either by distilling two molecules of saltpetre with one molecule of sulphuric acid, so that neutral sodium sulphate is formed (page 255), or by adding paraformaldehyde or a little starch to nitric acid and heating. This acid is far more energetic as an oxidizing agent than the colorless nitric acid. The U. S. P. reagent acid is of a gravity of from 1.48 to 1.52.

Detection.—Nitric acid is easily detected by its action on copper, which it dissolves with a blue color, giving off abundant brown-red fumes at the same time. When wool, silk, and animal tissues are brought in contact with strong nitric acid they are colored yellow, which is changed to orange by ammonia. The acid destroys the blue color of indigo solution, forms a dark ring when brought in contact with a crystal of ferrous sulphate and sulphuric acid, and gives off ammonia when made strongly alkaline with potassium hydroxide and heated with zinc. A very sensitive test (1 in 100,000) consists in adding a few drops of the solution of the acid or its salt to a solution of brucine, followed by sulphuric acid poured down the side of the test-tube; a rose color to red ring will appear at the zone of contact.

Impurities.—The chief impurities in the commercial nitric acid are chlorine, iodic acid, hydrochloric and sulphuric acids, and traces of metals. For tests see U. S. Pharmacopœia.

Uses.—Nitric acid is employed in the manufacture of sulphuric acid, of organic nitro compounds such as nitroglycerin, nitrobenzol, picric acid, gun cotton, tri-nitro-toluene, mercury fulminate, artificial silks, and indirectly many organic colors, as well as in the refining of precious metals. Vessels containing this acid should be packed in infusorial earth, for if leakage occurs, fire is liable to result on contact with sawdust, straw, or wood.

Nitrates.—Nitric acid is mono-basic, hence forms normal salts only. They may be prepared either by solution of the metal or its oxide in the acid.

The nitrates are nearly all soluble in water, the exceptions being a few of the basic salts (page 132) which this acid forms. When heated, nitrates fuse, and, if the temperature be sufficiently high, they undergo decomposition, the product depending upon the nature of the nitrate and the degree of heat. Thus the alkali nitrates yield nitrites and finally oxides, while the alkaline earth (and lead) nitrates yield nitrogen tetroxide and an oxide. Mercuric and silver nitrates yield nitrogen tetroxide and the metallic oxides, which at higher temperatures decompose into the metal and oxygen ($2AgNO_3 = Ag_2O + 2NO_2 = Ag_2 + O_2$). The alkali nitrates are employed in dry oxidations.

Acidum Nitrohydrochloricum, U.S.P.—This substance, which is also known by the names of aqua regia and nitromuriatic acid, was first prepared by Geber (eighth century), who dissolved ammonium chloride in nitric acid. Basil Valentine appears to have given it the name *aqua regia,* because of its solvent action upon gold, and suggested the method for preparing it, by mixing nitric and hydrochloric acids.

Preparation.—The U.S.P. directs the preparation of it by mixing 18 parts of nitric acid with 82 parts of hydrochloric acid, all by volume. The acids should be mixed in an open vessel, allowed to stand until effervescence has ceased, and preserved in partly filled bottles in a cool place. The compounds formed by the combination of the two acids are chlorine and nitrosyl chloride:

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

Properties.—Nitrohydrochloric acid is a "golden-yellow, fuming, very corrosive liquid, having a strong odor of chlorine" and a strongly acid reaction. The *acidum nitrohydrochloricum dilutum,* U.S.P., should be freshly prepared when needed, and dispensed only when it causes the immediate liberation of iodine when added to a solution of potassium iodide. It readily dissolves gold and platinum. This solvent action depends largely on the chlorine which is present.

PHOSPHORUS

Symbol, P. *Atomic Weight,* 31.04. *Valence,* III, V.

History.—Phosphorus was discovered by the alchemist Brandt, about 1675, at Hamburg, by distilling a mixture of evaporated urine and sand. Gahn in 1769 found it to be a constituent of bone-ash, and in 1775 Scheele published a method for preparing it from this source. The name phosphorus (*φως = light, φορος = carrier*) was given because of its luminous action in the dark.

Occurrence.—Phosphorus is never found native in the free state, but chiefly as tri-calcium phosphate, the principal constituent of bones, as well as of the minerals *apatite* [$3Ca_3(PO_4)_2 + CaF_2$] and *phosphorite* [$Ca_3(PO_4)_2$]. The latter, which is known as "phosphate rock," is extensively used for fertilizing purposes.

Phosphorus is, further, very widely distributed in comparatively small quantities. It is always found in plant and animal tissues, in the soil, and in sea water. This element is eliminated in the urine as calcium, magnesium, and sodium phosphate.

Isolation.—The bones are freed from fat by extraction with carbon disulphide or petroleum benzine, and from gelatin by superheated steam. They are then burned to whiteness. The resulting white bone-ash is composed of about 86 per cent. calcium phosphate, $Ca_3(PO_4)_2$, with small quantities of magnesium phosphate and calcium carbonate and fluoride. The following process, which is no longer used, is given because of the reactions involved.

The bone-ash or its equivalent, the calcined spent bone-black from the sugar refiners, is treated with sulphuric acid to convert the calcium into monocalcium phosphate and sulphate. This is then leached with hot water to dissolve the monocalcium phosphate, leaving the insoluble calcium sulphate; the solution is evaporated to dryness with ground coke and heated in earthenware retorts with silica to white heat. The reactions involved are as follows:

$$(1)\quad \underset{\text{Tricalcium Phosphate.}}{Ca_3(PO_4)_2} + 2H_2SO_4 = 2CaSO_4 + \underset{\text{Monocalcium Phosphate.}}{CaH_4(PO_4)_2}.$$

$$(2)\quad CaH_4(PO_4)_2 = 2H_2O + \underset{\text{Calcium Metaphosphate.}}{Ca(PO_3)_2}.$$

$$(3)\quad Ca(PO_3)_2 + 5C + SiO_2 = \underset{\text{Calcium Silicate.}}{CaSiO_3} + 2P + 5CO.$$

The yield is from 8 to 10 per cent. of the bones used. Phosphorus at this stage still contains impurities carried over mechanically in the process of distillation and must be further purified. This is accomplished by redistilling with steam in an atmosphere of carbon dioxide, or by treating the melted phosphorus under water with a mixture of sulphuric acid and potassium dichromate.

The molten phosphorus is then moulded into stick-form and placed in sealed cans containing water. It should always be cut under water.

The continuous acting electric furnace process utilizing powdered bones or phosphatic minerals has replaced the old, more expensive method. In an upright pear-shaped furnace, an intimate mixture of carbon, phosphate, and flux (sand) is heated at 1300–1450° by means of carbon electrodes. The phosphorous vapors pass off above to a condenser, while the slag is tapped off below.

$$\underset{\substack{\text{Calcium}\\\text{Phosphate.}}}{Ca_3(PO_4)_2} + \underset{\text{Silica.}}{3SiO_2} + \underset{\text{Coke.}}{5C} = \underset{\substack{\text{Phos-}\\\text{phorus.}}}{P_2} + \underset{\substack{\text{Calcium}\\\text{Silicate.}}}{3CaSiO_3} + \underset{\substack{\text{Carbon}\\\text{Monoxide.}}}{5CO}.$$

Physical Properties.—Phosphorus exists in several allotropic modifications, most important of which are the *yellow* and the *red phosphorus.*

Phosphorus, U.S.P., or *Yellow Phosphorus,* is that obtained by the above-described methods. This variety is a colorless, transparent to translucent, wax-like solid, sold in stick form. At ordinary temperatures it is sufficiently soft to be cut by a knife, but at lower temperatures it becomes more brittle. It has a specific gravity of about 1.83 at 10°, and at 44° it melts to a colorless refractive liquid. It boils at 279.3°, air, of course, being excluded. Vapor density as well as cryoscopical determinations give to phosphorus a molecular weight corresponding to P_4; that is, the molecule contains four atoms.

Phosphorus is insoluble in water; 1 gram is soluble in about 400 mils of anhydrous alcohol, in 102 mils of anhydrous ether, 17 mils of chloroform, 0.9 mil of carbon disulphide, and in about 50 parts of any fatty oil at 25° C. Carbon disulphide is probably its best solvent. From this phosphorus crystallizes in the regular system. All solutions of phosphorus in carbon disulphide should be preserved with the greatest care. When spilled or otherwise exposed, the solvent rapidly evaporates, leaving the phosphorus in such a finely divided condition that it inflames spontaneously. Phosphorus may be powdered by melting under water and agitating until cold; many saline solutions facilitate this division. When exposed to moist air it is slowly oxidized to phosphorous (H_3PO_3) and phosphoric (H_3PO_4) acids; the white vapors evolved contain ammonium nitrate, ozone, and hydrogen dioxide. The peculiar garlic-like odor of phosphorus is due to the formation of ozone ($P_2 + 3O_2 = P_2O_5 + O$), $O_2 + O = O_3$. The phosphorescence, visible in the dark, when exposed to the air appears to be due to slow oxidation. Phosphorus is a very inflammable element, igniting in the air spontaneously at 40°. For this reason it is kept and cut under water. Phosphorus, when kept under water and exposed to the light, undergoes slow oxidation, becoming covered first with a white, opaque film, which slowly turns red.

Chemical Properties.—Yellow phosphorus possesses a great affinity toward many elements, uniting directly with all except nitrogen, the rare gases, and carbon. With bromine and sulphur it reacts violently. Characteristic is its affinity for oxygen; when exposed to the air at a temperature above its melting-point, or at a lower temperature if in a finely subdivided state, ignition takes place, burning to phosphorous or phosphoric oxide, according to the supply of oxygen. The slow oxidation of phosphorus is accompanied by a faint glowing called phosphorescence; this is prevented by the presence of hydrocarbons, ammonia, ether, turpentine, etc.

Because of its great affinity for oxygen, phosphorus is an energetic reducing agent; sulphuric acid is reduced to sulphur dioxide. Nitric acid is deoxidized with explosive violence; salts of some metals, as Ag, Au, Cu, are reduced to their metals and phosphides. This property is made use of in copying delicate surfaces by the electrotype process. A dilute solution of phosphorus in ether is applied, followed by a solution of copper sulphate, which leaves a conducting metallic film.

Red or *Amorphous Phosphorus,* an allotropic modification, which possesses properties essentially different from the yellow, was discovered by Schrötter in 1845. It forms a dark-red to reddish-brown inodorous powder of specific gravity 2.34 (commercial 2.14 to 2.30), insoluble in carbon disulphide and all other solvents; does not phosphoresce and is stable in the air. It does not fuse at red heat, but when quickly heated to above 260° the vapors change to those of yellow phosphorus and ignite. Red phosphorus is prepared by heating the yellow variety to 300° in closed air-tight vessels, and, after the conversion, the product is treated with carbon disulphide to remove any of the unchanged phosphorus. If a little iodine be added, this change will take place at below 200°. Red phosphorus is not poisonous. Its chief use is in the manufacture of "safety matches"; is also extensively employed in organic syntheses.

Uses.—Medicinally, the *yellow* variety is very poisonous; it produces burning in the stomach, vomiting, and convulsions. The vapors, when breathed for any length of time, cause necrosis of the bones. The *red* modification, because of its insolubility, is inert medicinally.

The yellow phosphorus is employed in medicine, in the manufacture of the acids of phosphorus, also in making friction matches. The red variety is chiefly used in the preparation of various organic compounds.

The different ingredients which enter into the composition of matches may be classified as follows: the *oxidizable* components, as yellow and red phosphorus, antimony sulphide, sulphur, charcoal; the *oxidizing,* as potassium nitrate, chlorate, and bichromate, red lead, manganese dioxide; to sustain combustion, the sticks are impregnated with paraffin or sulphur. Such substances as powdered glass or quartz serve to impart the necessary friction. The ordinary "strike anywhere" match is made by dipping the wooden sticks into an emulsion of yellow phosphorus in a warm concentrated solution of glue, to which have been added potassium nitrate or chlorate, manganese dioxide, and powdered glass. The Swedish (or *safety*) *match* head consists of a mixture of potassium chlorate and dichromate with red oxide of lead and antimony sulphide. These ignite only on the box, the sides of which are covered with a mixture of red phosphorus, antimony sulphide, and powdered silica. The manufacture and sale of the yellow phosphorus match is now forbidden by law in most countries, due to the danger to which those employed in their manufacture are exposed.

Impurities.—The chief objectionable impurity liable to be present in phosphorus is arsenic. This enters into all the acids and salts prepared directly or indirectly from this element. German phosphorus has averaged from 0.01 to 0.015 per cent. of arsenic (as As_2O_3), while that of American manufacture has shown 0.03 per cent. The Pharmacopœia, through its test, permits a limit of not over 0.05 per cent., or 1 part of arsenous oxide in 2000 parts of phosphorus.

PHOSPHORUS AND HYDROGEN

Phosphorus combines with hydrogen in three proportions:

PH_3, gaseous hydrogen phosphide.
P_2H_4, liquid hydrogen phosphide.
(P_2H_6), solid hydrogen phosphide.

HYDROGEN PHOSPHIDE or PHOSPHINE, $PH_3 = 34.06$

PHOSPHORETTED HYDROGEN

Phosphine, which usually contains some of the liquid and solid varieties, may be prepared:

(1) *By heating phosphorus with a solution of the alkali hydroxides:*—

$$P_4 + 3KOH + 3H_2O = \underset{\text{Potassium Hypophosphite.}}{3KH_2PO_2} + PH_3.$$

(2) *By the action of water or dilute acids upon alkali phosphides:*—

$$Ca_3P_2 + 6HCl = 3CaCl_2 + 2PH_3.$$

(3) *By heating phosphorous or hypophosphorous acids or their salts:*—

$$\underset{\text{Phosphorous Acid.}}{4H_3PO_3} = PH_3 + \underset{\text{Phosphoric Acid.}}{3H_3PO_4}.$$

$$\underset{\text{Hypophosphorous Acid.}}{2HPH_2O_2} = PH_3 + \underset{\text{Phosphoric Acid.}}{H_3PO_4}.$$

The reactions involved are more complex than given above, owing to the formation of the liquid self-inflammable phosphide which is given off with the gaseous phosphide. Hence, in the preparation of this gas, care should be taken to displace the air from the apparatus by means of carbon dioxide, while the delivery-tube of the apparatus should terminate below the surface of water.

The escaping gas, as it comes in contact with air, inflames spontaneously with a slight report, forming white cloud rings of phosphorus pentoxide.

Properties.—*Pure* hydrogen phosphide is a colorless, very poisonous gas, of disagreeable fishy odor. Its density is 1.185 (Air = 1). It inflames when heated to 100°, liquefies when cooled to —85°, and solid at —133°. When ignited, it burns with a bright, luminous flame, yielding a white cloud of phosphoric oxide:—

$$2PH_3 + 4O_2 = 3H_2O + P_2O_5.$$

Mixed with chlorine it explodes violently, forming phosphorus pentachloride and hydrochloric acid. Phosphine gas readily reduces solutions of silver or copper to a mixture of the metal and its phosphide, $3CuSO_4 + 2PH_3 = 3H_2SO_4 + P_2Cu_3$.

Hydrogen phosphide is a compound analogous to ammonia, and combines with the halogen acids, forming phosphonium chloride, PH_4Cl; bromide, PH_4Br, and iodide, PH_4I. In contact with water they break up into PH_3 and HX.

Liquid Hydrogen Phosphide, P_2H_4, is formed in the preparation of phosphine, also in the decomposition of calcium phosphide with water, the gas is passed through a freezing mixture, by which the liquid phosphide is condensed.

This is a colorless, strongly refracting liquid boiling at 57° (735 mm.), which inflames spontaneously in contact with air. On exposure to light without access of air it readily decomposes into gaseous and yellow solid hydrogen phosphide, which is not spontaneously inflammable.

PHOSPHORUS AND THE HALOGENS

Phosphorus combines readily with the halogens to form compounds of the types $\overset{\text{III}}{P}X_3$ and $\overset{\text{V}}{P}X_5$.

Phosphorus Trichloride.—*Phosphorous Chloride,* PCl_3, is prepared by passing dry chlorine into a retort containing amorphous or red phosphorus; a moderate heat is applied to the retort, and the resulting vapors of the chloride are conducted into a well-cooled receiver. When the phosphorus is kept in excess the product is nearly pure, but if the chlorine be slightly in excess the distillate will also contain phosphorus pentachloride, which may be removed by redistilling from ordinary phosphorus.

Phosphorus trichloride is a colorless, pungent liquid, boiling at 76°. Its specific gravity at 0° is 1.612. It fumes in contact with moist air, and is decomposed by water into hydrochloric and phosphorous acids:

$$PCl_3 + 3H_2O = 3HCl + H_3PO_3.$$

Phosphorus Pentachloride.—*Phosphoric Chloride,* PCl_5, is formed by the action of dry chlorine on phosphorus trichloride. This is best accomplished by passing the dry chlorine over the surface of the trichloride through a wide tube, occasionally stirring until the whole solidifies to a crystalline mass. As there is considerable heat developed, the vessel in which the reaction takes place must be kept well cooled. This may also be prepared by passing chlorine through a solution of phosphorus in carbon disulphide, well cooled, which upon evaporation leaves prismatic crystals of the pentachloride.

Phosphorus pentachloride is a yellowish-white, crystalline powder, which fumes strongly on exposure to air, with a very irritating odor. It sublimes at 100° without previously melting; by higher temperatures (above 150°) it is dissociated into phosphorus trichloride and chlorine. Phosphorus pentachloride reacts energetically with water, yielding, according to the relative proportions of the reacting substances, phosphorus oxychloride ($POCl_3$), metaphosphoric acid (HPO_3) or orthophosphoric acid (H_3PO_4), and hydrochloric acid in variable proportions.

$PCl_5 + H_2O = 2HCl + POCl_3$ Phosphorus oxychloride.
$PCl_5 + 3H_2O = 5HCl + HPO_3$ Metaphosphoric acid.
$PCl_5 + 4H_2O = 5HCl + H_3PO_4$ Phosphoric acid.

On account of its affinity for the elements of water, phosphorus pentachloride is a useful laboratory reagent for determining the presence of the hydroxyl group and replacing the same by Cl, especially in organic compounds. For example, the reaction with ethyl alcohol:

$$\underset{\text{Ethyl Alcohol.}}{C_2H_5.OH} + PCl_5 = \underset{\text{Ethyl Chloride.}}{C_2H_5Cl} + \underset{\text{Phosphorus Oxychloride.}}{POCl_3} + HCl.$$

With acetic acid there is formed acetyl chloride, $CH_3CO.OH + PCl_5 = CH_3.CO.Cl + POCl_3 + HCl$; with sulphuric acid, chlorosulphonic acid, $SO_2(OH)_2 + PCl_5 = SO_2(OH)Cl + POCl_3 + HCl$.

Phosphorus Tribromide, PBr_3, is prepared like the trichloride, which it closely resembles. It has the specific gravity of 2.8847 at 0°, and boils at 175°.

Phosphorus Pentabromide, PBr_5, resembles the corresponding compound of chlorine in its mode of formation and properties. It is a yellow crystalline solid which melts below 100° and on heating decomposes into PBr_3 and Br_2.

Phosphorus Chlorbromide, PCl_3Br_2, is a compound formed by bringing together phosphorus trichloride and bromine in the proportion of their molecular weights. It is a yellowish-red, crystalline solid, which decomposes at 35°.

Phosphorus Tri-iodide, PI_3, is a dark-red, unstable, crystalline solid, melting at 55°.

Phosphorus Pentafluoride, PF_5, is formed by adding arsenic trifluoride to phosphorus pentachloride: $5AsF_3 + 3PCl_5 = 5AsCl_3 + 3PF_5$.

It is a colorless gas, possessing a density of 63 ($H = 1$). It is decomposed by water into phosphoric and hydrofluoric acids. Its chief use is in the manufacture of a number of compounds of fluorine.

PHOSPHORUS AND OXYGEN

Four oxides and six acids of phosphorus are known, as follows.

OXIDES		ACIDS	
		Hypophosphorous Acid,	H_3PO_2.
Phosphorus Protoxide,	P_2O.	Phosphorous Acid,	H_3PO_3.
Phosphorus Trioxide,	P_4O_6.	Metaphosphorous Acid,	HPO_2.
Phosphorus Tetroxide,	P_2O_4.	Orthophosphoric Acid,	H_3PO_4.
Phosphorus Pentoxide,	P_2O_5.	Metaphosphoric Acid,	HPO_3.
		Pyrophosphoric Acid,	$H_4P_2O_7$.
		Hypophosphoric Acid,	$H_4P_2O_6$.

The *meta-* and *pyro-phosphoric* acids are anhydride acids derived from orthophosphoric acid. These three acids may be considered as derived by the addition of water to phosphoric oxide, as follows:

$$P_2O_5 \left\{ \begin{array}{lcl} + \ H_2O & = & 2HPO_3\text{, Metaphosphoric Acid.} \\ + \ 2H_2O & = & H_4P_2O_7\text{, Pyrophosphoric Acid.} \\ + \ 3H_2O & = & 2H_3PO_4\text{, Orthophosphoric Acid.} \end{array} \right.$$

Phosphorus Protoxide (Phosphorus Suboxide), P_2O. Prepared by the reduction of phosphorus oxychloride by phosphine, $POCl_3 + PH_3 = 3HCl + P_2O$ an orange powder which is very stable.

PHOSPHORUS TRIOXIDE—PHOSPHOROUS ANHYDRIDE

Formula, P_4O_6 (*formerly* P_2O_3). *Molecular Weight,* 220.16.

This compound is prepared by gently heating phosphorus in a current of dry air, separating through condensation the P_2O_5 formed at the same time, by passing through a tube cooled to about 60°, the P_4O_6 being solidified by a freezing mixture. Its vapor density indicates the formula to be P_4O_6 and not P_2O_3.

It is a white, amorphous powder or colorless needles, of a garlic-like odor and fusing at 22.5°. In contact with air it rapidly oxidizes to form the pentoxide and where exposed to light it turns yellow. Phosphorous oxide dissolves slowly in cold water, forming phosphorous acid, $P_4O_6 + 6HOH = 4H_3PO_3$; with hot water it reacts violently. When heated to 440° it decomposes into red phosphorus and *phosphorus tetroxide.*

HYPOPHOSPHOROUS ACID

Formula, H_3PO_2, or HPH_2O_2, or $O{:}PH_2(OH)$. *Molecular Weight,* 66.06.

Preparation.—Hypophosphorous acid is prepared by heating yellow phosphorus with a concentrated solution of barium or calcium hydroxide, and subsequently precipitating the barium or calcium by means of sulphuric or oxalic acid. The insoluble barium sulphate or calcium oxalate is filtered off and the filtrate concentrated by evaporation *in vacuo:*

$$\underset{\text{Barium Hydroxide.}}{3Ba(OH)_2} + 2P_4 + 6H_2O = \underset{\text{Barium Hypophosphite.}}{3Ba(H_2PO_2)_2} + 2PH_3.$$

$$Ba(H_2PO_2)_2 + H_2SO_4 = \underset{\text{Barium Sulphate.}}{BaSO_4} + \underset{\text{Hypophosphorous Acid.}}{2HPH_2O_2}.$$

Properties.—Hypophosphorous acid is a colorless liquid of strong acid reaction. When heated, it decomposes into hydrogen phosphide and phosphoric acid.

$$2HPH_2O_2 = PH_3 + H_3PO_4.$$

Because of its great affinity for oxygen, being oxidized to phosphoric acid, it is a powerful reducing agent. Thus silver nitrate is reduced to metallic silver, mercuric chloride to mercurous chloride and metallic mercury, copper sulphate to its hydride, and iodine to hydriodic acid:

$$HPH_2O_2 + 4HgCl_2 + 2H_2O = H_3PO_4 + 4HgCl + 4HCl.$$
$$HPH_2O_2 + 4HgCl + 2H_2O = H_3PO_4 + 2Hg_2 + 4HCl.$$
$$HPH_2O_2 + 2I_2 + 2H_2O = H_3PO_4 + 4HI.$$
$$2HPH_2O_2 + 2CuSO_4 + 4H_2O = 2H_3PO_4 + Cu_2H_2 + 2H_2SO_4 + H_2.$$

The above test distinguishes hypophosphorous acid from phosphorous acid.

$$HPH_2O_2 + 2Cl_2 + 2H_2O = H_3PO_4 + 4HCl.$$
$$5HPH_2O_2 + 4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 5H_3PO_4 + 6H_2O.$$
$$2SO_2 + 2HPH_2O_2 = 2H_3PO_4 + S_2.$$

Acidum Hypophosphorosum, U.S.P., contains not less than 30 nor more than 32 per cent. by weight of absolute HPH_2O_2. It has a specific gravity of about 1.130 at 25°.

Acidum Hypophosphorosum Dilutum, U.S.P., contains not less than 9.5 nor more than 10.5 per cent. by weight of absolute HPH_2O_2. This acid has a specific gravity of about 1.042 at 25°.

Impurities and Tests.—The most probable impurities in these acids are hydrochloric, sulphuric, phosphoric, and oxalic acids, barium, arsenic, and calcium hypophosphite. Before testing for the presence of arsenic, the solution must be oxidized to phosphoric acid, for the nascent hydrogen generated in the arsenic test reduces the hypophosphorous acid to phosphine gas, which produces a yellow stain, similar to that of arsine, upon the mercuric chloride paper cap (U.S.P.).

Hypophosphites.—Hypophosphorous acid has but one hydroxyl hydrogen replaceable by metals; its salts are usually prepared from the barium salt by interaction with the sulphate of the base desired. They are all soluble in water. In the dry state they are stable, but in solution, or when exposed to moist air, they absorb oxygen and are gradually oxidized to phosphates. In pharmaceutical preparations they are usually preserved with sugar. When heated sufficiently high the hypophosphites (as well as hypophosphorous acid) are decomposed into phosphine, hydrogen, and a pyro- or meta-phosphate. The hypophosphites are reducing agents, becoming more active when acidulated.

PHOSPHOROUS ACID

Formula, H_3PO_3, *or* $HPO(OH)_2$. *Molecular Weight,* 82.06.

Preparation.—This acid is formed with hypophosphoric and phosphoric acids when phosphorus is exposed to moist air. It is prepared pure and in large quantity by passing a stream of chlorine into melted phosphorus under water. Phosphorus trichloride is first produced, which is decomposed, as fast as formed, by the water present:

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

The solution is evaporated until it attains a temperature of 180°, when a thick fluid mass remains, which, on cooling, solidifies to a mass of crystals, having a melting point of 70°. On heating above 180° decomposition takes place, with formation of phosphoric acid and hydrogen phosphide, as follows:

$$4H_3PO_3 = 3H_3PO_4 + PH_3.$$

Phosphorous acid is a powerful reducing agent, reducing sulphurous acid to hydrogen sulphide and sulphur ($H_2SO_3 + 3H_3PO_3 = 3H_3PO_4 + H_2S$), precipitating gold, silver, and mercury from solutions of their salts.

$$(a)\quad 2HgCl_2 + H_3PO_3 + H_2O = 2HgCl + H_3PO_4 + 2HCl.$$
$$(b)\quad 2HgCl + H_3PO_3 + H_2O = Hg_2 + 2HCl + H_3PO_4.$$

The phosphorous acid becomes oxidized to phosphoric, and the mercuric chloride is reduced to mercurous chloride and finally mercury.

The phosphites are distinguished from the hypophosphites by the former causing precipitates with barium chloride or lead acetate solutions.

Phosphorous acid is *dibasic,* only two of the hydrogens being replaceable by metals. The phosphites are not used in medicine.

PHOSPHORUS PENTOXIDE, PHOSPHORIC ANHYDRIDE

Formula, P_2O_5, or $O_2\overset{V}{P}—O—\overset{V}{P}O_2$. *Molecular Weight,* 142.08.

Phosphorus pentoxide is prepared by burning phosphorus in iron cylinders in a current of dry air. To obtain it free from "ous" oxides it is sublimed in a current of oxygen. It is a bulky, white, amorphous, or crystalline powder, the latter of which is obtained by subliming at 250°. It has a powerful affinity for water, hissing when thrown into it. The various acids produced with water are enumerated on page 263. Unless moist air be rigidly excluded deliquescence rapidly takes place. On account of this affinity for moisture, it is much used as a desiccating agent, especially in the drying of gases.

ORTHOPHOSPHORIC ACID

Formula, H_3PO_4, or $O{:}\overset{V}{P}(OH)_3$. *Molecular Weight,* 98.14.

History.—The existence of this acid was first noticed by Marggraf, in 1746, on account of the peculiar yellow precipitate it produced with silver nitrate. Graham, in 1833, first pointed out the difference between the ortho-, pyro-, and meta-acids.

Preparation.—Orthophosphoric acid may be prepared:

(1) *Through the solution of phosphorus pentachloride or bromide or pentoxide in water.* Technically, the acid may be prepared by burning phosphorus with an abundant supply of oxygen, and after the absorption of the oxides in water, the resulting mixture of phosphorous and phosphoric acids is completely oxidized to the ortho-acid.

(2) *Through the oxidation of phosphorus, in the presence of water, by means of nitric acid:*

$$3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO.$$

(3) More expeditiously and with less danger, the phosphorus may be *oxidized* by means of a mixture of *bromine* (*or iodine*) and *nitric acid* in presence of water. Phosphorus pentabromide is first formed, which, in contact with the water, is decomposed into phosphoric acid and hydrobromic acid.

$$PBr_5 + 4H_2O = H_3PO_4 + 5HBr.$$

The hydrobromic acid formed is decomposed by the nitric acid with formation of bromine, water, and nitric oxide:

$$6HBr + 2HNO_3 = 3Br_2 + 4H_2O + 2NO.$$

The liberated bromine now combines with a fresh portion of phosphorus and the reactions are repeated. In this way a limited amount of bromine is able to effect the conversion of a large quantity of phosphorus to its acid without the aid of heat.

(4) *From bone-ash, through treatment with an excess of sulphuric acid:*

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

Owing to the presence of arsenic in phosphorus (usually 0.01 to 0.03 per cent. As_2O_3), which is oxidized to arsenic acid (H_3AsO_4) in the process, the phosphoric acid is diluted and saturated with hydrogen sulphide. After the removal of the arsenous sulphide, the solution is brought up to the desired degree of concentration by evaporation.

Properties.—Anhydrous orthophosphoric acid crystallizes in six-sided rhombic prisms which fuse at 38.6°. On exposure to moist air, or on the addition of water, they deliquesce to a thick syrupy liquid.

The crystals are also easily soluble in alcohol. When heated from 200° to 215°, orthophosphoric acid is gradually converted into pyrophosphoric acid, $H_4P_2O_7$; when heated above 400° it is completely converted into metaphosphoric acid, HPO_3.

Acidum Phosphoricum, U.S.P., contains not less than 85 nor more than 88 per cent. of absolute H_3PO_4. It has a specific gravity of about 1.72 at 25°. The official *diluted* acid contains not less than 9.5 and not more than 10.5 per cent., by weight, of absolute acid.

Impurities.—The impurities liable to be present in phosphoric acid are arsenic acid, sulphuric acid, nitric acid, lead, and copper, which are introduced through the raw materials employed in its manufacture. Other impurities, such as phosphorous, meta- and pyro-phosphoric acids, are the results of the incomplete oxidation of the phosphorus, or, as with the latter two, the overheating of the acid. For tests see U. S. Pharmacopœia.

Phosphates.—Orthophosphoric acid, being tribasic, forms three classes of salts, according as one, two, or three atoms of hydrogen are replaced by metals; these are called *primary* (NaH_2PO_4), *secondary* (Na_2HPO_4), and *tertiary* (Na_3PO_4) phosphates. Since two of these salts contain replaceable hydrogen, they may also be termed mono-sodium phosphate (NaH_2PO_4), di-sodium phosphate (Na_2HPO_4), and tri-sodium (neutral) phosphate (Na_3PO_4). When the acid is neutralized by a carbonate, the secondary salt **Sodii Phosphas**, U.S.P., is obtained.

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + CO_2 + H_2O.$$

The alkali salts of all three kinds of acids are soluble in water; the primary alkaline earth salts are soluble, the others are insoluble. Aside from these all other phosphates are insoluble in water, but readily so in hydrochloric acid. Phosphoric acid yields a number of *double* or *mixed* salts through the replacement of the hydrogen by various metals, thus:

$HNaNH_4PO_4$ (hydrogen sodium ammonium phosphate).
NH_4MgPO_4 (ammonium magnesium phosphate).

Detection.—Orthophosphates, as well as the acid, are detected by adding silver nitrate to a neutral solution, when a yellow precipitate forms, consisting of silver phosphate, Ag_3PO_4. This precipitate is soluble in nitric acid and in ammonia. The hydrogen salts yield acid solutions with silver nitrate, while the tertiary salt solution remains neutral; by this we distinguish acid phosphates from the normal. With the primary and secondary phosphates, precipitation is not complete, owing to the liberation of free nitric acid.

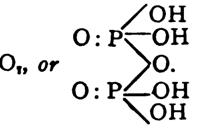
$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3.$$
$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3.$$

The free acid gives no precipitate until neutralized. Ammonium molybdate in nitric acid solution causes a yellow precipitate to separate slowly, consisting of ammonium phospho-molybdate, approximately

$(NH_4)_3PO_4(MoO_3)_{14} + 4H_2O$. In alkaline solutions, magnesia mixture causes a white precipitate of ammonium magnesium phosphate, $MgNH_4$-$PO_4.6H_2O$. Orthophosphoric acid does not coagulate albumin.

PYROPHOSPHORIC ACID

Formula, $H_4P_2O_7$, *or*



Molecular Weight, 178.11.

Preparation.—The acid is prepared by prolonged heating of the orthophosphoric acid at temperatures from 200° to 215°, until a portion neutralized with ammonia and treated with silver nitrate yields a pure white precipitate free from yellow color. Two molecules of the acid lose one molecule of water, $2H_3PO_4 - H_2O = H_4P_2O_7$.

Properties.—Pyrophosphoric acid forms colorless, opaque white masses. It is easily soluble in water, and in solution it slowly reverts to the ortho variety. This may be more quickly accomplished by heating with water to which a little nitric acid has been added.

$$H_4P_2O_7 + H_2O = 2H_3PO_4.$$

Pyrophosphates.—Pyrophosphoric acid is tetra-basic, but only two series of salts are known, the di- and tetra-salts.

The di- or acid salts have the general formula $H_2Me_2P_2O_7$, and the neutral or tetra-salts $Me_4P_2O_7$. The tetra-salts are usually obtained by heating the acid orthophosphates: $2Na_2HPO_4 = Na_4P_2O_7 + H_2O$. Acid pyrophosphates are converted into metaphosphates when heated to redness.

The pyrophosphates of the alkalies are soluble in water; those of other bases are mostly insoluble in water, but soluble in acids. Solutions of the salts in water remain unchanged, but when heated with water to 280°, or on boiling with dilute acids, or fusing with sodium carbonate, they are converted into normal phosphates.

Detection.—Pyrophosphoric acid and its salts are recognized and distinguished from the other varieties by the white precipitate of its solution with silver nitrate by giving no precipitate with barium chloride, by the absence of an immediate precipitation with ammonium molybdate in the presence of nitric acid, and by the inability of the free acid to coagulate albumin.

METAPHOSPHORIC ACID

Formula, HPO_3, *or* $O_2P—OH$. *Molecular Weight*, 80.05.

This acid is also known as glacial phosphoric acid. It is prepared by heating the ortho- or pyro-acid to about 316°. It is also produced by dissolving phosphorus pentoxide in a molecular quantity of cold water,

$$P_2O_5 + H_2O = 2HPO_3,$$

or by heating diammonium phosphate,

$$(NH_4)_2HPO_4 = 2NH_3 + H_2O + HPO_3.$$

Properties.—Metaphosphoric acid forms a glassy, deliquescent, pasty mass. When heated strongly it completely volatilizes. The commercial "stick" glacial acid consists of a variable mixture of pyro- and meta-acids with as much as 15 per cent. of sodium pyrophosphate, which is added to impart a more vitreous and stable appearance. The aqueous solution slowly changes to the ortho variety, quickly on boiling, and without formation of the intermediate pyro-acid.

$$HPO_3 + H_2O = H_3PO_4.$$

Metaphosphates.—Metaphosphoric acid is mono-basic and yields only normal salts, which may be obtained by neutralizing the acid or by heating the primary ortho-salts to redness,

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

When the aqueous solutions of these salts are boiled, they revert back to their ortho-salts.

Detection.—The free acid and its salts are detected and distinguished from the other varieties by the white precipitates with silver nitrate, barium and calcium chlorides, by not at once forming a precipitate with ammonium molybdate in presence of nitric acid, by the free acid coagulating albumin, and by the absence of a precipitate with magnesium sulphate in neutral solution.

Metaphosphorous Acid, HPO_2 or $O = P - OH$.—Obtained in the form of slender crystals by the slow oxidation of PH_3:

$$PH_3 + O_2 = H_2 + HPO_2.$$

It is transformed into phosphorous acid by steam.

Hypophosphoric Acid, $H_4P_2O_6$.—Obtained by the slow oxidation of moist phosphorus in air, together with phosphorous and phosphoric acids. It may be considered as being formed by the dehydration of one molecule each of phosphoric and phosphorous acid:

$$\left.\begin{matrix} H_3PO_4 \\ H_3PO_3 \end{matrix}\right\} - H_2O = H_4P_2O_6$$

OXYHALOGEN COMPOUNDS OF PHOSPHORUS

Phosphorus Oxychloride (Phosphoryl Chloride), $POCl_3$, may be obtained by the cautious oxidation of phosphorus trichloride with sodium chlorate or distilling phosphorus pentachloride with phosphorus pentoxide or crystallized boric acid, or by distilling 1 part of dry oxalic acid with 2 parts of PCl_5.

$$3PCl_3 + NaClO_3 = NaCl + 3POCl_3.$$

$$3PCl_5 + P_2O_5 = 5POCl_3.$$

$$3PCl_5 + 2H_3BO_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

Phosphorus oxychloride is a colorless, highly refractive liquid which boils at 107.2°. When cooled below 2° it solidifies to acicular crystals. With water it is decomposed into phosphoric and hydrochloric acids:

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Phosphorus Oxybromide ($POBr_3$) forms colorless plates which boil at 189°; the *oxy-iodide* (PO_2I_2), yellow to red crystals; the *oxyfluoride* (POF_3) is a gas.

COMPOUNDS OF SULPHUR AND PHOSPHORUS.

These are usually prepared by fusing red phosphorus and sulphur together. The two chief compounds correspond to the tri- and penta-oxides.

Phosphorus Trisulphide (Phosphorous Sulphide), P_4S_6, is a gray-yellow crystalline mass which fuses at 172° and boils at 408°. It is used to some extent in place of yellow phosphorus in the manufacture of matches

Phosphorus Pentasulphide (Phosphoric Sulphide), P_2S_5, is a gray-yellow crystalline mass which melts at 290° and boils at 515°.

ARSENIC

Symbol, As. *Atomic Weight,* 74.96. *Valence,* III, V.

History.—Arsenic in the form of its two sulphides, *realgar* and *orpiment,* was known to the ancients. Theophrastus (about 300 B.C.) was the first to apply the name *arsenikon* (αρσενικόν). Magnus (1193 to 1280) described the preparation of the metal from its oxide by means of reducing agents. Schroeder, in 1694, appears to have been the first to separate the metal.

Occurrence.—Arsenic is widely distributed in nature; in the free state it is occasionally found in distinct crystals. In the combined state it is abundantly distributed as *sulphides* (orpiment, As_2S_3, and realgar, As_2S_2), or as *metallic arsenides* (arsenical iron, Fe_2S_3; arsenical nickel, NiAs; white cobalt, $CoAs_2$), or as arseno-sulphides (arsenical pyrites or mispickel, FeAsS; cobalt-glance, $Co_2As_2S_2$, and nickel-glance, $Ni_2As_2S_2$). Small quantities of arsenic are found in many mineral waters and in sea water.

Isolation.—Metallic arsenic is obtained by reducing arsenous oxide with charcoal:

$$As_2O_3 + 3C = 2As + 3CO.$$

Probably the largest quantity is obtained by heating arsenical pyrites out of contact with air; the arsenic sublimes, leaving the iron as sulphide:

$$2FeAsS = 2As + 2FeS.$$

Physical Properties.—Arsenic appears usually in the form of a steel-gray, brittle, crystalline (hexagonal) mass of specific gravity 5.73 (14°), and is a good electric conductor. It sublimes under ordinary pressure (at about 180°) without fusion, but when heated in a sealed tube under the pressure of its own vapor it fuses at 840° (817–850°). Arsenic appears in two allotropic modifications, crystalline and amorphous. When sublimed in a current of hydrogen, an amorphous form separates. This latter form is also deposited upon heating arsine (AsH_3); it is black, amorphous, and when heated to 360° it reverts to the crystalline variety. The gray-white (hexagonal) crystalline variety is obtained by suddenly cooling arsenical vapors; this form closely resembles yellow phosphorus in physical properties. At about 860°, the vapor density indicates that the molecule of arsenic, like that of phosphorus, consists of four atoms (As_4), but at 1700° the vapor density is less than half, hence the molecule consists of two atoms.

Chemical Properties.—In dry air arsenic undergoes no change, but when heated it inflames at 180° and then burns with a bluish flame, forming As_2O_3, emitting a garlic-like odor. At higher temperatures it unites directly with most elements. It unites with metals to form *arsenides,* analogous to the sulphides. These arsenides and sulphides, being isomorphous, replace one another as FeS_2 — $FeAsS$ — $FeAs_2$.

Uses.—Metallic arsenic is used to impart a globular form to lead shot. Cobalt glance, a compound of arsenic and cobalt, has considerable use as a fly-poison under the name of *fly-stone.*

ARSENIC AND HYDROGEN

Hydrogen Arsenide or Arsine, AsH_3.—Analogous to nitrogen and phosphorus, arsenic also forms a gaseous hydride, which is produced through the action of nascent hydrogen on solutions of arsenic compounds, the hydrogen being generated through the action of dilute hydrochloric or sulphuric acid on zinc ($Zn + 2HCl = ZnCl_2 + H_2$) or solutions of caustic alkalies on zinc or aluminum [$Zn + 2KOH = Zn(OK)_2 + H_2$]:

$$As_2O_3 + 6H_2 = 3H_2O + 2AsH_3.$$

The pure arsine may be prepared by the action of dilute acids upon zinc arsenide:

$$As_2Zn_3 + 3H_2SO_4 = 3ZnSO_4 + 2AsH_3.$$

This reaction should be carried out with great precautions because of the extremely poisonous nature of this gas, there being no antidote when once inhaled.

Properties.—Arsine is a colorless gas of garlicky odor; when cooled to —55° it liquefies. It burns with a bluish-white flame, evolving white fumes of arsenic trioxide:

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

If a cold porcelain surface be held against the flame or the gas is passed through a heated tube, it decomposes into its elements with the deposition of a brilliant gray-black layer of metallic arsenic: $2AsH_3 = As_2 + 3H_2$.

Marsh's test (see page 277) depends on this property. When arsine is passed into a dilute solution of silver nitrate, metallic silver is precipitated, as follows:

$$6AgNO_3 + AsH_3 + 3H_2O = 3Ag_2 + 6HNO_3 + H_3AsO_3.$$

When arsine gas is passed over paper moistened with mercuric bromide or chloride a yellow to orange color is produced (see page 279).

ARSENIC AND THE HALOGENS

The halogen compounds of arsenic of the type AsX_3 are analogous to those of phosphorus and are usually produced through the direct union of the elements.

Arsenic Trichloride (*Arsenous Chloride*), $AsCl_3$, is prepared by passing dry chlorine over powdered arsenic, or it is formed when the trioxide is boiled with concentrated hydrochloric acid: $6HCl + As_2O_3 = 2AsCl_3 + 3H_2O$. It forms a colorless, fuming, oily liquid of specific gravity 2.2. It solidifies at —18° and boils at 130°. Excess of water decomposes it into hydrochloric acid, arsenous oxide, and water. Arsenous chloride is very poisonous.

The *Tribromide*, $AsBr_3$, forms deliquescent crystals which fuse at 31° and boil at 221°. The *Trifluoride*, AsF_3, is a fuming liquid which boils at 63°. The various possible penta-halogen compounds of arsenic are not known in free condition.

Arsenic Tri-iodide, AsI_3. **Arseni Iodidum,** U.S.P.—This may be prepared by extracting the powdered commercial article (made by fusing 1 p. of As with 5 p. of I) with chloroform or carbon tetrachloride and evaporating; or by pouring a hot solution of arsenous oxide in hydrochloric acid (10 in 250) into an aqueous solution of potassium iodide in water (51 gm. to 40 mils).

Properties.—Arsenic tri-iodide should form an orange-red, stable, crystalline or granular powder. When heated, it should not lose iodine; at higher temperatures it is volatilized, leaving not more than 0.5 per cent. of residue. It is soluble, with partial but temporary decomposition, in about 12 parts of water, 28 of alcohol, and completely in chloroform or carbon disulphide. It is one of the active ingredients of *Donovan's Solution,* **Liquor Arseni et Hydrargyri Iodidi,** U.S.P.

ARSENIC AND OXYGEN

Oxides.	Acids
III	
Arsenic Trioxide, As_2O_3.	Arsenous Acid, H_3AsO_3.* Metarsenous Acid, $HAsO_2$.†
V	
Arsenic Pentoxide, As_2O_5.	Orthoarsenic Acid, H_3AsO_4. Pyroarsenic Acid, $H_4As_2O_7$. Metarsenic Acid, $HAsO_3$.

Arsenic Trioxide, As_2O_3. **Arseni Trioxidum,** U.S.P.—*Arsenous oxide, Arsenous anhydride, Arsenous acid, White arsenic.*—This was known to Geber in the eighth century, being prepared through the ignition of arsenic trisulphide.

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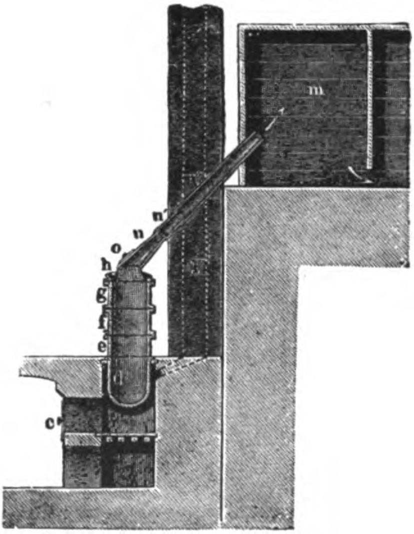
* Known only in solution.

† Known only in salts.

Preparation.—Arsenous oxide is obtained as a by-product in various metallurgical operations when roasting arsenical ores. Cobalt and nickel ores are especially rich in arsenic, and the fumes from the roasting of these ores are passed through a series of chambers, in which the arsenous oxide is condensed in an impure condition. In Silesia, arsenical pyrites are roasted especially for the arsenic. In England, large quantities are obtained in the roasting of tin ores. When resulting as a by-product, arsenous oxide is usually in fine powder and quite impure, and requires to be resublimed. This is accomplished by the apparatus shown in Fig. 104; *d* is an iron vessel in which the oxide is heated; on this are placed a number of iron cylinders, *e, f, g, h,* which are connected by the tubes *o, n, n',* with the chamber *m*. In the cylinders the oxide condenses as an amorphous, opaque, glassy solid, while in the tubes and chambers it is deposited as a crystalline powder.

FIG. 104.



Sublimation of arsenous oxide.

Physical Properties.—Arsenous oxide assumes three allotropic modifications.

The *Vitreous,* or *Amorphous,* form appears in transparent, colorless masses, odorless, of specific gravity 3.7, which gradually become opaque (porcelain-like), changing to the crystalline octahedral form. This variety requires about 30 and the crystalline about 80 parts of water at 25° for solution. Both varieties are freely soluble in glycerin and are dissolved by hydrochloric acid and alkaline solutions, the latter forming salts with the oxide.

The *Octahedral* variety is that usually assumed when the vapors of arsenous oxide are quickly cooled or when it crystallizes from hot water or hydrochloric acid. It forms regular octahedra of specific gravity 3.65, and sublimes without fusing above 218°; under pressure it fuses, solidifying to a glassy mass. The third or *Monoclinic* variety is formed when arsenic vapors crystallize slowly above 200°. The vapor density of arsenous oxide up to 800° indicates the formula of As_4O_6; at 1800° it corresponds to As_2O_3.

Chemical Properties.—The aqueous solution of arsenous oxide has a feeble acid reaction. When boiled with concentrated hydrochloric acid, it dissolves readily, large crystals of the oxide separating on cooling, while a small portion is converted into arsenous chloride ($AsCl_3$), which is volatilized. With a diluted acid it probably forms arsenous acid (H_3AsO_3), which evidences the feeble basic properties of this semi-metallic element. Arsenous oxide is readily oxidized to arsenic oxide; hence is employed as a reducing agent. It is readily dissolved by the alkali hydroxides, forming salts. Nascent hydrogen converts the trioxide into arsine (AsH_3); when heated with carbon the reduced arsenic is deposited as a metallic mirror.

Properties and Uses.—Arsenic trioxide is very poisonous, acting as an irritant poison. Beginning with very small doses, the system gradually establishes a toleration for large amounts. The usual antidote is ferric hydroxide (*Ferri Hydroxidum cum Magnesii Oxido,* U.S.P.), which as a colloid acts through adsorption of the arsenic, rendering it innocuous. Arsenous oxide is employed in large quantities in the preparation of inorganic colors, decolorizing glass, as well as medicinally.

Arsenous Acid, H_3AsO_3, is not known in the free state, for upon liberation from its salts and evaporation it breaks up into the anhydride and water: $2H_3AsO_3 = As_2O_3 + 3H_2O$. Arsenous acid is probably formed upon dissolving the anhydride in water or diluted hydrochloric acid ($As_2O_3 + 3H_2O = 2H_3AsO_3$). It is a very feeble acid; it reacts only in hot solution with alkali carbonates, while ammonium arsenite, being unstable, loses ammonia when exposed to the air. Being tribasic, three classes of salts (analogous to those of phosphoric acid) are possible. Those of the alkalies are all soluble in water, while those of metals are insoluble; they all dissolve readily in acids. Aqueous solutions of the alkali arsenites are active reducing agents, undergoing oxidation to arsenates, as, for example, in the presence of iodine, upon which reaction depends the volumetric determination of arsenic or its salts.

$$K_2HAsO_3 + I_2 + H_2O = K_2HAsO_4 + 2HI.$$

A neutral arsenite solution yields with silver nitrate a yellow precipitate of silver arsenite which is soluble in ammonia or nitric acid; with copper sulphate a green precipitate ($CuHAsO_3$), with magnesium sulphate a white precipitate ($MgHAsO_3$).

The following salts are the most important:

Potassium Arsenite. (K_2HAsO_3). **Liquor Potassi Arsenitis,** U.S.P. —The official process consists in boiling 10 grams of arsenous oxide with 20 grams of potassium bicarbonate and 100 grams of water until a clear solution is effected, and then diluting with sufficient water and 30 grams of compound tincture of lavender to make 1000 grams. The product is used in medicine under the name of *Fowler's solution.* Potassium bicarbonate is employed because of its comparative freedom from silica, other pharmacopœias using the neutral carbonate. The reaction is as follows:

$$As_2O_3 + 4KHCO_3 = 2K_2HAsO_3 + 4CO_2 + H_2O.$$

The alkali salts of arsenous acid also appear to have a constitution corresponding to $HAsO_2$, being then *metarsenites,* according to which the salt of Fowler's solution would be $KAsO_2$. Thus $As_2O_3 + 2KHCO_3 = 2KAsO_2 + 2CO_2 + H_2O$.

Metarsenous acid, $HAsO_2$, is not known free, but its salts are known. It is uncertain whether the hydrate $AsO(OH)$ or $HAsO_2$ is present in the aqueous solution of its anhydride (As_2O_3). When sodium dihydrogen arsenite is heated, one molecule of water is removed and sodium meta-arsenite remains. $NaH_2AsO_3 = NaAsO_2 + H_2O$.

Insoluble Arsenites.—The arsenites of the heavy metals are insoluble or nearly so. The addition of a soluble calcium salt to a soluble arsenite produces a white *insoluble calcium arsenite*, $CaHAsO_3$. The addition of soluble silver salts to a neutral arsenite yields a *yellow silver arsenite*, Ag_3AsO_3, which is readily soluble in aqua ammonia. $Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3$. Magnesium sulphide and zinc sulphide yield $MgHAsO_3$ and $Zn_3(AsO_3)_2$ respectively.

Cupric Arsenite, chiefly $CuHAsO_3$, *Scheele's Green*, is an insoluble green powder used as a pigment. It is prepared by adding a solution of copper sulphate to sodium arsenite, $Na_2HAsO_3 + CuSO_4 = CuHAsO_3 + Na_2SO_4$.

Paris or *Emerald Green* is a cupric aceto-arsenite made by boiling together solutions of copper acetate and arsenous oxide. It has the probable formula, $Cu(C_2H_3O_2)_2, 3Cu(AsO_2)_2$.

ARSENIC OXIDE AND ARSENATES

Arsenic Oxide, As_2O_5, *Arsenic Pentoxide*, or *Arsenic Anhydride*, is prepared by heating arsenic acid to low redness.

$$2H_3AsO_4 = 3H_2O + As_2O_5.$$

It forms a white, fusible, glassy mass which dissolves in water with formation of arsenic acid. High temperature converts it into arsenous oxide and oxygen:

$$As_2O_5 = As_2O_3 + O_2.$$

Arsenic Acid, H_3AsO_4, or $AsO(OH)_3$, or *Ortho-arsenic Acid*, is obtained by boiling (oxidizing) arsenous oxide with nitric acid diluted with ¼ its volume of water.

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3.$$

The solution is evaporated to a syrupy consistence, when crystals separate having the composition $2(H_3AsO_4)_2.H_2O$. These crystals deliquesce in the air, and give up their water of crystallization at 100°. On heating to about 180° they lose additional water and are converted into *pyro-arsenic acid*, $H_4As_2O_7$, and at about 206° a pearly, lustrous mass of *meta-arsenic acid*, $HAsO_3$, is formed. When meta-arsenic acid is heated to about 260°, water is evolved, and a glassy mass of *arsenic pentoxide*, As_2O_5, remains.

Arsenic oxide when heated to a high temperature gives off oxygen and arsenic trioxide remains. The pyro- and meta-arsenic acids are stable only in the solid state; their aqueous solutions revert quickly back into the ortho acid.

The *ortho-arsenates* are analogous to the orthophosphates, and may be prepared in the same manner. *Primary or monobasic* (MeH_2AsO_4), *secondary or dibasic* (Me_2HAsO_4), and *tertiary or tribasic* (Me_3AsO_4) salts are known.

Sodium Arsenate, $Na_2HAsO_4.7H_2O$, or $AsO(OH)(ONa)_2.7H_2O$. **Sodii Arsenas,** U.S.P.—This official salt, which is the *secondary* sodium arsenate, may be prepared by neutralizing arsenic acid with sodium carbonate, or by fusing together in a clay crucible 10 parts of arsenous oxide, 8.5 parts of sodium nitrate, and 5.5 parts of dried sodium carbonate. The fused product is poured while hot on a porcelain slab, dissolved in water, the solution filtered, and set aside to crystallize. The reaction involved is as follows:

$$As_2O_3 + 2NaNO_3 + Na_2CO_3 + H_2O = 2Na_2HAsO_4 + N_2O_3 + CO_2.$$

The crystals should be kept in well-stoppered bottles; they effloresce in dry air, and are somewhat deliquescent in moist air. Hence to secure greater uniformity they are first dried and then heated to 150°, whereby the *Sodii Arsenas Exsiccatus,* U.S.P., is produced.

Properties.—Sodium arsenate occurs in colorless, transparent, monoclinic prisms. It is soluble in 1.5 parts of water at 25° and about 1 part of boiling water. On the application of a gentle heat the salt loses 5 molecules of water, amounting to 28.8 per cent.; at 150° the remainder of the water is given off, yielding the anhydrous or exsiccated (U.S.P.) salt, which forms an amorphous white powder soluble in 3.1 parts of water at 25°; at a red heat this is converted into sodium pyro-arsenate. $2Na_2HAsO_4 = Na_4As_2O_7 + H_2O$.

The arsenates are distinguished from the arsenites as follows:

1. Arsenous acid solutions, acidulated, are precipitated at once by H_2S, while arsenic acid very slowly, only after its reduction to arsenous acid, in presence of dilute acids.

$$H_3AsO_4 + H_2S = H_3AsO_3 + H_2O + S.$$
$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O.$$

2. Neutral solutions of arsenous acid salts yield a *yellow,* while those of arsenic acid a *brick-red,* silver salt, both being readily soluble in ammonia water.

3. Arsenous acid only will decolorize solution of iodine. $H_3AsO_3 + I_2 + H_2O = H_3AsO_4 + 2HI$.

4. Magnesia mixture precipitates only arsenic acid, as a crystalline, insoluble double salt, $MgNH_4AsO_4.6H_2O$, magnesium ammonium arsenate.

Pyro-arsenic Acid, $H_4As_2O_7$, or $As_2O_3(OH)_4$, a crystalline mass, is obtained by heating ortho-arsenic acid to 180°. The salts by heating the secondary ortho-arsenates:

$$2H_3AsO_4 = H_4As_2O_7 + H_2O.$$
$$2Na_2HAsO_4 = Na_4As_2O_7 + H_2O.$$

Meta-arsenic Acid, $HAsO_3$, or $AsO_2(OH)$, a crystalline mass, is obtained by heating the ortho- or pyro-arsenic acid to about 206° and the salts by heating the primary ortho-arsenates:

$$H_4As_2O_7 = H_2O + 2HAsO_3.$$
$$NaH_2AsO_4 = H_2O + NaAsO_3.$$

ARSENIC AND SULPHUR

Arsenic Disulphide, As_2S_2, *Realgar*, is found native, crystallized in oblique rhombic prisms.

It is prepared by melting together 15 parts of metallic arsenic and 6.5 parts of sulphur, or by the sublimation of 4 parts of arsenous oxide and 2 parts sulphur. The product occurs in red, glassy masses, translucent on the edges. It is insoluble in water, but is readily dissolved by the alkali sulphides.

Realgar is used as a coloring in the manufacture of leather, rubber, and in the preparation of *white* or *Indian fire*. This consists of 24 parts saltpetre, 2 parts realgar, and 7 parts sulphur.

Arsenic Trisulphide, As_2S_3, *Orpiment*.—Under the latter name this compound is found in nature, crystallized in lemon-colored, rhombic prisms. It is prepared by melting together 6 parts of metallic arsenic and 4 parts of sulphur, or by subliming a mixture of 4 parts of arsenous oxide and 3 parts of sulphur. This compound is also formed when hydrogen sulphide is passed into a solution of arsenous oxide acidulated with hydrochloric acid. It fuses to a yellowish-red liquid when heated, and at 700° volatilizes without decomposition.

Arsenic Pentasulphide, As_2S_5 (King's yellow), is obtained by fusing arsenic trisulphide with the proper proportion of sulphur, or by subliming arsenous oxide with an excess of sulphur or by passing hydrogen sulphide into a cold solution of arsenic acid or arsenate in presence of a strong acid, $2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$. It is a yellow, poisonous, fusible mass which may be sublimed without decomposition, provided air is excluded.

Sulpho-salts of Arsenic.—The sulphides of arsenic or sulpho-anhydrides are readily soluble in alkali sulphides, forming thereby salts of the unknown acids, *sulpho-arsenous* (H_3AsS_3) and *sulpho-arsenic* (H_3AsS_4) acid. We may consider these as arsenous and arsenic acids in which the oxygen has been replaced by sulphur.

$$As_2S_3 + 3K_2S = 2K_3AsS_3 \quad \text{Potassium Sulpharsenite.}$$
$$As_2S_5 + 3K_2S = 2K_3AsS_4 \quad \text{Potassium Sulpharsenate.}$$

These salts are also formed by passing H_2S into salts of arsenous or arsenic acid:

$$K_3AsO_4 + 4H_2S = K_3AsS_4 + 4H_2O.$$

The sulpharsenites and sulpharsenates are readily soluble in water and decomposed by acids, arsenic tri- or penta-sulphide precipitating:

$$2K_3AsS_4 + 6HCl = As_2S_5 + 6KCl + 3H_2S.$$

Alkali hydroxides dissolve the sulphides, which are again precipitated without evolution of H_2S upon the addition of acids:

$$1\left\{\begin{array}{l} As_2S_3 + 6NaOH = Na_3AsO_3 + Na_3AsS_3 + 3H_2O. \\ Na_3AsO_3 + Na_3AsS_3 + 6HCl = As_2S_3 + 6NaCl + 3H_2O. \end{array}\right.$$

$$2\left\{\begin{array}{l} As_2S_5 + 6NaOH = \underset{\text{Sodium sulphoxy-arsenite.}}{Na_3AsO_3S} + \underset{\text{Sodium sulpharsenate.}}{Na_3AsS_4} + 3H_2O. \\ Na_3AsS_4 + Na_3AsO_3S + 6HCl = As_2S_5 + 6NaCl + 3H_2O. \end{array}\right.$$

ARSENIC TESTS

The following tests are for the detection of *traces* of arsenic present in inorganic substances. Organic materials cannot be tested for the presence of arsenic without special treatment for the destruction of the organic matter.*

The Marsh-Berzelius Test.†—This is the most sensitive and conclusive test known, its limit of delicacy being 0.001 mgm. of As_2O_3.‡ The apparatus consists of a generating flask A (Fig. 105) of 200 mils capacity, in which are placed about 20 grams of granulated zinc (U.S.P.); the funnel-tube, C, is for the intro-

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* See special books on Forensic Analysis, as Autenreith, "Detection of Poisons."

† Revised by British Joint Committee of Methods for the Detection of Arsenic. Jour. Soc. Chem. Industry, 1902, p. 95.

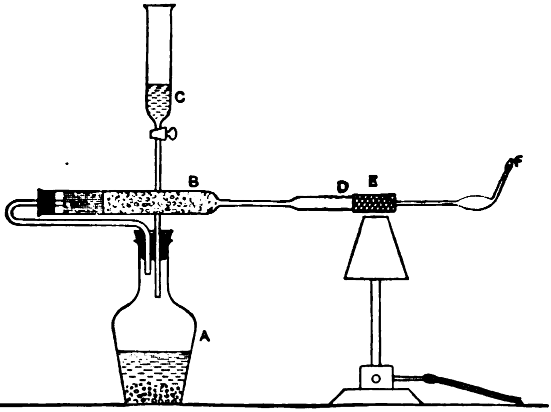
‡ By limiting the size of the generating flask and observing all possible precautions, 0.0005 mgm. of As_2O_3 can be detected.

duction of the arsenic-free hydrochloric acid (sp. gr. 1.10)* and solution to be tested. The drying tube, B, contains a wad of glass wool which has been dipped in lead acetate solution and dried, then a layer of cotton or glass wool, followed by granulated $CaCl_2$, and finally another wad of cotton or glass wool. The tube D is of hard glass, constricted to a diameter of about 2.5 mm. Close to this constriction the tube is heated, using a wire gauze, E, wrapped around the tube to insure uniform distribution of the heat.

The acid (10 to 20 c.c.) is run in through C, in sufficient quantities to insure a steady evolution of hydrogen, which is noted by the height (6 mm.) of the *round* flame at F. A blank experiment is then made to insure absence of arsenic, by heating the tube for ½ hour, whereby no trace of a metallic mirror should be discernible. The material to be tested, dissolved in a little of the diluted acid, is then introduced into the apparatus through C, washing it down with more acid; then after heating the tube for ½ hour all of the arsenic, if present, will have been deposited as a black metallic mirror. Excessive quantities of arsenical solution should not be introduced; by using dilutions as directed in the U.S.P., the test may be made quantitative by comparing the mirrors produced by 0.001 to 0.005 mgm. of As_2O_3 with those of the substances examined.

The zinc must not contain more than traces of iron (0.08 per cent., U.S.P.), for this latter metal retains arsenic tenaciously. The less iron present in zinc, the slower will be its reaction with diluted sulphuric acid. For its determination see Zincum Reagent, U.S.P. As activating agent use a piece of platinum.

FIG. 105.



Marsh-Berzelius test apparatus.

Solutions containing such metals as Bi, Pb, Hg, Sn, which are precipitated upon the zinc and form insoluble arsenides, should never be introduced into a Marsh or other generator containing zinc and a diluted acid.

Chemicals being tested should always be previously treated with a reducing agent (U.S.P., p. 584), since much of their arsenic is in the "ic" state and the nascent hydrogen of the test is not always sufficient for its complete reduction. The absence of antimony must be established (see U.S.P., page 585).

The Arsenic Test, U.S.P. (page 584).—This test, first suggested by Merçeron and Bergeret, differs from what is usually known as the "Gutzeit Test," in that an alcoholic solution of mercuric bromide is used for moistening the test-paper strips instead of a solution of silver nitrate, and the form of apparatus used. The limit of delicacy of this test is about 0.002 mgm. of As_2O_3, which produces a faint yet distinguishable yellow stain on the test-paper.

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* Since arsenic-free hydrochloric acid is difficult to obtain, diluted arsenic-free sulphuric acid (about 12 per cent.) may be used. To activate the zinc, which is necessary if very pure, introduce a piece of platinum wire or foil along with the zinc.

The arsine gas (representing from 0.002 to 0.005 mgm. of As_2O_3) passing over the test-paper strip will produce a faint yellow to light orange stain [$AsH(HgCl)_2$], while larger quantities (above 0.01 mgm.) produce a deep orange to red-brown ($As[HgCl]_3$). Traces of stibine (SbH_3) produce no change, larger quantities a gray to brown stain. The stain produced by *both* gases is brown; if the stained paper strip be immersed in a watch-glass containing alcohol, the antimony stain disappears, while the distinct bright yellow arsenic stain remains. Sulphides (H_2S) produce a black stain, and likewise blacken the lead acetate gauze; in most instances the gauze suffices to retain all hydrogen sulphide given off. Phosphine gas (PH_3) produces an orange stain, hence hypophosphorous acid and its salts must be first oxidized before testing.

Bettendorff's Test, U.S.P. (page 586).—To a solution of the substance in 5 mils of pure concentrated hydrochloric acid, contained in a test-tube, 10 mils of saturated, freshly prepared stannous chloride, T.S., are added. After setting aside for thirty minutes, no brownish tint or precipitate should be discernible. When the tube is viewed from above over a white surface, comparing with a mixture of 5 mils of concentrated hydrochloric acid and 30 mils of saturated stannous chloride, T.S.

This test is based on the reduction of the arsenous compound present to brown metallic arsenic by the stannous chloride ($SnCl_2$), the reaction being $As_2O_3 + 3SnCl_2 + 6HCl = As_2 + 3SnCl_4 + 3H_2O$, or $As_2O_5 + 5SnCl_2 + 10HCl = As_2 + 5SnCl_4 + 5H_2O$. This test fails to give distinct evidence with less than 0.1 mgm. of As_2O_3. The presence of readily reducible metals, also tellurium and selenium (which frequently occur in acids), produces reactions simulating those of arsenic. Antimony compounds are not reduced to the metal.

Reinsch's Test.—If a solution containing arsenic be boiled with hydrochloric acid (1 to 5) and a strip of bright copper foil, the arsenic will be deposited on the copper as a gray film. Wash, dry, and heat in a hard-glass tube; crystals (octahedral) of arsenous oxide will be deposited in the upper and cooler portions of the tube, which may be readily identified by means of a lens and also by chemical tests. Such metals as Sb, Bi, and Hg may likewise be deposited upon the copper, but only the Sb yields a sublimate which is amorphous and white; the Hg sublimate consists of minute gray globules.

ANTIMONY (Stibium)

Symbol, Sb. *Atomic Weight,* 120.2. *Valence,* III, V.

History.—Native antimony sulphide was used as a black cosmetic in prehistoric times. Metallic antimony was extracted and used for making vessels by the Chaldeans (at least 1000 B.C.). The initiative step to the present knowledge of the element was reserved for Basilius Valentinus, who, about the middle of the fifteenth century, prepared and described not only the metal but also a number of its compounds. At the same time he pointed out the value of the metal for the preparation of medicines and of alloys.

The names given to the element at present are the Chaldean term, *stibium,* and the Latin title, *antimonium,* both of which were applied to the native sulphide until the time of Lavoisier.

Occurrence.—The chief source of antimony is the antimony glance or *stibnite,* Sb_2S_3, which is found in Australia, East Indies, and Hungary; more recently, China and Japan have been supplying large quantities of antimony. Native antimony is usually accompanied by arsenic.

Isolation.—To separate antimony sulphide from the accompanying minerals advantage is taken of the easy fusibility of the sulphide. To obtain the metal, the purified sulphide, which contains about 50 per cent. of Sb, is either fused with metallic iron, $Sb_2S_3 + 3Fe = 2Sb + 3FeS$, or is roasted to form the oxide, $Sb_2S_3 + 9O_2 = 2Sb_2O_3 + 6SO_2$, which is afterwards reduced with charcoal, as follows: $2Sb_2O_3 + 3C = 4Sb + 3CO_2$.

The antimony so obtained may contain arsenic, from which it is freed by fusion with sodium carbonate and potassium nitrate, sometimes with the addition of a small quantity of antimony trisulphide, and subsequent reduction of the lixiviated mass by charcoal and sodium carbonate. Pure antimony is usually prepared by the reduction of the pure oxide, which is readily prepared.

Physical Properties.—Antimony is a lustrous, silver-white metal, more basic than arsenic, but less so than bismuth. It is harder than the last metal, and, like it, crystallizes in obtuse rhombohedra, a mass of which exhibits a granular or a coarsely laminated, fern-marked, crystalline fracture, according as it is rapidly or slowly cooled. This structure determines the great brittleness of the metal. Antimony has a specific gravity of 6.7 to 6.86, is scarcely tarnished by air, melts at 630°, boils at 1440°, and can be distilled in hydrogen at a white heat.

Chemical Properties.—On charcoal, before the blow-pipe it melts and evolves white fumes of trioxide, and, if the globule of molten metal is dropped from some height, it scatters in many small particles, which burn with a very bright flame to trioxide. Hot hydrochloric and sulphuric acid, as also cold nitro-hydrochloric acid, dissolve antimony, the latter forming the tri- or penta-chloride, according to the volume employed.

Nitric acid converts the metal into white antimony trioxide, Sb_2O_3, or ortho-antimonic acid, H_3SbO_4, according to concentration; while solutions of the alkali hydroxides produce no change. Antimony combines directly with the halogens, and with sulphur, phosphorus, and arsenic.

Uses.—From the metal a chloride, suitable for the preparation of some of the medicinal compounds, is prepared, but the largest amount of antimony is used in the form of alloys or of compounds, since it is too brittle to be employed as a metal except in thermo-electric couples. Along with bismuth, antimony finds use in the construction of thermo-electric piles.

When antimony is precipitated from a solution of the trichloride by zinc, the metal is obtained in a finely pulverulent condition. In this state it is called *antimony-black*, and is used to impart to the surface of gypsum and papier-maché figures and other objects the appearance of iron or steel.

Alloys.—These are useful because of their hardness and easy fusibility. *Type-metal* usually contains about 25 per cent. of Sb, 10 to 20 per cent. of Sn, the remainder consisting of Pb, with small amounts of Cu and Bi. Such an alloy expands upon cooling from the state of liquefaction, although its separate component elements when congealing contract.

Hard lead consists of lead containing 10 to 15 per cent. of antimony.

Britannia-metal consists of approximately nine parts of tin and one part of antimony, often with some addition of copper, zinc, and bismuth. *Pewter* is an alloy of variable composition, usually of tin and lead, also of tin, antimony, zinc, and copper.

ANTIMONY AND HYDROGEN

Hydrogen Antimonide (*Stibine*), SbH_3, is produced like arsine and closely resembles it in its reactions. Stibine is obtained by adding a solution of an antimony compound to a mixture of zinc and diluted sulphuric or hydrochloric acid from which nascent hydrogen is being evolved.

Properties.—Stibine gas is colorless, has a disagreeable smell unlike that of arsine or phosphine, and burns with a bluish-white or grayish flame, evolving white fumes of antimony trioxide.

If a cold porcelain plate is pressed into the flame, a sooty deposit of metallic antimony is obtained. $2SbH_3 = Sb_2 + 3H_2$.

Hydrogen antimonide, like arsine, is decomposed if passed through a red-hot tube, metallic antimony being deposited close to the heated spot. If the deposit be heated the minute particles coalesce to form microscopic globules.

These metallic antimony spots are distinguished from those produced under the same conditions by arsenic by the darker color of the former, their smoky appearance, their lesser volatility, when heated in a current of hydrogen, their insolubility in hypochlorite solutions, and their solubility in ammonium sulphide.

Strong sulphuric acid decomposes stibine, as do also alkali hydroxide solutions; the latter behavior accounts for the failure of antimony to produce its hydrogen compound in Fleitman's test for arsenic, wherein the necessary nascent hydrogen is obtained by interaction between zinc and potassium hydroxide solution.

When hydrogen antimonide is conducted into a solution of silver nitrate, a black precipitate containing silver antimonide, $SbAg_3$, and some metallic silver arising from the reduction of the silver salt by the hydrogen present, is precipitated. In the U.S.P. arsenic test, traces of stibine produce no reaction, while larger quantities give a gray-brown spot.

ANTIMONY AND THE HALOGENS

Antimony Trichloride, *Antimonous Chloride,* $SbCl_3$.—Prepared by dissolving the oxide or sulphide in concentrated hydrochloric acid, evaporating to dryness, and distilling:

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S,$$

or by the action of chlorine upon the metal or its sulphide.

The trichloride forms a deliquescent crystalline mass known as *butter of antimony,* which melts at 73.2° and boils at 223°. The solution of the chloride (*liquid butter of antimony*) is best made by boiling the trisulphide with strong hydrochloric acid, and evaporating to remove water and excess of acid. This solution is occasionally used in medicine as a caustic; but it is extensively employed for giving a bronze surface to iron and steel wares, such, for instance, as gun-barrels.

When the solution of the chloride is mixed with water there is precipitated an amorphous, white precipitate of the basic or oxychloride.

The composition of this product varies according to the temperature and volume of the water used; cold water generally yields SbOCl (antimonyl chloride), and hot water $2(SbOCl).Sb_2O_3$:

$$SbCl_3 + H_2O = 2HCl + SbOCl.$$
$$4SbCl_3 + 5H_2O = (SbOCl)_2.Sb_2O_3 + 10HCl.$$

The presence of free hydrochloric or of tartaric acid prevents the precipitation. Prolonged washing with boiling water converts antimony oxychloride into the oxide:

$$4SbOCl + 2H_2O = 4HCl + 2Sb_2O_3.$$

When antimony oxychloride is heated, or an aqueous solution acidified with hydrochloric acid is mixed with a large excess of hot water, white *powder of algaroth* is formed. This consists of a mixture of oxychloride and oxide. These compounds were much used towards the end of the sixteenth century by a Veronese physician, Algarotus.

Antimony Pentachloride, *Antimonic Chloride,* $SbCl_5$, results from the action of an excess of chlorine on antimony or upon saturation of the fused trichloride with chlorine gas. It is a colorless, hygroscopic, fuming liquid of suffocating odor, which crystallizes at 4°, and is decomposed by water. Heat decomposes this into the trichloride and chlorine Water in excess hydrolyzes it into the *pyro-antimonic* and hydrochloric acids:

$$2SbCl_5 + 7H_2O = H_4Sb_2O_7 + 10HCl.$$

Antimony pentachloride is used as a chlorinating agent in the preparation of certain organic chlorides.

Antimony Tribromide, $SbBr_3$.—Colorless, deliquescent needles, which melt at 94°, boil at 280°, and are changed by water to basic bromide.

A pentabromide is not known.

Antimony Tri-iodide, SbI_3, is a brownish-red crystalline mass obtained by directly uniting iodine and antimony with the aid of heat. It fuses at 170° and boils at 400°.

Antimony Penta-iodide, SbI_5, forms a dark-brown solid which fuses at 78°.

Antimony Trifluoride, SbF_3, obtained by solution of antimony oxide in hydrofluoric acid, forms colorless, deliquescent crystals, while the *pentafluoride,* SbF_5, is a gummy mass.

ANTIMONY AND OXYGEN

The oxides and acids (hydroxides) of antimony present many analogies to those of arsenic. Differing, however, in some respects—for example, the antimonous oxide is slightly basic, deporting itself like an acid anhydride; thus potassium and sodium hydroxides dissolve it, forming unstable *antimonites* ($NaSbO_2$), which are decomposed by water to Sb_2O_3. Antimonic oxide, which is distinctly acid, deporting itself like phosphoric acid, forms *antimonates* with caustic alkalies ($KSbO_3$). Hydrochloric acid (but not H_2SO_4 or HNO_3) dissolves antimonous oxide, forming a salt, which is decomposed by water. Salts of this type contain the monatomic *antimonyl* (SbO) group which is present in tartar emetic ($K.SbO.C_4H_4O_6$).

OXIDES	ACIDS (HYDROXIDES)
Antimony Trioxide, Sb_2O_3.	Ortho-antimonous Acid, H_3SbO_3. Meta-antimonous Acid, $HSbO_2$.
Antimony Tetroxide, Sb_2O_4.	
Antimony Pentoxide, Sb_2O_5.	Ortho-antimonic Acid, H_3SbO_4. Meta-antimonic Acid, $HSbO_3$. Pyro-antimonic Acid, $H_4Sb_2O_7$.

Antimony Trioxide, or *Antimonous Oxide,* Sb_2O_3.—It occurs native as senarmontite in octahedra or as valentinite in rhombic prisms.

Preparation.—Antimony oxide is prepared either by strong ignition of the metal (*flowers of antimony*) or in the wet way either by oxidizing antimony with dilute nitric acid or by diluting a solution of the chloride with a large excess of warm water, and after collecting the precipitate of oxychloride it is digested with a strong solution of sodium carbonate, then ignited till free from chloride.

Properties.—It forms a white, heavy, tasteless, crystalline powder, prepared by the wet method, in octahedra, and the dry, rhombic prisms. Thus prepared, antimony oxide is soluble in hydrochloric acid, alkalies, tartaric acid, and the acid tartrates ($KSbOC_4H_4O_6$) and insoluble in nitric and sulphuric acids. The commercial article is quite insoluble in all acids and is a mixture of unknown composition and origin. When boiled with sulphur and alkalies Sb_2O_3 is converted into a meta-antimonite ($NaSbO_2$) and sulphantimonite ($NaSbS_2$). Towards acids it (Sb_2O_3) deports itself like a base and to bases like an acid:

$$Sb_2O_3 + 2NaOH = \underset{\text{Sodium Antimonite}}{2NaSbO_2} + H_2O.$$

$$Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O.$$

The trioxide corresponds to the hydroxide $Sb(OH)_3$, which is precipitated upon adding dilute sulphuric acid to tartar emetic solution:

$$KSbOC_4H_4O_6 + H_2SO_4 + 2H_2O = Sb(OH)_3 + KHSO_4 + H_2C_4H_4O_6.$$

On boiling this trihydroxide with water, it gives up one molecule of water and is converted into the hydroxide SbO.OH, known as *meta-antimonous acid;* then finally into the oxide. The salts are derived from either antimonous acid, $Sb(OH)_3$, or meta-antimonous acid, SbO.OH. An example of the former class is *antimony sulphate,* $Sb_2(SO_4)_3$, while of the latter the *antimonyl* (SbO) group replaces hydrogen as antimonyl sulphate, $(SbO)_2SO_4$, or potassium antimonyl tartrate (tartar emetic), $KSbOC_4H_4O_6$.

The vapor density at 1560° corresponds to the formula Sb_4O_6, while above this to Sb_2O_3.

Ortho-antimonous Acid, H_3SbO_3, Normal Antimonous Hydroxide, $Sb(OH)_3$, separates as a white precipitate when weak sulphuric or nitric acid is cautiously added to tartar emetic solution. $KSbOC_4H_4O_6 + HNO_3 + 2H_2O = Sb(OH)_3 + H_2C_4H_4O_6 + KNO_3$. When dry it is a fine, white powder.

Meta-antimonous Acid, $HSbO_2$, or SbO.OH, is obtained as a white, amorphous precipitate when antimony trichloride is decomposed with a solution of an alkali-hydroxide or carbonate, in the former of which, when applied in excess, it redissolves: $2SbCl_3 + 3Na_2CO_3 + H_2O = 2SbO.OH + 6NaCl + 3CO_2$. $SbO.OH + NaOH = NaSbO_2 + H_2O$. Hot water decomposes it into trioxide: ($2SbO.OH = Sb_2O_3 + H_2O$). With alkalies it acts the part of an acid, although it saturates acids to give salts of antimony containing the *antimonyl* group, SbO.

Antimony Tetroxide, Sb_2O_4.—This is regarded as the antimonate of antimony, $(Sb)SbO_4$, and is produced by the ignition of Sb_2O_3 or nitrate or sulphide of antimony. It becomes yellow when heated, is soluble in caustic alkalies and hydrochloric acid.

Antimony Pentoxide, or *Antimonic Oxide* or *Anhydride,* Sb_2O_5, is obtained by heating antimonic acid at 300° or by evaporating the metal, or trioxide, with nitric acid and gently heating the residue. It is a yellowish, tasteless powder, which is soluble in hydrochloric acid, but not in water. Like arsenic oxide, it forms hydroxides which have acid characters. They are ortho-antimonic acid, H_3SbO_4, pyro-antimonic acid, $H_4Sb_2O_7$, and meta-antimonic acid, $HSbO_3$.

Ortho-antimonic Acid, H_3SbO_4, or $SbO(OH)_3$, is produced when antimony pentachloride is added to cold water ($SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl$), or on warming antimony with concentrated nitric acid, washing thoroughly with water and drying: $6Sb + 10HNO_3 + 4H_2O = 6H_3SbO_4 + 10NO$, or treating antimonous oxide with nitric acid: $Sb_2O_3 + 2HNO_3 + 2H_2O = 2H_3SbO_4 + N_2O_3$. Thus obtained, it is a gelatinous precipitate possessing a metallic, astringent taste and a distinct acid reaction, soluble in caustic alkalies, forming antimonates.

At 100° it loses water, and is changed to pyro-antimonic acid ($2H_3SbO_4 = H_4Sb_2O_7 + H_2O$), $H_4Sb_2O_7$, which is more soluble in water than antimonic acid. It also dissolves in ammonium hydroxide, forming ammonium pyro-antimonate, $(NH_4)_4Sb_2O_7$, which exists only in solution.

The Acid Sodium Salt, $Na_2H_2Sb_2O_7 + 6H_2O$, is remarkable as being the only insoluble compound of sodium, and its formation is sometimes used as a test for this element, but necessarily only in the absence of other metals.

Metantimonic Acid, $HSbO_3$, or $SbO_2.OH$, remains when ortho- or pyro-antimonic acid is heated at 275° ($H_4Sb_2O_7 = 2HSbO_3 + H_2O$), or when powdered antimony is heated with saltpetre, yielding K_3SbO_3. It is a white, infusible powder, which is insoluble in water, but soluble in tartaric and hydrochloric acids.

A basic lead metantimonate is used in oil painting, under the name of *Naples yellow.*

ANTIMONY AND SULPHUR

Antimony Trisulphide, Sb_2S_3, occurs native as stibnite, the most important ore of antimony. It usually forms columnar or striated masses which soil the fingers like graphite. The native sulphide is purified by fusion, whereby it is separated from the associated mineral matter. The crude sulphide of commerce consists of steel-gray masses of a metallic luster and a striated, crystalline fracture, which are easily pulverized and fused. When heated with hydrochloric acid, hydrogen sulphide is given off and antimony trichloride is formed.

This article is likely to contain arsenic, which is almost completely removed by macerating the finely divided substance with about one-half its weight of 10 per cent. ammonia water. It may also be obtained as an orange-red powder by passing hydrogen sulphide through a solution of antimony trichloride containing hydrochloric acid. It is soluble in alkalies and their sulphides (see below). When heated to above 200° the red trisulphide is converted into the gray crystalline variety.

When the purified native sulphide is boiled with about twelve times its weight of 5 per cent. sodium hydroxide solution for two hours, sodium meta-antimonite and sodium sulphantimonite are formed:

$$2Sb_2S_3 + 4NaOH = NaSbO_2 + 3NaSbS_2 + 2H_2O.$$

When this solution is acidified, the antimony is precipitated as sulphide.

Kermes Mineral is a variable mixture of antimony trisulphide and trioxide obtained by boiling Sb_2S_3 with a solution of sodium carbonate.

Uses.—Native crystalline antimony trisulphide is used not only for the preparation of the other antimony compounds, but also in fireworks, such as the *blue* or *Bengal lights,* and also for the preparation of Swedish matches. The amorphous orange-red variety (Sb_2S_5) is largely used as a means for vulcanizing caoutchouc, to which it imparts a reddish-brown color.

Antimony Pentasulphide, Sb_2S_5, sometimes called *golden sulphuret of antimony,* is obtained by passing hydrogen sulphide into a solution of antimony pentachloride containing hydrochloric acid ($2SbCl_5 + 5H_2S = Sb_2S_5 + 10HCl$) or by decomposing sodium sulpho-antimonate (Na_3SbS_4) with acids. It forms an orange-red powder, soluble in alkali sulphides, and decomposes on heating into Sb_2S_3 and S_2. The pentasulphide dissolves in solutions of the alkalies and alkali sulphides, forming *sulphantimonates* (Me_3SbS_4).

Antimony Cinnabar is an oxysulphide, Sb_2OS_2, found native as Kermesite, and is obtained by the action of a solution of sodium thiosulphate upon antimony trichloride. It is used in painting. *Crocus* and *glass of antimony* consist of varying proportions of oxide and oxysulphide, and are prepared by partly roasting the ore in air, or by incomplete oxidation by deflagration with potassium nitrate.

Sulpho-acids and Sulpho-salts.—Analogous to the sulphides of arsenic, antimony forms salts of the unknown free acids, namely: *Sulphantimonous acid,* H_3SbS_3, and *Sulphantimonic acid,* H_3SbS_4. These salts are prepared analogous to those of arsenic (page 277).

Sodium Sulphantimonate, $Na_3SbS_4 + 9H_2O$, known as Schlippe's Salt, may be made by boiling antimony trisulphide with sulphur and sodium hydroxide. It forms transparent tetrahedra. When its solution is acidified, antimony pentasulphide is precipitated.

TESTS FOR ANTIMONY

(1) By means of the Marsh-Berzelius Test (page 277), which consists in heating the tube through which stibine (or arsine) gas is passing, a dull and nearly black metallic-like deposit is obtained. If the tube containing this deposit be heated while passing a current of hydrogen sulphide through it, the antimony deposit changes to an orange-red (Sb_2S_3), while the arsenic deposit changes to a yellow (As_2S_3). Or if, when heated while passing a slow current of air through the tube, either a white crystalline sublimate of arsenous oxide or an amorphous white deposit of antimonous oxide is produced.

If a cold porcelain surface be held against the flame of the Marsh-Berzelius test-apparatus, a brownish-black to black mirror is deposited on the surface if either arsenic or antimony be present. When moistened with a freshly-prepared solution of sodium hypochlorite, the arsenical spot is dissolved, while that of antimony is not affected.

(2) Soluble salts of antimony, when added to water, give a white precipitate of basic antimony salts, which are soluble in tartaric acid (different from bismuth salts).

(3) Aqueous solutions of antimony salts give an *orange-red* precipitate with hydrogen sulphide. This precipitate is soluble in alkali hydroxides or ammonium sulphide

CHAPTER VI

BORON

Symbol, B. *Atomic Weight,* 11. *Valence,* III.

History.—The element boron was discovered simultaneously in 1808 by Davy in England and Gay-Lussac in France. It was known in combination as borax by Geber and the alchemists.

Occurrence.—Boron does not exist in the free state in nature, but is found native in combination with oxygen as boric acid, H_3BO_3, with sodium as borax (*tincal*), $Na_2B_4O_7 + 10H_2O$, with calcium as *borocalcite,* $CaB_4O_7 + 4H_2O$, with both sodium and calcium as *boronatrocalcite,* $Na_2B_4O_7.2CaB_4O_7 + 18H_2O$, and with magnesium (*boracite*), $2Mg_3B_8O_{15}.MgCl_2$. It is also found in smaller quantities in a number of other minerals, in sea-water, and in the ash of a few plants.

Isolation.—Boron is known in two allotropic modifications, the amorphous and crystalline.

1. *Amorphous Boron* is prepared by heating boron trioxide with magnesium to redness, then treating the powdered fused mass with hydrochloric acid and alkalies. The boron thus obtained contains some boron hydride. Amorphous boron is a brown powder which possesses the power of occluding gases, like fine platinum.

While this variety of boron is permanent in air or oxygen at ordinary temperatures, it readily oxidizes when heated, and when ignited it burns to boron trioxide. At very high temperatures it combines with nitrogen to form boron nitride, BN. When air is excluded boron may be heated to whiteness without melting; fusion may, however, be accomplished by a strong electric current. Boron ignites in presence of chlorine or fluorine. Boiling caustic alkalies dissolve boron, like aluminum, $2B + 2KOH + 2H_2O = 2KBO_2 + 3H_2$.

2. *Crystalline Boron.*—This variety is prepared by fusing amorphous boron or boron trioxide with an excess of aluminum:

$$B_2O_3 + Al_2 = Al_2O_3 + B_2.$$

The impure boron (AlB_{12}) crystallizes as the mass cools, and is separated by extracting with hydrochloric followed by boiling nitric acid. This variety of boron is in the form of yellow or brownish-yellow crystals, having a specific gravity of 2.6.

The crystals are highly refractive and very hard, being next to the diamond in this respect, and withstand a red heat without change. They are unacted upon by hydrochloric, nitric, or nitrohydrochloric acid. Solutions of the alkalies are without action. Boron is one of the few elements which unite directly with nitrogen when heated to redness.

BORON AND HYDROGEN

Boron Hydride, BH_3, only known in impure form mixed with hydrogen, is obtained by first fusing together boron trioxide and magnesium, whereby an impure magnesium boride is formed. The fused mass is then treated with diluted hydrochloric acid in an atmosphere of hydrogen:

$$B_2Mg_3 + 6HCl = 3MgCl_2 + 2BH_3.$$

It is a colorless gas, of peculiar odor, which burns with a green flame, yielding boron trioxide and water.

BORON AND HALOGENS

Boron Trichloride, BCl_3, is prepared by passing chlorine over boron carbide:

$$B_2C_2 + 3Cl_2 = 2BCl_3 + C_2.$$

It is collected in a well-cooled receiver and forms a colorless, fuming liquid which boils at 17°. It is decomposed by water, thus:

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl.$$

Boron Tribromide, BBr_3, boils at 90°, while the *iodide* (BI_3) forms large hygroscopic crystals.

Boron Fluoride, BF_3, is made by the action of hydrofluoric acid on boric oxide, or warming a mixture of the trioxide and calcium fluoride with sulphuric acid.

$$B_2O_3 + 3CaF_2 + 3H_2SO_4 = 3CaSO_4 + 3H_2O + 2BF_3.$$

It is a colorless, fuming gas, very soluble in water, forming boric and hydrofluoboric acids: $4BF_3 + 3H_2O = H_3BO_3 + 3HBF_4$.

BORON AND OXYGEN

BORON TRIOXIDE, BORIC ANHYDRIDE

Formula, B_2O_3. *Molecular Weight,* 70.00.

Preparation.—This oxide is formed when boron is burned in air or oxygen, but it is usually prepared by heating boric acid to redness: $2H_3BO_3 = B_2O_3 + 3H_2O$. The fluid should be poured out into thin layers and, when cold, broken into pieces of suitable size.

Properties.—Boron trioxide, when first prepared, is a colorless, transparent, hygroscopic, vitreous solid, becoming opaque when exposed to air, owing to absorption of moisture. At a white heat it is volatilized and when dissolved in water it forms boric acid.

BORIC ACID (ORTHOBORIC ACID)

Formula, H_3BO_3, *or* $B(OH)_3$. *Molecular Weight,* 62.02.

History.—This acid was first prepared and used in 1702 by Homberg, who obtained it by treating borax with a mineral acid. It was known under the name of sedative salt, or *sal sedativum Hombergii.* In 1774, Höfer, a Florentine apothecary, discovered the acid in the waters of the Tuscan lagoons.

Occurrence.—Boric acid occurs in the free state in nature. In certain volcanic districts, especially in Tuscany, there are localities where steam containing boric acid escapes from crevices in the ground termed *suffoni* or *fumaroles.* This steam contains, in addition to the boric acid, ammonia, hydrogen sulphide, and carbon dioxide.

Preparation.—The vapors escaping from these fumaroles are conducted into reservoirs filled with water, which become charged with boric acid, and at the same time the water is heated and evaporates.

Commercially, boric acid is prepared by treating borax in hot concentrated aqueous solution with sulphuric acid: $Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4$. Upon cooling, the boric acid crystallizes on iron or wooden rods suspended in the solution.

Properties.—Boric acid (**Acidum Boricum,** U.S.P.) consists of "transparent, colorless scales, of a somewhat pearly luster, or, when in perfect crystals, as six-sided, triclinic crystals, or as a white, bulky powder, slightly unctuous to the touch, odorless, having a faintly bitterish taste, permanent in the air." It is soluble in 18 parts of water, in 18 parts of alcohol, and 4 parts of glycerin at 25°; in 4 parts of boiling water and in 6 parts of boiling alcohol. The alcoholic solution burns with a green flame.

At 100° orthoboric acid loses one molecule of water and is converted into *metaboric* acid, $H_3BO_3 = HBO_2 + H_2O$ or $B(OH)_3 = BO.OH + H_2O$. The latter is a white powder, and is slowly volatilized when maintained at the above temperature for a long time. When *orthoboric* acid is kept at a temperature of 160° for some time, *pyroboric* acid ($H_2B_4O_7$) is produced, $4H_3BO_3 = H_2B_4O_7 + 5H_2O$.

It is a brittle, vitreous mass, and is also known under the name of *tetra* or *pyro*boric acid, ordinary borax ($Na_2B_4O_7 + 10H_2O$) being a salt of this acid.

If ignited, orthoboric acid is converted into boric trioxide: $2H_3BO_3 = 3H_2O + B_2O_3$.

Boric acid ionizes but slightly in solution, hence is readily displaced by other acids. However, in the dry state, owing to the non-volatile properties of its anhydride, it displaces most acids from their salts through fusion. Normal salts are unknown, while esters, $B(O.R)_3$, are readily made. The salts of metaboric acid (BO.ONa) are very unstable, being decomposed by carbon dioxide with the formation of tetra-borates: $4NaBO_2 + CO_2 = Na_2B_4O_7 + NaCO_3$.

Borates.—These are all salts of tetra or pyroboric acid, chief among which is the common borax (page 353). All borates give the reactions of boric acid in the presence of mineral acids.

Tests.—Boric acid solutions impart a faint red to blue litmus paper, and a reddish-brown to turmeric paper. Salts (as borax), when acidified with hydrochloric acid, also produce this color. (Alkalies brown turmeric paper, which is changed to yellow by acids.) The vapors of a boiling aqueous solution of boric acid impart to the flame a green color, due to the volatilization of the acid; likewise an ignited (methyl) alcoholic solution of boric acid, or a mixture of alcohol, borax, and sulphuric acid burns with a green flame.

Boron Trisulphide, B_2S_3, is formed by passing sulphur vapor over heated amorphous boron; or by passing the vapor of carbon disulphide over a heated mixture of boron trioxide and charcoal.

Boron trisulphide is a yellowish-white, friable, vitreous solid, easily decomposed by water into hydrogen sulphide and boric acid.

Boron Nitride, BN, is prepared by the direct union of amorphous boron and nitrogen at a red heat, or by heating to redness, in a platinum crucible, a mixture of one part anhydrous borax and two parts of dry ammonium chloride:

$$Na_2B_4O_7 + 4NH_4Cl = 2NaCl + 4BN + 2HCl + 7H_2O.$$

The fused mass is washed with water and hydrochloric acid, to remove the salt and some boric acid which is mixed with the nitride.

Boron nitride is a white, light, amorphous powder, which phosphoresces in a gas flame with a greenish-white light. It is decomposed when heated in a current of steam into boric acid and ammonia: $BN + 3H_2O = H_3BO_3 + NH_3$.

Boron Carbide, CB_6.—Prepared by heating in the electric furnace boron and carbon in the presence of copper, the latter being removed by treatment with nitric acid. This carbide forms black crystals harder than carborundum.

CHAPTER VII

THE CARBON GROUP

CARBON AND SILICON

Symbol, C. *Atomic Weight,* 12.00. *Valence,* IV.

In the Periodic System, this group embraces C, Si, Ge, Sn, and Pb. Owing to the marked electro-negative characters of carbon and silicon and their striking analogies to the preceding elements, they are separately considered, while the others are classed under the " Tin " group, following with the metals.

History.—Carbon in the form of charcoal has been known from the earliest times. Graphite was thought to be identical with molybdenite, and the diamond was supposed to be a kind of quartz crystal.

The diamond has been known since the earliest times and highly prized because of its extreme hardness. Splinters fastened in iron were used by the Greeks and Romans for engraving other stones. Early in the seventeenth century deBoot and also Newton assumed that the diamond was combustible because of its high refractive properties. This was proven by Avarani and Targioni in 1694, yet no credence was given this discovery, for it was firmly believed that the diamond was a form of quartz. During Lavoisier's time (1765 to 1790), it was conclusively demonstrated by various investigators that the product of the combustion of the diamond was carbon dioxide. In 1814 Davy proved that only carbon dioxide is produced through its combustion and that the diamond must therefore consist of pure carbon.

Occurrence.—Carbon exists in the free state in nature in three allotropic modifications—crystallized, as (1) *diamond,* (2) *graphite,* and (3) *amorphous carbon.*

In combination, carbon is widely distributed, being the principal element of all organic compounds, which constitute the separate division of organic chemistry. When combined with oxygen it forms carbon monoxide and carbon dioxide.

(1) *Diamond.*—Diamonds, the purest form of carbon, occur either in alluvial deposits, supposed to have resulted from the decomposition of certain kinds of micaceous rock, or else loose in sand, chiefly in South Africa and Brazil. When found they are usually covered with an opaque layer. This surface is removed and the gem given a great number of faces by cutting and polishing. These faces are so formed as to reflect the greatest amount of light. This is accomplished by so arranging the back planes or faces that nearly all the light strikes them at an angle greater than 24° 13′, when it is all reflected. Diamond dust is used in the cutting and polishing.

The diamond belongs to the regular or isometric system of crystallization, the prevailing form being the octahedron. It has a specific gravity of 3.5 to 3.6, and is the hardest substance known, being rated as 10 on the scale of hardness. It is insoluble in all known liquids.

The weight of the diamond is usually stated in carats, a carat being equal to 0.200 gram. A variety of black diamond from Brazil, which is worthless as a gem, is much used in drilling rocks. The specific gravity of the black variety is less than that of the transparent one, being about 3.0.

On the application of heat, diamonds remain unchanged in an atmosphere of hydrogen or when air is excluded, even at a white heat; but the intense temperature of the electric current causes them to swell to a mass of coke or graphite. At these temperatures in air or oxygen combustion takes place, carbon dioxide being formed, and a small quantity of ash remaining. This ash, which consists of silica and ferric oxide, amounts to from 0.05 to 0.20 per cent.

The diamond is a poor conductor of electricity and heat.

Microscopical diamonds were first made artificially by Moissan in 1893 by enclosing pure carbon (sugar) in a hollow block of cast-iron which was heated in an electric furnace and then suddenly cooled. The molten iron dissolved the carbon, and through the sudden chilling the inner portions were subjected to an enormous pressure, which caused the carbon to crystallize in the form of minute diamonds. These were removed from the mass of iron by solution in nitric acid.

(2) *Graphite* (*γράφω = I write*).—This substance, which is also known as plumbago or black lead, occurs in crystalline form, not well defined, but frequently approaching hexagonal prisms. It is found native in the oldest rock formations in Siberia (district Irkutsk), Ceylon, and several localities in the United States and Canada.

Molten iron will dissolve carbon, which on cooling separates as graphite. At Niagara Falls, graphite is now produced on an extensive scale by the Acheson process, which is based on the observation that graphite is formed by the vaporization of the silicon of silicon carbide. It was found that only a relatively small amount of carbide-forming material (as silicon), when intimately mixed with amorphous carbon, will convert the latter at moderately high temperatures into silicon carbide, then through catalytic action into graphite when heated to an extremely high temperature. The furnace consists of a long trough lined with fire-brick, containing large carbon cylinders, to both ends of which are connected the cables for conveying the current. The surface and spaces of the trough are filled with anthracite coal. A current beginning with 1500 amps., raising finally to 9000 amps., brings the mass to a very high temperature, so that the silicon of the anthracite ash combines with the carbon to form silicon carbide; eventually this is decomposed and the silicon is driven to the outside as an incandescent vapor which burns in the air, depositing silica as a fine white powder. When the furnace has cooled, the graphite is removed, crushed, and sorted. For commercial purposes from 1 to 10 per cent. of impurities are left in the graphite. It is possible to obtain graphite containing only 3 parts of ash in 10,000. The ash consists chiefly of silica, iron, and aluminum. The best qualities of natural graphite contain from 90 to 96 per cent. of carbon, while the poor qualities vary from 40 to 50 per cent.

Properties.—Graphite occurs in friable black masses of metallic luster. It feels soft and greasy between the fingers, and leaves a black mark when drawn across paper. Its specific gravity varies from 2.21 to 2.50. On the application of heat it remains unchanged, when air and oxygen are excluded; but at very high temperatures, in a stream of oxygen, it is slowly consumed, with more difficulty, however, than the diamond. Graphite is a good conductor of heat and electricity.

When heated with a chlorate and nitric acid, graphite is oxidized to graphitic acid. By an alkaline permanganate solution it is oxidized to mellitic acid.

Uses.—Graphite is used in the manufacture of lead pencils, antifriction compounds, paint, electrodes for metallurgical work, conducting surfaces in electrotyping, glazing powder grains. When mixed with fire clay it is used for making the black-lead or plumbago crucibles. For the manufacture of lead pencils the purified powder is mixed with a fine clay, and by the aid of water made into a plastic mass. The mixture is then forced through small holes by powerful pressure, which gives the mass the desired shape. The long cylinders are then cut into the required lengths and enclosed in wood.

(3) *Amorphous Carbon.*—Under this head may be included the following varieties: (*a*) Gas carbon, (*b*) Coke, (*c*) Wood charcoal, (*d*) Animal charcoal, (*e*) Lampblack.

(*a*) *Gas* or *Retort Carbon* is found in the upper part of the retorts in which coal is heated in the preparation of illuminating gas. It occurs in iron-gray masses of a metallic luster, and possesses considerable hardness. It is a good conductor of electricity, and is used for the carbon plates in several forms of batteries and for the carbon pencils in the arc electric light. The carbon after grinding fine is moulded into the desired form by aid of pitch.

Coke occurs in irregular, brittle, porous masses, of a grayish, somewhat metallic luster. It does not burn so easily as coal, and requires a constant draught of air. Its combustion is attended with great heat and but little smoke. Owing to its high carbon content and freedom from tarry matter, coke is used for obtaining high temperatures such as are necessary in metallurgical operations in blast furnaces. Where coal is subjected to distillation in the manufacture of illuminating gas, coke is a by-product. This form of coke cannot be used in metallurgic operations, since it is not free from volatile products. Metallurgic coke is prepared in specially constructed coke ovens, whereby the valuable volatile tarry products are collected, leaving a coke of a hard compact structure free from volatile compounds.

(*c*) *Wood charcoal,* usually known as charcoal, is obtained through the carbonization of wood.

Formerly this was altogether accomplished by covering piles of wood with earth and igniting at suitable openings. By regulating the access of air, slow combustion takes place, while the volatile products escape and charcoal remains.

Large quantities of charcoal are now the by-product of the dry distillation of wood, which is carried on in iron retorts. The volatile products, consisting of acetic acid, acetone, wood alcohol, oils and tar, are collected. The yield after the old process varies from 17 to 20 per cent., while from the dry distillation method it varies according to the temperature, from 33 per cent. (with 65 per cent. carbon) to about 18 per cent. (with 85 per cent. carbon).

The most esteemed charcoal for pharmaceutical purposes is that prepared from willow twigs or any soft wood. It is official as **Carbo Ligni**, U.S.P., which should not yield more than 7.5 per cent. of ash.

The best charcoal is hard and brittle, breaking with a dull fracture and emitting a metallic sound when struck. As ordinarily prepared it is a poor conductor of heat and electricity, but when prepared at a high temperature it is more compact and becomes a better conductor. Wood charcoal possesses in a marked degree the power to absorb gases. One volume will absorb about 90 volumes of ammonia, 55 of hydrogen sulphide, 65 of sulphur dioxide, and 35 of carbon dioxide (at 12°). This absorptive power increases at low temperatures. Charcoal obtained from hard woods absorbs larger volumes of gases than that from soft woods. That from cocoanut-shells will absorb 170 times its volume of ammonia gas.

On account of this property, charcoal becomes valuable for absorbing noxious gases, hence is employed for deodorizing putrefying animal or vegetable matter. It also possesses the power of decolorizing dark liquids, although not as readily as the next variety.

(*d*) *Animal charcoal* or bone-black is prepared by the dry distillation of bones in closed iron retorts, the volatile product being called "Dippel's animal oil." The charred bones are ground and sifted into different degrees of fineness, according to the various purposes for which it is intended. Animal charcoal contains about 90 per cent. of inorganic matter and about 10 per cent. of carbon; the former consisting of calcium and magnesium phosphates (80 per cent.), calcium carbonate (8 per cent.), with small quantities of the alkalies, ferric oxide, and silica. When ignited, it leaves about 85 per cent. of ash, which should completely dissolve in hot hydrochloric acid.

Animal charcoal forms dull-black, granular fragments or powder; it is odorless, tasteless, and insoluble.

It possesses the power of absorbing coloring matter from solution, and absorbs alkaloids and astringent compounds from their solutions, but gives them up again to boiling alcohol. Many of the domestic filters for the filtration of water are constructed of animal charcoal and sand. Perhaps the most extensive application of animal charcoal is in the decolorizing of raw sugar, also the removal of coloring matter from crude alkaloids and fusel oil from spirits. The superior decolorizing power of animal charcoal is probably due to its porous structure and surface, which afford greater adhesion for coloring matter.

After using a number of times, this charcoal ceases to decolorize, hence must be revivified; this is accomplished by washing with hydrochloric acid, then boiling with a solution of caustic soda, washing with water, steaming, and, after drying, heating to redness in closed retorts.

(*e*) *Lampblack.*—This variety of carbon is in very fine powder. It is obtained from the smoky flame of many bodies rich in carbon, as resins, when their combustion takes place without much access of air, and the products are condensed. This condensation is accomplished by passing the products through a series of chambers. Rosin and petroleum are most frequently employed in the preparation of lampblack, but the product is not pure. The purification is effected by heating for some time in a current of chlorine. A very pure lampblack is made from the natural gas of Western Pennsylvania and Ohio which is sometimes known under the name of *diamond* or *carbon black*. Lampblack, when pure, is a velvety black, impalpable powder. It should mix readily with water, and yield no color to alcohol or ether when agitated with them, showing the absence of oily impurities. It is used to give a black color to paints and inks, not only on account of its intense black color, but also because of its indestructibility.

COAL

Coal is classified as a variety of carbon, although it contains, besides that element, considerable quantities of oxygen, hydrogen, nitrogen, mineral matter, and frequently sulphur.

Our present supply is the product from the decomposition of buried vegetable matter of a former age, this decomposition having taken place under great pressure without access of air, and in the presence of moisture.

Owing to the differences under which their formation took place, we have several different varieties of coal. They may, however, be arranged into three classes, *Anthracite* and *Bituminous* coals, and *Lignite,* which represent different stages of carbonization.

Anthracite is found in this country most abundantly in Pennsylvania, also in Wales, France, and Southern Russia. It contains about 92 to 95 per cent. of carbon and only very small quantities of sulphur. It is hard, with a conchoidal fracture and an iron-back color, frequently displaying iridescence. It burns with but little flame and gives out an intense heat. The volatile matter is contained in it in small amount, being from 6 to 7 per cent.

Bituminous coal is found in all parts of the world. It is much softer than anthracite, and contains from 10 to 30 per cent. of volatile matter. It is used extensively in producing coke and in the manufacture of illuminating gas, in which process it yields many useful by-products.

Cannel coal is a variety of this class which, on account of its large percentage of volatile matter, is much used in England for gas making.

The carbon of bituminous coal varies from 70 to 91 per cent., the sulphur from 0.40 to 2.25 per cent., the nitrogen from 1.00 to 2.50 per cent., and the ash from 0.75 to 20 per cent.

Lignite is a brown coal of more recent formation than the two preceding varieties. It frequently retains the structure of the wood from which it was formed and contains from 50 to 80 per cent. of carbon and 15 to 20 per cent. of moisture.

Jet is a variety of this brown coal, so compact as to take a fine polish.

Silicon Carbide, or Carborundum, SiC, is made by heating a mixture of 100 parts of coke, 100 parts of sand, 25 parts of common salt with some sawdust in an electric furnace to about 3500°: $SiO_2 + 3C = SiC + 2CO$. When pure, silicon carbide is colorless, the crystals obtained in the commercial manufacture are blue, black, or brown, with beautiful iridescence. It is insoluble in ordinary solvents and is attacked by fused caustic alkalies, nitre, and chlorine above 600°. In hardness, carborundum ranks next to boron carbide and the diamond; hence its use as an abrasive, the crystals being crushed and moulded into the desired forms.

The Metallic Carbides.—These are compounds of the various metals and carbon obtained through solution of carbon in the fused metal, or more usually by the reduction of metallic oxides with carbon, by means of the high temperature of the electric furnace. According to their deportment to water, they may be divided into the following classes:

1. Those decomposed by cold water: the carbides of lithium (Li_2C_2), potassium, calcium, barium (BaC_2), strontium, aluminum (Al_4C_3), manganese (MnC), uranium (U_2C_3), etc.

2. Those not decomposed by water: chromium (Cr_4C, Cr_3C_2), molybdenum (MoC), titanium, boron, etc.

Aluminum carbide, in contact with water, yields methane:

$$Al_4C_3 + 12H_2O = 3CH_4 + 4Al(OH)_3.$$

Uranium carbide, with water, yields methane, ethane, and hydrogen:

$$C_3Ur_2 + 8H_2O = CH_4 + C_2H_6 + H_4 + 2(UO_2[OH]_2).$$

The most important of this group is calcium carbide, obtained by heating in an electric furnace an intimate mixture of pulverized lime and coke. The commercial article contains about 80 per cent. of CaC_2 and is used for preparing acetylene gas (page 298) and calcium cyanamide (page 240).

CARBON AND HYDROGEN

These two elements occur in a great variety of combinations known as hydrocarbons, which constitute the petroleums, benzene, and its homologues, most of the essential oils, etc. The compounds of carbon and hydrogen, when associated with oxygen and nitrogen, become well-nigh innumerable, and make up the material of *Organic Chemistry*.

The subject of organic chemistry, therefore, is confined to the consideration of the compounds of carbon and their derivatives, and the classification of these is based on several series of *hydrocarbons*, or compounds of carbon and hydrogen.

It will be sufficient at this point to give some description of two or three compounds of these two elements for comparison with the hydrogen compounds of the preceding elements.

METHANE

MARSH GAS

Formula, CH_4. *Molecular Weight*, 16.032.

Marsh gas is the first member of the *paraffin* or *aliphatic* or *marsh gas series* of hydrocarbons. It occurs free in nature wherever vegetable matter is undergoing decomposition in the presence of moisture. This is always noticeable where leaves and other vegetable matter are under water, and the bubbles which rise when such a mass is disturbed are composed chiefly of this gas. It also occurs in coal seams, giving rise to the *fire-damp* of the miners, and is the explosive element in mine disasters. The very lightest part of petroleum consists largely of this gas, and escapes as soon as the oil is relieved of its pressure on coming to the surface. Closely associated with this is the *natural gas*, which consists essentially of marsh gas and hydrogen. Natural gas is found in great abundance in Pennsylvania, Ohio, West Virginia, and Indiana. In all these places it has been successfully used for heating, and, after treatment, also for lighting. It has been found especially valuable in metallurgical operations and glass furnaces.

Preparation.—Marsh gas may be prepared by heating dried sodium acetate, 1 part, and soda-lime, 4 parts. Soda-lime is made by slaking calcium oxide with a solution of sodium hydroxide of such strength that 2 parts of calcium oxide shall be mixed with 1 part of sodium hydroxide. The mixture is then dried and heated in an iron or Hessian crucible, after which it is preserved in a tightly closed bottle:

$$CH_3COONa + NaOH = Na_2CO_3 + CH_4.$$

Another method of preparation consists in passing a mixture of carbon disulphide vapor and hydrogen sulphide over red-hot metallic copper:

$$2H_2S + CS_2 + 8Cu = 4Cu_2S + CH_4.$$

This process is of interest because of the fact that every one of the compounds employed is strictly inorganic and may be made directly from elementary matter, thus rendering it possible to prepare some of what are considered organic compounds synthetically.

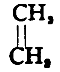
Properties.—Marsh gas is colorless, odorless, tasteless, insoluble in water, and lighter than air. It is combustible, and when mixed with 2 volumes of oxygen or 10 volumes of air (fire-damp of the miners) it explodes with considerable violence on ignition:

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

By the electric spark marsh gas is slowly decomposed into its constituent elements. When a mixture of 1 volume of marsh gas and 2 volumes of chlorine is exposed to direct sunlight or the flame of a taper, a sudden reaction takes place, with the formation of hydrochloric acid, and the separation of carbon as a black, very finely divided powder. Marsh gas is not considered poisonous.

ETHYLENE

OLEFIANT GAS

Formula, C_2H_4, or  $\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}$ *Molecular Weight*, 28.032.

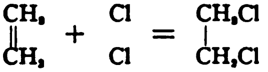
This gas is the first member of the second series of hydrocarbons, known as the *olefine series*, to which it has given the name.

Preparation.—Ethylene is formed in the destructive distillation of coal, wood, and many substances rich in carbon. It is one of the constituents of illuminating gas. The gas is best prepared by heating, in a capacious glass flask, a mixture of 1 part of alcohol with 6 parts of sulphuric acid; when the gas is evolving rapidly, a further quantity of a mixture of 1 part alcohol and 2 parts acid is run slowly in, so as not to cool the contents of the flask sufficiently to retard the evolution of the gas. The reaction involved may be expressed as follows:

$$\underset{\text{Alcohol.}}{C_2H_6O} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O.}$$

The sulphuric acid simply plays the part of a dehydrating agent, and brings about the reaction by its affinity for the water.

Properties.—Ethylene is a colorless gas, having a peculiar suffocating, ethereal odor. It is soluble in 8 parts of water. Ethylene is a combustible gas, burning with a very luminous flame, and decomposes first into marsh gas and free carbon: $C_2H_4 = CH_4 + C$. It forms a mixture with 3 volumes of oxygen, which explodes violently on the application of flame. Being an unsaturated compound, it unites directly with two atoms of bromine or chlorine to form an oily liquid which is known as the "oil of the Dutch chemists." From this the name of "olefiant gas" is derived.



$$\begin{array}{c}CH_2\\ \|\\ CH_2\end{array} + \begin{array}{c}Cl\\ \\ Cl\end{array} = \begin{array}{c}CH_2Cl\\ |\\ CH_2Cl\end{array} \quad \text{(Ethylene Chloride).}$$

ACETYLENE

Formula, C_2H_2, or  $\begin{array}{c}CH\\ |||\\ CH\end{array}$. *Molecular Weight*, 26.016.

Preparation.—Acetylene is present in coal gas and is formed in considerable quantities through its incomplete combustion, *e.g.*, the "struck-back" flame of a Bunsen burner. When calcium carbide (page 382) is brought into contact with water, acetylene is produced according to the following reaction:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

One hundred pounds of the carbide yield about 450 cu. ft. of acetylene gas.

Properties.—Acetylene is a colorless gas, with a peculiar, disagreeable odor. It is condensed to a liquid at 15° and under a pressure of 83 atmospheres. It is moderately soluble in water. The hydrogen of acetylene is readily replaced by metals; thus, by passing the gas into ammoniacal solutions of copper and silver salts, explosive copper and silver acetylides are precipitated. Acetylene is combustible, burning with a bright but smoky flame. It is employed as an illuminating agent, requiring, however, specially constructed burners. Since acetylene is an unsaturated hydrocarbon, it combines readily with halogens or their acids to form saturated compounds. Mixtures of acetylene with from 1¼ to 20 volumes of air are explosive, the mixture of 1 in 12 being the most dangerous. The compressed gas is quite explosive, but when dissolved in acetone under pressure it is not explosive.

For illuminating purposes, cylinders containing charcoal or asbestos are saturated with this mixture of acetone and acetylene under about 15 pounds pressure. These can be handled with safety. When burned with oxygen in a blowpipe, a temperature of about 2500° is produced, which suffices for welding and melting iron or steel plates.

ILLUMINATING GAS

COAL GAS

History.—Gas was first used for illuminating purposes in the house of William Murdock, at Redruth, in Cornwall, England. He distilled coal in an iron retort, and lighted his house with the gas which he thus manufactured. This occurred about 1792. Gas was used for lighting the streets of London in 1812, and those of Paris in 1815.

Preparation.—Illuminating gas is prepared by the destructive distillation of bituminous coal or petroleum, although other substances rich in carbon, like rosin or wood, may be used. Carburetted water gas, made by enriching "water gas" with volatilized hydrocarbons (from naphtha), is now chiefly employed in our various city plants.

Coal or Illuminating Gas.—Prepared by the destructive distillation of bituminous coal is still made by the smaller gas companies of this country and some European ones. The process is accomplished in iron or fire-clay retorts, ten to twelve feet in length and two or three feet in diameter. The temperature employed approaches low redness. The products of this dry distillation process are as follows:

1. Coal gas, a mixture of hydrocarbons (see table).
2. Coal tar. This consists of a mixture of light oils (benzene, toluene, aniline, etc.) and heavy oils (phenol, cresols, naphthalene, etc.) with pitch.
3. Ammoniacal liquor. The water used for washing the gas dissolves the ammonia and ammonium compounds.
4. Gas-carbon and coke. These remain in the retorts.

The volatile products are first passed into the hydraulic main, where the water and tar separate. From thence the gas passes into condensers, in which more tarry and oily liquids are removed. It then passed into the scrubbers, which consist of one or more columns of coke over which a spray of water trickles; this serves to wash the gas and remove the ammonia. Next come the purifiers, in which the gas is brought in contact with slaked lime (which removes the carbon dioxide and sulphur):

$$\left\{\begin{array}{l} Ca(OH)_2 + H_2S = CaS + 2H_2O \\ CaS + CS_2 = CaCS_3 \\ Ca(OH)_2 + CO_2 = CaCO_3 + H_2O \end{array}\right.$$

$$Fe_2O_3.3H_2O + 3H_2S = 2FeS + S + 6H_2O$$

or ferric oxide (bog iron ore), which serves to remove only the sulphur compounds, the carbon dioxide being removed before the gas enters the iron oxide purifiers. From the purifiers the gas passes into the gasometers for storage and distribution.

The average yield per ton of coal is from ten to twelve thousand cubic feet.

Coal gas is considerably lighter than air, its specific gravity varying from 0.4 to 0.75 (air = 1).

Water Gas.—This is produced when steam is passed through incandescent carbon:

$$C + 2H_2O = 2H_2 + CO_2.$$

$$C + CO_2 = 2CO.$$

It consists chiefly of hydrogen and carbon monoxide (50 per cent.) is non-luminous, of high heating value, and poisonous when inhaled.

Carburetted Water Gas.—This is the illuminating gas of our cities and is made by blowing steam with air into the glowing coal of the generator. The water gas thus generated is then carburetted (rendered luminous) by mixing with the vapors of petroleum or benzene or other suitable hydrocarbons and passing through long fire-clay retorts kept at white heat. This cracks the oil vapors into hydrocarbons (ethane, ethylene, acetylene, etc.), which render the gas luminous. For 1000 cubic feet of gas, about 50 pounds of anthracite coal and 4 to 5 gallons of naphtha are used.

Oil (Pintsch) Gas.—This is made by "cracking" petroleum or shale oils in hot retorts, in which the vapors are heated to about 1000°. This oil when compressed in cylinders under low pressure is used as a transportable illuminant.

Acetylene Gas.—Made by treating calcium carbide with water, is used in many districts not supplied with coal gas, owing to the readiness with which small plants can be installed. Specially constructed generators containing the calcium carbide and water supply the gas automatically, and when burned in a special form of burner under high pressure, it yields a very brilliant light. With air, acetylene gas forms explosive mixtures. The carbide furnishes upward of 5 cubic feet of acetylene per pound.

Blau Gas.—Petroleum is injected into steel retorts heated to about 600°, whereby gaseous and liquid products result. The gases are freed from sulphur compounds and carbon dioxide by means of lime and iron oxide, then compressed to 100 atmospheres, whereby a part liquefies and holds the fixed gases in solution. Blau gas is furnished in steel cylinders and is adapted for lighting and heating where ordinary illuminating gas is not available.

The value of gas for illuminating purposes is determined by comparing the light from a jet burning five cubic feet per hour with the light from a standard candle consuming one hundred and twenty grains per hour. Such a gas flame should be equal to thirteen or fourteen candles.[*]

CARBON AND OXYGEN

There are two well-known compounds of these two elements:

Carbon Monoxide, CO.

Carbon Dioxide, CO_2.

CARBON MONOXIDE

CARBONIC OXIDE

Formula, CO. *Molecular Weight*, 28.

This compound is formed when coal or carbon burns with an insufficient supply of air. It may be easily recognized in the combustion of anthracite coal by its peculiar blue flame. Practically the same reaction is involved when carbon dioxide is passed over red-hot coals, $CO_2 + C = 2CO$, or when steam is subjected, as in water-gas, to the same treatment, $C + H_2O = CO + H_2$.

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[*] The average composition of different varieties of gas may be seen from the following:[†]

	Coal	Carburetted Water	Water (Fuel)
Candle Power	17.5	25.	
Illuminants	5.	16.6	
Marsh Gas	34.5	19.8	1.0
Hydrogen	49.0	32.1	36.
Carbon Monoxide	7.2	26.1	51.
Nitrogen	3.2	2.4	7.
Carbon Dioxide	1.1	3.0	4.

[†] Thorp's Industrial Chemistry.

The carbon may be replaced by iron or zinc and the same result attained. Carbon monoxide is readily prepared by heating oxalic acid and concentrated sulphuric acid together:

$$H_2C_2O_4 = CO_2 + CO + H_2O.$$

The sulphuric acid, through its affinity for water, causes a breaking down of the oxalic acid molecule.

The mixed gases are passed through a strong solution of sodium hydroxide to absorb the carbon dioxide.

In a similar manner formic acid, or a formate, may be decomposed by sulphuric acid; in this case, however, no carbon dioxide is formed:

$$HCHO_2 = CO + H_2O.$$

An economical method and one that will yield the gas rapidly consists in gently heating powdered potassium ferrocyanide with about ten times its weight of concentrated sulphuric acid:

$$K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO.$$

As soon as the reaction commences the heat must be removed and the vessel cooled, if necessary, in order to prevent too rapid evolution of the gas. The water in the above reaction is derived from the water of crystallization in the potassium ferrocyanide. If heated too long SO_2 is given off through interaction between the $FeSO_4$ and H_2SO_4.

Physical Properties.—Carbon monoxide is a colorless, inodorous gas, of specific gravity 0.967 (air = 1). It is very slightly soluble in water and has no effect on litmus paper. It is very difficult to liquefy, requiring a pressure of 35 atmospheres and temperature of —140°. The liquid boils at —190°, and is solid at —211°.

Chemical Properties.—Carbon monoxide burns with a peculiar blue flame, the product of its combustion being carbon dioxide. Combustion does not take place if the gas and air are very dry. Carbon monoxide unites directly with chlorine to form *phosgene*, $COCl_2$; at elevated temperature, with sulphur to form *carbon oxysulphide*, COS; both of these are gases. The temperature of the CO flame is about 1400°.

Because of the readiness with which it is oxidized, carbon monoxide is a reducing agent, most metallic oxides being reduced to their metals at red heat. $CuO + CO = Cu + CO_2$. Hence its extensive use in metallurgic operations where sufficient coal, coke or charcoal is used to reduce the carbon dioxide to monoxide. One of the best examples of this is the reduction of iron ore.

Palladium, platinum, and gold chlorides are reduced from their solutions, thus paper moistened with the former ($PdCl_2$) is blackened. This is a sensitive test for CO.

When passed over finely divided nickel or cobalt (at 25 to 30°) and iron (at 80°), this gas unites with them to form volatile metallic carbonyls.

Nickel carbonyl ($Ni[CO]_4$) is a colorless, refractive liquid which boils at 43°. Cobalt carbonyl melts at 51° and iron carbonyl ($Fe[CO_4]$) boils at 102.8°.

Physiological Properties.—When inhaled, carbon monoxide acts as a narcotic poison, producing dizziness, headache, nausea, convulsions, and death. The presence of 1 liter in 100 cubic meters of air will produce poisoning. The gas unites with the hæmoglobin of the blood, forming the undecomposable carboxy-hæmoglobin which prevents the absorption of oxygen and causes suffocation. Poisoning by coal gas is essentially caused by its carbon monoxide. The *after-* or *choke-damp* resulting from the explosion of fire-damp (air and gaseous hydrocarbons) is a mixture of carbon monoxide and dioxide.

PHOSGENE, OR CARBONYL CHLORIDE, OR CARBON OXYCHLORIDE

Carbonyl chloride ($COCl_2$), or phosgene (φῶς = *light*, γεννάω = *I produce*), is a colorless, suffocating gas which may be prepared by the action of the sunlight on a mixture of carbon monoxide and chlorine, also by passing these gases over platinized asbestos. Industrially phosgene is prepared by heating a mixture of calcium oxide, calcium chloride, and coke in an electric furnace, $CaO + CaCl_2 + 5C = 2CaC_2 + COCl_2$. Water and alkalies decompose it into hydrogen chloride and carbon dioxide: $COCl_2 + H_2O = CO_2 + 2HCl$.

Phosgene is readily condensed to a liquid which boils at 8.4°; it is employed in the preparation of various organic compounds and dyes, also in asphyxiating shells of modern warfare.

CARBON DIOXIDE

CARBONIC ANHYDRIDE, CARBONIC ACID GAS

Formula, CO_2. *Molecular Weight*, 44.

History.—The presence of this gas in certain caves, grottos and springs was observed from the earliest times. Van Helmont (1577 to 1644) distinguished between air and "*spiritus sylvestris,*" which was evolved through the action of acids on chalk and alkalies, was given off from burning charcoal and during the process of fermentation, and found in caves. Black (1755) confirmed Van Helmont's assertions, identifying carbon dioxide by its absorption in lime water, and called the gas "fixed *air.*" After the discovery of oxygen, Lavoisier (1781) recognized the chemical nature of the gas and proved the presence of carbon and oxygen. Dalton demonstrated its volume composition. Faraday was the first to liquefy it.

Occurrence.—Carbon dioxide (incorrectly called *carbonic acid*) occurs free in the atmosphere to the extent of three or four volumes in ten thousand. It is found in all terrestrial waters, some springs being heavily charged, and is given off in large quantities from the earth in many volcanic districts. It collects in caves, mines, and wells, and is usually termed *choke-damp*. Combined with calcium and magnesium as carbonates, it makes up mountain ranges. Marble, limestone, and chalk consist chiefly of calcium carbonate, while magnesite is magnesium carbonate, and dolomite a mixture of the latter two.

Preparation.—Carbonates and bicarbonates when heated yield the gas according to the following:

$$CaCO_3 = CaO + CO_2.$$
$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

When small quantities are desired it is rapidly and conveniently made from marble and hydrochloric acid:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

Carbon dioxide is a product of fermentation and putrefaction.

When a current of air is passed over red-hot carbon the product is carbon dioxide, provided the air be kept in excess. This and the method by heating a carbonate are used for furnishing the gas in the manufacture of carbonates on the large scale.

Physical Properties.—Carbon dioxide is a colorless, odorless gas with a faint acid taste. It is 1.529 times heavier than air, 21.945 times heavier than hydrogen. At 0° 100 mils of water dissolve 171 mils (0.335 gm.); at 20°, 87.8 mils (0.169 gm.), and at 30°, 66.5 mils (0.126 gm.) of the gas at 760 mm. pressure. This solubility of the gas is increased approximately 1 volume for every increase of 1 atmosphere in pressure; one liter of the gas at 0° and 760 mm. weighs 1.9652 gm.

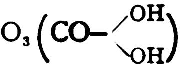
The gas is more soluble in alcohol than in water—about 3 volumes in 1 at 20°.

A solution containing about 5 volumes of the gas in water constitutes the so-called "soda-water."

The critical temperature of carbon dioxide is 31.3°; that is, it can only be liquefied at this temperature by a pressure of 73 atmospheres (its critical pressure). At 0° it liquefies under 35 atmospheres to a colorless mobile liquid, which boils at —78.2° (760 mm.). When liquid carbon dioxide is suddenly released from pressure, a part instantly volatilizes, absorbing so much heat as to produce an intense degree of cold, causing thereby a portion of the liquid to solidify to snow-like flakes. These fuse at —56.4° with a vapor tension of 5 atmospheres, hence solid carbon dioxide passes into vapor without fusing (see page 53). When solid carbon dioxide is mixed with ether and allowed to evaporate, a temperature of —80° is produced, and with acetone a temperature of —110°, which may be still further reduced to —140° by facilitating volatilization through a vacuum. This solid may be handled with safety, as it is always surrounded by a thin layer of the gas; when, however, it is pressed into contact with the skin it will cause a blister.

Chemical Properties.—Carbon dioxide is a very stable compound. At 2000° (760 mm. pressure) about 7.5 per cent. is dissociated:

$$2CO_2 = 2CO + O_2.$$

When passed over heated potassium or sodium, carbon separates, while the oxygen unites with the alkali metal to form an oxide, and this with the excess of carbon dioxide to a carbonate. This gas when in aqueous solution colors blue litmus a faint red, which disappears on drying. This acid reaction is due to the presence of the hypothetical compound H_2CO_3  $\left(CO\!\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}\right)$ *carbonic acid,* of which many salts are known. The acid has not been isolated, for when liberated from its salts, it immediately breaks up into carbonic acid gas (CO_2) and water. Practically all inorganic acids liberate carbon dioxide from its salts.

Carbon dioxide is readily separated from other gases by passing into a solution of or over moist caustic potash, soda, or lime,

$$2KOH + CO_2 = K_2CO_3 + H_2O.$$

Carbon dioxide is neither combustible nor a supporter of combustion. This property may be illustrated by lowering a lighted taper into a vessel of it, or, since it is heavier than air, by pouring it down an inclined board on which are placed a number of lighted candles, each of which is extinguished in turn when reached by the descending volume of gas. Under the name of "choke-damp" it sometimes collects in old wells, and is detected by lowering a lighted candle, which will be extinguished if the gas is present.

Physiological Properties.—Carbon dioxide occurs in ventilated rooms in from 5 to 6 parts per 10,000. Expired air contains from 4 to 5 per cent. by volume, or averages about 0.78 cu. ft. per hour, with a consumption of about 0.9 cu. ft. of oxygen. A gas jet (12-candle) burning 3 to 5 cu. ft. of gas per hour gives off about 1.7 cu. ft. of CO_2 per hour. In order that an adult may not receive more than 2 cu. ft. of CO_2 per 10,000 cu. ft. of air, it is estimated that at least 2000 cu. ft. of air per hour should be furnished. Internally, the gas is an agreeable, mild stimulant.

Uses.—Carbon dioxide is employed in the manufacture of carbonates; its solution in water is extensively used as a beverage; and it forms an important constituent of the chemical fire extinguishers. Apart from these, and on a much larger scale, it assists in the growth of plant life. Carbon dioxide as a waste-product in the atmosphere is absorbed by plants and decomposed by the chlorophyll, aided by sunlight; the carbon resulting from this decomposition goes to make up the structure of the plant, while the oxygen is rejected and returns to maintain the proper proportion of that element in the atmosphere.

Liquid Carbon Dioxide, contained in steel cylinders, is extensively used in making carbonated mineral waters, soda water, carbonating alcoholic beverages, in sugar refineries, etc. The CO_2 may be obtained from furnace gases, which are dissolved by forcing into a solution of potassium carbonate under pressure; this when released gives up the CO_2. The gas is also obtained by pumping such artesian wells as contain spring waters highly charged with the gas. The Manheim Springs in Germany give off about one million pounds of carbon dioxide annually.

Carbonates.—The soluble salts of carbonic acid are usually prepared by passing carbon dioxide into a solution of a hydroxide of the base; or, when insoluble, they are formed by interaction between a soluble carbonate and a soluble salt of the base:

$$FeSO_4 + Na_2CO_3 = FeCO_3 + Na_2SO_4.$$

The carbonates of the alkalies are soluble in water; all others are insoluble. Being dibasic, this acid forms well-defined *neutral* salts, called carbonates (Na_2CO_3) of alkaline reaction in aqueous solution and *acid* or *bi-carbonates* ($NaHCO_3$). The various bases readily absorb the gas, forming the acid or neutral (normal) salt, thus:

$NaOH + CO_2 = NaHCO_3$, sodium hydrogen (bi or acid) carbonate.
$2NaOH + CO_2 = H_2O + Na_2CO_3$, sodium carbonate (normal).

The carbonates of the alkaline earths and most metals are insoluble, but upon passing carbon dioxide into them when suspended in water, soluble bicarbonates result.

$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$
$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$ calcium bicarbonate.
$FeCO_3 + H_2O + CO_2 = Fe(HCO_3)_2$ iron bicarbonate.

Basic carbonates occur frequently among the alkaline earths and heavy metals; they may be considered as oxy- or hydroxy-carbonates, as *white lead*, $2PbCO_3.Pb(OH)_2$; magnesium carbonate, $3MgCO_3.Mg(OH)_2$; bismuth oxycarbonate, $(BiO)_2CO_3$, etc.

All of the carbonates except those of the alkalies are decomposed by heat into oxides and CO_2, the bicarbonates into carbonates, water, and CO_2.

$CaCO_3 = CaO + CO_2.$
$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$

Through the presence of dissolved carbon dioxide, spring waters hold in solution considerable quantities of calcium, magnesium, and iron as bicarbonates, which are redeposited as neutral carbonates upon exposure or boiling: $Fe(HCO_3)_2 = FeCO_3 + CO_2 + H_2O$.

Percarbonates.—These (like the persulphates) are formed through the electrolysis of concentrated solutions of the carbonates at —10°. Potassium carbonate is decomposed by the current into the ions KCO_3, which unite to form the percarbonate $K_2C_2O_6$. This is a bluish, deliquescent, amorphous powder, which when heated from 200° to 300° rapidly decomposes into carbonate and oxygen. The aqueous solution of a percarbonate gives off oxygen at 45°, while the addition of dilute acids causes the liberation of hydrogen peroxide: $K_2C_2O_6 + 2HCl = 2CO_2 + 2KCl + H_2O_2$; caustic alkalies will do the same, $K_2C_2O_6 + 2KOH = 2K_2CO_3 + H_2O_2$. The percarbonates are therefore active oxidizing and bleaching agents.

COMBUSTION AND ILLUMINATION

History.—Stahl (1660–1734) was the first to formulate a theory of the phenomenon of combustion based on the old ideas of Basilius Valentinus, Paracelsus and Becher; that is, the presence of a constituent (a "fire material") common to combustible bodies. Stahl assumed that all combustible substances, including metals capable of calcination, contained a common substance termed ***phlogiston*** which escaped through combustion or calcination. The more readily the substance burned, the richer it was in phlogiston, hence charcoal was regarded as nearly pure phlogiston. When a metal was calcined, phlogiston escaped and the *calx* remained; in order to reproduce ("revive") the metal, the metallic calx (metallic oxide) was heated with coal or charcoal. Upon a similar erroneous assumption, sulphur was considered to consist of sulphuric acid and phlogiston, for on heating sulphuric acid or any sulphate with coal (phlogiston), sulphur was obtained. A natural sequence to the above assumption would be that substances become lighter through combustion, and although many experiments demonstrated the reverse (for example, the calcination of metals), no attention was given such conclusive facts, which proofs finally caused the abandonment of this doctrine. The discovery of oxygen by Priestley and Scheele, followed by the experiments of Lavoisier, who was the first to explain the true nature of combustion and reduction—that is, it was a combination with or the separation from oxygen—caused the downfall of the phlogistic theory (1786).

1. Chemical Nature of Combustion.—All phenomena of combustion are manifestations of chemical energy accompanied by evolution of heat and in the common use of the term, light. In this same sense, the combustible body withdraws oxygen from the air, which is the supporter of combustion, forming oxides as products of decomposition. These may be solids, liquids, or gases.

As these combustions involve direct chemical union of the elements concerned, it matters not which is the combustible body and which the supporter of combustion. We may in many cases easily reverse the ordinary conditions. Thus, a jet of hydrogen or illuminating gas will burn in an atmosphere of air or oxygen because the hydrogen or the hydrocarbons of the illuminating gas combine chemically with the oxygen. For the same reason, a jet of oxygen will burn in an atmosphere of hydrogen or illuminating gas if such be arranged. A jet of air will also burn in the atmosphere of illuminating gas, the air being for the time called the combustible body and the illuminating gas the supporter of combustion. The terms "*combustible*" and "*supporter of combustion*" are therefore merely relative in their use.

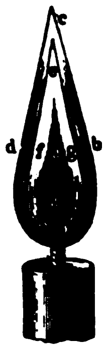
2. Conditions of Combustion.—Combustion may be slow or rapid, accompanied by flame or not, according to conditions. The appearance of flame indicates the presence of a gas or vapor which has been raised to a temperature at which it becomes luminous.

In order to bring about combustion, the substance must be heated to its *ignition-temperature*. Thus zinc methyl or hydrogen-phosphide ignites when brought into contact with the air, phosphorus ignites at 40°, carbon disulphide at 149°, other substances at red heat. Combustion continues as long as the heat produced by the reaction is sufficient to retain the temperature of ignition. Therefore we define a *flame* as the phenomenon produced at the surface where two gases or vapors meet and combine, giving off heat and usually light. If, for example, a piece of metallic gauze be lowered over a lighted gas jet, the flame will not pass through the gauze, or, if the gas be ignited above the gauze, the flame will not communicate to the gas issuing below. This is due to the excellent conducting power of the metal, which lowers the temperature below the ignition-point. Of course, if the gauze is held in a very hot flame, it soon becomes sufficiently heated to cause the entire gas jet to ignite. The Davy safety-lamp is an application of this principle.

3. The Structure of Flame.—An ordinary candle flame or gas-jet as shown in Fig. 106 is composed of several cones. The inner cone, *a, a'*, consists of gaseous hydrocarbons not as yet ignited; in the middle cone, *e, f, g,* which consists of the burning lighter hydrocarbons, acetylene is formed as intermediary product. This, through its decomposition with separation of incandescent particles of carbon, emits the light. In the outer cone, *c, d, b,* where the flame comes in contact with the atmospheric oxygen, complete combustion of the liberated carbon is secured. This part of the flame is therefore the least luminous as well as the hottest.

The fact that unconsumed hydrocarbon gases exist in the inner cone of a gas flame can be demonstrated by introducing a small glass tube obliquely from one side and taking off this gas to be burned, or holding a porcelain surface in the cone when a layer of soot is deposited.

FIG 106.



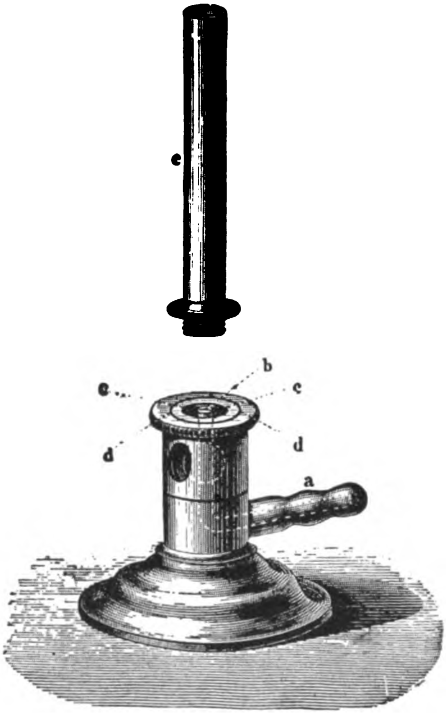
Candle flame.

4. Distinction Between Luminous and Non-Luminous Flames.—The luminosity of a flame depends upon the presence of solid particles heated to a state of incandescence. The incandescent matter may be a product of the combustion, as in the gas, oil, candle, or acetylene flame. In these instances it consists of highly heated carbon in a minute state of subdivision, liberated through the decomposition of hydrocarbons in the presence of an insufficient supply of oxygen. A non-luminous flame, like that of hydrogen or the Bunsen burner or oxy-hydrogen blow-pipe, may be rendered highly luminous by introducing an infusible oxide, the oxy-hydrogen flame with lime forming the lime or Drummond light. By introducing the incandescent Welsbach mantle, which consists of a mixture of thorium oxide with 1 per cent. of cerium oxide, into a Bunsen or alcohol (colorless) flame, these become intensely luminous through the incandescence of the particles of the rare earth oxides.

Such chemical reactions as are accompanied by the development of heat energy, which cause the splitting up of complex molecules (gas, acetylene, phosphorus, arsenic), yield light energy. In the latter two, vapors of phosphoric and arsenous oxides form, which become incandescent. If sufficient oxygen or air be admitted to the cone of a gas flame, the hydrocarbon gases will be consumed without separation of carbon. This may be done in either one of two ways—by the aid of the blow-pipe or blast lamp, which directs a current of air directly into the cone of the flame, or by mixing air with the illuminating gas before it is burned, as in the Bunsen burner.

The Bunsen burner (Fig. 107) is of a specially contrived form for securing complete combustion of the gas hydrocarbons through admixture with air. If the movable ring *d*, at the base of the burner, be turned so as to close the openings for admission of air, the stream of gas passing into the tube from *b* will burn with a luminous, smoking flame. If this ring be turned so as to admit air gradually from below, the flame becomes less luminous and hotter with the increase of the volume of air admitted. If the proportion of air and gas be properly regulated, a non-luminous flame of high temperature will be secured. A burner consuming 6 cubic feet of gas per hour may give a temperature of from 1000 to 1200°.

FIG. 107.



Bunsen burner.

FIG. 108.

Bunsen flame.

The structure of the Bunsen flame, which is the same as that of the blow-pipe or blast-flame, is shown in Fig. 108. The mixture of cold air and gas constitutes the inner colorless cone *a;* the luminous cone *b,* which contains the partially consumed hydrocarbons, constitutes the *reducing*-flame, so called because of its deficiency in oxygen, while the outer edge of the cone or main body of the flame, with the tip *c,* where combustion is complete and the temperature is the highest, is known as the *oxidizing* flame.

The *blow-pipe* is a hollow tapering brass tube bent at a right angle near the tip; a blast of air from this when directed over a small flame (alcohol, gas, or candle) produces a long, pointed, exceedingly hot flame similar in structure to that of the Bunsen burner. It is, however, more convenient in analysis, since it can be directed whenever desired, and its oxidizing or reducing effect upon substances studied. Higher temperatures may be produced by means of the oxyhydrogen blow-pipe (page 196) in which a blast of air is forced through an illuminating gas flame, whereby a temperature of below 2000° is obtained; if the gas be replaced by hydrogen and the air by oxygen, the temperature will be increased to about 2500°. The electric arc will give a temperature varying between 3690 and 3720°, and the oxygen acetylene lamp about 3000°.

CARBON AND SULPHUR

CARBON DISULPHIDE

Formula, CS_2. *Molecular Weight,* 76.14.

Carbon disulphide was discovered by Lampadius of Freiburg in 1796 while heating pyrites with charcoal. It is prepared by passing the vapors of sulphur over coke or charcoal which has been heated to a cherry-red in retorts of cast-iron or earthenware. It is also prepared electrothermally (see p. 709).

Purification, consisting in removing uncombined sulphur, hydrogen sulphide, sulphur dioxide, etc., is accomplished by washing with milk of lime and distilling from a solution of lead acetate or mercury salts and paraffin; the latter serves to retain volatile odoriferous compounds.

Physical Properties.—Carbon disulphide is a colorless, mobile, strongly refracting liquid, of specific gravity of 1.27 at 15°, which, as it comes in commerce, usually has a fetid odor, due to the presence of various polysulphides, but when purified it has a mild ethereal odor. When inhaled for any length of time, CS_2 vapors produce fatal poisoning. It is soluble in about 530 parts water, mixes in all proportions with absolute alcohol, ether, chloroform, and the fixed and volatile oils. It boils between 46 and 49°. The vapor of carbon disulphide is very inflammable, taking fire in the air at 149°; this may be effected by introducing a heated glass rod into its vapors. Carbon disulphide is the best solvent for sulphur, phosphorus, rubber, fats, iodine, etc., the latter dissolving with an intense violet color. Traces of iodine can be more readily detected by its color imparted to this solvent than through the iodide of starch reaction.

Chemical Properties.—Carbon disulphide burns with a pale-blue flame to carbon dioxide and sulphur dioxide:

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

A mixture of its vapors with oxygen gives rise to a violent explosion on ignition. When mixed with nitric oxide, the vapors burn with an intensely brilliant flame, rich in actinic rays. If the vapors of carbon disulphide and chlorine are passed through a hot tube, sulphur monochloride (S_2Cl_2) and carbon tetrachloride (CCl_4) are produced. A similar reaction results through the action of chlorine on a boiling solution of iodine in carbon disulphide.

The vapors of carbon disulphide, when passed over heated, finely divided metals, convert most of them into sulphides:

$$CS_2 + 2Zn = 2ZnS + C.$$

Carbon disulphide is the anhydride of thio- or sulpho-carbonic acid, H_2CS_3.

Uses.—Carbon disulphide is used extensively in the arts on account of its solvent action on oils, fats, resins, rubber, etc. Its vapor is poisonous to man, animals, and insect life. As a germicide and insecticide it is used for destroying insects, weevils in wheat, the grape pest or *phylloxera.* For the latter purpose it is usually converted into the sulphocarbonate of sodium. This salt is also useful in destroying mice, rats, gophers, and other burrowing animals which damage crops.

Carbon disulphide is employed in the manufacture of carbon tetrachloride, thiocyanates, rubber cements, and for filling glass refracting prisms.

Detection.—Carbon disulphide is detected by mixing a small quantity of the liquid with alcoholic ammonia, and evaporating on a water-bath, when ammonium sulphocyanate is formed:

$$\underset{\text{Carbon Disulphide.}}{CS_2} + \underset{\text{Ammonia.}}{4NH_3} = \underset{\text{Ammonium Sulphocyanate.}}{NH_4SCN} + \underset{\text{Ammonium Sulphide.}}{(NH_4)_2S.}$$

On acidifying the residue with hydrochloric acid, and adding ferric chloride solution, the red color of ferric sulphocyanate is developed. Or dissolve the CS_2 in alcoholic potassium hydroxide and add copper sulphate, T.S., which gives a yellow precipitate of cuprous xanthate, $Cu_2S.CS.OC_2H_5$.

Sulphocarbonic or Thiocarbonic Acid, H_2CS_3.—This salt may be prepared either through the union of carbon disulphide and alkali sulphides: $Na_2S + CS_2 = Na_2CS_3$; or by the action of carbon disulphide on alkali hydroxides:

$$6NaOH + 3CS_2 = 2Na_2CS_3 + Na_2CO_3 + 3H_2O.$$

On adding hydrochloric acid to solutions of this salt the free acid (H_2CS_3) separates as a yellowish-brown heavy oil, which readily decomposes into hydrogen sulphide and carbon disulphide: $H_2CS_3 = H_2S + CS_2$. The thiocarbonates of the alkalies and earths are soluble in water and are chiefly used for the destruction of *phylloxera*. Their action depends on the carbon disulphide which is liberated.

On adding an acid to solutions of these salts, the sulpho-carbonic acid separates as a reddish-brown oil, already described.

Carbonyl Sulphide, or Carbon Oxysulphide, COS.—It may be obtained by the direct union of carbon monoxide and sulphur vapor, when passed through a red-hot tube; but it is more easily made by acting on potassium sulphocyanate with sulphuric acid:

$$\underset{\substack{\text{Potassium}\\ \text{Sulphocyanate.}}}{KCNS} + \underset{\substack{\text{Sulphuric}\\ \text{Acid.}}}{2H_2SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid Ammo-}\\ \text{nium Sulphate.}}}{NH_4HSO_4} + \underset{\substack{\text{Acid Potas-}\\ \text{sium Sulphate.}}}{KHSO_4} + \underset{\substack{\text{Carbonyl}\\ \text{Sulphide.}}}{COS.}$$

It is a colorless gas, with a disagreeable, sulphuretted odor, very inflammable, burning with a bright blue flame. It is soluble in an equal volume of water, which solution gradually decomposes into carbon dioxide and hydrogen sulphide: $COS + H_2O = CO_2 + H_2S$.

SILICON

Symbol, Si. *Atomic Weight,* 28.3. *Valence,* IV.

History.—Amorphous silicon was first isolated by Berzelius in 1823 by fusing together iron, carbon, and silica. The crystallized variety was prepared by Deville in 1854, by fusing sodium silico-fluoride with aluminum or zinc and sodium:

$$Na_2SiF_6 + 4Na = 6NaF + Si.$$

Occurrence.—Next to oxygen, silicon is the most abundant element known. It is not found in the free state, but in combination with oxygen in quartz as silicon dioxide (SiO_2) it is widely distributed. It is, further, the chief constituent of nearly all rocks, and consequently, also, of the soils which have resulted from the decomposition of rocks. It is also found in the ashes of many plants, owing to its presence in their mineral structure. Silicon exists in two allotropic conditions, the *amorphous* and the *crystalline.*

Isolation.—Amorphous silicon may be prepared by mixing equal parts of powdered and well-dried white sand (SiO_2) and magnesium. This mixture is placed in a test-tube and heated with a Bunsen flame. The reaction soon begins with a glowing which rapidly extends throughout the entire mass: $SiO_2 + 2Mg = Si + 2MgO$. The cooled, hardened product is powdered and washed with dilute hydrochloric acid to remove the magnesium oxide. It may be obtained by the Acheson process in which a mixture of quartz sand and crushed coke is fused in an arc-type furnace at about 3000°, when the metal collects at the bottom. The product by the former process is an amorphous, brown powder. By the latter process a crystalline molten black mass of high luster.

Silicon is also prepared in the electric furnace through the reduction of quartz with charcoal, adding some CaO and Mn_3O_4. The crude silicon resulting is purified by washing with HCl and HF.

Properties.—The silicon of the silico-fluoride process is in the form of dark, lustrous, octahedral crystals, and a degree of hardness sufficient to scratch glass. They withstand a white heat without igniting, and resist the action of all acids, excepting hydrofluoric. Hydrogen chloride gas, when passed over silicon heated to a high temperature, combines to form silicon tetrachloride and silicon chloroform. Hot concentrated solution of sodium hydroxide dissolves silicon with formation of sodium silicate and evolution of hydrogen.

$$Si + 4NaOH = Na_4SiO_4 + 2H_2.$$

The silicon obtained in the electric furnace is in crystalline masses or ingots of a dark silver luster. It is quite brittle, of specific gravity 2.49 and fuses at about 1450° C. In hardness, it is between six and seven of the scale. Metallic silicon is a powerful reducing agent and is also used in hardening iron and making it resistive to acids (ferrosilicon).

Silicon Hydride, Silico-methane, SiH_4, is prepared like arsine or stibine by treating magnesium silicide with hydrochloric acid:

$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4.$$

The magnesium silicide is prepared by heating together powdered quartz 1 p. with powdered magnesium 1.5 p.

Silicon hydride is a colorless gas, which may be collected over water or mercury. When pure, the gas does not inflame spontaneously, but when mixed with traces of silico-ethane (Si_2H_6), present as impurity, it ignites, a phenomenon analogous to phosphine. In burning it evolves dense fumes of silicon dioxide, SiO_2, with formation of water. When mixed with chlorine, it inflames, forming chlorine derivatives. When passed into solutions of alkali hydroxides their silicates are formed:

$$SiH_4 + 2NaOH + H_2O = 4H_2 + Na_2SiO_3.$$

Silicon Tetrachloride, $SiCl_4$, is usually prepared by passing a current of dry chlorine over a mixture of silicon dioxide and carbon contained in a porcelain tube heated to redness, the product being condensed in a receiver cooled with ice:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

Silicon tetrachloride is a colorless, fuming liquid, having the specific gravity at 0° of 1.58, and boiling at 59.6°. It is decomposed by water into hydrochloric and silicic acids:

$$SiCl_4 + 4H_2O = H_4SiO_4 + 4HCl.$$

Silicon Hexachloride (Trichloride), $Cl_3Si\text{-}SiCl_3$, is formed in small quantity when the vapor of silicon tetrachloride is passed over fused silcon at high temperature. It is a colorless, fuming liquid, which solidifies at —1° and boils at 147°.

Silico-chloroform, $SiHCl_3$, which corresponds to chloroform ($CHCl_3$), is produced when silicon is heated to redness in a current of dry hydrochloric acid gas:

$$Si + 3HCl = SiHCl_3 + H_2.$$

It is a colorless, inflammable liquid, which boils at 33 to 34°, burns with a greenish flame, and decomposes with water into silicic and hydrochloric acids.

Silico-bromoform, $SiHBr_3$, and Silico-iodoform, $SiHI_3$, have also been prepared.

Silicon Tetrabromide, $SiBr_4$, and **Tetraiodide,** SiI_4, are prepared in the same manner as the chloride. The bromide is a colorless liquid which boils at 153°. The iodide forms colorless octahedra which fuse at 120° and boil at 290°. Both are decomposed by water, like the chloride.

Silicon Hexabromide, Si_2Br_6 and Hexaiodide, Si_2I_6, are prepared like the hexachloride.

Silicon Tetrafluoride, Fluosilicic Acid, SiF_4, is prepared by heating silicon dioxide (sand) with fluorspar and sulphuric acid:

$$SiO_2 + 2CaF_2 + 2H_2SO_4 = SiF_4 + 2CaSO_4 + 2H_2O.$$

Silicon tetrafluoride is a colorless, very pungent, fuming gas, which when liquefied boils at —65°, is decomposed by water into silicic and hydrofluosilicic acids:

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6.$$

The volatile properties of HF are made use of in the analysis of silicates, in which the pulverized silicate is heated with a mixture of H_2SO_4 and HF; the silica is expelled as SiF_4, leaving the bases as sulphates. The etching of glass depends on the formation of SiF_4

Silicon Carbide.—See page 294.

Hydrofluosilicic Acid, H_2SiF_6, known only in aqueous solution, is formed when the vapor of silicon tetrafluoride is led into water (preceding equation). The gelatinous silicic acid, which separates at the same time, would quickly stop the tube, if it were not prevented by keeping the latter under mercury, on the surface of which is placed the water. Each bubble of escaping gas forms a mass of silicic acid as it enters the water from the mercury. The hydrofluosilicic acid is obtained in aqueous solution and is decomposed by boiling or concentrating to a certain point into silicon tetrafluoride and hydrofluoric acid. It is useful as a laboratory reagent, since it forms a number of insoluble salts termed hydrofluosilicates, among which are those of potassium, lithium, and barium.

Silicides.—These are compounds of silicon with the metals, produced through the heat of the electric furnace. Among these are Ni_2Si, Cu_2Si, etc.

SILICON DIOXIDE

SILICIC ANHYDRIDE, SILICA

Formula, SiO_2. *Molecular Weight,* 60.30.

This compound of silicon is the most abundant of all those in which the element occurs. There are three well-defined varieties of silica. Two of them are crystalline and one is amorphous. The most abundant of these is represented by *quartz,* which, when pure, consists of colorless, transparent, hexagonal prisms, having a specific gravity of 2.6, and represented in the scale of hardness by 7. These prisms are of two varieties, one of which rotates the plane of polarization to the right and the other to the left, when polarized light is passed through a section cut parallel to the vertical axis. Hence these crystals are called dextro- and lævo-rotary. It is sometimes slightly colored, as in amethyst, smoky quartz, and rose quartz.

Many of our most abundant rocks, as granite, gneiss, and syenite, also sand, are made up chiefly of quartz. Olivine, serpentine, talc, and asbestos are silicates of magnesium; clays, slate, fuller's earth, and pumice are silicates of aluminum, while mica and feldspar, silicates of potassium.

Amorphous silicates are generally hydrated, of waxy luster and conchoidal fracture, the type of which is *chalcedony.* This variety frequently occurs with varying amounts of coloring impurities, as shown in *agate, onyx agate, jasper,* and *flint.* The precipitated silica formed when silicon fluoride is passed into water and dried, or when a soluble silicate is treated with an acid, the precipitate collected and dried, also belongs to this variety. An amorphous form, known as *kieselguhr,* or diatomaceous earth, occurs in large deposits in Germany, and in several localities in the United States. This consists of about 63 per cent. of soluble silica, about 18 per cent. of organic matter, 11 of sand or clay, and about 8 per cent. of water. *Opal* is a compact hydrated silicic oxide, as is also *geyserite.*

The opal is softer than the quartz and is of various colors, exhibiting opalescence with beautiful iridescence. Silicon dioxide is also found widely distributed in the vegetable and animal kingdoms, although not in such large amounts as among minerals. In the stalks of various grasses, and in the hair of man and animals, it is an important constituent.

The silicified wood found in many localities, but especially in the vicinity of the Yellowstone National Park in this country, is formed by silicon replacing the carbon of the wood.

Chemical Properties.—All the varieties of silica are insoluble in water and acids, except in hydrofluoric acid, which dissolves it, forming silicon fluoride (SiF_4). Quartz, even in fine powder, is practically insoluble in boiling solutions of the alkaline hydroxides or carbonates, while the other two varieties will dissolve, the amorphous variety completely. This serves to distinguish quartz from the other two. All varieties on fusing with dry sodium or potassium carbonate form soluble silicates of the alkalies; the aqueous solution of sodium silicate is commonly termed *water glass:*

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2.$$

On treating this solution of sodium silicate with hydrochloric acid, evaporating to dryness, adding water, collecting the precipitate, and washing thoroughly with boiling water, the purest amorphous silica is obtained.

Quartz crystal and sand are largely used in the manufacture of pottery and glass; many of the colored varieties are used as imitation gems; the amorphous kieselguhr is employed as a polishing agent, in filtration of liquids, as an absorbent packing for bromine, also as an absorbent of nitroglycerin, forming dynamite; and agate, on account of its hardness, is used to make mortars for pulverizing minerals.

Fused quartz laboratory utensils, which were first produced in 1839 by Gandin, are now extensively employed, owe their commercial introduction to Heraeus and Achendstone in 1900, who, through the agency of the oxyhydrogen or oxy-acetylene flame, were able to fuse quartz and work it into various forms of apparatus, which resist sudden temperature changes, wet or dry. These vessels are not affected by boiling acids (except HF and H_3PO_4), nor by temperature changes, provided not more than traces of calcium are present. The coefficient of expansion of quartz is about $^1/_{17}$ that of the best glass, hence quartz vessels withstand sudden temperature changes without fracture.

Orthosilicic Acid, H_4SiO_4 or $Si(OH)_4$ or $SiO_2 2H_2O$.—When hydrochloric acid is added to a dilute solution of sodium silicate, no precipitate occurs:

$$Na_4SiO_4 + 4HCl = 4NaCl + H_4SiO_4.$$

If this solution be submitted to dialysis the sodium chloride and excess of hydrochloric acid will pass through, while a transparent colorless solution remains, supposed to contain orthosilicic acid; this also forms in the decomposition of silicon fluoride by water (page 311).

This feeble acid solution upon evaporation and drying loses one molecule of water, being transformed into amorphous *meta-silicic* acid, H_2SiO_3 or $SiO(OH)_2$, which when heated to redness loses a further molecule of water, leaving silicon dioxide, SiO_2. This ortho acid is represented in a few silicates, as *olivine,* Mg_2SiO_4 or $2MgO.SiO_2$; *zircon,* $ZrSiO_4$ or $ZrO_2.SiO_2$; *garnet,* $Ca_3Al_2(SiO_4)_3$ or $3CaO.Al_2O_3.3SiO_2$; *chrysolite,* $MgFeSiO_4$ or $MgO.FeO.SiO_2$; and *anorthite,* $CaAl_2(SiO_4)_2$ or $CaO.Al_2O_3.2SiO_2$.

A large number of metasilicates are known, for example:

Steatite (talc), $Mg_3H_2(SiO_3)_4$ or $3MgO.4SiO_2.H_2O$.
Wollastonite, $CaSiO_3$ or $CaO.SiO_2$.
Emerald, $Be_3Al_2(SiO_3)_6$ or $Al_2O_3.3SiO_2.(BeO.SiO_2)_3$.
Enstatite, $MgSiO_3$ or $MgO.SiO_2$.
Sodium silicate, Na_2SiO_3 or $Na_2O.SiO_2$.

Polysilicates.—Through the removal of one of more molecules of water from two or more molecules of orthosilicic acid a variety of polysilicic acids * may be obtained, thus:

DISILICIC ACIDS

$2H_4SiO_4 - H_2O = H_6Si_2O_7$. Hexabasic disilicic acid.
$2H_4SiO_4 - 2H_2O = H_4Si_2O_6$. Tetrabasic disilicic acid.
$2H_4SiO_4 - 3H_2O = H_2Si_2O_5$. Dibasic disilicic acid.

TRISILICIC ACIDS

$3H_4SiO_4 - H_2O = H_{10}Si_3O_{11}$.
$3H_4SiO_4 - 2H_2O = H_8Si_3O_{10}$.
$3H_4SiO_4 - 3H_2O = H_6Si_3O_9$.

These polysilicic acids are not known free, but many occur in nature among the amorphous forms of silica as agate, opal, and chalcedony. Our natural silicates are salts of these acids. The hydrated silicates (zeolites) are soluble in hydrochloric acid, while the anhydrous silicates are insoluble and are rendered soluble by fusion with alkali carbonates and hydroxides.

Glass.—This is an amorphous mixture of the silicates of calcium or lead with those of an alkali (K or Na), obtained by fusing sand (SiO_2), lime or lead oxide with sodium or potassium carbonates. For the cheaper grades of glass the alkali carbonates are replaced by a mixture of either one of the sulphates and coal dust. The sulphates are thereby reduced to sulphides, which form silicates with the sand. Since the degree of fusibility, hardness, and refrac-

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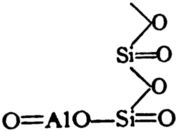
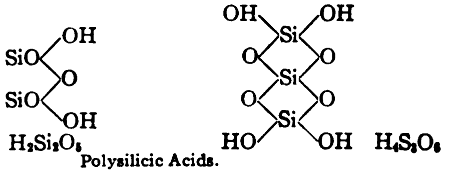
* As illustration of the linkage in these polyacids the following examples are given:



Orthoclase.



$H_2Si_2O_5$ $H_4S_3O_8$

Polysilicic Acids.

tive properties of glass depend upon its composition, we distinguish between the following varieties:

1. *Lime* (**Plate**) *Glass.*—This is either a soda-lime glass or potash-lime glass. It is cheaper, harder, and less fusible than the "lead" glass. The *soda-lime* glass, which is readily fusible, is the commoner sort such as is used for window-glass, plate glass, bottles, etc. The *potash-lime* glass (Bohemian or Crown glass), which is a silicate of lime and potassium, fuses only at a very high temperature, is harder and withstands the action of water and acids better than soda-glass, hence is especially adapted for the manufacture of chemical glassware. Increasing the content of alkali renders these glasses softer, more fusible, and less resistive to chemicals. Increasing the percentage of lime decreases the fusibility and hardens the glass.

2. *Lead* (**Flint or Crystal**) *Glass.*—In this variety, litharge (PbO) or red lead (Pb_3O_4) replaces the CaO of the lime glass. It is heavy, possesses great luster and brilliancy, and is chiefly used for cut-ware and optical glass (lenses, prisms).

Through the replacement of a portion of the lead oxide by thallium oxide or boron tri-oxide, the refractive property of the glass is very much increased; the boron glass is called "*strass,*" and is used for making imitation gems.

The chemical composition of glassware employed in various physical and chemical operations varies according to its uses. Various oxides, such as BaO, ZnO, MgO, Al_2O_3, B_2O_3, may be added to the glass mass, each of which serves a specific purpose in imparting the desired physical properties to the glass. The following summary illustrates:

Baryta increases the index of refraction, brilliance, and density of glass, adapting it for pressed and cut ware.

Zinc oxide glass possesses a high resistance to tension, compression, and chemical action, therefore adapted for thermometers. Jena instrument glass (16 III) contains 7 per cent. of ZnO. When used in conjunction with boric oxide, it imparts resistive action to sudden temperature changes, hence these two oxides enter into the composition of what is known as "resistive" glass.

Alumina in small amounts facilitates fusion of the glass mixture and renders it resistive to the action of alkaline solutions.

Boric anhydride up to 20 per cent. raises the refractive index of glass; over this it is lowered. It decreases the coefficient of expansion of glass, hence is used (also with ZnO) in making chemical ware which must withstand sudden temperature changes without breaking. Boric acid glass will not withstand the action of alkaline solutions. As much as 80 per cent. of SiO_2 enters into the composition of a temperature change resistive glass.

Phosphates are important in optical glass, but render it quite soluble.

Glass is colored through the addition of various metallic oxides or salts. Amber glass is made by adding sulphur or carbon to the flux which produces alkali sulphides. *Blue* glass is made with cobaltic oxide (Co_2O_3) or cupric oxide (CuO); *violet* glass, by the use of manganese dioxide; *red,* by metallic copper, cuprous oxide (Cu_2O), selenium oxide, or gold; *yellowish-green,* by uranium oxide; *green,* by ferrous, chromic, or cupric oxides; *milk* or *opal* glass is made by adding cryolite, bone-ash, tin, or zinc oxides. The green color of common window or bottle glass is due to the presence of ferrous oxide in the sand; to remove this coloration, manganese dioxide is added. This serves to oxidize the ferrous to ferric oxide, which imparts a yellow tint; this color, with the violet produced by the manganese, neutralizes the other as a complementary color. A little cobalt oxide is generally used with the manganese. Arsenous oxide or nitre ($NaNO_3$) is frequently added in producing colorless glass.

Enamels.—The enameling of cooking vessels must be very thin so as not to chip off, free from poisonous substances, and of low melting-point so that the iron vessel may not lose its shape when coated. The glass used usually consists of borax 26 p., quartz 17 p., feldspar 34 p., sodium silico-fluoride 13 p., soda 4 p., saltpetre 3 p., and kaolin 3 p. These are fused together, ground to paste with water, clay added, and then, after coating, the vessel is baked at 800° for about one minute. For white opaque enamel stannic acid or zirconium oxide is added.

CHAPTER VIII

CLASSIFICATION OF THE ELEMENTS

PERIODIC SYSTEM

IT had long been noted that certain elements possess striking similarities in their physical and chemical properties. For example, the metals sodium and potassium, discovered by Davy in 1807, closely resembled one another in physical appearances, ready oxidizability, and their salts presented analogous physical and chemical properties. Also the metals lithium, rubidium, and cæsium, which were discovered later, were found to bear a striking resemblance to potassium and sodium, and when arranged in a series their atomic weights formed a progressive series: Li, 6.94; Na, 23; K, 39.1; Rb, 85.45; Cs, 132.8. Similar striking relationships were subsequently found to exist between such other elements as Cl, Br, I, and F; Ca, Sr, and Ba. The first attempt at classifying the elements was made by Doebereiner, who, in 1829, proposed arranging certain elements which showed a close similarity in their chemical and physical properties in groups or families of three, called triads; and among other striking relationships he noted that the atomic weight of the middle members of such groups was nearly the mean between those of the first and last.* Since the proposed classification could not be applied to the majority of the elements and other discrepancies arose, it was dropped.

In 1864 Newlands proposed his law of octaves, in which he pointed out if the elements be arranged in order of their increasing atomic weights, in horizontal rows of seven, one row above the other, they fall into groups, and those elements which constitute the perpendicular columns show such striking similarities that they may be classed into families. Those members which make up the rows of seven are related to one another as the several octaves in music.† Thus related are Li, Na, K, Rb, and Cs; F, Cl, Br, and I.

In 1869 Mendeléeff and Lothar Meyer independently elaborated these views and formulated what is known as the *periodic law of the elements,* —namely, *the properties of the elements are periodic functions of their*

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* For convenience, the figures have been rounded into their nearest whole numbers.

$$\begin{array}{lrlrlr}
\text{Ca} = 40. & 40. & \text{Cl} = 35.5 & 35.5 & \text{Li} = 7. & 7. \\
\text{Sr} = 87.6 & \underline{137.4} & \text{Br} = 80. & \underline{127.0} & & \underline{39.} \\
 & 2)\underline{177.4} & & 2)\underline{162.5} & \text{Na} = 23. & 2)\underline{46.} \\
\text{Ba} = 137.4 & 88.7 & \text{I} = 127. & 81.25 & \text{K} = 39 & 23.
\end{array}$$

† Upon referring to the table, it will be seen that the number of elements in the horizontal series is eight and not seven. This is due to the recent discovery of new elements which have been assigned to a new vertical column or group.

atomic weights. This means that if the atomic weight of an element is known, its position in the table and consequent physical and chemical characteristics are all fixed.

The Periodic Table (page 317) of Mendeléeff contains all of the known elements, with spaces for the undiscovered, which are systematically blocked off into spaces. To each one of these spaces are assigned certain fixed physical and chemical properties due to its position in the horizontal row or *series* and in the vertical column or *group*. Starting with the elements arranged in the columns (groups), we find under Group I*a* the elements which constitute the family of alkali metals, namely Li, Na, K, Rb, Cs; these are all monads, strongly electro-positive, forming *bases* with oxygen of the type Me'_2O. In Group II*a* are the alkaline earths, Be, Mg, Ca, Sr, Ba, which are dyads, less electro-positive than Group I*a*, and form bases of the type $M''O$ and haloid salts of the type $M''X_2$. Group III*a* are triads which yield derivatives of the type $\overset{\prime\prime\prime}{M}_2O_3$ or MX_3; all resemble aluminum closely, and as a group possess but feeble basic properties.

The tetrads C, Si, Ge, Sn, and Pb, under Group IV*a*, from their slight electro-negative characters, as well as their central position between Groups I and VII, serve as a turning point from the electro-positive groups preceding, which gradually diminish in their positive characters from left to right, and the electro-negative groups following, which, increasing in their negative properties, culminate in the *acid*-forming halogen group (VII) consisting of Fl, Cl, Br, and I. The groups (V) N, P, As, Sb, and (VI) O, S, Se, Te, as well as the halogen group (VII), all form volatile compounds with hydrogen. The metals in Group I*b* (Cu, Ag, Au) are monivalent, and form compounds isomorphous to those of the sodium group (Ia). They exhibit among themselves great similarities physically and chemically; as, for example, the insolubility of their oxides and sulphides, also their chlorides, CuCl, AgCl, and AuCl, are insoluble in water, and soluble in ammonia and thiosulphates. Corresponding similarities may be cited for Group II*b*, and so on.

Beginning with the periods, we find there is a gradual and regular change in the chemical and physical properties of the elements, showing a maximum or minimum value at either extremity or the middle of the period. For example:

	Na	Mg	Al	Si	P	S	Cl.
a. Valency, hydrogen	I	II	III	IV	III	II	I.
b. Valency, oxygen.	I	II	III	IV	V	VI	VII.
c. Specific gravity....	0.97	1.75	2.7	2.49	1.83	2	1.4 (liq.)
d. Atomic volume*...	24	14	10	11	14	16	27
e. Hydroxides.......	NaOH	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$			

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* The atomic volume (specific volume) of an element is the quotient obtained by dividing its atomic weight by its density. It expresses the number of mils (c.c.) occupied by a gram.

PERIODIC SYSTEM OF THE ELEMENTS (MENDELÉEFF).*

GROUP.		O	I		II		III		IV		V		VI		VII		VIII		
	SERIES		*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*	*a*	*b*			
Hydrogen or Halogen Types			MX		MX_2		MX_3		MX_4		MX_3		MX_2		MX				
Highest Oxides				M_2O		MO		M_2O_3		MO_2		M_2O_5		MO_3		M_2O_7	MO_3	MO_2	MO
Period I	1		H 1.008																
	2	He 3.99	Li 6.94		Gl. 9.1			B 11.0		C 12.0		N 14.01		O 16.0		F 19.0			
Period II	3	Ne 20.2	Na 23.0		Mg 24.32			Al 27.1		Si 28.3		P 31.04		S 32.07		Cl 35.46			
Period III	4	A 39.88	K 39.1		Ca 40.07		Sc 44.1		Ti 48.1		V 51.0		Cr 52		Mn 54.93		Fe 55.84	Co 58.97	Ni 58.68
	5	—		Cu 63.57		Zn 65.3		Ga 69.9		Ge 72.5		As 74.96		Se 79.2		Br 79.92			
Period IV	6	Kr 82.9	Rb 85.45		Sr 87.63		Y 89.0		Zr 90.6		Nb 93.5		Mo 96.0		—		Ru 101.7	Rh 102.9	Pd 106.7
	7	—		Ag 107.88		Cd 112.4		In 114.8		Sn 119.0		Sb 120.2		Te 127.5		I 126.92			
Period V	8	X 130.2	Cs 132.81		Ba 137.37		Rare Earth Metals		Ce 140.25		Nd 144.3		—		Sa 150.4		—	—	—
	9	—		Gd 157.3		—				—	Er 167.7			—		Tu 168.5			
Period VI	10	—	—		—				—		Ta 181.5		W 184		—		Os 190.9	Ir 193.1	Pt 195.2
	11	—		Au 197.2		Hg 200.6				Pb 207.1		Bi 208		—		—			
		Nt 222.4	—		Ra 226.4		—		Th 232.4		—		U 238.5		—	—	—	—	—

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*The figures representing the atomic weights have been rounded off for convenience.

The above comparisons may be extended to the other periods. Some doubt exists as to where hydrogen, the element with the lowest atomic weight, shall be placed. Some place it at the head of the column VII*b*, but there are better reasons for its present place in Group I. The hydrogen valencies (*a*) and the specific gravities (*c*), p. 316, form two curves which rise gradually from the extremities and unite at the middle to form a maximum [$NaCl$, $MgCl_2$, $AlCl_3$, $SiCl_4$, PCl_3, SCl_2 (WCl_2)]. The oxygen valencies (*b*) and hydroxides (*e*) form a curve which reaches a maximum with chlorine (Na_2O, MgO, Al_2O_3 SiO_2, P_2O_5, SO_3, Cl_2O_7). It should also be noted that sodium (Na_2O or $NaOH$) is more basic than magnesium (MgO or $Mg[OH]_2$), while aluminum begins to show slightly acid properties in its hydroxide [$Al(OH)_3$]. Passing from the neutral acid anhydride SiO_2 to phosphorus, we find this latter element possesses strong acid-forming properties which are exceeded by those of sulphur and still more so by chlorine. The Rare Earth Metals which occupy Group III and Periods V and VI are omitted from the table.

In classifying the various elements, it was found necessary to assign a special place (Group VIII) to certain metals which apparently did not fit in elsewhere. These are characterized by their gray color, low atomic volume, and high fusing-point (Os = 2500°, Ir = 2300°, Fe = 1505°, etc.).

The melting-point of iron is higher than cobalt, and this is higher than nickel. A similar gradation fall occurs with ruthenium, rhodium, and palladium, as also with osmium, iridium, and platinum. They all form stable, well-defined double salts with potassium cyanide; iron, ruthenium, and osmium form compounds of the type $K_4R(CN)_6$; cobalt, rhodium, and iridium form $K_3R(CN)_6$, while the elements of the last column, nickel, palladium, and platinum, form double salts of the type $K_2R(CN)_4$. All these elements form colored salts; those of cobalt are red or blue; the nickel salts are green, while the remainder, various shades of brown.

This group either permits the passage of hydrogen at red heat (especially Fe and Pt), or occludes the gas as palladium and the other platinum metals.

Through the systematic gradation afforded by this table we are able to verify the atomic weights of all elements; these may also be determined when the equivalent or combining weights of elements are known. It not only enables us to distinguish between the combining weights or multiples of these and the atomic weights, but also to correct them in case of error. Further, this table affords us information relative to the physical and chemical properties of the various compounds of all the elements, for when the position of an element is once fixed in this system, its properties naturally follow as a sequence of its relations to its surrounding elements. Based on the above facts, Mendeléeff predicted the existence of a number of elements unknown previous to 1875 and possessing an atomic weight below 75, such being indicated by means of blank spaces in the table. Two of these elements were to fit in Group III below Al, and one in Group IV below Ti. These elements were provisionally termed *eka-boron, eka-aluminum,* and *eka-silicon.* Their atomic weights were set, the physical and chemical properties of their various compounds, as well as those of the metals themselves, were minutely described. True to the prediction, gallium was discovered in 1875, scandium in 1879, and germanium in 1887. The properties of these elements and their compounds were found to closely correspond with those predicted.

Professor Ramsey, in endeavoring to find a place in the periodic table for the element argon discovered by him in 1895, was led to the belief that this element constituted a member of a new period which Mendeléeff had suggested might exist. With this in view, he instituted a search for other possible elements which, like argon, might be associated with nitrogen in the atmospheric air. This resulted in the discovery of helium, neon, krypton, and xenon, which, because of the total absence of chemical affinity, thus differing from all other elements, were assigned to a new Group (Zero) placed before Group I which consists of monads.

It should also be noted that the atomic weight of the newly discovered element radium places it directly under barium, to which it is apparently related.

PART III.

CHEMISTRY OF THE METALS.

CHAPTER I

THE ALKALI METALS

General Characters.—The alkali group of metals consists of **Potassium, Sodium, Lithium, Rubidium, Cæsium,** and the atomic group **Ammonium.** They are taken up in the order of their commercial importance, excepting ammonium.

This group of monovalent metals possesses marked alkaline (basic) properties, increasing in electro-positive intensity in the following order: Li, Na, K, Rb, Cs. Their chemical characters, as a group, are directly opposite to the electro-negative halogen group, which present similar gradations of properties. Thus iodine, which is the least electro-negative member of the halogen group, shows the highest atomic weight, while cæsium, the heaviest of the alkali group, is the most electro-positive. These metals are all of soft wax-like consistence, of low melting-points, oxidize in the air, energetically decompose water, evolving hydrogen, and form hydroxides which have a strongly alkaline reaction. Of this group, cæsium, rubidium, and potassium form a sub-group possessing properties in common; for example, their carbonates are deliquescent, while those of sodium and lithium are not, the former being efflorescent and the latter insoluble. Cæsium, rubidium, and potassium form comparatively insoluble tartrates and chloroplatinates, while the same salts of the other sub-groups are more soluble.

POTASSIUM

Symbol, K. *Atomic Weight,* 39.1. *Valence,* I.

History.—The salts of potassium have been known from the earliest times. They were probably first extracted from wood ashes under the name *alkali.* Previous to 1736 there was no distinction between the salts of potassium and sodium. Later the former became known as *potashes.*

The metal potassium was discovered in 1807 by Davy, who separated it by the electrolysis of potassium hydroxide. Its elementary character was not finally admitted until 1811, after the investigations of Gay-Lussac and Thénard.

Occurrence.—Potassium is widely distributed in nature, but never in the metallic state. In the mineral kingdom it is found as nitrate, or *nitre,* as the chloride, or *sylvite,* as the double magnesium and potassium chloride, or *carnallite,* and as the double magnesium and potassium sulphate known as *schoenite* and *kainite.* It occurs most extensively as silicate in many rocks—especially in potash-feldspar, a double silicate of aluminum and potassium, where it is found to the extent of 10 to 15 per cent. As feldspar is a constituent of granite, it will be seen that the distribution is very wide. The other abundant rocks that contain potassium are syenite, gneiss, and micaceous schist. Many mineral waters, and the waters of the ocean, contain small proportions of the potassium salts.

Potassium is found abundantly in the vegetable and animal kingdoms. It is a necessary constituent of plants, and is absorbed by them from the soil. The soil retains more potassium than it does sodium. The animal body contains a considerable proportion of potassium salts. The salts of sodium are eliminated from the system, while those of potassium are retained.

Sources.—The world's supply of potassium salts is chiefly derived from the carnallite and sylvite of the Stassfurt deposits * near Magdeburg, Germany. Formerly the carbonate was the most important salt, being derived from wood ashes by leaching, evaporating and igniting. As a by-product, some potassium carbonate is obtained from the wash-water in the scouring of wool, 25 per cent. of the solid matter consisting of potash. In the manufacture of alcohol from cane molasses, the residue remaining in the stills contains about 5 per cent. of solids; these average about 10 per cent. of potassium carbonate. Kelp obtained along the Pacific coast, after drying, will yield about 15 per cent. of potassium carbonate. Large deposits of *alunite* [$K(AlO)_3(SO_4)_2.3H_2O$] in Utah, Nevada, and Colorado are being worked for potassium sulphate. In addition to a number of small brine lakes in Wyoming which average from 10 to 15 per cent. of total solids, of which one-fourth is potash, Searles Lake, in San Bernardino County, California, is a prolific natural source. This brine contains 30 per cent. of the chlorides, sulphates, carbonates and borates of potassium and sodium, of which 5 per cent. is potassium chloride.

Isolation.—Potassium is chiefly prepared by electrolysis from potassium chloride or hydroxide analogous to the methods described under Sodium.

A recent method consists in distilling a mixture of potassium fluoride or fluosilicate with aluminum.

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* The more important Stassfurt salts are:
Anhydrite, $CaSO_4$.
Kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$.
Carnallite, $KCl.MgCl_2.6H_2O$.
Kieserite, $MgSO_4.H_2O$.
Polyhalite, $K_2SO_4.MgSO_4.2CaSO_4.2H_2O$.
Rock Salt, NaCl.
Sylvite, KCl.
Tachydrite, $CaCl_2.2MgCl_2.12H_2O$.
Astrakanite, $MgSO_4.Na_2SO_4.4H_2O$.
Schoenite, $K_2SO_4.MgSO_4.6H_2O$.

Properties.—On account of the rapidity with which potassium combines with oxygen, it is preserved under petroleum or other hydrocarbon, to protect it from the air. Potassium appears in commerce chiefly in the form of small globular pieces of the size of cherries.

Potassium is of a waxy consistence, and when freshly cut exhibits the true appearance of the metal, which is silver-white in color and of bright metallic luster. This freshly cut surface tarnishes immediately on exposure to the air, leaving a thin, white incrustation of potassium oxide. Next to lithium, it is the lightest metal known, having a specific gravity of 0.875 (13°). On the application of heat it melts at 62.5°, and boils at 762° C. in dry air or an atmosphere of some inert gas, like nitrogen, yielding a greenish vapor.

Potassium has a strong affinity for oxygen, but when perfectly dry little or no action takes place. If air be absolutely free from moisture, it will not combine with the metal at ordinary temperatures. When thrown on water, the latter is immediately decomposed and sufficient heat is liberated to fuse the metal on the surface of the water and ignite the liberated hydrogen, which with some potassium vapor bursts into a violet-colored flame.

Potassium combines with the halogens with great energy; a small fragment dropped on bromine causes a violent explosion. Since potassium on dissociating into ions liberates an immense amount of kinetic energy, it is capable of abstracting chlorine from the chlorides of boron and silicon, hence can be used in the isolation of these elements.

POTASSIUM AND HYDROGEN

Potassium Hydride, KH.—When potassium is heated in an atmosphere of hydrogen to 300°, a silver-white, brittle mass results, which begins to decompose at 410°, or, under reduced pressure, dissociation begins at 200°. Potassium hydride inflames spontaneously on contact with air.

POTASSIUM AND THE HALOGENS

The halogen compounds of potassium are:

Potassium Fluoride,	KF.
Potassium Chloride,	KCl.
Potassium Bromide,	KBr.
Potassium Iodide,	KI.

Potassium Fluoride, KF, is prepared by neutralizing aqueous hydrofluoric acid, in a platinum dish, with potassium carbonate or hydroxide. On concentrating the solution the salt crystallizes out in cubes. When formed at ordinary temperatures these crystals have the formula $KF.2H_2O$, but at or above 35° they form without water of crystallization.

The salt is deliquescent, and its solution attacks glass. Hydrofluoric acid has the property of forming an acid double haloid, which is characteristic of potassium, KF.2HF. The other halogens do not exhibit this property of forming acid double salts.

Potassium Chloride, KCl.—This salt was first used in medicine by Sylvius de le Boé, under the name of *sal febrifugum* or *sal digestivum.*

It occurs in sea-water, in many mineral springs, and in the Stassfurt deposits as *carnallite,* $KCl.MgCl_2.6H_2O$, and *sylvite,* KCl.

Preparation.—Since potassium chloride occurs so abundantly in nature, it is rarely prepared on the small scale. It can, however, readily be made by neutralizing hydrochloric acid with potassium carbonate, according to the following reaction:

$$K_2CO_3 + 2HCl = 2KCl + CO_2 + H_2O.$$

On a large scale carnallite is mixed with three-fourths its weight of water and the mixture treated for some time with live steam, whereby the carnallite is resolved into its constituent salts, magnesium chloride and potassium chloride. The hot solution is allowed to cool, and the less soluble potassium chloride crystallizes. It is further purified through removal of the more soluble magnesium salt by washing with a little cold water and recrystallizing.

Properties.—Potassium chloride occurs in permanent, white, cubical crystals; soluble in 3 parts of cold water, in about 2 parts of hot water, and insoluble in alcohol. On the application of strong heat the salt melts, and at a red heat it volatilizes.

Uses.—Potassium chloride is used for the preparation of a number of other potassium salts, notably the chlorate and carbonate. The impure salt is used largely as a fertilizer.

Potassium Bromide, KBr. **Potassii Bromidum,** U.S.P.—This salt is prepared by one of two methods (also compare page 178).

(1) One part of iron wire is covered with 10 parts of water; 2 parts of bromine are slowly added, in small portions at a time, allowing the combination with the iron to take place after each addition. This part of the operation should be conducted in a well-ventilated fume chamber, in order that the operator may avoid inhaling the irritating fumes that are evolved. In the reaction which takes place ferrous bromide is formed, as follows:

$$Fe + Br_2 = FeBr_2.$$

The resulting solution is of a green color, and to this sufficient bromine is added to oxidize the ferrous bromide to a ferroso-ferric bromide:

$$3FeBr_2 + Br_2 = (2FeBr_3 + FeBr_2) = Fe_3Br_8.$$

To this solution is added a sufficient quantity of potassium carbonate and the whole boiled to facilitate the precipitation of the iron as a hydrated ferroso-ferric oxide:

$$Fe_3Br_8 + 4K_2CO_3 + 4H_2O = 8KBr + 4CO_2 + Fe_3(OH)_8.$$
$$Fe_3(OH)_8 = Fe_2O_3.3H_2O + FeO.H_2O.$$

The whole is then filtered and the precipitate washed free of potassium bromide by means of hot water. The clear filtrate, containing the potassium bromide, is evaporated to crystallization.

(2) To a convenient quantity of potassium hydroxide solution bromine is added, in small portions at a time, until, after agitation,

the orange color of the bromine remains permanent, indicating a slight excess of that element. This reaction takes place:

$$\underset{\text{Potassium Hydroxide.}}{6KOH} + \underset{\text{Bromine.}}{3Br_2} = \underset{\text{Potassium Bromide.}}{5KBr} + \underset{\text{Potassium Bromate.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O.}$$

The solution is evaporated to dryness, and a quantity of wood charcoal stirred in amounting to one-tenth of the amount of bromine. The mixture is then dried and heated to low redness in an iron vessel, when the reduction of the potassium bromate is accomplished as follows:

$$KBrO_3 + 3C = KBr + 3CO.$$

The cooled mass is treated with water, the solution filtered and evaporated to crystallization.

Properties.—When perfectly pure, potassium bromide occurs in colorless, translucent, cubical crystals, permanent in the air, odorless, with a sharp saline taste and a neutral reaction. The commercial salt usually occurs in white, opaque crystals with a slightly alkaline reaction. The salt is soluble in 1.5 parts of water at 25°, and in less than one part of boiling water. It is soluble in 250 parts of cold and in 21 parts of boiling alcohol; also soluble in 4.6 parts of glycerin. When heated the salt decrepitates somewhat, and at 700° it fuses without decomposition. At a bright red heat it volatilizes, imparting to the flame a violet color. Potassium bromide is identified by the usual potassium tests and the bromine by adding to 10 mils of its aqueous solution (1 in 20) a few drops of chloroform and then, a little at a time, chlorine water until the solution smells distinctly of chlorine; an orange color is imparted to the chloroform on agitation. If a violet color be produced iodide is indicated. If silver nitrate, T.S., is added to a solution of potassium bromide a yellowish-white precipitate of silver bromide is formed which is insoluble in nitric acid or in a moderate excess of ammonia water. An admixture of potassium bromate is indicated when an immediate yellow color appears on the addition of diluted sulphuric acid. This test depends on the following reaction:

$$5KBr + KBrO_3 + 6H_2SO_4 = 6KHSO_4 + 3H_2O + 3Br_2.$$

Potassium Iodide, KI. **Potassii Iodidum**, U.S.P.—This salt (compare page 185) is prepared by mixing in a capacious porcelain dish 1 part of iron wire with 8 parts of water, and adding in small portions at a time 4 parts of iodine, $Fe + I_2 = FeI_2$. The pale-green solution is filtered from the undissolved iron, and treated with one part of iodine, forming ferroso-ferric iodide:

$$3FeI_2 + I_2 = Fe_3I_8.(FeI_2.2FeI_3).$$

To this solution are added 2.2 parts or a sufficient quantity of pure potassium carbonate, previously dissolved in 10 parts of water. The following reaction takes place:

$$\underset{\text{Ferroso-Ferric Iodide.}}{Fe_3I_8} + \underset{\text{Potassium Carbonate.}}{4K_2CO_3} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Potassium Iodide.}}{8KI} + \underset{\text{Carbon Dioxide.}}{4CO_2} + \underset{\text{Hydrated Ferroso-Ferric Oxide.}}{Fe_3(OH)_8}.$$

If necessary, a small additional quantity of potassium carbonate may be added until the solution is faintly alkaline. The whole mixture is then boiled for a few minutes, which causes the precipitate to become more dense; it is then filtered and washed. The filtrate and washings are concentrated to a small volume and set aside for the potassium iodide to crystallize.

Another method consists in adding to a convenient quantity of potassium hydroxide solution sufficient powdered iodine in small portions at a time to produce a permanent yellowish color. Potassium iodide and iodate are formed as follows:

$$\underset{\text{Potassium Hydroxide.}}{6KOH} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Potassium Iodide.}}{5KI} + \underset{\text{Potassium Iodate.}}{KIO_3} + \underset{\text{Water.}}{3H_2O}.$$

The solution is evaporated to a syrupy consistence, and a quantity of wood charcoal, equal to one-tenth the amount of iodine employed, is stirred in. The mixture is then dried and heated to low redness. The iodide is unchanged by this treatment, while the iodate is converted into iodide according to the following reaction:

$$KIO_3 + 3C = KI + 3CO.$$

The residue, after cooling, is treated with water, filtered, and the filtrate, after concentration, is set aside to crystallize.

Some potassium iodide is prepared from the "mother liquors" obtained in the preparation of sodium nitrate from Chili saltpetre, iodine being recovered as cuprous iodide, CuI. This is converted into hydrogen iodide as follows:

$$2CuI + H_2S = Cu_2S + 2HI.$$

The hydrogen iodide, after removal of cuprous sulphide by filtration, is neutralized with potassium carbonate.

Properties.—Potassium iodide is ordinarily found in large, white, opaque crystals, having been crystallized from a faintly alkaline solution. When the crystals are formed in neutral solutions, they are colorless and nearly transparent, but soon become discolored on storing. The salt has a faint odor, and a sharp, saline taste with a faint, bitterish after-taste. The crystals are permanent in dry air, but slightly deliquescent in moist air.

The salt is soluble in 0.7 part water at 25°, and in 0.5 part of boiling water, in 22 parts of alcohol, and in 8 parts boiling alcohol; it is also soluble in 2 parts of glycerin.

When heated the salt decrepitates, and at a low red heat it fuses; at a bright red heat it volatilizes without decomposition. The aqueous solution should be neutral or slightly alkaline to litmus paper. If the salt does not contain a sufficient excess of alkali it is liable to turn a faint yellowish color when exposed to light and air, on account of the liberation of traces of iodine.

The usual tests for potassium serve to identify the salt as containing that base, and the iodine is indicated by adding a few drops of chloroform to the aqueous solution, and then chlorine water in small portions at a time with agitation, when a violet color will be imparted to the chloroform; excess of chlorine water should be avoided, since decolorization is liable to take place, due to the formation of iodine chlorides and iodic acid; iodine is also liberated from this salt by fuming nitric acid, by concentrated sulphuric acid, and by ferric chloride. Silver nitrate produces a yellow precipitate of silver iodide when added to a solution of potassium iodide. This precipitate is insoluble in nitric acid and in ammonium hydroxide.

Uses.—Potassium iodide is extensively used in medicine.

POTASSIUM AND OXYGEN

Potassium Oxide, K_2O, is obtained, together with some peroxide, by heating the metal in dry air. When this mixture is strongly heated, it evolves oxygen and the monoxide remains. It is also prepared by heating a mixture of the metal and potassium nitrate:

$$KNO_3 + 5K = 3K_2O + N.$$

The oxide, when pure, is a white powder or brittle mass; it fuses at a high temperature. Its affinity for water is so intense that when moistened with that liquid it becomes red-hot. Potassium hydroxide is the result of this combination with water.

Potassium Peroxide, K_2O_2, is obtained when the metal is heated with an excess of oxygen. It is a yellow powder which gives up oxygen at white heat. On treatment with water, it dissolves, with the formation of potassium hydroxide, hydrogen peroxide, and oxygen. Great care should be exercised when adding to water, owing to the intense heated generated.

Potassium Hydroxide, KOH. **Potassii Hydroxidum**, U.S.P.—This compound, which is also incorrectly termed potassium hydrate, also caustic potash, appears to have been first observed by Geber in the eighth century, and was considered to be an element until Davy demonstrated its compound nature in 1807.

Preparation.—Potassium hydroxide may be prepared by adding calcium hydroxide (slaked lime), made into a thin paste with water, to a boiling dilute solution of potassium carbonate. Water must be added from time to time during the heating, for if the solution becomes too concentrated, a reverse reaction sets in. The operation is known to be complete when a portion of the clear solution gives no effervescence on supersaturating with an acid. The reaction which takes place in the formation of the hydroxide is as follows:

$$\underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Calcium}\\\text{Hydroxide.}}}{Ca(OH)_2} = \underset{\substack{\text{Potassium}\\\text{Hydroxide.}}}{2KOH} + \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{CaCO_3}.$$

The clear liquid is removed from the sediment by a siphon, and evaporated in an iron dish to a specific gravity of 1.16, when it begins to attack the iron, and further concentration must be conducted in a silver vessel. When the liquid has assumed an oily consistence and a drop removed on a glass rod solidifies on cooling, it is poured into silver moulds if the stick form is desired. Prepared by this process, potassium hydroxide is quite impure, containing sulphates, chlorides, alumina, calcium, iron, and silica.

Potassium hydroxide is more generally prepared from potassium chloride electrolytically analogous to the method described under sodium hydroxide (page 343). Electrolytic caustic potash is practically free from foreign salts and is generally supplied when "potassium hydroxide by alcohol" is called for. Formerly this latter compound was prepared from the "lime process" alkali by dissolving in alcohol, decanting the solution from the insoluble sulphate, chloride, alumina, and silica, and distilling off the alcohol, subsequently fusing and moulding into stick form. A still purer potassium hydroxide is sometimes prepared by adding metallic potassium to water.

Properties.—Potassium hydroxide, when pure, occurs in dry white or nearly white flakes, fused masses or sticks, hard and brittle, with a crystalline fracture. It is odorless, and has a sharp, caustic taste and strong alkaline reaction. It is soluble in about 0.9 part of water at 25°, and in 3 parts of alcohol; it is very soluble in boiling water and in boiling alcohol. When heated to a temperature of 530° it fuses to a clear oily liquid, and at a bright red heat it is volatilized unchanged. It absorbs carbon dioxide and water from the air. When dissolved in water heat is generated. Potassium hydroxide possesses a very caustic action on the skin and readily saponifies fats, forming soap. Potassium hydroxide readily dissociates in aqueous solution into $K^{\cdot}$ and OH' ions, which readily interchange when mixed with ionizable solutions of salts of the heavy metals, with precipitation of an insoluble hydroxide of the metal. When the concentrated aqueous solution is cooled, a compound containing two molecules of water, $KOH.2H_2O$, crystallizes out in tabular or octahedral crystals. The solution in alcohol (if not free from aldehydes) rapidly assumes a dark-yellow to brown color.

The Liquor Potassii Hydroxidi of the Pharmacopœia contains not less than 4.5 per cent. and not more than 5.5 per cent. of the hydroxide and has a specific gravity of about 1.046. The official process directs this to be made by solution of 60 gm. of KOH in water to make 1000 gm. This solution readily absorbs CO_2 from the air, hence should be kept in well-closed containers.

The commercial caustic potash usually contains from 80 to 90 per cent. of absolute potassium hydroxide and 10 to 20 per cent. of water. The "stick" form contains the largest percentage of water.

OXYGEN SALTS OF POTASSIUM AND THE HALOGENS

Potassium Hypochlorite, $KClO$, is known only in solution. It is the active ingredient in "Eau de Javelle," which is prepared by passing chlorine into a cold dilute solution of potassium carbonate or hydroxide. The result is a solution of potassium hypochlorite and chloride. This solution was formerly much used for bleaching purposes, but has been replaced by sodium hypochlorite. When the solution is boiled or evaporated, potassium chlorate and chloride are obtained:

$$3KClO = 2KCl + KClO_3.$$

Potassium Chlorate, $KClO_3$. **Potassii Chloras, U.S.P.**—This salt was discovered and first prepared by Berthollet in 1786.

Preparation.—In the preparation of hypochlorites a limited amount of chlorine is passed into a *cold* solution of the alkali hydroxide, but if an exess of chlorine be passed into a hot solution of the alkali, chlorates are formed.

$$2KOH + Cl_2 = KCl + KClO + H_2O.$$
$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O.$$

Owing to the formation at the same time of a considerable quantity of potassium chloride, this is an expensive process, hence on a commercial scale other methods have been introduced.

The commercial production of potassium chlorate was formerly accomplished by treating milk of lime with an excess of chlorine in a vessel in which the mixture was constantly agitated, the solution then boiled to decompose the hypochlorite into calcium chlorate and chloride, as follows:

$$\underset{\text{Calcium Hydroxide.}}{6Ca(OH)_2} + \underset{\text{Chlorine.}}{6Cl_2} = \underset{\text{Calcium Chloride.}}{5CaCl_2} + \underset{\text{Calcium Chlorate.}}{Ca(ClO_3)_2} + \underset{\text{Water.}}{6H_2O.}$$

After allowing the mixture to settle, the clear liquid was drawn off and evaporated with potassium chloride to a specific gravity of 1.28, when the following reaction took place between the calcium chlorate and the potassium chloride:

$$Ca(ClO_3)_2 + 2KCl = 2KClO_3 + CaCl_2.$$

The very soluble calcium chloride remained in solution while the less soluble potassium chlorate crystallized as the solution cooled.

Chlorates are now prepared by the electrolysis of hot solutions of potassium or sodium chloride. Commercially it is preferred to first prepare the sodium chlorate, which is afterwards converted into potassium chlorate by interaction with potassium chloride. In the preparation of sodium hydroxide by the Griesheim process (page 344), the electrolysis is continued instead of stopping to remove the hydroxide formed whereby the oxygen liberated at the anode oxidizes the NaCl to $NaClO_3$. This latter salt is very soluble, hence can be handled in concentrated solutions, while the potassium chlorate, owing to its slight solubility, retards the electrolytic process by constant precipitation as it accumulates. If potassium chloride be added to the hot solution of sodium chlorate, interaction takes place with separation of the less soluble potassium chlorate, while the more soluble chloride remains in solution. When the anodes and cathodes are placed opposite each other in a solution of potassium chloride, but without being separated by a porous diaphragm, the electric current gives rise to the formation of potassium hypochlorite. If the solution of this compound be boiled, or if the electrolysis be carried out with warm solutions, potassium chlorate is obtained:

$$\underset{\text{Potassium Hypochlorite.}}{3KClO} = \underset{\text{Potassium Chlorate.}}{KClO_3} + \underset{\text{Potassium Chloride}}{2KCl.}$$

Properties.—Potassium chlorate occurs in colorless, lustrous, monoclinic prisms or plates, or as a white granular powder, odorless, and having a cooling, characteristic taste. Permanent in the air. Soluble in 11.5 parts of water at 25° and in 1.8 parts of boiling water; insoluble in absolute alcohol and but slightly soluble in diluted alcohol.

When heated to 360° the salt fuses and commences to decompose into oxygen, potassium chloride, and perchlorate. At about 400° the perchlorate is decomposed, with further evolution of oxygen, potassium chloride only remaining. Analytically, the chlorates are distinguished from the chorides by not giving a precipitate with silver nitrate. For further properties of the chlorates see page 209.

Uses.—One of the principal uses of potassium chlorate is in the preparation of oxygen on a small scale. It is also largely employed in chemical operations as an oxidizing agent. In the manufacture of colored fires, matches and explosives this salt plays an important part. It has considerable use in medicine, especially in diseases of the throat.

Potassium chlorate should never be ground or rubbed with organic substances or with sulphur, as violent explosions are almost sure to occur. In case it is necessary to make such mixtures, the ingredients should be powdered separately and then carefully mixed without friction.

Mixtures of potassium chlorate and ammonium chloride have exploded violently after standing for some time.

Colored fires are made by taking 25 to 50 parts of potassium chlorate and 25 parts of powdered sugar or shellac as a base; to this mixture are added 25 parts of strontium nitrate for red, 25 parts of barium nitrate for green, 10 parts of copper nitrate for blue, and 10 parts of sodium nitrate or chloride for yellow. Sulphur may be used in place of sugar or shellac, but the resulting powder is more liable to spontaneous decomposition with combustion or explosion.

Potassium Perchlorate, $KClO_4$, is prepared by heating potassium chlorate to 360°, when it is decomposed into perchlorate, chloride, and oxygen; the oxygen escapes, and the two salts remain behind as a pasty mass. This is cooled, powdered, and treated with cold water, which removes the potassium chloride. The undissolved residue is digested with warm hydrochloric acid to decompose any remaining chlorate into chloride, which is then washed out with cold water. The residue consists of nearly pure perchlorate. This salt may be produced electrolytically from a cold concentrated solution of potassium chlorate.

The perchlorate is one of the most insoluble of potassium salts, requiring 65 parts of cold and 5.04 parts of boiling water to dissolve it. It is decomposed at 400° into KCl and O_4. (See Perchloric Acid, page 211.)

Potassium Bromate, $KBrO_3$.—When bromine is added to a moderately concentrated solution of potassium hydroxide until it attains a yellow color, the following reaction takes place:

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O.$$

From the solution, if sufficiently concentrated by evaporation, potassium bromate separates as a granular powder, owing to its comparative slight solubility. The bromide may be recovered from the mother liquor upon further concentration. Potassium bromate may also be prepared by saturating an alkaline solution of the bromide with chlorine,

$$KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O,$$

or by heating the bromide with potassium chlorate above 300°, $KBr + KClO_3 = KCl + KBrO_3$. The bromates are readily separated by crystallization. Potassium bromate is soluble in about 15 parts of water at 25° and 2 parts at 100°. (See page 211.)

Potassium Iodate, KIO_3, may be extemporaneously prepared by adding a mixture of 3 grams of powd. iodine and 5 grams of potassium chlorate to 15 mils of nitric acid and digesting until decolorized. Dry and heat to about 100°.

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

This salt when mixed with starch paste gives a blue color with SO_2. (See HIO_3, page 213.)

Iodates of the alkali metals or the alkaline earths may be prepared by heating the iodide with potassium chlorate on a sand-bath at above 300°, when oxygen is given off. This oxidizes the iodide to iodate: $BaI_2 + 2KClO_3 = Ba(IO_3)_2 + 2KCl$. (See Iodic Acid, page 211.)

Potassium Periodate, KIO_4, is prepared by passing chlorine into a concentrated solution of potassium iodate and hydroxide. The salt separates in small rhombic crystals, and requires 300 parts of cold water for solution. Between 250° and 300° it decomposes into potassium iodate and oxygen, and at a higher temperature it parts with all of its oxygen, leaving a residue of potassium iodide.

POTASSIUM AND SULPHUR

Potassium Monosulphide, K_2S Potassium Hydrosulphide, KSH

Potassium Monosulphide, K_2S, is prepared by heating to redness in a well-covered vessel an intimate mixture of 7 parts of potassium sulphate and 2 parts of finely powdered charcoal, when the following reaction takes place:

$$K_2SO_4 + 4C = K_2S + 4CO.$$

The same compound is obtained when one volume of potassium hydroxide solution is saturated with hydrogen sulphide and then mixed with an equal volume of the same strength of potassium hydroxide solution:

$$KOH + H_2S = KSH + H_2O.$$
$$KSH + KOH = K_2S + H_2O.$$

Properties.—When potassium monosulphide is treated with a small proportion of water, it dissolves unchanged, and will crystallize from its solution with 5 molecules of water. When, however, it is treated with a larger quantity of water, it decomposes into the hydrosulphide and hydroxide, as follows:

$$K_2S + H_2O = KSH + KOH.$$

On standing, this solution absorbs oxygen from the air, being converted into thiosulphate and hydroxide:

$$2K_2S + H_2O + O = K_2S_2O_3 + 2KOH.$$

On the application of heat potassium sulphide melts to a black liquid, which cools to a reddish, crystalline mass.

Potassium Hydrosulphide, KSH, is formed when hydrogen sulphide is passed into a solution of potassium hydroxide; by evaporating this solution in a vacuum, crystals are formed containing 1½ molecules of water.

If sulphur be heated with a solution of potassium sulphide, large quantities of the former are dissolved; such solutions contain what might be termed *polysulphides,* potassium salts of the ions S_4'' and S_5''. If hydrochloric acid is added to such a solution, " milk of sulphur " precipitates.

Potassa Sulphurata, U.S.P. (Hepar Sulphur or Liver of Sulphur), is a mixture of potassium polysulphides and thiosulphate, containing an amount of sulphides corresponding to not less than 12.8 per cent. of sulphur. It is prepared by fusing together sulphur 2 p. and potassium carbonate 1 p. When fresh it forms irregular pieces of a liver-brown color, which, by exposure to the air, gradually absorb moisture, oxygen, and carbon dioxide, and change to a greenish-yellow and finally to a gray mass containing potassium carbonate, thiosulphate, and sulphate.

OXYGEN SALTS OF POTASSIUM AND SULPHUR

Potassium Sulphite, $K_2SO_3.2H_2O$.—The salt of this formula is the normal potassium sulphite. It is prepared by passing sulphur dioxide into a solution of potassium carbonate until the mixture reacts strongly acid:

$$K_2CO_3 + 2SO_2 + H_2O = 2KHSO_3 + CO_2.$$

To this solution of acid potassium sulphite potassium carbonate is added to a neutral or faintly alkaline reaction. The slight excess of sulphur dioxide forms the acid sulphite, which, on the addition of the carbonate, is converted into neutral or normal sulphite, as follows:

$$2KHSO_3 + K_2CO_3 = 2K_2SO_3 + CO_2 + H_2O.$$

The solution is concentrated at low temperature for crystallization.

Potassium sulphite is somewhat deliquescent, odorless, and has a bitter, saline, sulphurous taste. It has a neutral or feebly alkaline reaction. It is more soluble in cold than in hot water, requiring 4 parts of water at 15° and 5 parts of boiling water for solution; alcohol has a very slight solvent action. The sulphites are gradually oxidized to the sulphates on standing.

Acid Potassium Sulphite, or *Bisulphite,* $KHSO_3$, is prepared from potassium carbonate and sulphur dioxide, according to the equation given under the normal sulphite. The salt is very soluble in water, has a neutral or slightly acid reaction, and emits the odor of sulphur dioxide. On exposure to air it gradually changes to sulphate.

Potassium Metasulphite, or Pyrosulphite, $K_2S_2O_5$, is formed when sulphur dioxide is passed into a hot saturated solution of potassium carbonate until effervescence ceases and the liquid assumes a greenish tinge. On cooling, the salt separates in granular crystals. It is employed in photography in place of the other sulphites, owing to its greater stability. When dissolved in water it dissociates into HSO_3' and $\dot{K}$ ions.

Potassium Sulphate, K_2SO_4.—This salt occurs in many mineral waters, in sea-water, and in the ashes of many plants. The chief locality of its occurrence is in the Stassfurt salt-beds. *Kainite* is a double sulphate of potassium and magnesium with magnesium chloride, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$; *Schoenite* is a double sulphate of potassium and magnesium, $K_2SO_4.2MgSO_4.6H_2O$. Since the potassium sulphate is much less soluble than magnesium chloride or sulphate, it is readily separated on concentrating the aqueous solution of these salts.

It may be obtained as a by-product in the manufacture of nitric acid from potassium nitrate and hydrochloric acid from sodium chloride.

Properties.—Potassium sulphate occurs in "hard, colorless, transparent crystals having a somewhat bitter, saline taste. Permanent in the air. Soluble in about 9 parts of water at 25°, and in 4 parts of boiling water; insoluble in alcohol." It is employed as a reagent in the U.S.P.

Potassium sulphate has some uses in medicine, and it is extensively employed in the preparation of potash alum and potassium carbonate.

Acid Potassium Sulphate (Potassium Bisulphate), $KHSO_4$.—Its usual source and method of preparation is from the residue of the manufacture of nitric acid from potassium nitrate when an excess of sulphuric acid has been used.

When the salt is separated from an acid solution, it is obtained in the form of tabular rhombic crystals, which are very soluble in water. From dilute solutions of the acid sulphate the neutral sulphate crystallizes; following this, as the solution is concentrated, there separates a salt having the composition $K_2SO_4KHSO_4$, and then the acid salt crystallizes. There are present in this solution the ions $\dot{K}$, $\dot{H}$, SO_4'', with some undissociated HSO_4. Since K_2SO_4 is less soluble, it will be the first to separate.

Potassium bisulphate is used in the analysis of silicates, owing to its solvent and decomposing effect on silicates.

Acid potassium sulphate fuses at 200°, and above that temperature is converted into *potassium pyrosulphate,* $K_2S_2O_7$. This salt at a temperature of about 600° decomposes into neutral sulphate and sulphur trioxide.

Potassium pyrosulphate crystallizes in long needles, and when brought in contact with water evolves much heat and is converted into the acid sulphate.

Acid Potassium Disulphate, KHS_2O_7, is formed when the pyrosulphate is dissolved in fuming sulphuric acid, and from this liquid it is deposited in transparent prismatic crystals.

OXYGEN SALTS OF POTASSIUM AND NITROGEN

Potassium Nitrate (Saltpetre, Nitre), KNO_3. **Potassii Nitras,** U.S.P. —Saltpetre was known in the eighth century. It is very widely distributed in nature, mixed more or less with other salts, chiefly calcium nitrate. It is found most abundantly in the warm climates of India, Egypt, and South America. Formerly most of the salt came from India, where it was prepared from the leachings of the nitre heaps. These consisted of heaps of manure, animal and vegetable refuse mixed with limestone over which stable drainings with urine were poured. After a time, nitrates formed on the surface, which were collected, leached, and treated with potassium carbonate, which precipitated the calcium, and the clear liquid was separated and concentrated for crystallization. The formation of nitrates under these conditions is due to the influence of micro-nitrifying organisms (see page 240).

The chief present source of this salt is from Chile saltpetre (sodium nitrate), prepared by interaction with potassium chloride, as follows:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The hot saturated solutions of these two salts (containing the ions $\dot{K}$, $\dot{Na}$, $\acute{Cl}$, and $N\acute{O}_3$) are mixed and concentrated until the solution reaches a specific gravity of 1.5, when those ions which form the less soluble sodium chloride separate, while the solution is still hot. The liquid is then drawn off and allowed to cool, when the potassium nitrate separates as a granular crystalline powder. This is removed and washed with a small quantity of cold water, which removes the last of the sodium chloride. The salt is then purified by recrystallization.

In order more fully to explain this method of preparing the salt, the following solubilities are given:

	15°	100°
100 parts of water dissolve KNO_3	26 parts.	247 parts.
100 parts of water dissolve $NaNO_3$	86.3 parts.	168.2 parts.
100 parts of water dissolve KCl	33.4 parts.	56.6 parts.
100 parts of water dissolve NaCl	36 parts.	39.2 parts.

Properties.—Potassium nitrate occurs as "colorless, transparent, six-sided, rhombic prisms, or as a white crystalline powder, odorless, and having a cooling, saline, and pungent taste. Slightly hygroscopic in moist air. Soluble in 2.8 parts of water at 25°, and in 0.5 part of boiling water; very sparingly soluble in alcohol. When heated to 353° the salt melts. When fused and moulded into balls it is commercially known as *sal prunelle.* At a higher temperature it is decomposed, giving off oxygen at first, and then some of its nitrogen, leaving a residue of potassium nitrate, nitrite, and oxide. Thrown on red-hot coals, the salt deflagrates. The aqueous solution is neutral to litmus paper."

Uses.—Potassium nitrate is used in medicine and to a limited extent as a preservative for meat. The chief use of potassium nitrate is in the manufacture of gunpowder. The average composition of this is as follows:

Potassium nitrate	74 to 77 parts.
Charcoal	12 to 16 parts.
Sulphur	9 to 12.5 parts.

The quantitative composition of gunpowder varies according to the purposes for which it is intended. It has been displaced in warfare by the "smokeless powders."

Potassium Nitrite, KNO_2.—This may be prepared by reducing 1 part of the nitrate through fusion with 2 parts of lead (or Fe or Cu): $KNO_3 + Pb = KNO_2 + PbO$. The insoluble metal oxide is removed by solution of the flux in water and filtration.

Industrially, potassium nitrite may be prepared by passing a current of sulphur dioxide through a hot mixture of CaO and concentrated potassium nitrate solution: $KNO_3 + CaO + SO_2 = CaSO_4 + KNO_2$. The insoluble calcium sulphate is removed by filtration, while the filtrate yields on evaporation a white crystalline mass of nitrite. Potassium nitrite is deliquescent in moist air, very soluble in water, and insoluble in alcohol. It is also sold in fused stick form.

OXYGEN SALTS OF POTASSIUM AND PHOSPHORUS

There are three potassium salts of orthophosphoric acid.

Tripotassium Orthophosphate, K_3PO_4, is prepared by heating to redness phosphoric acid and potassium carbonate or hydroxide. It is readily soluble in water, and separates in small, colorless, acicular crystals.

Dipotassium Orthophosphate, K_2HPO_4.—This salt is formed when orthophosphoric acid is neutralized with potassium carbonate. The resulting compound is difficult to crystallize.

Monopotassium Orthophosphate, KH_2PO_4, is produced when the above dipotassium compound is heated with an excess of orthophosphoric acid. It usually separates in large, colorless, rhombic crystals.

There are two potassium salts of pyrophosphoric acid, according as two or four atoms of hydrogen are replaced by the base.

Potassium Pyrophosphate, $K_4P_2O_7$, is obtained by neutralizing pyrophosphoric acid with potassium hydroxide, or, perhaps more conveniently, by heating the dipotassium orthophosphate to redness. It is a deliquescent salt, which separates from solution in fibrous crystals containing three molecules of water.

Dipotassium Pyrophosphate, $K_2H_2P_2O_7$.—This is the acid salt, and is prepared by dissolving the neutral salt in acetic acid and precipitating with alcohol.

Potassium Metaphosphate, KPO_3, is prepared by heating the monopotassium orthophosphate to redness. As thus obtained it is in translucent masses, nearly insoluble in water, but readily soluble in dilute acids. Although monobasic, metaphosphoric acid possesses the property of polymerization, so that there are at least five compounds of potassium with the acid, having the following formulas: KPO_3, metaphosphate; $K_2P_2O_6$, dimetaphosphate; $K_3P_3O_9$, trimetaphosphate, etc.

Potassium Hypophosphite, KH_2PO_2. **Potassii Hypophosphis,** U.S.P.—This salt is prepared by interaction between solutions of calcium or barium hypophosphite and potassium carbonate, as follows:

$$\underset{\substack{\text{Calcium}\\ \text{Hypophosphite.}}}{Ca(H_2PO_2)_2} + \underset{\substack{\text{Potassium}\\ \text{Carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\ \text{Hypophosphite}}}{2KH_2PO_2} + \underset{\substack{\text{Calcium}\\ \text{Carbonate.}}}{CaCO_3}.$$

The details of the process are to add a solution of 5.75 parts of potassium carbonate in 8 parts of water, to 6 parts of calcium hypophosphite in 64 parts of water, allow to stand until the precipitate settles, filter, and evaporate the filtrate at a temperature not exceeding 100° until granulation is effected. The product may be purified by dissolving in diluted alcohol, filtering, evaporating to a syrupy consistence, and crystallizing.

Potassium hypophosphite occurs in "white, opaque, hexagonal plates, or crystalline masses, or as a granular powder, odorless, and having a pungent, saline taste; very deliquescent. Soluble at 25° in 0.6 part of water and in 9 parts of alcohol, in 0.4 part of boiling water and in 5 parts of boiling alcohol; insoluble in ether. When heated in a dry test-tube, the salt at first loses moisture, and then evolves spontaneously inflammable hydrogen phosphide gas, which burns with a bright yellow flame."

This salt should not be triturated or heated with nitrates, chlorates, permanganates, or other oxidizing agents, as explosion is liable to occur.

OXYGEN SALTS OF POTASSIUM AND SILICON

The composition of potassium silicate varies between $K_2O.2SiO_2$ and $K_2O.4SiO_2$, according to the relative proportions of sand and alkali used. It is usually prepared by fusing together 47 p. of sand, 30 p. of potassium carbonate and 25 p. of charcoal. The latter aids in the disengagement of the CO_2 as CO. The flux is dissolved in 5 times its weight of boiling water and concentrated to any density desired. When dried, it forms a vitreous opaque mass.

Potassium Fluosilicate, K_2SiF_6, is prepared by precipitating any salt of potassium with hydrofluosilicic acid. The resulting compound is quite insoluble in cold water, but readily dissolves in that solvent when hot.

OXYGEN SALTS OF POTASSIUM AND CARBON

Potassium Carbonate, K_2CO_3.—The more or less pure carbonates of potassium are known as *potash, pearlash,* and *salt of tartar,* according to their degree of purity.

Source.—Potassium carbonate was originally obtained from wood ashes by leaching with water, evaporating in open pans, and calcining the residue in furnaces, hence the name *pot-ash.* Another, somewhat limited source, is from the molasses of beet-root sugar, from which, after undergoing fermentation and distillation to remove the alcohol, the residue is evaporated to dryness and ignited. The washings from sheep's wool, when evaporated, yield a residue which contains about 30 per cent. of carbonate. This is ignited, re-dissolved in water, and again ignited, the operation being repeated until the potash is sufficiently white and pure. The purer form of carbonate is sometimes called *pearlash.*

Most of the potassium carbonate is obtained from the chloride and sulphate by either the Leblanc process (see under Soda) or the Engel-Precht process. This latter consists in passing carbon dioxide through a mixture of a solution of potassium chloride with magnesium carbonate:

$$3MgCO_3.3H_2O + 2KCl + CO_2 = 2(MgCO_3.KHCO_3.H_2O) + MgCl_2.$$

The double salt of magnesium and potassium separates, which is then decomposed by heating with water under pressure at 80°. Basic magnesium carbonate precipitates with an evolution of carbon dioxide; the solution of potassium carbonate is removed by filtration; and, after evaporating, calcined. Potassium carbonate thus prepared is free from sodium, since this, if present as an impurity, does not react with the magnesium carbonate.

Crude potassium carbonate, or potash, is in hard, solid masses or coarse powder. The color varies from whitish, through gray-greenish and blue, to reddish-brown, according to the proportions of manganese and iron. The purer compound, known as pearlash, is a white granular powder. All the different grades absorb moisture from the air, becoming damp and then liquid.

The commercial potassium carbonate contains considerable quantities of other salts, chiefly potassium chloride, sulphate, and silicate, and sodium carbonate. There is also present more or less hydroxide, depending on the method of manufacture. Potassium carbonate prepared by the ignition of potassium bitartrate, leaching with water, filtering and again igniting is very pure and is known by the name of *salt of tartar*.

The pure salt is official under the name of **Potassii Carbonas.**

Preparation.—The chemically pure salt is made by igniting crystallized potassium bicarbonate, as this salt is capable by crystallization of being prepared of a high degree of purity; a superior product may thus be obtained.

$$\underset{\substack{\text{Acid}\\\text{Potassium}\\\text{Carbonate.}}}{2KHCO_3} = \underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O.}$$

Properties.—Potassium carbonate is a white, dry, granular powder, without odor, and possessing a strongly alkaline taste. It is very deliquescent, absorbing moisture readily from the air; soluble in 0.9 part of water at 25°, and in 0.7 part of boiling water; insoluble in alcohol. On heating to 180° the salt loses the adhering moisture, which should not be more than 15 per cent., and at about 890° it melts. The solution of the salt reacts strongly alkaline to litmus, and effervesces with acids.

From the concentrated aqueous solution crystals separate, having the formula $K_2CO_3.3H_2O$.

Potassium Bicarbonate, $KHCO_3$. **Potassii Bicarbonas,** U.S.P.—On passing carbon dioxide into a concentrated solution of the normal carbonate, the acid carbonate crystallizes out according to the following reaction:

$$K_2CO_3 + CO_2 + H_2O = 2KHCO_3.$$

The same result is sometimes accomplished by passing the carbon dioxide over the moistened pearlash. The product by either process is dissolved in water, filtered clear, and allowed to crystallize. This procedure serves to remove the silica, which is the chief impurity in the normal carbonate.

Properties.—Potassium bicarbonate occurs in colorless, transparent monoclinic prisms. It is without odor, and has a saline and slightly alkaline taste. It is soluble in 2.8 parts of water at 25°, and in 2 parts at 50°. Above 50°, in aqueous solution, it rapidly decomposes into normal carbonate and carbon dioxide. It is insoluble in alcohol. When first dissolved in water the resulting solution has a neutral reaction, but on standing it becomes alkaline, owing to the formation of the normal carbonate.

Potassium Percarbonate, $K_2C_2O_6$.—Prepared by the electrolysis of a concentrated solution of potassium carbonate at 30° to 40°. It separates as a bluish deliquescent powder at the anode, being formed by the union of the two ions, $CO_3K + CO_3K$. Its solutions give off oxygen at 45°, and with dilute acids or alkalies hydrogen peroxide forms, hence it is used as an oxidizing agent, $K_2C_2O_6 + 2HCl = 2KCl + 2CO_2 + H_2O_2$. $K_2C_2O_6 + 2KOH = 2K_2CO_3 + H_2O_2$. Percarbonates liberate iodine immediately upon addition to a solution of KI, while H_2O_2 solution reacts very slowly unless a ferrous salt be present.

Percarbonates, like hydrogen peroxide, reduce such oxides as Ag_2O, MnO_2, and PbO_2.

Potassium Trithiocarbonate, K_2CS_3.—This is used in solution only in destroying phylloxera and other insect life. It is prepared by the action of potassium sulphide on carbon disulphide: $K_2S + CS_2 = K_2CS_3$. When in contact with the soil the moisture and carbon dioxide decompose it into carbon disulphide: $K_2CS_3 + CO_2 + H_2O = H_2S + CS_2 + K_2CO_3$. Compare Thiocarbonic Acid, page 308.

POTASSIUM AND CYANOGEN

Potassium Cyanide, KCN.—This salt was formerly obtained by heating in an iron crucible to redness a mixture of dried potassium ferrocyanide (8 parts) and dried potassium carbonate (3 parts) with a little charcoal to prevent the formation of cyanate.

$$\underset{\substack{\text{Potassium}\\\text{Ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Potassium}\\\text{Carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{Cyanide.}}}{5KCN} + \underset{\substack{\text{Potassium}\\\text{Cyanate.}}}{KCNO} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Iron.}}{Fe}.$$

$$2KCNO + C = CO_2 + 2KCN.$$

When effervescence ceases, and the liquid becomes clear, it is poured carefully into an iron dish to solidify.

Commercially, potassium cyanide is prepared either by passing dry ammonia gas into a fused mixture of potassium carbonate and carbon,

$$K_2CO_3 + C + 2NH_3 = 2KCN + 3H_2O,$$

or from calcium carbide and nitrogen (see page 240).

The pure potassium cyanide contains about 40 per cent. of cyanogen, while the sodium salt contains 53 per cent. The commercial salt usually consists of a mixture of the two, and when the cyanogen content is determined as KCN the result shows from 95 to 100 per cent.

Properties.—Potassium cyanide occurs either in white, amorphous, opaque pieces, or as a white, granular powder. When perfectly dry it is odorless, but as ordinarily found it has an odor of hydrocyanic acid, owing to the presence of moisture and carbon dioxide in the air, which cause the formation of alkali carbonate with liberation of hydrocyanic acid. The salt is soluble in 2 parts of water at 25°, and in an equal weight of boiling water; at the latter temperature, however, it is rapidly decomposed. It is sparingly soluble in alcohol. When exposed to damp air, the salt readily deliquesces. The aqueous solution has an alkaline reaction. When heated to low redness the salt fuses, and absorbs oxygen from the air, forming cyanate. Its aqueous solution when heated or allowed to stand undergoes a gradual decomposition into ammonia and potassium formate:

$$KCN + 2H_2O = NH_3 + HCOOK.$$

All alkali cyanides are decomposed by the weakest acids, even carbonic acid being able to displace the hydrocyanic radicle. Violent explosions occur when this salt is mixed with nitric acid or with potassium chloride. Owing to the readiness with which alkali cyanides absorb oxygen, they are used as a flux in assaying and metallurgy.

When soluble alkali cyanides are added to solutions of salts of the heavy metals, most of the latter yield at first insoluble cyanides, which, however, are dissolved by an excess of the alkali cyanide, forming soluble double cyanides, among which are $AgCN.KCN$, $Ni(CN)_2.2KCN$, $Hg(CN)_2.2KCN$, $AuCN.KCN$. The constituent parts of these compounds are loosely combined, and through the addition of acids they break up with liberation of HCN.

The alkali cyanides are used in electroplating solutions and extensively in the extraction of gold from low-grade ores.

Potassium Cyanate, KCNO.—This is formed when a cyanide is oxidized by fusion with metallic oxides or when equal parts of potassium ferro-cyanide and manganese dioxide are intimately mixed, and fused until the mass begins to soften. After allowing the mass to cool, it is extracted with hot 80 per cent. alcohol, which, on cooling, deposits the salt in transparent tabular crystals. It is readily soluble in water and in alcohol. The salt in aqueous solution generally decomposes into water and potassium bicarbonate. It is chiefly used in the preparation of alkyl isocyanates.

Potassium Thiocyanate, or Sulphocyanate, KCNS.—May be prepared by fusing potassium cyanide with sulphur or boiling a solution of the former with the latter, or by gently heating together 46 parts of potassium ferrocyanide, 17 parts of potassium carbonate, and 32 parts of sulphur. The fused mass is extracted with hot alcohol, which deposits the crystallized salt, on cooling, in long, striated, transparent prisms.

When hydrochloric acid is added to a concentrated solution of a sulphocyanate, a yellow persulphocyanic acid precipitates. When heated with a mixture of equal volumes of sulphuric acid and water, alkali sulphocyanates yield carbon oxysulphide, $KSCN + 2H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + COS$.

The alkali sulphocyanates are all very soluble in water and alcohol and because of the intense red color which they give when in contact with ferric salts, sulphocyanates serve as a sensitive test for ferric iron. They are also employed in volumetric analysis.

SODIUM

Symbol, Na. *Atomic Weight,* 23. *Valence,* I.

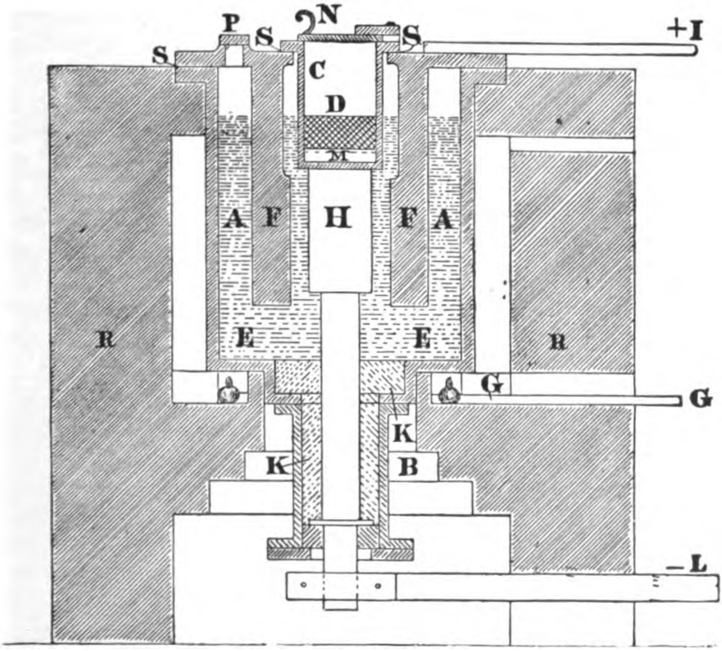
History.—As stated under the preceding element, the salts of sodium and potassium were not distinguished from each other until

1736. Those of sodium were probably the first known. *Nitrum*, which later came to be a name for saltpetre, was probably in earlier times applied to an impure sodium carbonate, since it effervesced on application of vinegar. Sodium chloride, because of its presence in sea water, was known in the earliest times.

The metal sodium was discovered by Davy in 1807, in the same manner as potassium—namely, by the electrolysis of the hydroxide.

Occurrence.—Sodium, like the other alkali metals, is not found in nature in the free state; but in combination it is very widely distributed. Sodium chloride is found as rock-salt in the earth; it is a constituent of sea water, of the water of many mineral springs, and it is universally distributed in animal and vegetable organisms.

Fig. 109.



Electrolytic preparation of sodium.

Sodium silicate is a constituent of *albite*, or soda-feldspar ($Na_2O.Al_2O_3.6SiO_2$), and in smaller quantity in many other minerals. The nitrate, as Chile saltpetre, is found in the warm and rainless districts of Chile and Peru. Cryolite, found in large deposits in Greenland, is the double fluoride of sodium and aluminum (page 437). Sodium carbonate occurs as a natural deposit in the warm and rainless districts of many countries, notably in Egypt, India, South America, and in Wyoming and California; in the latter places, however, it is usually associated with larger quantities of sodium sulphate or borate.

Isolation.—Sodium is prepared chiefly by the electrolytic process of Castner (Fig. 109), in which fused caustic soda contained in A is heated by the gas jets G. The current passes from the iron anode F to the cathode H, which generates sufficient heat to keep the bath fused. At the anode, oxygen is liberated and at the cathode, sodium and hydrogen; the metal, being lighter than the electrolyte, rises into the receiver cage C, where it is removed by a ladle. Fresh charges of caustic soda are introduced through P.

Properties.—Sodium is a silver-white metal, of a waxy consistence at ordinary temperatures. It has a specific gravity of 0.972 at 15°.

On the application of heat sodium melts at 97.5°, and at 882.9° it boils; under these conditions it is necessary to exclude air. The metal is easily oxidized at ordinary temperatures, becoming covered with a layer of sodium oxide. It is usually kept in dry tins and when wanted for use the thin layer of oxide is pared from the surface with a knife, taking care to avoid contact with moist surfaces. When heated in air, a mixture of Na_2O and Na_2O_2 forms.

The behavior of sodium towards most other elements is similar to that of potassium, but less energetic; for instance, potassium and bromine combine with explosive violence, while sodium may be warmed with it without violent action.

When thrown on water, sodium combines with the oxygen of the water, liberating hydrogen, but the action is not sufficiently energetic to inflame the latter, unless the metal be held in one position by a piece of filter paper, or water be warmed to 60°, when the gas ignites and burns with a yellow flame. This yellow color is characteristic of sodium compounds.

Uses.—Because of its reducing action on the oxides of metals sodium is sometimes used in the preparation of silicon, boron, and magnesium. It is employed for removing the last traces of moisture in the preparation of anhydrous alcohol and ether. If more than traces of water be present in the alcohol or ether or liquid to be dehydrated, an amalgam of sodium with either mercury or lead (hydrone) is employed, otherwise the reaction between pure sodium and the water would be too violent.

SODIUM AND HALOGENS

The halogen compounds of sodium are:

Sodium Fluoride, NaF.
Sodium Chloride, NaCl.
Sodium Bromide, NaBr.
Sodium Iodide, NaI.

Sodium Fluoride, NaF, is prepared by neutralizing hydrofluoric acid with sodium carbonate or fusing fluorspar (CaF_2) with Na_2CO_3. The compound crystallizes in anhydrous cubes. It is soluble in 25 parts of cold water, and scarcely more so in hot water. It has a tendency to form double compounds with other salts, as instanced in cryolite, the double fluoride of sodium and aluminum, $3NaF.AlF_3$. Its chief use is in softening water used for feeding boilers.

Sodium Chloride, NaCl. **Sodii Chloridum**, U.S.P.—Sodium chloride, or common salt, is found abundantly throughout the globe. As rock-salt it occurs in large deposits, alternating with strata of clay and gypsum, at an average depth of 100 meters. Probably the most celebrated mines are at Wieliczka, in Galicia, the deposit there being 500 miles long, 20 miles broad, and 1200 feet thick. Enormous quantities are also found in England, at Stassfurt, Germany, and in America.

Numerous saline springs also occur in many parts of the world, in which common salt is the chief constituent.

Sea water contains 3 to 4 per cent. of solid residue, three-fourths to nine-tenths of which is sodium chloride, or 2.4 to 2.8 per cent. of the sea water, the remainder consisting of the chlorides, bromides, and sulphates of potassium, magnesium, and calcium. Many inland seas contain a greater proportion of salt than exists in the ocean. For instance, the water of the Great Salt Lake in Utah contains over 22 per cent. of saline matter, about 90 per cent. of which is sodium chloride.

Extraction.—When sufficiently pure, rock-salt is mined and sent at once into commerce without further purification; since it is not as readily soluble as the finely crystallized salt, it is usually employed in curing meat, preserving green hides, feeding stock, preparing hydrochloric acid, etc. If it is more inaccessible, or mixed with earthy matter, holes are drilled into the deposits, water is run in, and the saturated solution is either forced out by the water which enters, or it is pumped out. The salt is recovered by evaporating the solution in iron or lead boilers. Weaker salt solutions or brines obtained from bored wells are evaporated by exposure to the sun's rays while exposed in shallow wooden vats. First, crystals of gypsum, $CaSO_4.2H_2O$, separate, then the brine is transferred to other vats, where evaporation is continued until the salt crystals separate. If the brine contains iron (ferrous carbonate) with some calcium and magnesium salts, these may be removed by means of a little soda ash.

When a purer compound is desired for chemical purposes, the purest commercial salt is carefully treated with barium chloride solution so long as a precipitate is produced, by which the sodium sulphate is decomposed, barium sulphate and sodium chloride resulting; the barium sulphate is filtered off, and the warm filtrate is treated with a slight excess of sodium carbonate; this precipitates aluminum, barium, calcium, iron, and magnesium compounds; after filtering clear, the solution is carefully neutralized with hydrochloric acid, and evaporated to the crystallizing point.

Properties.—Sodium chloride ordinarily occurs in transparent cubical crystals, or as a white, crystalline powder. It is permanent in the air, odorless, and has a pure saline taste. The impure commercial article is more or less hygroscopic, due to the presence of calcium or magnesium chlorides. Pure sodium chloride is non-hygroscopic. Soluble in 28 p. of H_2O at 25°, and in 2.7 p. at 100°; it is almost insoluble in alcohol. The solution in water has a neutral reaction. When heated the salt decrepitates; at a red heat (about 804°) it fuses, and at a white heat it is slowly volatilized with slight decomposition.

Uses.—Sodium chloride is used as a condiment, in medicine, and chiefly as a source for the preparation of other sodium salts, the most important of which are sodium sulphate and carbonate.

Sodium Bromide, NaBr. **Sodii Bromidum,** U.S.P.—The preparation of this salt is carried out similarly to the potassium salt, either by interaction between ferroso-ferric bromide and sodium carbonate or by the formation of sodium bromide and bromate by the combination of bromine and sodium hydroxide. The bromate is converted into bromide by fusion with charcoal (see page 325).

Properties.—Sodium bromide occurs in colorless or white cubical crystals, without odor, and with a saline, slightly bitter taste. The salt slowly attracts moisture from the air without deliquescing; this is probably due to the fact that at ordinary temperatures it crystallizes with two molecules of water, but as found in commerce it is free from water of crystallization, the latter condition having been attained by crystallizing from a warm solution, or above 30°.

Sodium bromide is soluble in 1.1 parts of water at 25°, and in 0.8 part of boiling water; in 16 parts of alcohol at 25°. When heated the salt melts at 712°, and at higher temperatures it is slowly volatilized with some decomposition.

Uses.—The principal use of sodium bromide is in medicine.

Sodium Iodide, NaI. **Sodii Iodidum,** U.S.P.—This salt is prepared as the corresponding potassium salt (see page 326).

Properties.—Sodium iodide occurs in colorless cubical crystals, or as a white, crystalline powder; it is odorless, and has a saline, slightly bitter taste. It is deliquescent in moist air, and when exposed to air and sunlight it undergoes a slight decomposition into sodium carbonate and free iodine, thereby becoming slightly discolored.

The salt is soluble in 0.5 part of water at 25°, and in 0.4 part of boiling water; in 2 parts of alcohol, and in 1.4 parts of boiling alcohol. When it crystallizes from water at ordinary temperatures it contains two molecules of water of crystallization, but above 40° it crystallizes as an anhydrous salt. When heated it fuses, and at a higher temperature it volatilizes with partial decomposition. Its aqueous solution is neutral to litmus paper.

Uses.—Sodium iodide is employed chiefly in medicine.

SODIUM AND OXYGEN

Sodium Monoxide is prepared from sodium and sodium nitrate, as described under potassium oxide (page 327).

It is a gray mass with a conchoidal fracture. When brought in contact with water, violent action occurs with generation of heat and formation of sodium hydroxide.

Sodium Peroxide, Na_2O_2.—This compound is formed when sodium contained in aluminum trays is heated at 300° in a current of dry air or oxygen until the weight becomes constant.

Properties.—As found in commerce, sodium peroxide is a yellowish-white powder. It is very deliquescent. When thrown into water, considerable heat is evolved, and sodium hydroxide and oxygen are formed, as follows:

$$Na_2O_2 + H_2O = 2NaOH + O.$$

Owing to the intensity of the reaction, sometimes accompanied by flaming, only small quantities of the peroxide should be added to the water at a time. Water should never be added to the peroxide.

When, however, a cold dilute acid is used, hydrogen dioxide results:

$$Na_2O_2 + 2HCl = 2NaCl + H_2O_2.$$

Sodium peroxide is a very energetic oxidizing agent, and is used for bleaching silk and wool. Owing to the formation of caustic soda, this must be neutralized gradually with acetic acid or the peroxide is mixed with magnesium sulphate, forming magnesium peroxide.

$$Na_2O_2 + MgSO_4 = Na_2SO_4 + MgO_2.$$

Sodium peroxide contains about 20 per cent. of available oxygen. It has recently been brought on the market in a compact fused state under the name of "oxone." One volume of this oxone will generate on contact with water 315 times its volume of oxygen.

Sodium Hydroxide, **Sodii Hydroxidum,** U.S.P. (Sodium Hydrate, Caustic Soda), NaOH.—This is formed when sodium is added to water; care should be exercised, owing to the violence of the reaction.

$$Na_2 + 2H_2O = 2NaOH + H_2.$$

The oldest method for the preparation of commercial caustic soda consists in adding calcium hydroxide (milk of lime) to a 10 per cent. boiling solution of sodium carbonate (soda ash), air or steam being blown into the liquor to assist mixing (see page 358).

$$\underset{\text{Sodium Carbonate.}}{Na_2CO_3} + \underset{\text{Calcium Hydroxide.}}{Ca(OH)_2} = \underset{\text{Sodium Hydroxide.}}{2NaOH} + \underset{\text{Calcium Carbonate.}}{CaCO_3}.$$

The clear liquid is decanted from the precipitate and evaporated in an iron dish to a specific gravity of 1.170, when the concentration is completed in a silver dish and the fused product poured into silver moulds. Caustic soda is now prepared electrolytically either from a solution of sodium chloride or from the fused sodium chloride.

A variety of methods are now in use, more important among which are the *amalgamation* electrolytic processes of Castner-Keller (page 706) and Acker.

Electrolysis of sodium chloride by the dry Acker process is based on the decomposition of the fused salt, carbon anodes and a molten lead cathode being used. The liberated sodium alloys itself with the lead, which is afterwards decomposed by steam in a separate vessel under proper precautions, producing anhydrous fused sodium hydroxide.

Among the *diaphragm* processes, that of Griesheim is one of the most successful. In this, the cathode and anode are placed in compartments separated by a porous diaphragm. The cathode is of cast-iron and the anode of fused and moulded ferrous-ferric oxide (Fe_3O_4), which resists the corrosive action of chlorine. A solution of sodium chloride is introduced into the compartments, and in the one containing the cathode sodium is liberated by the current; this reacts with the water to form sodium hydroxide. When the concentration of NaOH reaches about 8 per cent., the solution is drawn off and concentrated by evaporation to about 50 per cent. NaOH, whereby the unchanged sodium chloride separates and is returned to the cell.

Properties.—Commercial sodium hydroxide is usually supplied in large iron drums, the alkali forming a solid hard mass. For pharmaceutical or analytic purposes it is supplied in small fused pieces or stick form, the latter containing more water than the lumps, which is necessary in order to remove the sticks from the moulds. Caustic soda " by alcohol " was formerly prepared from the lime-process alkali by solution in alcohol, decanting from the insoluble impurities, evaporating and fusing. What is now sold under this name is chiefly electrolytic caustic soda. When exposed to moist air sodium hydroxide rapidly deliquesces; in dry air it first becomes coated with a dry film of carbonate. It is soluble in 0.9 part of water at 25°, and in 0.3 part of boiling water; very soluble in alcohol.

On the application of heat nearly anhydrous sodium hydroxide melts at about 300° to a clear oily liquid, and at a bright red heat it is slowly volatilized unchanged. The solution, even when very dilute, gives a strongly alkaline reaction with litmus paper, being highly ionized into $Na^{\cdot}$ and OH' ions.

A very concentrated aqueous solution of sodium hydroxide when cooled to 0° deposits crystals of several different hydrates. Water is always present in the commercial article; that coming in sticks contains from 15 to 25 per cent. of moisture.

Liquor Sodii Hydroxidi, U.S.P., which contains not less than 4.5 and not more than 5.5 per cent. of the alkali, is prepared by dissolving 56 gm. of NaOH in 944 gm. of distilled water. Solutions of caustic soda readily attack glass, hence potassium hydroxide, which shows but little or no such action, is preferred in making the volumetric standard solutions.

Uses.—Sodium hydroxide is used in the manufacture of soap, of paper pulp from wood, for purifying petroleum and absorbent cotton, in the preparation of phenol, resorcinol, naphthol, and many dyes.

Soda Lime consists of a variable mixture of caustic lime and soda which from its chemical deportment contains such compounds as $Ca(ONa)_2$ and OH.Ca.ONa. It is an efficient absorptive for poisonous and irritating gases of all kinds, since it absorbs Cl, Br, halogen acids, CO_2, SO_2, $COCl_2$, HCN, halogen cyanides, AsH_3, SbH_3, H_2S, H_2Se,

$SOCl_2$, NOCl, and many others. One hundred grammes of soda lime will absorb as much as 35 liters of hydrogen sulphide. Soda lime is used in the laboratory for drying gases and some volatile liquids.

OXYGEN SALTS OF SODIUM AND HALOGENS

Sodium Hypochlorite, NaClO.—This compound is employed only in solution. Officially it is known as **Liquor Sodæ Chlorinatæ,** or Labarraque's Solution. This solution is prepared according to the Pharmacopœia by mixing solutions of sodium carbonate and chlorinated lime; the reaction is as follows:

$$\underbrace{Ca(ClO)_2 + CaCl_2}_{\text{Chlorinated Lime.}} + \underset{\text{Sodium Carbonate.}}{2Na_2CO_3} = \underset{\text{Labarraque's Solution.}}{2NaClO + 2NaCl} + \underset{\text{Calcium Carbonate.}}{2CaCO_3}.$$

The clear supernatant liquid, after decantation, should contain not less than 2.5 per cent. of available chlorine, and, in addition to the hypochlorite, sodium chloride and carbonate.

The corresponding potassium hypochlorite is known as "Javelle Water." Under the name of "bleach liquor," immense quantities of sodium hypochlorite solution are produced by the direct electrolysis of cold dilute solutions of sodium chloride. No diaphragms are employed, so that the products of the electrolysis, chlorine liberated at the positive pole, reacts with the sodium hydroxide liberated at the negative pole (with hydrogen), yielding NaClO. The bleaching action of hypochlorous acid or the hypochlorites is due to the nascent oxygen they liberate, which is double that of the chlorine present, were it to act in the free state, thus:

$$(a)\quad 2Cl + H_2O = 2HCl + O.$$
$$(b)\quad 2NaClO = 2NaCl + O_2.$$

In equation *a,* two atoms of Cl liberate one atom of O; in equation *b,* two atoms of combined Cl (in NaClO) liberate two atoms, or twice as much oxygen, hence two atoms of chlorine in hypochlorous acid or its salts possess twice the bleaching effect as two atoms of chlorine gas in water. Sodium hypochlorite may also be prepared by passing Cl through a weak cold solution of sodium carbonate, avoiding an excess of chlorine.

$$2Cl_2 + Na_2CO_3 + H_2O = 2HClO + 2NaCl + CO_2.$$

Such a solution reacts like the above, but deteriorates more quickly than the official slightly alkaline solution, with the formation of chlorate and chloride (see page 208). Slightly alkaline solutions will keep not only much longer, but even when exposed to a temperature of 50° C. For this reason it is possible to warm the official reacting solutions as directed in the U.S.P., without causing appreciable decomposition.

Exposure to the light, heating, or evaporating solutions of the hypochlorites (above 50° C.) causes rapid decomposition into chloride and chlorate. In the dark decomposition proceeds more slowly. The addition of very weak acids, as boric or carbonic, liberates HClO, while the inorganic diluted acids, as HCl or H_2SO_4, cause liberation of chlorine:

$$2NaClO + H_2SO_4 = Na_2SO_4 + H_2O + 2Cl.$$

Hydrochloric acid reacts as follows:

a. $NaClO + HCl = NaCl + HClO.$
b. $HClO + HCl = Cl_2 + H_2O.$

The hypochlorites oxidize and destroy organic colors, more rapidly if used in connection with a very weak acid, which causes the liberation of HClO (see page 208).

Dakin's Solution.—This, important because of its use in antiseptic surgery, consists of a solution of sodium hypochlorite which should contain not less than 0.4 per cent. nor more than 0.5 per cent. of NaOCl. The solution is alkaline to alcoholic phenolphthalein T.S. and not alkaline to powdered phenolphthalein. If the solution is alkaline to powdered phenolphthalein, it is irritating; if acid to the alcoholic T.S., the solution is unstable. If the solution is prepared too alkaline, it may be neutralized with boric acid; if the alkalinity be too low, a 1 per cent. solution of sodium bicarbonate may be added. Dakin's solution may be prepared, first, by the electrolysis of a solution of sodium chloride; second, by the action of chlorine on a dilute solution of sodium hydroxide or carbonate cooled below 30°; third, by interaction between solutions of calcium hypochlorite and sodium carbonate. The NaOCl content of this solution should be accurately determined.

Sodium Chlorate, $NaClO_3$.—Sodium chlorate is prepared by the electrolysis of solutions of sodium chloride as described under potassium chlorate (page 329). It may also be prepared by interaction between hot concentrated solutions of molecular quantities of sodium bitartrate and potassium chlorate. After removing the potassium bitartrate which crystallizes out, the filtrate is concentrated to small volume for the crystallization of the very soluble sodium chlorate.

$$NaHC_4H_4O_6 + KClO_3 = NaClO_3 + KHC_4H_4O_6.$$

Sodium chlorate occurs in colorless, transparent crystals, or as a white, crystalline powder. Its taste is more decidedly saline and cooling than the corresponding potassium salt. It is soluble in 1 part of water at 25° and in 0.5 part of boiling water, in 100 parts of alcohol, and in 40 parts of boiling alcohol; it is also soluble in 5 parts of glycerin. When heated, the salt melts and gives off oxygen, leaving a residue of sodium chloride.

On account of its greater solubility the salt has been used considerably in place of the potassium chlorate in oxidations, calico printing and in the manufacture of aniline black.

Sodium Bromate, $NaBrO_3$, is prepared in like manner to potassium bromate. It is soluble in about 3 parts of water at 15°. In other respects it resembles the potassium salt.

Sodium Iodate, $NaIO_3$, which occurs in Chile saltpetre, is prepared similarly to potassium iodate, and crystallizes with a variable proportion of water. It is soluble in about 14 parts of water.

SODIUM AND SULPHUR AND THEIR OXYGEN SALTS

The compounds of sodium and sulphur are similar to those of potassium and are used in preference, since they are cheaper.

Sodium Hydrosulphide, NaHS.—This is obtained commercially from the calcium sulphide of the Leblanc soda residues by treatment with sodium acid sulphate: $CaS + NaHSO_4 = CaSO_4 + NaSH$. Sodium hydrosulphide solutions undergo decomposition through boiling: $2NaSH = Na_2S + H_2S$.

Sodium Sulphide, $Na_2S.9H_2O$.—This is made by heating sodium sulphate with powdered coal, leaching the mass and crystallizing: $Na_2SO_4 + 4C = Na_2S + 4CO$. This is used in preparing sulphurated dyes, in tanning, denitrating artificial silk, cleaning cotton and silk, etc. The Pharmacopœia recognizes the purified salt as a reagent for preparing sodium sulphide, T.S., owing to its greater stability in comparison with ammonium sulphide. When dissolved in water, sodium sulphide breaks up into the hydrosulphide and hydroxide as follows: $Na_2S + H_2O = NaSH + NaOH$. The salt is hygroscopic and must be kept in well-stoppered bottles.

Various *polysulphides* are known, Na_2S_2, Na_2S_4, and Na_2S_5.

Sodium Sulphite, $Na_2SO_3.7H_2O$.—Normal sodium sulphite is prepared by saturating a solution of sodium carbonate with sulphur dioxide, and then neutralizing with an equal amount of sodium carbonate previously dissolved in water.

a. $Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2$.

b. $2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O$.

The solution is then carefully evaporated to crystallization.

If the solution be heated to the boiling point, the anhydrous sodium sulphite separates, which redissolves on cooling. The Pharmacopœia recognizes only the **Sodii Sulphis Exsiccatus**, which should assay not less than 90 per cent. In the exsiccated state the salt is more stable, since it does not as readily absorb oxygen from the air, as is the case with the crystalline form, which slowly oxidizes to the sulphate.

Properties.—The official salt is an inodorous white powder of a cooling, saline, somewhat sulphurous taste.

It is soluble in 3.2 parts of water at 25° and is scarcely soluble in alcohol. At a red heat the salt fuses to a reddish-yellow mass of sodium sulphate and sulphide.

The aqueous solution is alkaline to litmus paper. Sodium sulphite is a reducing agent in that it abstracts oxygen from other chemicals, forming sodium sulphate. Its chief commercial use is in the paper and cotton goods industries, where bleaching has been effected by means of chlorine, the excess of chlorine being neutralized with sodium sulphite, which is commonly known as "antichlor."

$$Na_2SO_3 + H_2O + Cl = Na_2SO_4 + 2HCl.$$

Sulphites are also used to prevent the cane-juice from browning while being concentrated.

Acid Sodium Sulphite, or *Bisulphite,* $NaHSO_3$ (U.S.P. Reagent), is prepared, as stated under the preceding salt, when a solution of sodium carbonate is saturated with sulphur dioxide; the salt separates in turbid crystals on cooling the solution.

Commercially it is much used in solution, from which, however, it may be crystallized, or precipitated by alcohol.

Properties.—The salt slowly evolves sulphur dioxide, and has a disagreeable, sulphurous taste. It is soluble at 25° in 3.5 parts of water and in 70 parts of alcohol, and in about 2 parts of boiling water and in 49 parts of boiling alcohol. When strongly heated, the vapors of sulphur and sulphur dioxide are evolved, and a residue of sodium sulphate remains. The aqueous solution imparts an acid reaction to litmus paper.

Uses.—The salt has been used as a preservative for foods; it is extensively used as an "antichlor," like the normal sulphite, and as a bleaching agent. Sulphur dioxide is readily and abundantly evolved on the addition of an acid.

Sodium Sulphate, $Na_2SO_4.10H_2O$. **Sodii Sulphas,** U.S.P.—The anhydrous salt is known as *salt-cake,* while the official compound with 10 molecules of water is known as *Glauber's salt,* after Glauber, who, in 1658, first described it under the name of *sal mirabile.* Sodium sulphate is widely diffused in nature. In the anhydrous condition it is found as the mineral *thenardite,* and in the hydrous form as *mirabilite;* it occurs in sea water and in many mineral springs, chief among which are those of Carlsbad. Large amounts occur in a nearly pure state, in solution, in many lakes throughout the arid regions of western United States. Sodium sulphate is produced at Stassfurt from the mother liquors of carnallite and kieserite. The largest portion of commercial sodium sulphate is a product of the Leblanc soda process, the first step of which is the conversion of sodium chloride into sulphate through treatment with sulphuric acid.

The official salt occurs in transparent monoclinic prisms or granular crystals. The commercial salt is frequently covered with efflorescence; it is without odor, and has a bitter, saline taste. Sodium sulphate is soluble in 1 part of water at 25°, and when heated at about 33° it fuses in its crystal-water, and at 100° it loses all its water (55.87 per cent.). At a red heat the anhydrous salt fuses.

Uses.—Sodium sulphate is used in medicine as a purgative, but its greatest consumption is in the manufacture of sodium carbonate by the Leblanc process; it is also extensively employed in the manufacture of glass, ultramarine, dye-stuffs. When the crystalline salt is mixed with half of its weight of concentrated HCl the temperature drops to —18°.

Acid Sodium Sulphate, $NaHSO_4$, is also known as bisulphate of soda, primary sodium sulphate, and sodium hydrogen sulphate. It is prepared by heating 16 parts of sodium sulphate with 10 parts of pure concentrated sulphuric acid until they liquefy, and then dissolving the cooled, white, crystalline mass in twice its weight of water; by evaporating at 50° the anhydrous salt is obtained in triclinic prisms. When the crystallization takes place at the ordinary temperature, monoclinic prisms, with one molecule of water, $NaHSO_4.H_2O$, are formed.

It is also obtained in the manufacture of nitric acid from sodium nitrate and sulphuric acid, hence called *nitre cake:* $NaNO_3 + H_2SO_4 = HNO_3 + NaHSO_4$. This salt is used as an acid flux in the decomposition of minerals, also, to a certain extent, in the dyeing industry.

Sodium Thiosulphate, $Na_2S_2O_3.5H_2O$. **Sodii Thiosulphas,** U.S.P.—This salt is commercially, but incorrectly, known as hyposulphite of soda.

Preparation.—Sodium thiosulphate may be prepared by boiling a solution of sodium sulphite with sulphur:

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The commercial source is from the *black ash* (tank or soda waste) residue, after extraction of sodium carbonate in alkali manufacture (page 357). When this residue is exposed to air for some time, the calcium sulphide, or oxysulphide, contained therein is oxidized to thiosulphate, as follows:

$$\underset{\substack{\text{Calcium}\\ \text{Sulphide.}}}{2CaS} + \underset{\text{Oxygen.}}{2O_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Calcium}\\ \text{Thiosulphate.}}}{CaS_2O_3} + \underset{\substack{\text{Calcium}\\ \text{Hydroxide.}}}{Ca(OH)_2}.$$

The thiosulphate is extracted from the mass with water, and the resulting solution decomposed with sodium sulphate, as follows:

$$\underset{\substack{\text{Calcium}\\\text{Thiosulphate.}}}{CaS_2O_3} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} = \underset{\substack{\text{Sodium}\\\text{Thiosulphate.}}}{Na_2S_2O_3} + \underset{\substack{\text{Calcium}\\\text{Sulphate.}}}{CaSO_4.}$$

Properties.—Sodium thiosulphate forms large, colorless, well-defined monoclinic crystals; odorless, with a saline, cooling, afterwards bitter taste. It is neutral to litmus, and is permanent in dry air. Above 33° it effloresces, and at 56° melts in its water of crystallization. At 100° it loses all its water (36.26 per cent.), with partial decomposition, and at a red heat it is completely decomposed, evolving sulphur, which escapes, leaving a residue of sodium sulphate and sulphide.

Sodium thiosulphate is soluble in 0.5 part of water at 25°; at the boiling temperature its solution is rapidly decomposed. It is insoluble in alcohol.

The chloride, bromide, and iodide of silver are readily soluble in solutions of sodium thiosulphate, forming a double salt, sodium-silver thiosulphate, as follows:

$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$

This property of dissolving the halogen salts of silver explains its use as a *fixing* agent in photography.

Iodine is also soluble in an aqueous solution of sodium thiosulphate, sodium iodide and tetrathionate being formed:

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI.$$

This reaction is of great importance in iodometric determinations with tenth-normal volumetric solution of sodium thiosulphate. A similar reaction taking place with chlorine is responsible for its extensive use in removing the excess of chlorine present after certain bleaching operations; for this reason it is called "*antichlor.*" Exposure to air containing carbon dioxide causes a gradual decomposition of this solution.

Aqueous solutions of thiosulphate are decomposed by acids with evolution of sulphur dioxide (recognized by its odor and blackening paper moistened with mercurous nitrate T.S.) and deposition of sulphur (distinction from a sulphite):

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3.$$
$$H_2S_2O_3 = SO_2 + H_2O + S.$$

OXYGEN SALTS OF SODIUM AND NITROGEN

Sodium Nitrate, $NaNO_3$.—In 1683 Bohn discovered this salt, which was more thoroughly investigated by Duhamel in 1736, and Marggraf in 1761. In 1820 it was first shipped from South America to European ports.

Occurrence.—Sodium nitrate is found as a natural deposit in parts of South America, chiefly in Chile, Peru, Bolivia, and the province of Bahia in Brazil. The Atacama Desert extends through the northern part of Chile into the southern part of Peru. It is in Atacama, Chile, Tarapaca, Peru, and the interlying region that the most extensive deposits occur. The district covers hundreds of miles, is practically rainless, and is especially favorable for the recovery of a salt like this, which is soluble in water. The crude deposit is termed "caliche," and one tract alone extends 40 miles in length, and 1 to 2 miles in width.

A characteristic nitrate, *pampa,* or *calichero,* as it is called, consists of about the following strata: First, a layer of sand and gravel, about 1 to 2 inches deep; then a 6-inch layer of a white friable substance consisting largely of calcium sulphate; below this is a stratum from 2 to 10 feet in thickness, consisting of earth and stones; then there is a layer 1 to 3 feet thick of a substance known as *costra,* which is low-grade *caliche,* composed of chlorides, feldspar, and earthy matter. The *caliche,* or crude sodium nitrate, lies below this; it forms a layer 1½ to 2 feet in thickness. In the Tarapaca district this layer is much thicker, ranging from 4 to 12 feet. Below the sodium nitrate deposit is a stratum of fine clay 3 feet in depth, resting on porphyritic rock.

The assay of the *caliche* varies from 15 to 55 per cent. sodium nitrate; the impurities present are sodium perchlorate, sodium iodate (up to 0.5 per cent.), potassium nitrate, and up to 20 per cent. of sodium chloride.

Extraction.—The ground crude *caliche* is boiled with water, and the clear solution run into crystallizing tanks. The residue is boiled with water a second time, which usually completes the exhaustion. The liquor in the crystallizing tanks deposits its crystals of the nitrate in from 4 to 6 days.

The mother liquor is then run off to the iodine house, where that valuable element is removed (see page 180). The crystals of sodium nitrate are thrown out on drying-boards, washed once with a little cold water, allowed to dry, and are then packed in bags for shipment. As water is scarce in this dry region, all washings are saved and all steam is condensed as far as possible. The commercial sodium nitrate, prepared as above described, consists of 95 per cent. nitrate, with small quantities of chlorides, sulphates, moisture, and insoluble matter. For the preparation of nitrates from atmospheric nitrogen, see page 255.

Properties.—For medicinal use the commercial salt requires purification by recrystallization. It occurs in colorless, transparent, rhombohedral crystals, odorless, and having a cooling, saline, and slightly bitter taste. Deliquescent in moist air. Soluble at 25° in 1.1 parts of water, and in about 100 parts of alcohol; in 0.6 part of boiling water, and in 40 parts of boiling alcohol.

When 75 parts of sodium nitrate are dissolved in 100 parts of water at 13.2°, the temperature falls to —5.2°.

On application of heat, sodium nitrate melts at 318°, without decomposition; at a higher temperature it evolves oxygen and is converted into nitrite.

Uses.—Sodium nitrate, frequently termed "Chili saltpetre," is used extensively as a fertilizer, and for the preparation of potassium nitrate by interaction with potassium chloride. Since it is cheaper than the potassium salt, it is used in the preparation of nitric acid. It cannot replace the potassium salt in the manufacture of gunpowder, because of its tendency to absorb moisture.

Sodium Nitrite, $NaNO_2$. **Sodii Nitris,** U.S.P., is prepared by heating 100 parts of sodium nitrate with 285 parts metallic lead, in an iron vessel, between 450° and 500°:

$$NaNO_3 + Pb = NaNO_2 + PbO.$$

The fused mass is treated with water, filtered, and carbon dioxide passed through the filtrate in order to remove the last traces of lead. Finally, the salt is purified by repeated crystallization. Another method consists in heating a mixture of concentrated solutions of sodium nitrate and calcium oxide while saturating with SO_2.

$$NaNO_3 + CaO + SO_2 = CaSO_4 + NaNO_2.$$

Properties.—As usually found in commerce, sodium nitrite is in white or yellowish-white opaque, fused masses or sticks, hexagonal crystals or as a granular powder. The salt is odorless, has a mild, saline taste, and when exposed to the air deliquesces and is gradually oxidized to nitrate.

Sodium nitrite is soluble in about 1.5 parts of water at 25°; very soluble in boiling water, and only slightly soluble in alcohol. On the application of heat, the salt melts, and at a red heat it decomposes, with the formation of oxygen, nitrogen, nitrogen dioxide, and sodium oxide. Aqueous solutions give off brown vapors of nitrogen trioxide upon the addition of acids.

This salt was made official because of its use in the manufacture of spirit of nitrous ether. The Pharmacopœia requires that it shall contain not less than 95 per cent. of the pure salt.

Sodium nitrite has considerable use as a chemical reagent, being usually employed when a soluble nitrite is demanded; it is also employed by the color manufacturers in preparing Azo dyes as well as in diazotizing.

OXYGEN SALTS OF SODIUM AND PHOSPHORUS

Sodium Orthophosphates.—There are three compounds of sodium with orthophosphoric acid, which are less soluble and crystallize more readily than the corresponding potassium salts.

Trisodium Orthophosphate, $Na_3PO_4.12H_2O$, Tribasic.
Disodium Orthophosphate, $Na_2HPO_4.12H_2O$, Dibasic.
Monosodium Orthophosphate, $NaH_2PO_4.H_2O$, Monobasic.

When a solution of orthophosphoric acid is neutralized with an alkali carbonate or hydroxide, *dibasic* phosphate is obtained:

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + CO_2 + H_2O.$$

If a dibasic phosphate be evaporated with an excess of phosphoric acid, a *monobasic phosphate* results:

$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4.$$

If a dibasic phosphate be evaporated with an alkali carbonate or hydroxide, a *tribasic* phosphate is formed:

$$Na_2HPO_4 + NaOH = Na_3PO_4 + H_2O.$$

Of these, the mono- and di-basic salts are used in medicine.

When an alkali is added to phosphoric acid with methyl orange as indicator, neutrality is reached with the formation of the monobasic salt. If phenolphthalein is used as indicator, neutralization is complete with the formation of the dibasic salt. The tribasic salt is strongly alkaline.

The aqueous solutions of these salts of phosphoric acid exhibit marked differences in their reaction towards indicators, which may be explained through the trend of their ionizations.

The *primary salt* (NaH_2PO_4) owes its acid reaction to the splitting of its anion H_2PO_4' into the (acid) $H^{\cdot}$ and HPO_4'' ions, the former predominating.

The *secondary* salt (Na_2HPO_4), which is of slight alkaline reaction, ionizes into $2Na^{\cdot}$ and HPO_4''; the latter ions unite with $H^{\cdot}$ ions in the water ($H^{\cdot} + HPO_4'' \rightleftarrows H_2PO_4'$), liberating sufficient OH' ions to impart an alkaline reaction.

The *tertiary* salt (Na_3PO_4) hydrolyzes into the ions PO_4'''; these possess a stronger attraction for the $H^{\cdot}$ ions than the HPO_4'' ions, hence the PO_4''' ion induces the formation of a greater percentage of OH' ions not compensated by $H^{\cdot}$ ions, therefore a strong alkaline reaction.

Disodium Orthophosphate, $Na_2HPO_4.12H_2O$.—This salt is official under the name of **Sodii Phosphas,** U.S.P., but is generally known in commerce as "phosphate of soda." It is widely distributed in the animal economy, especially in the urine, where it is found to the extent of from 0.3 to 0.5 per cent.

Sodium phosphate is formed when sodium carbonate is added to phosphoric acid until a faintly alkaline reaction is obtained. Below 30° crystallization takes place. From solutions of a higher temperature than 30° the salt crystallizes with $7H_2O$, which does not effloresce.

Properties.—These crystals contain twelve molecules of water, and rapidly effloresce on exposure to the air, losing 5 molecules of water (25.1 per cent.). They occur in large, colorless, monoclinic prisms, odorless, and having a cooling, saline taste. The salt is soluble in 2.7 parts of water at 25° and in 1.5 parts of boiling water; it is insoluble in alcohol.

On the application of heat, sodium phosphate fuses at 40°; at 110° it loses all its water of crystallization, amounting to 60.3 per cent., yielding **Sodii Phosphas Exsiccatus,** U.S.P., and at a red heat it is converted into sodium pyrophosphate. The aqueous solution reacts slightly alkaline towards litmus paper and phenolphthalein.

Uses.—Sodium phosphate is used in medicine, as a reagent, and to a certain extent in the dyeing industry.

Monosodium Orthophosphate, $NaH_2PO_4H_2O$.—This salt is formed when orthophosphoric acid is added to a solution of disodium orthophosphate till barium chloride no longer produces a precipitate after evaporation. The salt separates with one molecule of water of crystallization.

Trisodium Orthophosphate, Na_3PO_4, is obtained either by heating one molecule of Na_2HPO_4 with 1 molecule of NaOH, or igniting 2 parts of Na_2HPO_4 with 1 part of Na_2CO_3. This tribasic salt is not used in medicine.

Sodium Pyrophosphate, $Na_4P_2O_7.10H_2O$.—The simplest method of obtaining this salt is by heating the ordinary sodium phosphate to 300°, or more rapidly by increasing the temperature to low redness, until a sample taken out and dissolved in water gives no yellowish precipitate with silver nitrate. The following expresses the reaction:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

This operation may be conducted in an iron vessel, but one of silver is preferable. After the conversion is complete, the cooled mass is dissolved in 5 parts of hot water, filtered, and the filtered solution allowed to crystallize.

Sodium pyrophosphate occurs in colorless, transparent, monoclinic prisms, or a crystalline powder, odorless, and having a cooling, saline, and feebly alkaline taste. The crystals are permanent under most circumstances, but effloresce slightly in dry air.

The salt is soluble in 11.5 parts of water at 25°, and in 1.1 parts of boiling water; alcohol does not dissolve it. The aqueous solution is slightly alkaline to litmus and phenolphthalein. When heated to 100° the salt loses its water of crystallization, amounting to 40.35 per cent. When boiled with diluted nitric acid the pyrophosphate is converted into monosodium phosphate.

Disodium Pyrophosphate, $Na_2H_2P_2O_7.6H_2O$, is prepared by heating disodium phosphate to 150° with strong hydrochloric acid: $2Na_2HPO_4 + 2HCl = Na_2H_2P_2O_7 + H_2O + 2NaCl$; or by dissolving the normal pyrophosphate in acetic acid and precipitating by alcohol. As thus obtained, it occurs as a white, crystalline powder. Its aqueous solution has an *acid reaction.*

Sodium Metaphosphate, $NaPO_3$, is formed by heating the ordinary phosphate to bright redness for some minutes, or by heating disodium dihydrogen pyrophosphate to 240°: $Na_2H_2P_2O_7 = 2NaPO_3 + H_2O$. This compound is scarcely soluble in water; it exists in several polymeric modifications, corresponding to the various polymeric metaphosphoric acids; these modified salts are more soluble in water.

Sodium Hypophosphite, $NaPH_2O_2.H_2O$. **Sodii Hypophosphis,** U.S.P.—Sodium hypophosphite is obtained by adding a solution of sodium carbonate to one of calcium hypophosphite as long as a precipitate is produced. The filtered solution is evaporated at a low temperature, and concentration is completed in a vacuum. Explosion may result from too rapid evaporation or slight overheating of this solution, even on a water-bath.

Properties.—This salt occurs in pearly, tabular crystals, or in a white, granular powder; it is without odor, and possesses a saline taste. It is very deliquescent on exposure to moist air. The aqueous solution is neutral or slightly alkaline to litmus paper.

Sodium hypophosphite is soluble in 1 part of water and in 25 parts of alcohol at 25°; it is dissolved by 0.15 part of boiling water and by 1 part of boiling alcohol.

On carefully heating a small quantity of the salt in a test tube it first loses water of crystallization, and at 200° it is decomposed with the evolution of spontaneously inflammable hydrogen phosphide, which burns with a yellow flame:

$$2NaPO_2H_2 = PH_3 + Na_2HPO_4.$$

Sodium hypophosphite should not be triturated with nitrates, chlorates, permanganates, or other oxidizing agents, as violent explosions are liable to occur.

OXYGEN SALTS OF SODIUM AND BORON

Sodium Borate, $Na_2B_4O_7.10H_2O$. **Sodii Boras,** U.S.P.

History.—Borax was known to the ancients and to the alchemists.

Its true chemical character was not understood until 1747, when Baron pointed out the fact that it consisted of boric acid (then called sedative salt) and soda.

Occurrence.—Originally borax was found in certain lakes of Thibet; later it was brought from India and Persia, and was found in smaller quantities in various parts of the world. The abundant deposits of borax in the United States were not discovered until 1856. It was formerly obtained through the evaporation of the water of various ponds in Southern California; later from dry lake beds or desert marshes in the Death Valley region, where it occurs as dry, incrusted masses. In some of these localities the base is calcium instead of sodium; in South America, for instance, the mineral *boronatrocalcite,* $Na_2B_4O_7.2CaB_4O_7.18H_2O$, is chiefly found, while the *borocalcite,* $Ca_2B_6O_{11}.5H_2O$, is found in these as well as in many other places. One bed of this latter mineral, near Death Valley, California, has an average depth of six feet. It is locally known as *colemanite,* from Coleman, its discoverer. This mineral, with ulexite (cotton ball), $NaCaB_5O_9.8H_2O$, furnishes practically all the borax of this country.

Extraction.—Crude borax, obtained from the East, is known as *tincal,* containing lime, magnesia, sulphates, and chlorides as impurities. The deposits in this country, however, are of such purity as merely to require recrystallization. When *borocalcite* or *ulexite* is used, it is boiled with water, sodium carbonate, and bicarbonate, the result being sodium borate and calcium carbonate. This is permitted to settle and the solution of borax is run into vats containing iron rods upon which the borax crystallizes.

$$2Ca_2B_6O_{11}.5H_2O + 2Na_2CO_3 + 2NaHCO_3 = 4CaCO_3 + 3Na_2B_4O_7 + 11H_2O.$$
$$4NaCaB_5O_9.8H_2O + 2Na_2CO_3 + 2NaHCO_3 = 4CaCO_3 + 5Na_2B_4O_7 + 9H_2O.$$

Properties.—Sodium borate occurs in colorless, transparent, monoclinic prisms, or as a white powder; it is odorless, and has a sweetish, alkaline taste. In warm, dry air it is slightly efflorescent.

The salt dissolves in 15 parts of water at 25°, and 0.6 part of boiling water; it is insoluble in alcohol. At 25° it is soluble in 1 part of glycerin. On the application of heat, borax first loses a part of its water of crystallization, and, without melting, swells to a white, porous mass. When the heat is increased to redness, the remainder of the water is driven off, amounting to 47.14 per cent., and the salt fuses to a colorless liquid, which on cooling hardens to a transparent glass known as borax glass. The aqueous solution of the salt reacts alkaline towards litmus paper, and colors yellow turmeric paper reddish-brown.

Uses.—On account of its solvent action on metallic oxides, borax is largely used in soldering and welding. Its extended use in metallurgical operations and in blowpipe analysis is well known. It enters into the composition of hard-water soaps, is used as a mordant in dyeing, and is employed in the manufacture of certain kinds of glass, in some enamels, and in glazes for metal ware and pottery.

Sodium Metaborate, $NaBO_2.4H_2O$.—This salt is formed when 1 molecule of borax is fused with 1 molecule of sodium carbonate; the product is the anhydrous salt, which, when dissolved in water and allowed to crystallize, separates with 4 molecules of water.

Sodium Orthoborate, Na_3BO_3.—When boron trioxide is fused with sodium carbonate the following reaction takes place:

$$B_2O_3 + 3Na_2CO_3 = 2Na_3BO_3 + 3CO_2.$$

This salt is very unstable, and cannot exist in solution, since it is converted by water into the metaborate.

Sodii Perboras, U.S.P., *Sodium Perborate,* $NaBO_3.4H_2O$. It contains not less than 9 per cent. of available oxygen, corresponding to about 86.5 per cent. of the pure salt. It may be prepared either by adding boric acid to a very cold solution of sodium peroxide, or by adding to a saturated solution of borax an equivalent quantity of sodium hydroxide, followed by twice the theoretical quantity of hydrogen peroxide: $Na_2B_4O_7 + 2NaOH + 4H_2O_2 = 4NaBO_3 + 5H_2O$. When heated above 40°, sodium perborate solution begins to give off oxygen. It occurs as white crystalline granules or powder, odorless and having a saline taste; stable in cool and dry air but decomposes with evolution of oxygen in warm or moist air. The aqueous solution of sodium perborate breaks up into sodium metaborate and hydrogen dioxide, gradually giving off oxygen. $NaBO_3 + H_2O = NaBO_2 + H_2O_2 = NaBO_2 + H_2O + O$. The solution of sodium perborate is an energetic oxidizing agent, converting ferrous salts to ferric, chromic acid to perchromic acid (same as H_2O_2), manganous salts to manganese dioxide, liberating chlorine from hydrochloric acid, iodine from its salts, etc. Sodium perborate is used in medicine and as a bleaching agent.

OXYGEN SALTS OF SODIUM AND SILICON

SODIUM SILICATES

Sodium silicate is a constituent of many minerals and of glass (see page 313). Like the potassium silicate, it is obtained by fusing powdered quartz (SiO_2) with calcined soda (Na_2CO_3) or sodium sulphate and powdered coal or charcoal. When sodium sulphate and powdered coal are used, the fused silicate is of a brown color, due to the formation of sodium sulphide (Na_2S). This may be decolorized by oxidation through a current of air or by adding an oxide of copper or lead. According to the proportions of soda and silica, the solid silicate varies in composition from $Na_2O.4SiO_2$ to $Na_2O.2SiO_2$. Its solubility in water decreases with increase in silica.

Commercial sodium silicate, or *water glass,* consists chiefly of sodium tetrasilicate, $Na_2O.4SiO_2$. It is prepared by fusing together 45 parts of powdered quartz or fine sand, 23 parts of dry sodium carbonate, and 3 parts of charcoal. The fused product is run into a tank of water, which has the effect of converting it into small porous masses, which are more easily dissolved in water. The solution in water is a thick, viscid liquid, which sets to form a translucent jelly. As ordinarily found in practical use, it is a semi-transparent, almost colorless, or yellowish, or pale greenish-yellow, viscid liquid, odorless, and of an alkaline reaction. Soluble glass must be kept in well-closed vessels, owing to its ready decomposition through contact with the carbon dioxide of the air, with separation of silicic acid.

Soluble glass enters into the composition of many cements, and is used in large quantities in the manufacture of silicated soaps, sizing of paper, and fire-proofing.

OXYGEN SALTS OF SODIUM AND CARBON

Sodium Carbonate, $Na_2CO_3.H_2O$. **Sodii Carbonas Monohydratus,** U.S.P. Commercial Sodium Carbonate or Sal Soda, $Na_2CO_3.10H_2O$.

History.—Sodium carbonate, or soda, has been known since the earliest times. It was not originally distinguished from potash, both being designated by the term *nitrum.*

Duhamel, in 1736, and Marggraf, in 1759, were the first to draw a sharp distinction between the two; the former showed the base of common salt, borax, and the ashes of sea plants to be one and the same; the latter designated soda as *mineral alkali,* and distinguished it from potash by the yellow color it imparted to the flame.

Nearly all the soda was obtained previous to 1793 from the ashes of sea plants, called *varec* or *kelp.* These sea-weeds were collected on the northwest coasts of France, Spain, Ireland, and Scotland.

One of the immediate results of the French wars and Revolution at the close of the eighteenth century was the imperative demand for various war staples, among which was sal soda, which up to this time had been prepared from the ashes of sea-weed. Upon investigation of the various processes that had been proposed, the government found that an apothecary, Nicolas Leblanc, associated with Dizé, was operating a small plant at St. Denis, in which sea salt was used to furnish the source for his sodium carbonate. This factory was taken over and was in successful operation in 1794. The industry was established in England in 1823 by Muspratt.

There is probably no operation in the whole field of industrial chemistry that has undergone so few fundamental changes, owing to the perfection and completeness of the original process. So far as the material employed and the reactions involved are concerned, they remain the same. Improvements have been introduced, but they have been of a mechanical nature or have related to the utilization of waste material, its chief by-products being hydrochloric acid and bleaching powder. In more recent times entirely different processes have been established, the most successful ones being that by Thomsen (1851), in which *cryolite* was used, that by Solvay (1873), known as the *ammonia-soda* process, and the several processes which electrolyze sodium chloride.

Occurrence.—Sodium carbonate is found in the ash of all plants, but especially in that from sea plants and those growing near salt waters. It is also found in the waters of many mineral springs, often in the form of bicarbonate. An efflorescence or deposit, consisting largely of sodium carbonate, occurs in the soil of many rainless localities, as in Egypt, Mexico, parts of South America, and in the drier parts of the United States, there being unknown quantities in California, Wyoming, and Nevada, and some other Western States.

Preparation.—(1) *Native Soda.*—The soda which occurs in nature consists almost entirely of a double carbonate, having the formula $2NaHCO_3.Na_2CO_3.2H_2O$. In early times that which was brought from Egypt was known as *Trona-soda*, that from South America (Colombia) and that from Mexico was called *Urao-soda.*

(2) *Soda from the Ashes of Plants.*—The amount found in the ashes of sea and sea-coast plants is from 5 to 30 per cent. The soda from Spain is usually known as *Salsola* soda and *Barilla;* that from the south of France is called *Salicox* or *Blanquette* soda; and that prepared from the species of Fucus, used also in the preparation of bromine and iodine, is called *Kelp* soda in Scotland, and *Varec* soda in Normandy and the Channel Islands. Potassium is far more widely distributed in plants than sodium, but those plants growing in or near the salt water take up large quantities of sodium chloride and convert it into salts of the organic acids. Soda from these sources is only of historic interest.

(3) *The Leblanc Process.*—When sodium carbonate is manufactured by this method, the first step consists in converting sodium chloride into sulphate; this part of the operation is known as the *salt-cake process.* It consists in decomposing the sodium chloride, in a specially constructed furnace, with chamber acid (sulphuric acid having a specific gravity of 1.60 to 1.70), hydrochloric acid vapors being given off, according to the following reaction:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Acid Sodium}\\\text{Sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{HCl.}$$

The hydrochloric acid is passed into coke towers to be condensed and dissolved by cold water, forming the commercial hydrochloric or muriatic acid. The residue from this reaction consists of acid sodium sulphate, with some undecomposed chloride. This is raked into a hearth or roaster, where the reaction is completed at a higher temperature, as follows:

$$\underset{\substack{\text{Acid Sodium}\\\text{Sulphate.}}}{NaHSO_4} + \underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} = \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{HCl.}$$

The hydrochloric acid which is evolved is recovered as in the preceding part of the operation. The salt which remains consists of about 95 per cent. sodium sulphate, with small quantities of the acid sulphate, sodium chloride, calcium sulphate, ferric oxide, and insoluble matter; it is commercially known as *salt-cake*, or frequently simply as *sulphate.*

The sulphate is converted into carbonate by the *black-ash process.* This operation consists in fusing an intimate mixture of salt-cake, limestone, and coal. The reaction takes place in two steps, as follows:

$$\underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{Na_2SO_4} + \underset{\text{Carbon.}}{2C} = \underset{\substack{\text{Sodium}\\\text{Sulphide.}}}{Na_2S} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{2CO_2.}$$

The sodium sulphate is first reduced to sulphide, and the latter reacts with the calcium carbonate, forming calcium sulphide and sodium carbonate:

$$\underset{\substack{\text{Sodium}\\\text{Sulphide.}}}{Na_2S} + \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{CaCO_3} = \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{Sulphide}}}{CaS.}$$

After the salt-cake is all decomposed, a supplementary reaction between the limestone and the remaining carbon takes place, whereby quicklime is formed with evolution of carbon monoxide, the blue flame of which marks the end of the treatment:

$$CaCO_3 + C = CaO + 2CO.$$

When the black ash is leached, this quicklime, becoming calcium hydroxide, reacts with some of the sodium carbonate to form sodium hydroxide, or caustic soda.

Crude soda or black-ash has about the following composition:

	Per cent.
Sodium carbonate	45
Calcium sulphide	30
Calcium oxide	10
Sodium sulphate, silicate, aluminate, and chloride with calcium carbonate and iron oxide ....about	15

Considerable quantities of this crude soda are used without further purification in the manufacture of green glassware, in soap-making, and in bleaching.

The next step in the Leblanc process consists in leaching the black-ash, evaporating the solution, and crystallizing.

The mother liquor ("tank liquor") from the first crystallization of the soda contains considerable quantities of sodium hydroxide ($CaO + H_2O + Na_2CO_3 = CaCO_3 + 2NaOH$) ; it also contains some chloride, sulphate, cyanide, and sulphide as impurities. These are in part removed by allowing the liquor to run down a coke tower in which it meets a current of air and carbon dioxide (chimney gases), which convert the hydroxide into carbonate, oxidize the sulphides and cyanides, while the alumina, iron, and silica are precipitated. The liquor is then concentrated until on cooling it deposits crystals of sodium carbonate.

Soda made by this process contains a little caustic soda with traces of sulphide, sulphite, sulphate, and chloride. The secondary products of this process are hydrochloric acid and alkali waste (chiefly CaS and $CaCO_3$), the latter being utilized in the manufacture of sodium thiosulphate. The Leblanc process has been largely supplanted by that of Solvay.

Caustic soda is made from soda-ash or "tank liquor" by adding calcium hydroxide, $Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$. Usually air with steam is blown into the liquor, which aids the reaction and converts the sodium sulphide into thiosulphate and sulphate:

$$2Na_2S + H_2O + 2O_2 = 2NaOH + Na_2S_2O_3.$$

The thiosulphate is removed through oxidation to sulphate.

(5) *The Ammonia-Soda (or Solvay) Process.*—As long ago as 1838 this process was patented by Dyer and Hemming, but the numerous practical difficulties were not overcome until Solvay, in 1865, established a factory near Brussels.

The ammonia-soda process is based on the interaction that takes place at ordinary temperature between solutions of sodium chloride and ammonium bicarbonate with formation of sodium bicarbonate, as follows:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\substack{\text{Acid}\\\text{Ammonium}\\\text{Carbonate.}}}{NH_4HCO_3} = \underset{\substack{\text{Acid}\\\text{Sodium}\\\text{Carbonate.}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\\text{Chloride.}}}{NH_4Cl.}$$

In practice this is effected by running the salt solution down through a column, which meets in its descent the ammonia gas. The ammonia enters through a perforated iron plate, by which it is broken up into small bubbles. Considerable rise of temperature takes place during the absorption, and the saturated brine is passed through a cooler into another vessel, in which it is saturated with the carbon dioxide. The reaction may be summed up as follows:

$$\underset{\substack{\text{Sodium}\\\text{Chloride.}}}{NaCl} + \underset{\text{Ammonia.}}{NH_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid}\\\text{Sodium}\\\text{Carbonate.}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\\text{Chloride.}}}{NH_4Cl.}$$

The sodium bicarbonate produced in this process separates owing to its insolubility in the cold concentrated ammonium chloride solution and is collected on a vacuum filter, washed with a small quantity of cold water, and dried. It is converted into normal carbonate by heat:

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

The carbon dioxide is used to furnish a part of that required to saturate the ammoniacal brine. The solution, which contains ammonium chloride and some free ammonia, is heated with burnt lime for the regeneration of ammonia ($2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O$). Part of the carbon dioxide used in this process is obtained by heating limestone, while the residue of calcium oxide is utilized as outlined above. This process cannot be utilized for the preparation of potassium carbonate because its bicarbonate is too soluble to separate.

(6) *Soda from Cryolite.*—The mineral cryolite, a double fluoride of sodium and aluminum, $AlF_3.3NaF$, occurs in enormous deposits in Greenland. When the finely divided mineral is mixed with chalk or limestone and heated, the following reaction takes place:

$$\underset{\text{Cryolite.}}{2(AlF_3.3NaF)} + \underset{\substack{\text{Calcium}\\\text{Carbonate.}}}{6CaCO_3} = \underset{\substack{\text{Sodium}\\\text{Aluminate.}}}{Al_2O_3.3Na_2O} + \underset{\substack{\text{Calcium}\\\text{Fluoride.}}}{6CaF_2} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{6CO_2}.$$

The fused mass is treated with water, whereby the soluble sodium aluminate is dissolved; carbon dioxide is then passed through this solution under pressure, which precipitates the aluminum hydroxide and forms sodium carbonate:

$$\underset{\substack{\text{Sodium}\\\text{Aluminate.}}}{2AlO_3Na_3} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{3CO_2} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{3Na_2CO_3} + \underset{\substack{\text{Aluminum}\\\text{Hydroxide.}}}{2Al(OH)_3}.$$

The clear solution is run off from the precipitate, and the sodium carbonate allowed to crystallize.

Properties.—At ordinary temperature, sodium carbonate crystallizes in monoclinic prisms with 10 molecules of water, from a saturated solution; between 30° and 50° it crystallizes in rhombic system with 7 molecules of water; if crystallization takes place below 30° it separates in granular crystals with *one* molecule of water. The salt is odorless, and has an alkaline taste and reaction. When exposed to air the crystals become white, and gradually crumble to a fine white powder, losing about one-half of their water of crystallization, amounting to 31.46 per cent. The official salt (monohydrate) is a white crystalline, granular powder, odorless, and with a strongly alkaline taste. When exposed to the air under ordinary conditions it absorbs only a slight percentage of moisture. Exposed to warm, dry air at or above 50° C. the salt effloresces, and at 100° C. it loses its water of crystallization (14.52 per cent.). Soluble in 3 parts of water at 25° C. and 1.8 parts of boiling water. The salt fuses at a bright red heat, or about 850°.

Sodium carbonate is perhaps used in larger quantity and in a greater variety of ways than any other alkali salt. In addition to its own uses, it forms the base from which many other sodium salts are prepared.

Pure sodium carbonate is prepared by dissolving the commercial crystals in one-half their weight of water at 30° to 40°, filtering the solution, and allowing it to stand in a cool place. The small crystals which separate are collected in a funnel, allowed to drain well, and then washed with a small quantity of cold water, or with a saturated solution of pure sodium carbonate. It may also be obtained by washing sodium bicarbonate with cold water till free from chloride and sulphate, drying, and heating the residue to redness.

The chief impurities in the commercial carbonate are chlorides, sulphates, silica, calcium, alumina, and iron.

Anhydrous Sodium Carbonate.—This is obtained from the commercial crystals by allowing them to effloresce at a temperature of about 50° until they disintegrate, and then drying at 100° C. until constant weight is obtained. Anhydrous soda is soluble in about 14 parts of water at 20° and about 1.6 parts at 37.5°. This salt is employed either alone or in conjunction with saltpetre in making fusions in the analysis of minerals and other analytic operations (see U.S.P., p. 545).

Sodium Bicarbonate (*Acid Sodium Carbonate, Sodium Hydrogen Carbonate*). **Sodii Bicarbonas,** U.S.P.—This salt was first prepared by Valentine Rose in 1801. It occurs in many mineral waters, especially those of Ems and Vichy.

Preparation.—Sodium bicarbonate was originally prepared by passing carbon dioxide into a concentrated solution of neutral sodium carbonate; the bicarbonate, on account of its sparing solubility, separates:

$$Na_2CO_3 + CO_2 + H_2O = 2NaHCO_3.$$

Commercially it is prepared altogether by the Solvay process.

Properties.—Sodium bicarbonate occurs in small monoclinic, tabular crystals, which are frequently united into crusts. Commercially it is a white, opaque powder, permanent in the air under ordinary circumstances, but decomposing slowly in moist air. It has a mild alkaline taste; the cold solution, when freshly prepared, gives a faintly alkaline reaction to litmus paper. Its alkalinity increases through loss in carbon dioxide and conversion into normal carbonate on long standing, agitation, or heat. The commercial bicarbonate contains traces of normal carbonate, chloride, and sulphate. These may be removed by washing with cold distilled water, afterwards drying at low temperature.

The salt is soluble in 10 parts of water at 25°; when heated with water above 15° it loses carbon dioxide, the neutral carbonate being formed; at the boiling temperature, or one-half hour heating of the *dry salt* at 270°, it is entirely converted into the normal salt as follows:

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

Uses.—Sodium bicarbonate (sometimes called *saleratus*) enters into the composition of most baking powders; it has considerable use in the textile industries, especially in degumming silk and scouring wool, as it attacks the fibre less than soap or ammonia. Medicinally, it is used as an antacid.

AMMONIUM

Formula, NH_4. *Molecular Weight*, 18,042. *Valence*, I.

History.—The salts of ammonium were known to the ancients, but ammonia gas was first collected by Priestley in 1774, although it was previously known that a pungent odor was developed on adding an alkali to sal ammoniac. Berthollet, in 1785, determined it to be composed of nitrogen and hydrogen.

Theoretical Considerations.—Ammonia when dissolved in water combines to form a hydrate ($NH_3 + H.OH = NH_4OH$), which dissociates into the cation $\dot{N}H_4$, called ammonium, and the anion OH′. The former deports itself as though it were a metallic element, forming salts possessing physical and chemical properties analogous to those of sodium and potassium. The anion OH′ imparts the alkaline reaction to ammonia water. This view of the existence of an elemental NH_4 group has been verified by the formation of an amalgam composed of the radical NH_4 and mercury, a property characteristic of metallic elements only. When ammonium chloride in contact with mercury is subjected to the electric current, a bulky, buttery mass is formed which is considered to be ammonium amalgam. The same product is obtained by placing sodium amalgam containing 1 per cent. of sodium in a concentrated solution of ammonium chloride, adding at the same time a few fragments of the salt. The bulky amalgam which is formed becomes crystalline at —80°, and at —29° begins to decompose, forming 2 volumes of ammonia gas and 1 volume of hydrogen. Ammonium hydroxide has not been isolated. When the solution is evaporated it splits up into NH_3 and H_2O. The salts of ammonium most closely resemble those of potassium, with which they are isomorphous.

Occurrence and Sources.—The salts of ammonium are widely distributed in nature. The carbonate, nitrate, and nitrite are found in small quantities in the atmosphere, in rain, in snow, in the soil, and in the secretions of plants and animals.

One of the chief inorganic sources of ammonium salts is the native carbonate in the guano deposits of South America; the salt which exists in this guano is the acid carbonate, NH_4HCO_3.

The organic sources of ammonium salts are of importance, since they yield nearly all of the commercial salts; at the present time practically the entire supply comes from gas-liquor, from the condensed gases of coke-ovens, and from the watery distillate of shale-works. These various ammoniacal liquors are treated according to the salt required, usually the chloride or sulphate, the details of which will be considered under the respective salts. For the industrial sources of ammonia see page 246.

HALOGEN SALTS OF AMMONIUM

Ammonium Chloride, NH_4Cl (Sal Ammoniac). **Ammonii Chloridum, U.S.P.**—Sal ammoniac was prepared in earlier times in Egypt by the sublimation of the ashes and soot resulting from the burning of camel's dung, which was there used as fuel. The salt may be prepared by the direct union of equal volumes of the gases, ammonia, and hydrochloric acid.

At the present time the ammoniacal water from gas-works or similar sources is neutralized with hydrochloric acid, or the ammonia gas is liberated from these liquors by lime and passed into the hydrochloric acid. The salt is first partly purified by crystallization, and then it is sublimed in earthenware pots or iron retorts. The ammonium chloride collects on the cover or dome of the retort as a thick fibrous cake. When prepared in iron vessels sal ammoniac is usually contaminated with some of this metal. A crystalline and granular ammonium chloride may be prepared by adding to the powdered salt a hot, saturated solution of the same, so as to form a magma of crystals, which are placed in moulds, and, after thorough draining, the whole is dried. A former official process for the preparation of a purified granular salt consisted in adding to a hot solution of the salt some ammonium hydroxide, filtering, evaporating, and granulating; this procedure was for the purpose of removing iron.

Properties.—Ammonium chloride comes in commerce as *sublimed sal ammoniac,* in masses of fibrous crystals, or else as *crystallized sal ammoniac,* or *muriate of ammonia,* in the form of small, white octahedra or cubes. The salt is odorless, with a cooling, saline taste, and permanent in the air. It is soluble in 2.6 parts of water at 25°, in 1.4 parts of boiling water, and in 100 parts of alcohol at 25°. On the application of a low red heat, the salt is completely volatilized without residue. At 350° it dissociates into two gases, NH_3 and HCl, which upon cooling reunite, forming NH_4Cl. Its aqueous solution shows a weak acid reaction to litmus, owing to the hydrolysis of the NH_4 ions with the hydroxyl ions of the water to form NH_3 and H_2O, leaving unchanged acid H ions of the water.

Ammonium chloride reacts slightly acid towards phenolphthalein, and as this property is characteristic of the other ammonium salts, this indicator cannot be used in their presence.

Uses.—Ammonium chloride is used extensively as a medicinal agent, for soldering (heat liberating HCl, which dissolves the oxides on the metal surface), in calico printing and dyeing, and in the manufacture of a number of pigments; considerable quantities are also used as a reagent in the laboratory.

Ammonium Bromide, NH_4Br. **Ammonii Bromidum, U.S.P.**—This salt may be prepared by neutralizing hydrobromic acid with ammonium hydroxide or carbonate or by interaction between ferrous bromide and ammonium hydroxide:

$$\underset{\text{Ferrous Bromide.}}{FeBr_2} + \underset{\text{Ammonium Hydroxide.}}{2NH_4OH} = \underset{\text{Ammonium Bromide.}}{2NH_4Br} + \underset{\text{Ferrous Hydroxide.}}{Fe(OH)_2}.$$

It may also be made by adding slowly 35 parts of bromine to 52 parts of ammonia water (20 per cent.); the hypobromite formed during this reaction is reduced by passing hydrogen sulphide through the solution. After removing the excess of sulphide by heating, and filtering off the separated sulphur, the filtrate is evaporated to dryness on a water-bath while ammonia is being added in small portions. This is necessary to prevent the formation of the explosive nitrogen bromide: $NH_4Br + 3Br_2 = 4HBr + NBr_3$.

The ferrous hydroxide is bulky and not completely precipitated until the solution is boiled, by which it is converted into ferric hydroxide, $Fe(OH)_3$.

Properties.—Ammonium bromide occurs in colorless, transparent, prismatic crystals, or as a white, crystalline powder. It is odorless, has a pungent, saline taste, and is neutral or of a slightly acid reaction towards litmus paper. When exposed to the air the salt undergoes slight decomposition, becoming yellowish. It is soluble in 1.3 parts of water at 25°, and in 0.9 part of boiling water, in 12 parts of alcohol at 25°, and in 1.2 parts of boiling alcohol. When heated, the salt volatilizes completely without melting, dissociating into NH_3 and HBr.

Uses.—The chief use of ammonium bromide is in medicine.

Ammonium Iodide, NH_4I. **Ammonii Iodidum,** U.S.P.—Concentrated hot solutions of 33 parts potassium iodide and 13 parts ammonium sulphate are mixed, stirred well, mixed with double their volume of alcohol, and the whole cooled to 40°:

$$2KI + (NH)_2SO_4 = 2NH_4I + K_2SO_4.$$

The mixture is then thrown into a funnel, previously stopped with cotton, allowed to drain, and the residual potassium sulphate washed with a mixture of 2 volumes of water and 1 volume of alcohol. The filtrate containing the ammonium iodide is then evaporated carefully to dryness while adding small portions of ammonia water, stirring in order to granulate the salt. When prepared according to this process ammonium iodide always contains small quantities of ammonium sulphate. Ammonium iodide may also be prepared like the bromide, by interaction between ferrous iodide and ammonia water. The product, which is very hygroscopic, should be kept in small, well-stoppered vials protected from the light, owing to its tendency to lose ammonia with liberation of iodine, becoming yellow.

Properties.—Ammonium iodide occurs in minute, colorless, cubical crystals, odorless, and having a sharp, saline taste. It is soluble at 25° in 0.6 part of water, in 3.7 parts of alcohol, and in 0.5 part of boiling water. When heated it completely volatilizes without melting, dissociating at first into NH_3 and HI; the latter decomposing evolves vapors of iodine. Its aqueous solution is neutral or slightly acid to litmus.

Ammonium iodide deliquesces when exposed to the air, and gradually undergoes decomposition, becoming yellow to yellowish-brown, due to the liberation of free iodine. The colored salt has a faint odor of iodine. It should not be dispensed when colored, but may be reclaimed by dissolving in very little water, decolorizing with a small quantity of freshly prepared ammonium sulphide; then, after filtering off the separated sulphur, the filtrate is evaporated quickly to dryness on a water-bath while adding a little ammonia water.

Ammonium Fluoride, NH_4F.—This salt is obtained in prismatic crystals by the sublimation of a mixture of ammonium chloride and sodium fluoride:

$$NH_4Cl + NaF = NH_4F + NaCl.$$

Its aqueous solution has an acid reaction, due to liberation of HF, and should be stored in rubber or cerasin containers. It is used for etching glass and was at one time employed as a food and beverage preservative now legally prohibited.

AMMONIUM AND SULPHUR

Ammonium Monosulphide $(NH_4)_2S$.—When 2 volumes of ammonia gas and 1 volume of hydrogen sulphide are mixed at a temperature of —18°, ammonium monosulphide is formed. It forms colorless, glittering crystals, which commence to decompose at ordinary temperatures into ammonia and ammonium sulphydrate. This compound (Ammonium Sulphide, T.S.) is prepared in aqueous solution by saturating 3 parts of solution of ammonia with hydrogen sulphide and then adding 2 parts of ammonia water. This is the official test-solution. It is a valuable reagent in the laboratory, and is very extensively used. Owing to the instability of this solution, the Pharmacopœia recognizes Sodium Sulphide, which is stable and is used in the extemporaneous preparation of Sodium Sulphide, T.S.

Ammonium Hydrosulphide, NH_4SH.—This compound is obtained by saturating ammonia water with hydrogen sulphide; on cooling to 0°, colorless, acicular crystals separate. These crystals are formed when alcoholic ammonia is saturated with hydrogen sulphide:

$$NH_4OH + H_2S = NH_4SH + H_2O.$$

This solution and the preceding one of ammonium monosulphide are colored yellow on standing, owing to the formation of the ammonium polysulphides and water.

OXYGEN SALTS OF AMMONIUM

Ammonium Sulphate, $(NH_4)_2SO_4$.—The only natural source of this salt is the ammonium sulphate of the suffioni of Tuscany, where it is met with as a by-product in the manufacture of boric acid. It is usually prepared by saturating ammoniacal gas-liquor with sulphuric acid, evaporating rapidly, and removing, with perforated ladles, the crystals as they form. As thus obtained the crystals are of a dark color. They are first allowed to drain well, then recrystallized until sufficiently white.

Properties.—Ammonium sulphate occurs in large, transparent, rhombic crystals, isomorphous with potassium sulphate. They are soluble in 1.3 parts of water at 15° and in 1 part of boiling water; insoluble in absolute alcohol, but slightly soluble in ordinary alcohol. On the application of heat the crystals melt at 140°; then at higher temperatures (about 300°) it decomposes into ammonia and NH_4HSO_4.

which in turn yield NH_3, SO_2, N, and H_2O. The aqueous solution of ammonium sulphate when boiled evolves ammonia gas with formation of the acid sulphate.

Uses.—Ammonium sulphate is chiefly used as a basis for the preparation of the other ammonium salts. It is employed in the manufacture of ammonia-alum and as a fertilizer. When dipped into ammonium sulphate solution and dried, fabrics, wood, etc., become non-inflammable. Purified ammonium sulphate is used as a U.S.P. Reagent.

Ammonium Persulphate, $(NH_4)_2.S_2O_8$.—This salt is obtained by the electrolysis at 7° of a saturated solution of ammonium sulphate in dilute sulphuric acid. The white prisms are very soluble in water. It is used extensively as an oxidizing and bleaching agent and in photography.

Ammonium Nitrate, NH_4NO_3.—The usual process for obtaining this salt is by saturating nitric acid with ammonium hydroxide or carbonate and evaporating to crystallization, or by interaction between ammonium sulphate and barium nitrate:

$$(NH_4)_2SO_4 + Ba(NO_3)_2 = 2NH_4NO_3 + BaSO_4.$$

filtering, washing and evaporating. According to a patented process, a solution of calcium nitrate is mixed with an excess of ammonia and saturated with carbon dioxide.

Properties.—Ammonium nitrate (U.S.P. Reagent) is found in commerce in long, thin, colorless, rhombic prisms, or in white, fused masses, or as a white, granular powder; it is odorless, has a sharp, bitter, saline taste, and is somewhat deliquescent. Its aqueous solution is neutral to litmus paper. The salt is soluble at 15° in 0.5 part of water and in 10 parts of alcohol. It melts at 160°, and between 230° and 250° it is decomposed into nitrogen monoxide and water, as follows:

$$NH_4NO_3 = N_2O + 2H_2O.$$

A small proportion of the salt is sublimed unchanged at the same time. The fused salt acts as an energetic oxidizing agent.

Uses.—Ammonium nitrate is used largely in the production of nitrogen monoxide, or "laughing gas." The salt when dissolved in water produces a decided fall in temperature, hence is used in freezing mixtures. It is also used in the preparation of some explosives.

Ammonium Nitrite, NH_4NO_2.—This may be prepared by interaction between concentrated aqueous solutions of barium nitrite and ammonium sulphate; the insoluble barium sulphate is removed by filtration and the filtrate evaporated spontaneously over sulphuric acid in a desiccator. The barium nitrite may be prepared by boiling a concentrated solution of barium nitrate with spongy lead until the latter is converted into lead oxide. The latter is removed from the filtrate by passing carbon dioxide followed by hydrogen sulphide through the solution, which, after filtration, is evaporated to crystallization. Ammonium nitrite is also formed by an electric discharge through moist air. Ammonium nitrite occurs in indistinct crystalline masses, which decompose when heated, yielding water and nitrogen:

$$NH_4NO_2 = N_2 + 2H_2O.$$

Normal Ammonium Phosphate, $(NH_4)_3PO_4.3H_2O$, is sometimes found in guano; it is also obtained by mixing a concentrated solution of hydrogen diammonium phosphate, or phosphoric acid, with concentrated water of ammonia. Small prismatic or acicular crystals are deposited which decompose into the secondary phosphate $[(NH_4)_2HPO_4]$ when exposed to the air, or when the solution is boiled.

Hydrogen Diammonium Phosphate, $(NH_4)_2HPO_4$, is also found in some guanos, and is prepared by evaporating a solution of phosphoric acid with a slight excess of ammonia. The salt is deposited in transparent monoclinic prisms.

Dihydrogen Ammonium Phosphate, $NH_4H_2PO_4$.—When phosphoric acid is in slight excess over ammonia, or a concentrated solution of the secondary salt is boiled, crystals of this compound separate.

Hydrogen Ammonium Sodium Phosphate, $NaNH_4HPO_4.H_2O$.—Microcosmic salt occurs in guano and in putrid urine. The salt is prepared by dissolving 5 parts of ordinary sodium phosphate, $Na_2HPO_4.12H_2O$, in hot water, adding it to a hot solution of the ordinary ammonium phosphate, $(NH_4)_2HPO_4$, and allowing the solution to cool. The salt separates in transparent, monoclinic, prismatic crystals. They have a distinctly saline taste, and are readily soluble in water. On the application of heat the salt melts, gives off water and ammonia, and leaves a residue of the dihydrogen sodium phosphate; the further application of heat melts this salt to clear liquid with further loss of water, and with the formation of sodium metaphosphate, which forms a clear glass on cooling: $NaNH_4HPO_4 = H_2O + NaPO_3$. Because of this property of forming a clear glass the salt is largely used in blowpipe analysis.

Ammonium Carbonate, $NH_4HCO_3.NH_4NH_2CO_2$. **Ammonii Carbonas,** U.S.P.—As will be seen from the above formula, the official salt is a compound of the acid ammonium carbonate with ammonium carbamate, which yields not less than 30 per cent. nor more than 32 per cent. of NH_3. Normal ammonium carbonate, $(NH_4)_2CO_3$, is obtained when the official salt is dissolved in water.

$$\underset{\text{Official Ammonium Carbonate.}}{NH_4HCO_3.NH_4NH_2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Acid Ammonium}\\ \text{Carbonate.}}}{NH_4HCO_3} + \underset{\substack{\text{Normal Ammonium}\\ \text{Carbonate.}}}{(NH_4)_2CO_3}.$$

The normal carbonate may be prepared by passing ammonia gas over the official compound or digesting it for 2 hours at a temperature at 12° with strong aqueous ammonia:

$$NH_4NH_2CO_2.NH_4HCO_3 + NH_3 + H_2O = 2(NH_4)_2CO_3.$$

the resulting white, crystalline powder is dried by pressing between folds of absorbent paper. These crystals readily lose NH_3 and pass over into the acid carbonate.

The official, which is also the commercial, salt is prepared by heating in iron retorts ammonium sulphate and calcium carbonate, or chalk, sometimes with a small quantity of charcoal:

$$\underset{\substack{\text{Ammonium}\\ \text{Sulphate.}}}{2(NH_4)_2SO_4} + \underset{\substack{\text{Calcium}\\ \text{Carbonate.}}}{2CaCO_3} = \underset{\substack{\text{Official Ammonium}\\ \text{Carbonate.}}}{NH_4HCO_3.NH_4NH_2CO_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Calcium}\\ \text{Sulphate.}}}{2CaSO_4}.$$

After the condensation of the ammonium carbonate, the uncondensed vapors, containing water and ammonia, are led into sulphuric acid in order to recover the ammonia.

Crude ammonium carbonate may also be prepared by passing ammonia liberated from gas-liquors by lime, into leaden chambers along with carbon dioxide and water.

$$\underset{\text{Ammonia.}}{3NH_3} + \underset{\text{Carbon Dioxide.}}{2CO_2} + \underset{\text{Wa}}{H_2O} = \underset{\text{O}\quad\text{Ammonium Carbonate.}}{NH_4HCO_3.NH_4NH_2CO_2}.$$

Properties.—The official ammonium carbonate occurs in “ white, hard, translucent, striated masses, having a strong odor of ammonia, without empyreuma, and a sharp, saline taste. On exposure to the air, the salt loses both ammonia and carbon dioxide, becoming opaque, and is finally converted into friable, porous lumps, or a white powder.” The salt is soluble in about 4 parts of water at 25°; it is decomposed by hot water, with the elimination of carbonic acid and ammonia, resulting finally, after prolonged boiling, in complete dissipation of the salt. *Alcohol dissolves the carbamate, leaving the acid carbonate behind.* On the application of heat, ammonium carbonate is completely dissipated without darkening or charring. The aqueous solution reactions alkaline to litmus, and effervesces strongly with acids.

Ammonium Carbamate, $NH_4NH_2CO_2$, may be prepared by saturating absolute alcohol with dry ammonia gas and then dry CO_2, whereby the carbamate separates in crystalline form. Ammonium carbamate when heated in aqueous solution forms the normal carbonate: $NH_4NH_2CO_2 + H_2O = (NH_4)_2CO_3$.

Ammonium Hydrogen Carbonate, NH_4HCO_3. Ammonium Bicarbonate.—When the commercial carbonate is exposed to the air for some time a white powder results, consisting of the bicarbonate, $NH_4NH_2CO_2 + H_2O = NH_4HCO_3 + NH_3$; it may also be prepared by passing carbon dioxide into an aqueous solution of the ordinary carbonate. It is usually found as a white, mealy powder, but may be obtained in large rhombic crystals by allowing them to form slowly from aqueous solution. At 60° it is slowly decomposed into ammonia, water, and carbon dioxide. The salt is soluble in 8 parts of water at 15°, *and is insoluble in alcohol.*

LITHIUM

Symbol, Li. *Atomic Weight,* 6.94 *Valence,* I.

History.—Discovered by Arfvedson in 1817 in the mineral *petalite.* Named lithium (λίθος = *stone*) because it was thought to exist only in the mineral kingdom.

Occurrence.—While lithium is not found in large quantities, it is still widely distributed in the three kingdoms. In the mineral kingdom it is found in *petalite,* a silicate of aluminum, sodium, and lithium, to the extent of 2.7 to 3.7 per cent.; in *lepidolite,* a lithia mica (consisting of alumina silicate with fluorides of potassium and lithium containing 1.3 to 5.7 per cent.; and in *spodumene,* a silicate of aluminum, sodium, and lithium, 3.8 to 5.6 per cent. It is found in a number of mineral waters, the most notable in the United States being the springs at Gettysburg. In the vegetable kingdom, lithium has been detected in the ash of certain plants, as tobacco. The animal kingdom contains small quantities of this metal, as shown by its detection in the ashes of blood and milk and in muscular tissue.

Isolation.—The oxide cannot be reduced by carbon, as in the case of sodium and potassium, hence the metal is obtained by the electrolysis of fused lithium chloride, or of a pyridine solution of the salt.

Properties.—Lithium possesses the silver-white luster of sodium and potassium, but does not tarnish by oxidation so easily as they do. It is the lightest of all known solids, having a specific gravity of $0.534^{20°}$.

It floats on ordinary petroleum, and can only be preserved under the lightest gasoline.

When heated to 180° lithium melts, and at a higher temperature ignites, and burns with a brilliant red flame. In contact with water it does not oxidize so actively as sodium, as not sufficient heat is evolved to melt it. Most of the acids act on it slowly, but concentrated nitric acid attacks it with explosive violence.

COMPOUNDS OF LITHIUM

The soluble salts of lithium resemble those of calcium in some respects, and in others sodium and potassium. Like calcium, lithium forms an insoluble carbonate and phosphate; like the alkali metals, metallic lithium burns to form an oxide.

The color of the lithium flame is crimson.

Lithium Chloride, $LiCl$.—This salt is usually prepared by dissolving the carbonate in hydrochloric acid, or it is made directly from one of the minerals. When the aqueous solution is evaporated slowly over sulphuric acid at ordinary temperatures, the salt is obtained in octahedra. It is very soluble in water, being one of the most deliquescent salts known. It is soluble in alcohol and in a mixture of absolute alcohol and ether. Lithium chloride fuses at a low red heat, and at a higher temperature is slowly volatilized. On evaporating its aqueous solution to dryness, the salt is slightly decomposed, hydrochloric acid being given off, and the residue becoming alkaline.

Lithium Bromide, $LiBr$. **Lithii Bromidum,** U.S.P.—This salt is obtained by neutralizing hydrobromic acid with lithium carbonate. It occurs as a white, granular, crystalline powder, odorless, and with a sharp, slightly bitter, saline taste, and a neutral reaction. It is soluble in 0.6 part of water at 25°, and in 0.4 part of boiling water; very soluble in alcohol, and soluble in ether. On the application of heat, lithium bromide melts at low redness, and at a higher temperature is slowly volatilized.

Lithium Oxide, Li_2O, is formed when the metal is burned in air. It is prepared by heating the nitrate to redness in a silver basin. It forms a white, crystalline mass, which dissolves slowly in water with the formation of the hydroxide, $LiOH$. The latter behaves in many respects like sodium hydroxide, but is less energetic.

Normal Lithium Sulphate, $Li_2SO_4.H_2O$, is formed in the decomposition of petalite, or other lithia minerals, by sulphuric acid, as described under the carbonate, or dilute sulphuric acid is neutralized with lithium carbonate. It crystallizes in thin monoclinic plates, and is easily soluble in water and in alcohol. The acid salt, $LiHSO_4$, is also known.

Double Potassium and Lithium Sulphate, $KLiSO_4$, is obtained by dissolving the molecular weight of each salt in water, mixing, and allowing to crystallize, when rhombic crystals of the double salt separate.

Lithium Phosphate, Li_3PO_4, is quite insoluble in water, which gives it some analytic interest, since lithium salts are thereby separated from the other alkali metals.

Normal Lithium Carbonate, Li_2CO_3. **Lithii Carbonas,** U.S.P.—On account of its sparing solubility in water, this salt differs from the carbonates of sodium and potassium. It rather forms a connecting link between this group of metals and the next, consisting of calcium, strontium, and barium, whose carbonates it resembles.

Lithium carbonate may be prepared by a precipitation of a soluble salt, like the sulphate or chloride, with sodium or ammonium carbonate, and boiling. It is, however, prepared from its source, lepidolite, by powdering and heating the mineral and then digesting it with sulphuric acid. The mass with the acid is gently heated, and the cooled product extracted with water. The aqueous solution is boiled with milk of lime, by which iron and aluminum are removed; the filtrate from them consists of potassium, sodium, and lithium hydroxides, with a small quantity of lime; the latter is removed by evaporating to dryness and dissolving in a small quantity of hot water, by which a solution is obtained containing the hydroxides of the alkalies; from this the lithium carbonate is precipitated by boiling with ammonium carbonate.

This may be purified by suspending 1 part of the carbonate in 20 parts of water and effecting solution by saturating with carbon dioxide, which forms the bicarbonate, $LiHCO_3$; after filtering, the solution is boiled, whereby a pure salt is precipitated.

Properties.—Lithium carbonate is a light, white, odorless powder, with an alkaline taste and reaction. It is permanent in the air; soluble in 78 parts of water at 25° and in 140 parts of boiling water, insoluble in alcohol. On the application of a temperature approaching redness, lithium carbonate melts, and gives off some carbon dioxide; when this melted mass cools, it forms a crystalline mass of lithium carbonate and oxide. Lithium carbonate is quite soluble in water charged with carbon dioxide. The carbonate is partially decomposed when boiled for a long time with water, carbon dioxide escaping with formation of some lithium hydroxide.

Lithium Bicarbonate, $LiHCO_3$, is not known except in aqueous solution.

Uses.—The salts of lithium are employed as uric acid solvents, also diuretics.

RUBIDIUM

Symbol, Rb. *Atomic Weight,* 85.45. *Valence,* I.

History.—Rubidium was discovered in 1861 by Bunsen and Kirchhoff, in the Duerkheimer Mineral Springs, by means of the spectroscope. The name rubidium (*rubidus* = dark-red) refers to its spectral lines.

Occurrence.—It is found in nature, usually along with potassium, in many mineral waters, chiefly those of Dürkheim, in Baden; in some minerals, as *lepidolite and petalite;* and in the ashes of some plants. It is widely distributed, but only in small quantities.

Isolation.—The separation of this element, as well as cæsium, from sodium and potassium is based on the lesser solubility of certain salts of these rarer metals in water. Difficultly soluble are rubidium alum ($RbAl(SO_4)_2.12H_2O$), rubidium borofluoride ($RbBF_4$), and rubidium chloroplatinate ($2RbCl.PtCl_4$). The same compounds of cæsium are but slightly soluble in water. The RbCl and CsCl may be separated from the chlorides of the alkali metals by their ready solubility in alcohol.

Metallic rubidium is obtained by heating its hydroxide with magnesium or calcium in a current of dry hydrogen: $2RbOH + 2Mg = 2Rb + 2MgO + H_2$.

Properties.—Rubidium is a silver-white metal of a waxy consistence as low as -10°. Its specific gravity is $1.532^{20°}$, and it melts at 39°. Below a red heat it gives off a bluish vapor. When exposed to the air it oxidizes, forming dark brown crystals; when thrown on water it acts energetically, decomposing the latter, burning with a violet flame.

SALTS OF RUBIDIUM

Many of these salts have been prepared, and found to closely resemble those of potassium, with which they are isomorphous. Rubidium iodide is sometimes used in medicine in place of potassium iodide.

Their behavior in the colorless flame is very similar to that of potassium, the flame being reddish. The flame spectrum exhibits two characteristic lines in the violet, which forms the most certain means of detecting rubidium salts. Bunsen stated that he could detect 0.002 milligram by this reaction.

CÆSIUM

Symbol, Cs. *Atomic Weight,* 132.81. *Valence,* I.

History.—Cæsium, which accompanies rubidium, was discovered by Bunsen and Kirchhoff by means of the spectroscope in 1860. The name cæsium (cœsius = *sky blue*) refers to its spectral lines.

Occurrence.—Cæsium is widely distributed in nature, but in small quantities, the most abundant source being the mineral *pollax,* a silicate of cæsium and aluminum, found in the island of Elba; contains 32 per cent. of cæsium; this same mineral has also been found at Hebron, Maine, under the name of *pollucite.*

Cæsium is also found in many mineral springs, but not in the ashes of plants, as it is claimed that, in the absence of potassium compounds, cæsium acts as a poison toward plant life.

Properties.—Cæsium is a silver-white, very soft metal, melting at 28.5°, and having a specific gravity of 1.87. It inflames on exposure to the air, and is the most electro-positive metal known.

Isolation.—The method of preparation of metallic cæsium is like that of rubidium. Cæsium carbonate, unlike rubidium and potassium carbonates, is soluble in alcohol. The bitartrate of cæsium is nine times more soluble in water than the rubidium salt.

The metal was discovered by its characteristic spectrum, which consists of two intense blue lines and one less intense orange-red line.

SALTS OF CÆSIUM

The properties of the salts of this metal closely resemble those of rubidium and potassium. They color the flame still more reddish, form a double chloroplatinate, and react similarly with other reagents. Among the soluble salts of cæsium are the *hydroxide,* $CsOH$; *chloride,* $CsCl$; *nitrate,* $CsNO_3$; *sulphate,* Cs_2SO_4; *acid sulphate,* $CsHSO_4$, and *carbonate,* Cs_2CO_3. Almost insoluble are *cæsium chloroplatinate,* Cs_2PtCl_6; the double *cæsium and lead chloride,* $2CsCl.PbCl_2$, and *cæsium aluminum sulphate,* $CsAl(SO_4)_2\ 12H_2O$, one of the alums.

CHAPTER II

THE ALKALINE EARTH GROUP

THE alkaline earth metals, all of which are bivalent, are CALCIUM, STRONTIUM, and BARIUM; they are closely related to one another, and, like the alkali metals, their relative electro-positive intensities increase with their atomic weights. They are termed alkaline earth metals because their oxides and hydroxides resemble those of the alkali metals on the one hand and the earths (alumina, etc.) on the other. A marked characteristic of the alkaline earth group is the insolubility of their carbonates, phosphates, and sulphates.

The metals of the alkaline earths possess a distinct luster and a white or yellow color. They do not change so rapidly when exposed to the air as do the metals of the alkali group. The oxides of these metals are white in color, and possess many properties peculiar to the earths. They fuse only at the temperature of the electric furnace and are not reduced by hydrogen or carbon under these circumstances. The metals are heavier than water, and decompose it at ordinary temperatures, but not so energetically as the alkali metals.

CALCIUM

Symbol, Ca. *Atomic Weight*, 40.07. *Valence*, II.

History.—The use of lime in mortar for building purposes by the ancients indicates that this substance was well known to them. A description of the process of lime-burning is found in the writings of Dioscorides and of Pliny. Lime and many of its compounds were designated as *earths* by the ancients, and not distinguished from many other substances possessing this generic name. Towards the middle of the eighteenth century it was found that different kinds of earths existed, and lime was recognized as a distinct kind of earth.

The metal was first obtained by Davy, in 1808, by the electrolysis of calcium chloride in the presence of mercury; an amalgam of calcium and mercury resulted, which, when heated, gave off mercury, and left the calcium as a powder.

Occurrence.—The compounds of calcium are widely distributed in nature, the carbonate being the most abundant. The latter is found as calcite, arragonite, chalk, marble, and limestone, in a comparatively pure condition, but many other minerals contain the carbonate as one of the constituents. The most abundant of these is dolomite, a magnesian limestone, which frequently forms whole mountain ranges.

Calcium fluoride or fluor-spar, CaF_2, is found in considerable quantities; the chloride, $CaCl_2$, occurs in sea water and in many mineral springs. The sulphate is found in the anhydrous condition as anhydrite, $CaSO_4$, or in the hydrated form as selenite or gypsum, $CaSO_4$-$2H_2O$. The phosphate is found, with chloride or fluoride, in apatite $[3Ca_3(PO_4)_2.CaF_2.(CaCl_2)]$ and osteolite. Nearly all silicates contain a considerable proportion of calcium. Calcium in some form is an essential constituent of all plants and animals.

Calcium has also been detected in meteorites, in the sun, and in some fixed stars.

Isolation.—Metallic calcium is now isolated by electrolysis at 800° of a solution of 100 p. of $CaCl_2$ in 16 p. of CaF_2, using a hollow cylinder of Acheson graphite as anode and an iron cathode, to which the calcium gradually attaches itself as a rod of metal, which when freed from adhering calcium chloride is preserved in very dry containers or under a hydrocarbon oil.

Properties.—Calcium is silver-white, lustrous, tough, and malleable. It is about as hard as aluminum, melts at 800°, and has the specific gravity of 1.52 at 29.2° C. It does not oxidize readily in dry air, but in moist air it quickly becomes covered with hydroxide, the action gradually extending through the whole mass. The halogens react with calcium only at higher temperatures. Water is decomposed by calcium at ordinary temperatures with violent evolution of hydrogen; the heat developed, however, is not sufficient to inflame the latter. On the application of heat, calcium burns in the air with a very brilliant whitish flame, forming calcium oxide and some calcium nitride (Ca_3N_2); when this is added to water NH_3 is given off. Since calcium combines with all gases except those of the argon group, it is employed in producing high vacua. Dilute nitric acid dissolves the metal with such energy that the latter sometimes inflames, but concentrated nitric acid does not attack it until the temperature is raised to the boiling point of the acid. In metallurgy calcium is used for removing the last traces of carbon from alloys and metals; it may also be used in place of magnesium in Grignard's reaction. The salts of calcium impart a red color to the Bunsen flame.

Calcium Hydride, CaH_2.—This is prepared by passing hydrogen into fused calcium; when added to water, hydrogen is given off, $CaH_2 + 2H_2O = Ca(OH)_2 + 2H_2$. One kilo of CaH_2 yields about 1 cu. meter of H.

CALCIUM AND THE HALOGENS

Calcium Chloride, $CaCl_2$. **Calcii Chloridum**, U.S.P.—This salt was first prepared by Isaac Hollendus, in the fourteenth century, who designated it by the title *sal ammoniacum fixum*, because he prepared it by heating a mixture of sal ammoniac and lime.

It is found in sea water and in many mineral waters; also as tachydrite at Stassfurt; a compound having the formula $CaCl_2,2MgCl_2.12H_2O$.

Preparation.—Crude calcium chloride is a by-product in various chemical operations; for example, it is the residue in the preparation of ammonia from ammonium chloride; it is obtained in the preparation of potassium chlorate, in the ammonia-soda process and in the preparation of carbon dioxide from limestone and hydrochloric acid. For many uses this crude product, which is in aqueous solution, is evaporated to dryness in an iron kettle, and then heated until it melts. The product is sent into commerce for dehydrating purposes as fused calcium chloride.

It is also furnished in the crystallized, powdered, and granulated form.

Purified calcium chloride is made by nearly saturating hydrochloric acid with marble, adding chlorine water to oxidize the iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime (calcium hydroxide). The clear, filtered solution, which is slightly alkaline, is carefully neutralized with hydrochloric acid. This solution is then evaporated to the crystallizing point or to dryness, according to the uses to which it is to be applied.

Properties.—The crystallized salt occurs in large, hexagonal prisms, having the composition $CaCl_2.6H_2O$. On the application of heat it melts at 30°. These crystals rapidly deliquesce on exposure to the air, forming a thick, oily liquid, formerly known as *oleum calcis.*

When the crystals dissolve in water a considerable fall in temperature (—12°) takes place. A temperature of —48° is obtained by mixing it with three-fourths of its weight of snow. When heated to 200°, or when kept for some time over concentrated sulphuric acid, the crystals lose 4 molecules of water of crystallization, a white powder resulting, which possesses energetic dehydrating properties. Above 200° the remaining 2 molecules of water are gradually driven off, and at 719° the anhydrous salt fuses.

The official salt contains not less than 75 per cent. of $CaCl_2$ and occurs in slightly translucent, hard fragments, granules, or sticks, which are very deliquescent. It is soluble in 0.62 p. of cold and 0.7 p. of boiling water, and 10 p. of alcohol at 25°.

The anhydrous salt is soluble in 1.3 parts of water, and in 8 parts of alcohol at 25°, in 1.5 parts of boiling alcohol. Since the aqueous solution is used for maintaining a temperature above that of boiling water, it is useful to know the boiling point of such a solution; that containing 50 parts of the anhydrous salt in 100 of water boils at 112°; that containing 200 parts in 100 boils at 158°, and that containing 325 parts in 100 boils at 180°.

The pure salt dissolves in water without residue, and has a neutral reaction. If, however, it be kept at or above the fusing point for some time, a slight decomposition takes place with loss of HCl, so that it leaves a residue of basic chloride insoluble in water, and the solution has a faintly alkaline reaction.

Uses.—Calcium chloride has some use in the laboratory as a reagent, but its chief value is as a desiccating agent, in the drying of gases (except $NH_3 = CaCl_2.8NH_3$). Its solution is valuable, as above stated, for use in baths, where it is desired to maintain a constant temperature above that of boiling water, and for use on a large scale in refrigerating plants as a circulating liquid.

Calcium Bromide, $CaBr_2$. **Calcii Bromidum,** U.S.P.—Like the preceding salt, calcium bromide is found in certain mineral waters.

It is prepared by neutralizing hydrobromic acid with calcium carbonate, adding bromine water to oxidize iron and manganese compounds, and precipitating these by the addition of a slight excess of milk of lime. The solution is filtered and the filtrate carefully neutralized with hydrobromic acid. The resulting solution is then evaporated to dryness, preferably *in vacuo,* and carefully heated to fusion, whereby an anhydrous salt is obtained. Calcium bromide may be prepared in same manner as calcium iodide.

The Pharmacopœia directs that the hydrated salt be employed containing not less than 84 per cent. of $CaBr_2$. In this state it occurs as white, granular, very deliquescent salt, without odor, and with a sharp, saline taste. At 25° it is soluble in 0.7 part of water, and in 1.3 parts of alcohol. At 680° the salt melts; above this temperature it is slowly decomposed with loss of bromine. The aqueous solution is neutral or slightly alkaline to litmus paper.

Uses.—The principal use of this salt is in medicine.

Calcium Iodide, CaI_2, is prepared like the bromide, which it resembles in many particulars. Or 100 p. of calcium sulphite ($CaSO_3$) are suspended in 400 p. of warm water; to this is added in small portions powd. iodine (158 to 160 p.) until the solution retains a permanent yellow tint. Add sufficient $CaSO_3$ to remove the tint, then 63 p. of $CaCO_3$, and warm till all carbon dioxide escapes, fill into a flask, cork, let settle, filter, and evaporate filtrate to dryness *in vacuo,* heat to fusion, then pour on a cold slab.

Calcium iodide is extremely deliquescent and readily discolors from liberation of iodine on exposure to light and air.

Calcium Fluoride, CaF_2, under the name of fluor-spar, occurs quite abundantly in a crystalline state in nature. It occurs in cubes and octahedra, and in some other forms belonging to the regular system.

It is also found in the ashes of some plants, in bones, in the enamel of the teeth, and in sea water and mineral springs. The salt may be prepared by interaction between solutions of $CaCl_2$ and NaF.

In the pure condition calcium fluoride is colorless, but it is much oftener of a violet, blue, red, green, or brown color, and at times shows the phenomena of dichroism. At a red heat calcium fluoride fuses without decomposition; while hot it fluoresces in the dark.

Fluor-spar is extensively employed as a flux in many metallurgical operations.

CALCIUM AND OXYGEN

Calcium Monoxide, CaO. **Calx,** U.S.P. (Quicklime).—Lime is prepared by heating calcium carbonate. If a pure carbonate is used a correspondingly pure product results. Between 850° and 900° calcium carbonate is decomposed into CaO and CO_2; this must be carried out in a draught for the removal of the CO_2, otherwise decomposition will not be complete, hence crucibles cannot be used for this purpose. Small quantities of lime may be prepared by heating in clay or silica trays placed in a gas furnace provided with a good draught:

$$CaCO_3 = CaO + CO_2.$$

On a commercial scale lime-kilns are used. These were formerly constructed so as to be filled with limestone and fuel in alternate layers. Fire was then started at the bottom, and the temperature regulated by the air-supply below. Such a furnace, however, could only be emptied when cool. At the present time continuous furnaces are used, in which limestone and coke are introduced above, while the quicklime is removed from the bottom outlet. The furnace gases, consisting chiefly of CO_2, are commercially utilized.

Properties.—Pure lime occurs in white, amorphous masses. Calx of the U. S. P. contains, when freshly ignited to constant weight, not less than 95 per cent. of CaO. It generally contains iron, and consequently is frequently of a grayish or yellowish shade of color. When exposed to the air it gradually absorbs moisture and carbon dioxide, and crumbles to a white powder. Lime is without odor, but has a sharp, caustic taste. It is soluble in about 840 parts of water at 25° C., and in 1740 parts of boiling water. The oxyhydrogen flame causes it to emit an intense white light, and in the electric furnace at a temperature of about 2570° it fuses.

When lime is treated with about one-third of its weight of water, added drop by drop, it gradually becomes hot, swells to about twice its bulk, and then falls to a white powder of calcium hydroxide or slaked lime, $Ca(OH)_2$. Lime which readily slakes is termed *fat lime,* while such as slakes partially is known as *lean* or *poor lime;* this is usually due to the presence of considerable quantities of silica, alumina, or magnesia. *Overburnt* lime contains hard masses of calcium silicate formed through excessive heating, hence slakens imperfectly.

The solubility and some of the other properties of lime are closely associated or identical with those of calcium hydroxide, since, in the presence of water, the oxide is first converted into hydroxide.

Calcium Hydroxide, $Ca(OH)_2$.—When lime is treated with one-third its weight of water, as stated above, the product is calcium hydroxide. Considerable heat is developed in this operation; where the proportions are carefully adjusted a temperature of 150° is easily attained. The reaction involved is as follows:

$$CaO + H_2O = Ca(OH)_2.$$

The resulting product is a fine, white, impalpable powder, which is much less soluble in cold water than either the barium or strontium hydroxides. One part of calcium hydroxide requires 700 parts of cold and about 1400 parts of hot water for solution. Its solution in water forms **Liquor Calcis,** U.S.P., or lime water, which must contain not less than 0.14 per cent. of $Ca(OH)_2$. The percentage of hydroxide varies with the temperature at which the solution is prepared, being about 0.17 per cent. at 15° and diminishing as the temperature rises. This solution has a saline and somewhat caustic taste and an alkaline reaction. On boiling it becomes turbid, owing to the lesser solubility of the hydroxide in hot than in cold water. When the clear solution is exposed to the air, a pellicle forms on the surface, due to the formation of calcium carbonate, resulting from the absorption of carbon dioxide from the atmosphere.

Crystals of calcium hydroxide, in the form of tablets or small prisms, may be obtained by evaporating the clear solution of lime water in a vacuum over sulphuric acid.

Milk of lime is a mixture of calcium hydroxide and water. It may be made of any desired strength by agitating the freshly slaked lime with water.

Uses.—Calcium oxide, and therefore also the hydroxide, is largely used as a laboratory reagent. The oxide finds much use as a desiccating agent for gases. Industrially in making high temperature crucibles, in glass making, and the smelting of metals. The hydroxide is used in the manufacture of mortar, and large quantities are employed in the manufacture of chlorinated lime.

Mortars and Cements.—Mortar is prepared by mixing freshly slaked lime with water and sand.

The process of hardening which mortar undergoes is called "setting." This setting is sufficiently complete in a few days to give stability to a structure in which it is employed, but the hardening process continues for years. The peculiar action of mortar appears to be due to loss of water and subsequent absorption of carbon dioxide, rather than to the formation of calcium silicate. The value of a mortar depends to a great degree upon the thorough mixing of the ingredients in the process of manufacture. The nature of hydraulic cements will be explained in the section on alumina, page 444.

Calcium Dioxide, or *Peroxide,* CaO_2, is prepared by mixing lime water with hydrogen dioxide. This precipitate has the composition $CaO_2 8H_2O$; it is a light, cream-colored, odorless and tasteless powder, almost insoluble in water and insoluble in alcohol. It also occurs in crystals which effloresce when exposed to the air; at higher temperatures they give off half of their oxygen without undergoing fusion.

A commercial calcium peroxide is now produced by adding sodium peroxide to a solution of a calcium salt. This contains 60 to 70 per cent. of CaO_2 with some calcium hydroxide and carbonate, and is capable of yielding, when mixed with diluted acids, 13 to 15 per cent. of available oxygen, or 10 liters of oxygen gas per 100 grams of material. It is used as a bleaching agent for edible oils, as a food preservative, and in treatment of acidosis.

Soda Lime.—This is prepared by heating a mixture of equal parts of caustic soda and calcium hydroxide to low redness. Also it may be made by adding a hot solution of 20 per cent. of NaOH in 60 mils of water to 80 gm. of $Ca(OH)_2$, stir while heating till dry, and granulate. Soda lime is used as a desiccant for gases and liquids as well as for absorbing CO_2.

OXYGEN SALTS OF CALCIUM AND THE HALOGENS

Calcium Hypochlorite.—The exact constitution of this substance has not been established because it has not yet been obtained in a pure state. The chief constituent of the commercial *chlorinated lime* is calcium hypochlorite, Ca(OCl)Cl, a mixed salt of HClO and HCl, mixed with CaO and

$Ca(OH)_2$. Commercially it is known as *chloride of lime, chlorinated lime, bleaching powder* or *bleach,* also as **Calx Chlorinata,** U.S.P.

Chlorinated lime was first prepared on a commercial scale by Tennant, of Glasgow, in 1798, by saturating slaked lime with chlorine, the reaction being

$$Ca(OH)_2 + Cl_2 = Ca(OCl)Cl + 2H_2O.$$

Preparation.—This important substance is prepared in enormous quantities wherever chlorine is produced on a large scale. The slaked lime is prepared from a pure limestone free from iron and manganese, sifted and placed in lead chambers supported by a wooden framework, the walls and floor being covered with asphalt. These chambers are about 60 feet long, 30 feet wide, and 5 feet high. The chlorine which passes into the top rapidly settles to the bottom of the chamber, passing through the layers of lime, saturation taking place in about 24 hours. In other forms of apparatus the manufacture is carried on more expeditiously by the use of rotating drums in which the calcium hydroxide is propelled by an endless screw in a direction opposite to that of the current of chlorine gas and so passes from drum to drum until it comes out completely converted into bleaching powder. As soon as the lime contains about 36 per cent. of available chlorine it is removed. But little $CaCl_2$ is formed, while some CaO with $Ca(OH)_2$ remains mixed with the hypochlorite.

Properties.—Chlorinated lime is officially described as " a white, or grayish-white, granular powder, having an odor of chlorine. It becomes moist and gradually decomposes on exposure to the air, and when in such a condition must not be used or dispensed."

It is only partly dissolved by water or alcohol; the aqueous solution first colors red litmus paper blue, and then bleaches it. It is decomposed by weak acids with evolution of chlorine; carbon dioxide will also decompose it.

The Pharmacopœia requires that chlorinated lime shall contain not less than 30 per cent. of available chlorine. Much of it comes in commerce packed in sealed paper boxes, coated on the inside with a water-proof material, so that the powder maintains its original strength satisfactorily until opened. When exposed to moist air it rapidly deteriorates, due to the action of the carbon dioxide of the air. Old chlorinated lime always contains calcium chlorate, $6CaOCl_2 = 5CaCl_2 + Ca(ClO_3)_2$.

A solution of this hypochlorite turns litmus paper first blue, then, after standing for a while, or through the addition of a very weak acid, such as carbon dioxide or boric acid, it is bleached. This is due to the liberation of hypochlorous acid. On treating bleaching powder with an excess of *dilute* hydrochloric or sulphuric acid all of the chlorine present, whether linked directly or indirectly to the Ca, is liberated, as follows:

$$CaCl.OCl + 2HCl = CaCl_2 + H_2O + Cl_2.$$
$$CaCl.OCl + H_2SO_4 = CaSO_4 + H_2O + Cl_2.$$

The hydrochloric acid liberated by the sulphuric reacts with the hypochlorous acid with the generation of chlorine, $HCl + HClO = H_2O + Cl$. If a molecular quantity of the mineral acid be added, then hypochlorous acid is liberated.

The chlorine thus obtained is known as "available chlorine."

The process of bleaching by free chlorine is one of oxidation; it combines with the hydrogen of the moisture present to form hydrochloric acid, while the liberated oxygen in the nascent state readily bleaches organic colors.

$$H_2O + Cl_2 = 2HCl + O.$$

If a solution of chlorinated lime be warmed with a cobalt salt, oxygen is given off. The cobalt oxide, CoO, formed is oxidized to Co_2O_3, which with the chlorinated lime yields oxygen and CoO (see page 153).

Uses.—Chlorinated lime is used most extensively for bleaching purposes; it is also largely employed as a disinfecting agent, and is undoubtedly one of the best substances for this purpose. Enormous quantities are now being used in the purification of municipal water supplies. A quantity of chlorinated lime equivalent to 0.15 gm. Cl per liter of water will destroy bacteria in 10 minutes (see page 201). This is generally used with a small quantity of sodium chloride. When used as a bleaching agent, the goods are first immersed, after cleansing in a solution of sal soda, in a weak solution of chlorinated lime, then in a dilute solution of an acid, after which it is thoroughly rinsed. For disinfecting rooms, cloths saturated with the solution are suspended in the air, the carbonic acid present causes a slow decomposition with evolution of hypochlorous acid, which breaks up into chlorine and chloric acid, $5HClO = HClO_3 + 2H_2O + 2Cl_2$. Where rapid action of chlorine is desired, any dilute acid is poured over the chlorinated lime. When ammonia or its salts are warmed with solutions of the hypochlorites, nitrogen is evolved:

$$6CaOCl_2 + 4NH_3 = 6CaCl_2 + 6H_2O + 2N_2.$$

Where chlorine is desired in the free state, chlorinated lime forms one of the most convenient and economical means of obtaining it, the simple addition of a dilute acid being sufficient to produce it in liberal quantity, according to a reaction given above.

Calcium Chlorate, $Ca(ClO_3)_2$, is prepared by passing chlorine into hot milk of lime, or solutions of calcium silicofluoride and potassium chlorate are mixed, when potassium silicofluoride crystallizes out, leaving the calcium chlorate in solution, and the latter is crystallized from the very concentrated solution. Calcium chlorate is a very deliquescent salt, and is crystallized with considerable difficulty. The crystals contain 2 molecules of water of crystallization.

Calcium Bromate, $Ca(BrO_3)_2.H_2O$, and *Calcium Iodate,* $Ca(IO_3)_2.6H_2O$, are also known.

CALCIUM AND SULPHUR

Calcium Monosulphide, CaS.—In 1750 Marggraf noticed that this substance had the property of remaining luminous in the dark after it had been exposed to bright light. It is obtained by heating calcium sulphate with powdered charcoal, or it may be prepared by leading the vapor of carbon disulphide and carbon dioxide over incandescent lime. It is official under the title of

Calcii Sulphidum Crudum, U.S.P. (**Calx Sulphurata,** Sulphurated Lime), a crude calcium sulphide, prepared by heating 70 parts of dried calcium sulphate, 10 parts of charcoal, and 2 parts of starch. The official preparation should contain at least 55 per cent. of calcium sulphide and contains in addition varying amounts of calcium sulphate and carbon.

Pure calcium sulphide occurs in white masses. The official product is described as "a pale gray or yellowish powder, having a faint odor of hydrogen sulphide, and a nauseous and alkaline taste. It gradually decomposes on exposure to air. Very slightly soluble in cold water ($Ca(SH)_2$ being formed), more readily in boiling water, which partially decomposes it with evolution of H_2S; insoluble in alcohol."

Sulphurated lime is decomposed by dilute acids with evolution of hydrogen sulphide, even acetic acid effecting this change.

The pure salt is not luminous, but when impure it is phosphorescent, like the sulphides of barium and strontium, giving off bluish, greenish or violet light in the dark after it has been exposed to sunlight. It is an ingredient of luminous paints; has some use in medicine, and may be employed as a source of arsenic-free H_2S.

Calcium Sulphydrate, $Ca(SH)_2$, is prepared by saturating milk of lime with hydrogen sulphide:

$$\underset{\text{Calcium Hydroxide.}}{Ca(OH)_2} + \underset{\text{Hydrogen Sulphide.}}{2H_2S} = \underset{\text{Calcium Sulphydrate.}}{Ca(SH)_2} + \underset{\text{Water.}}{2H_2O.}$$

It is known only in solution, and is employed as a depilatory when freshly prepared.

Calcium Polysulphides. When equal quantities of slaked lime and sulphur are boiled with water, an orange-colored liquid is obtained, which contains calcium disulphide, pentasulphide (CaS_5) and thiosulphate. Used as insecticide, also in preparing Sulphur Præcipitatum.

OXYGEN SALTS OF CALCIUM AND SULPHUR

Calcium Sulphite, $CaSO_3$, is precipitated when solutions of calcium chloride and sodium sulphite are mixed. It occurs as a white powder soluble in 800 parts of cold water. This salt is obtained in crystals by allowing its solution in sulphurous acid to stand exposed to the air; they have the composition $CaSO_3.2H_2O$. A solution of this salt in excess of sulphurous acid is found in commerce under the name of *bisulphite of lime,* $Ca(HSO_3)_2$; it is made by passing sulphur dioxide into milk of lime. Calcium bisulphite is used in cleansing wine and cider casks before refilling, also in paper and cellulose manufacture.

Calcium Sulphate, $CaSO_4 + 2H_2O$. *Gypsum.*—This compound was known to the ancients; likewise the property which the dried gypsum possesses of hardening when moistened with water. Marggraf determined its composition in 1780.

Calcium sulphate is found native as *anhydrite* associated with limestone, or crystallized with 2 molecules of water as selenite. Two other varieties of this compound are known as satin spar or fibrous gypsum, and crystalline translucent gypsum or *alabaster*.

This salt may be prepared by treating calcium carbonate, marble, or limestone with sulphuric acid.

Exsiccated calcium sulphate is prepared by heating the native gypsum to between 120° and 130° until it loses three-fourths of its water, becoming $2CaSO_4.H_2O$; it then contains about 95 per cent. by weight of calcium sulphate and 5 per cent. of water. When thus dried it is commercially known as *burnt gypsum*, or *plaster of Paris*. If overheated (overburnt)—that is, above 200°—it will not take up water so readily, and will not harden. The addition of 0.1 to 0.5 per cent. of sodium phosphate causes plaster of Paris to set more rapidly.

Properties.—Plaster of Paris forms a fine, white powder, without odor or taste. From moist air it attracts water, becomes granular, and then loses the property of hardening with water. When mixed with half its weight of water, it forms a smooth, cohesive paste, which rapidly hardens. It is soluble in about 378 parts of water at 25°, in 388 parts at 38°, and in 451 parts at 100°. In alcohol it is insoluble. It readily dissolves in dilute nitric or hydrochloric acid, also in saturated solutions of potassium nitrate, sodium thiosulphate, and of various ammonium salts. When calcium sulphate is dissolved in hot hydrochloric or nitric acid and the solution is allowed to cool, it separates in glittering, silky, acicular crystals. Calcium sulphate is present in most natural waters, causing "permanent hardness" (page 202).

Uses.—Gypsum is used in large quantities as a fertilizer; it has some use as a cement, is employed somewhat in surgery, and is the material employed in making plaster casts and certain kinds of ornamental work. The artificially prepared salt, made by precipitating a concentrated solution of calcium chloride with dilute sulphuric acid, is used as a filling for writing-paper under the name of *pearl hardening*.

Calcium Thiosulphate, $CaS_2O_3.6H_2O$, is made by warming a mixture of calcium sulphite, sulphur, and water. It forms oblique, six-sided prisms, which are soluble in their own weight of water. The solution is decomposed at a temperature of 60°, sulphur separating. Commercially it is used for the manufacture of sodium thiosulphate (see page 348).

OXYGEN SALTS OF CALCIUM AND NITROGEN

***Calcium** Nitrate*, $Ca(NO_3)_2.4H_2O$, occurs as an efflorescence on walls of stables and other places where organic matter is undergoing decomposition through the agency of nitrifying bacteria in the presence of lime. It is abundant in some soils, especially that of the Chile nitre deposits (page 350).

Calcium nitrate is prepared by dissolving chalk or marble in nitric acid. It is a very deliquescent salt, soluble in both water and alcohol. It is sometimes known as *lime saltpetre* or *wall saltpetre*. Calcium nitrate was formerly used in the preparation of ordinary saltpetre. Now it is employed largely as a fertilizer in place of the Chile saltpetre. Very large quantities of calcium nitrate are manufactured synthetically from atmospheric nitrogen (see page 255).

OXYGEN SALTS OF CALCIUM AND PHOSPHORUS

Tertiary or Tricalcium Phosphate, $Ca_3(PO_4)_2$.
Secondary or Dicalcium Phosphate, $Ca_2H_2(PO_4)_2$.
Primary or Tetra-hydrogen Calcium Phosphate, $CaH_4(PO_4)_2$.

Calcium Phosphate, $Ca_3(PO_4)_2$.—Also known as ***tricalcium phosphate*** or ***tertiary calcium phosphate*** or ***normal calcium orthophosphate*** and ***bone phosphate.*** It is found native with calcium fluoride in the minerals apatite and phosphorite, $3Ca_3(PO_4)_2.CaF_2$. By far the most extensive occurrence of calcium phosphate is in what is known as the phosphate rock of South Carolina, Florida, and other parts of the Southern United States. This rock frequently contains as much as 90 per cent. of calcium phosphate. Bones consist chiefly of tertiary calcium phosphate; when burned the ash contains from 80 to 85 per cent. of it.

Preparation.—Calcium phosphate may be prepared by adding calcium chloride and ammonium hydroxide to sodium phosphate:

$$3CaCl_2 + 2NH_4OH + 2(Na_2HPO_4.12H_2O) = Ca_3(PO_4)_2 + 2NH_4Cl + 4NaCl + 26H_2O.$$

Properties.—Calcium phosphate precipitates in the above reaction as a white, amorphous powder; it is odorless and tasteless, and permanent in the air. It is almost insoluble in cold water; decomposed by boiling water into an insoluble basic salt, and a soluble acid salt. This reaction takes place very slowly in the presence of cold water. Tertiary calcium phosphate is readily soluble in solutions of ammonium salts, sodium nitrate, sodium chloride, and a number of other salts, also in diluted HCl or HNO_3, being again precipitated upon the addition of ammonia water.

Uses.—Calcium phosphate has some use in medicine, and is extensively used as a fertilizer.

Secondary or Dicalcium Phosphate, $Ca_2H_2(PO_4)_2.2H_2O$.—This compound is precipitated when a solution of sodium phosphate is added to one of calcium chloride in the presence of a little acetic acid; it is a white, crystalline powder, decomposing with an excess of water into tricalcium phosphate. Urinary concretions and deposits are made up largely of this phosphate.

Primary or Tetrahydrogen Calcium Phosphate, $CaH_4(PO_4)_2$, is prepared by dissolving either of the preceding phosphates in phosphoric acid ($Ca_3PO_4 + 4H_3PO_4 = 3CaH_4(PO_4)_2$), and allowing the solution to evaporate spontaneously, or by decomposing tricalcium phosphate with sulphuric acid: $Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$; after removing the calcium sulphate the superphosphate remains in solution. This compound is also known sometimes as calcium superphosphate. What is commercially known as *superphosphate of lime* is a mixture of this compound and calcium sulphate, and is prepared by treating bones or phosphate rock with two-thirds of their weight of sulphuric acid. The product is extensively employed as fertilizer.

Calcium Hypophosphite, $Ca(H_2PO_2)_2$. **Calcii Hypophosphis,** U.S.P. —This salt is prepared by taking 1 part of finely divided phosphorus and 2 parts of calcium oxide which has been slaked with 1 part of water and then stirred with sufficient water to make a thin mixture.

These ingredients are mixed, placed in a well-ventilated fume chamber, and warmed between 30° and 40° until combination is complete, or until hydrogen phosphide ceases to be evolved:

$$3Ca(OH)_2 + 2P_4 + 6H_2O = 3Ca(H_2PO_2)_2 + 2PH_3$$

When the reaction is ended the mixture is filtered and the calcium hydroxide removed from the filtrate by carbon dioxide. It is again filtered, and the clear filtrate evaporated at a low temperature in a vacuum, finally, over sulphuric acid until crystallization takes place.

The finely divided phosphorus is obtained by placing 1 part of phosphorus in a flask with 2 parts of powdered glass and 5 parts of water, applying a gentle heat until the phosphorus is melted, and then agitating until cold. By this means the phosphorus is obtained in small particles which more readily combine with the calcium hydroxide. Instead of crystallizing the salt from its aqueous solution, it may be precipitated by the addition of alcohol.

Properties.—Calcium hypophosphite occurs in small, water-free, transparent, monoclinic prisms or scales, or as a white crystalline powder of not less than 98 per cent. purity (U.S.P.). It is odorless, has a nauseous, bitter taste, and is permanent in the air.

The salt is soluble in 6.5 parts of water at 25° and in 6 parts of boiling water; it is insoluble in alcohol.

On the application of heat calcium hypophosphite decrepitates, and above 300° it begins to decompose, giving off water, hydrogen, and hydrogen phosphide, and leaving a residue of calcium pyrophosphate and metaphosphate with some red phosphorus. The aqueous solution is neutral to litmus paper.

Uses.—Calcium hypophosphite has a considerable use in medicine, and at the same time furnishes a convenient salt from which to prepare the other hypophosphites.

Calcium Silicate, $CaSiO_3$ or $CaO.SiO_2$.—The compound of this formula occurs native as the mineral *wollastonite; okenite, gyrolite,* and *xonotlite* are polymeric compounds of this. Most natural silicates contain more or less calcium silicate. This compound may also be obtained by adding calcium chloride to a solution of sodium silicate, when it forms a gelatinous precipitate.

Calcium silicate enters into the composition of many varieties of glass.

CALCIUM AND CARBON

Calcium Carbide, CaC_2.—This was first prepared by Wöhler in 1862; obtained accidentally in 1892 by T. L. Wilson. Calcium carbide is an artificial compound of considerable technical importance prepared by heating a mixture of powdered lime and coke-dust in an electric furnace:

$$CaO + 3C = CaC_2 + CO.$$

It is a grayish-brown, dense substance, having a crystalline metallic fracture of blue or brown appearance and a specific gravity of 2.26; when pure it forms transparent crystals. It evolves a peculiar odor when exposed to a moist atmosphere, due to acetylene (C_2H_2), which is always produced when calcium carbide is brought into contact with water or its vapor at ordinary temperatures:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2.$$

It also decomposes with snow at a temperature of —31° C. It is not acted upon by the vapor of water at high temperatures.

In a dry atmosphere it is odorless. When exposed to the air in lumps it becomes coated with a layer of calcium hydroxide, which to a great extent protects the rest of the substance from further deterioration by atmospheric moisture. Calcium carbide is not inflammable, and can be exposed to the temperature of the ordinary blast-furnace without melting.

Commercial calcium carbide, which contains about 80 per cent. CaC_2, is used as a source of acetylene for illuminating purposes, also for the manufacture of calcium cyanamide ($CaC_2 + N_2 = CaCN_2 + C$), page 240. One pound of the pure material yields 5.9 cubic feet of acetylene gas at 18° C.

OXYGEN SALTS OF CALCIUM AND CARBON

Calcium Carbonate, $CaCO_3$. **Calcii Carbonas Præcipitatus,** U.S.P.— In the form of chalk, limestone, and marble this compound occurs in nature so abundantly that whole mountain ranges are formed of it. It is also the chief constituent of egg shells, of the shells of mollusks, coral, and pearls. In chalk it is amorphous, in marble it is in crystalline masses, while in calcite and arragonite it occurs in distinct crystals. These two minerals illustrate its dimorphous character. Calcite or calc-spar has a specific gravity of 2.70 to 2.75, and crystallizes in hexagonal prisms, while arragonite has a specific gravity of 2.92 to 3.28, and occurs in the form of rhombic prisms. When carbon dioxide in small quantity is passed into cold lime water, the precipitate is at first amorphous, but soon becomes crystalline in the form of calc-spar; when, however, the lime water is hot, crystals of the arragonite form are deposited.

Preparation.—The official salt, which after drying at 200° should be 98 per cent. pure, is prepared by adding a hot solution of calcium chloride to one of sodium carbonate:

$$Na_2CO_3 + CaCl_2 = CaCO_3 + 2NaCl.$$

The product is a fine, white powder, without odor or taste, and permanent in the air. Calcium carbonate is produced through the action of furnace gases on slaked lime, and is also a by-product in the purification of potable waters. It is almost entirely insoluble in water, 1 liter dissolving about 18 milligrams. In the presence of ammonium hydroxide or carbonate it is less soluble, but with the other ammonium salts its solubility is increased. Carbon dioxide also increases its solubility: a liter of water saturated with this gas will dissolve 0.385 gram of the salt through the formation of a bicarbonate ($Ca(HCO_3)_2$). This solubility is increased under pressure up to 3 grams per liter, but not beyond this point. Such a solution when allowed to stand at ordinary temperatures deposits crystals having the composition $CaCO_3.5H_2O$.

Dilute acetic, hydrochloric, or nitric acid dissolves calcium carbonate with effervescence, leaving no residue.

On heating calcium carbonate to redness with access of air it parts with its carbon dioxide, leaving a residue of calcium oxide.

Creta Præparata, U.S.P., *Prepared Chalk,* is an amorphous calcium carbonate prepared by the elutriation of chalk containing when dried at 200° not less than 97 per cent. of $CaCO_3$.

Prepared chalk is " a white to grayish-white, very fine, amorphous powder, often moulded into conical drops, odorless and tasteless; permanent in the air." In other characters it is practically identical with the precipitated compound.

Uses.—Both of the above preparations are used in medicine; the prepared chalk is preferred by some of the manufacturers of tooth powders on account of its non-crystalline character.

Whiting and *Paris White* are commercial varieties of prepared chalk, not so carefully washed, and therefore not so white. They are used for polishing and for many other purposes where chalk is required in the arts.

STRONTIUM

Symbol, Sr. *Atomic Weight,* 87.63. *Valence,* II.

History.—The mineral in which strontium was first found was called *strontianite* from its occurrence near the village of Strontian in Scotland. The fact that this mineral contained a peculiar earth was first pointed out by Crawford in 1790. In 1792 Hope identified strontium as an element, and in 1855 Bunsen and Matthieson isolated the metal by the electrolysis of fused strontium chloride.

Occurrence.—Strontium is found in nature in the same combinations which characterize barium and calcium—namely, as carbonate, $SrCO_3$, or *strontianite,* and as sulphate, $SrSO_4$, or *celestite.* Some calcium minerals also contain small quantities of strontium. Smaller amounts are found in sea water, in mineral waters, and in certain salt springs.

Isolation.—Strontium is readily obtained by the electrolysis of the fused chloride, or by heating the oxide (3 mol.) with granulated aluminum (2 atoms).

Properties.—Strontium is a white metal of sp. gr. 2.54, melts at about 800°, and is soft enough to be cut with a knife. If heated in the air it burns with a crimson flame. All salts of this metal impart a crimson color to a colorless flame. When placed in water it decomposes it with some violence. The salts of strontium show great similarities to those of barium.

STRONTIUM AND THE HALOGENS

Strontium Chloride, $SrCl_2.6H_2O$.—This salt is prepared by saturating hydrochloric acid with the native carbonate and digesting the solution for some time with excess of carbonate, by which metals like aluminum, iron, and manganese are removed. The hot concentrated solution deposits, on cooling, acicular crystals of the hexagonal system.

These crystals have a sharp, bitterish taste, and deliquesce on exposure to the air. They are soluble in 1.8 parts of water at ordinary temperatures, and in 0.9 part of boiling water. The ready solubility of this salt in alcohol offers a ready means for its separation from barium chloride.

On the application of heat the salt loses its water of crystallization at 100°, and at 873° it melts. The anhydrous salt is soluble in absolute alcohol.

Strontium Bromide, $SrBr_2.6H_2O$. **Strontii Bromidum,** U.S.P.—To hydrobromic acid, diluted with an equal volume of water, a slight excess over an equimolecular quantity of strontium carbonate is added in portions until the effervescence has subsided. The mixture is then digested for a few hours, filtered, washed, and the filtrate concentrated for crystallization.

$$SrCO_3 + 2HBr = SrBr_2 + H_2O + CO_2.$$

Strontium bromide may also be prepared by boiling a concentrated solution of a molecular quantity of ammonium bromide with an equimolecular quantity of strontium hydroxide until ammonia gas ceases to be given off. After filtration and concentration the strontium bromide is permitted to crystallize:

$$2NH_4Br + Sr(OH)_2 = SrBr_2 + 2NH_3 + 2H_2O.$$

Properties.—Strontium bromide, which should be of not less than 98 per cent. purity, occurs in transparent, colorless crystals, odorless, and having a bitter, saline taste and an alkaline reaction. It is a very deliquescent salt; dissolves in 0.35 part of water at 25°, and is readily soluble in alcohol, and is insoluble in ether.

On the application of heat the crystals melt in their water of crystallization, and then lose all their water, amounting to 30.4 per cent., at above 180°.

Uses.—Same as the other alkali bromides in medicine.

Strontium Iodide, $SrI_2.6H_2O$. **Strontii Iodidum,** U.S.P.—This is most conveniently prepared by boiling a concentrated solution of a molecular quantity of ammonium iodide with an equimolecular amount of strontium hydroxide until ammonia gas ceases to be given off. After filtering, the solution is set aside for crystallization of the strontium iodide:

$$2NH_4I + Sr(OH)_2 = SrBr_2 + 2NH_3 + 2H_2O.$$

Properties.—Strontium iodide of not less than 99 per cent. purity is officially described as occurring in " colorless, transparent, hexagonal plates, white granular powder, or crystalline crusts, odorless, and having a bitterish, saline taste. Deliquescent, and colored yellow by exposure to air and light," on which account it is directed to be kept in " dark amber-colored, glass-stoppered vials." The salt is soluble in 0.2 part of water at 25°, also soluble in alcohol, and slightly in ether.

On the application of a gentle heat, the crystals melt in their water of crystallization, and at a higher temperature lose all of their water, amounting to 24.05 per cent. When the temperature approaches redness the salt is decomposed with loss of iodine, strontium oxide remaining. The aqueous solution is neutral, or very slightly acid, to litmus paper.

STRONTIUM AND OXYGEN

Industrially, most of the compounds of strontium are prepared indirectly from the sulphide, which is made by roasting the sulphate with charcoal or coal dust. The sulphide is then heated in a current of steam or with copper oxide in presence of water, which yields strontium oxide. $SrS + H_2O = SrO + H_2S$; $SrS + CuO = CuS + SrO$.

Strontium Monoxide, SrO.—This compound of strontium is usually prepared from the sulphide as given above or by igniting the nitrate or carbonate.

Properties.—When prepared by heating the nitrate, this compound forms grayish-white, porous, infusible masses. That made by heating the carbonate is found in the form of powder or pressed into bricks. The latter form, after hydrating, is that in which it is best adapted for use in the sugar industry.

Strontium Dioxide, SrO_2, is formed when the hydroxide is mixed with hydrogen dioxide. It occurs in pearly scales, having the formula $SrO_2.8H_2O$. When these crystals are heated they lose water, leaving the dioxide as a light, white powder, in an anhydrous condition.

Strontium Hydroxide, $Sr(OH)_2$, is usually obtained by dissolving the monoxide in water, but it may be prepared in small quantity by precipitation of a solution of strontium nitrate with sodium hydroxide. This hydroxide is soluble in about 81 p. of water at 10° and 2.1 p. at 100°; when the hot solution cools, crystals are deposited having the formula $Sr(OH)_2.8H_2O$. Strontium hydroxide is extensively used in the extraction of sugar from the beet-root molasses, as it forms an insoluble saccharate, readily decomposable by carbon dioxide, yielding strontium carbonate and pure crystallizable sugar.

OXYGEN SALTS OF STRONTIUM

Strontium Sulphate, $SrSO_4$, occurs in nature as celestite, in transparent rhombic prisms or in fibrous masses, having the specific gravity of 3.89. Celestite usually has a light-bluish shade of color, from which it takes its name. The sulphate may be prepared by adding sodium sulphate to a soluble salt of strontium, as the nitrate. It is soluble in 6895 parts of cold water, and in 9638 parts of boiling water. The salt is quite easily decomposed by boiling it with solution of potassium or sodium carbonate. It fuses when strongly heated.

Strontium Nitrate, $Sr(NO_3)_2$.—This salt is prepared by dissolving strontium carbonate in dilute nitric acid. As ordinarily obtained, it separates in anhydrous octahedrons; these are permanent in the air. When a hot, dilute solution of strontium nitrate is allowed to cool slowly, monoclinic prisms or plates separate with 4 molecules of water of crystallization; these crystals readily effloresce on exposure to the air.

The anhydrous salt is easily soluble in water, both hot and cold, but scarcely soluble in alcohol.

On the application of heat the salt melts, and at a red heat is decomposed, a residue of strontium oxide remaining.

The principal use of strontium nitrate is in pyrotechnics. Nearly all red fires contain this salt. The following formula will furnish a good red fire: Strontium nitrate, 50 parts; potassium chlorate, 25 parts; pulverized shellac or sugar, 25 parts; powder separately, and carefully mix without friction. An intimate mixture is best made by passing the powders through a sieve.

Strontium Carbonate, $SrCO_3$, occurs native as strontianite in the form of rhombic prisms. It is prepared by precipitating a soluble salt of strontium with sodium carbonate. The salt is insoluble in water. On ignition (1100°) it gradually dissociates into SrO and CO_2. For conversion into its oxide, strontium carbonate requires a higher temperature than calcium and a lower temperature than barium carbonate.

The chief use of strontium carbonate is in the preparation of the other strontium salts. It is constantly formed and again converted into oxide in the recovery of sugar from beet-root molasses.

Such salts of strontium as have not been described in the preceding pages may be prepared by processes similar to the corresponding barium or calcium salts.

BARIUM

Symbol, Ba. *Atomic Weight*, 137.37. *Valence*, II.

History.—The metal barium (βαρυς = *heavy*) was first prepared by Davy in 1808, although its compounds were previously well known.

Occurrence.—Barium sulphate as *heavy spar*, $BaSO_4$, and barium carbonate as *witherite*, $BaCO_3$, are the chief natural forms of this metal. Barium is, further, found in sea water, in sea plants, and in the ash of certain woods, notably that of the beech. Germany has been the chief source of supply for barium salts. Recently the extensive deposits of barium in Tennessee, Kentucky, Virginia, and Missouri have been commercially utilized.

Isolation.—Davy obtained barium by electrolysis of the chloride in the presence of mercury; the resulting amalgam was heated in a tube containing petroleum, whereby the metallic barium was left behind as a white powder. It may be obtained by electrolysis of a barium chloride solution in which a mercury cathode is used. The resulting amalgam is distilled in a current of hydrogen, leaving barium hydride, which, when heated *in vacuo*, leaves barium metal.

Properties.—Barium is a yellowish-white metal, which melts at 850°. It is not volatile under ordinary circumstances. When exposed to the air it readily oxidizes, and if sufficiently heated takes fire. Its specific gravity is about 3.75. Barium decomposes water at ordinary temperatures, like sodium. The salts of barium are poisonous.

BARIUM AND THE HALOGENS

Barium Chloride, $BaCl_2.2H_2O$.—This salt may be prepared by dissolving native barium carbonate, witherite, in dilute hydrochloric acid. The resulting solution contains, in addition to barium, the chlorides of calcium, iron, manganese, etc.; these are removed by allowing the solution to remain for some time in contact with an excess of the carbonate, whereby the impurities are precipitated. The clear filtered solution is then neutralized with hydrochloric acid, and evaporated for crystallization.

Commercially, barium chloride is prepared by heating a mixture of finely-powdered heavy spar, charcoal, and a concentrated solution of calcium chloride in a furnace to 900°. The reaction is as follows:

$$BaSO_4 + 4C = BaS + 4CO.$$
$$BaS + CaCl_2 = BaCl_2 + CaS.$$

Or heavy spar is ignited with charcoal in the electric furnace and the resulting barium oxide dissolved in HCl.

$$(a)\ 4BaSO_4 + 4C = BaS + 3BaSO_4 + 4CO.$$
$$(b)\ 3BaSO_4 + BaS = 4BaO + 4SO_2.$$

Properties.—Barium chloride occurs in colorless, glistening, rhombic tables, permanent in the air, having a disagreeable, bitterish, saline taste and a neutral reaction. It is soluble in 2.5 parts of water at 15°, and in about 1.5 parts of boiling water. It is insoluble in concentrated hydrochloric acid and in absolute alcohol. At ordinary temperatures over sulphuric acid the salt loses one molecule of water of crystallization; at 120° it becomes anhydrous, and at about 800° it melts. When it is melted with free access of air it loses chlorine.

The anhydrous salt on exposure takes up two molecules of water.

Barium chloride, like other barium salts, is an active poison.

Uses.—The chief uses of barium chloride are as a reagent (see U. S. P. Reagent) for the detection and determination of sulphuric acid, as a preventive against boiler incrustation, and in ceramics.

Barium Bromide, $BaBr_2.2H_2O$, is prepared by adding bromine to an excess of barium hydroxide in water, $6Ba(OH)_2 + 6Br_2 = 5BaBr_2 + Ba(BrO_3)_2 + 6H_2O$; to complete the precipitation of the bromate, alcohol is added, and after filtration the filtrate is distilled to recover the alcohol and set aside for crystallization of the bromide. The bromate ($Ba(BrO_3)_2$) is ignited with charcoal to convert into the bromide. Other bromides may be prepared from barium bromide by interaction in aqueous solution with their soluble sulphates, removing the barium sulphate by filtration. *Barium Iodide,* $BaI_2.2H_2O$, may be prepared in the same manner as the barium bromide, reducing, however, the barium iodate by means of hydrogen sulphide, heating to remove the excess of H_2S, filtering and evaporating to crystallizing point. Other iodides may be prepared from barium iodide as outlined under barium bromide.

BARIUM AND OXYGEN

Barium Monoxide, Baryta, BaO, is prepared by heating barium nitrate in an iron crucible until there is no further evolution of red fumes. It may also be prepared by igniting barium carbonate mixed with charcoal, or, better, by heating a mixture of barium hydroxide and barium carbide with a heavy hydrocarbon oil. This yields a porous oxide which is desirable for making the peroxide.

This compound usually occurs as a grayish-white, porous mass. In contact with water it slakes with considerable evolution of heat, forming barium hydroxide, $Ba(OH)_2$.

Barium monoxide is used in the manufacture of oxygen by the Brin process.

Barium Dioxide, BaO_2. *Barium Peroxide.*—Prepared from the oxide, which is obtained by calcining the nitrate, by heating in a current of air free from carbon dioxide, between 400° and 500°. It is then cooled away from contact with the air to avoid absorption of carbon dioxide.

Properties.—Barium dioxide occurs as a heavy white to grayish-white, amorphous, coarse powder, odorless and tasteless. When exposed to the air it slowly absorbs moisture and carbon dioxide, and is gradually decomposed. It is almost insoluble in cold water, with which, however, it forms, on standing, a definite hydroxide, $BaO_2 + H_2O = BaO(OH)_2$. This hydration of barium peroxide is necessary before attempting to prepare solution of hydrogen peroxide.

When heated to a bright redness barium dioxide fuses, and loses one atom of oxygen. Hydrochloric and the other mineral acids decompose it with the formation, in the cold, of hydrogen dioxide and a barium salt:

$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Barium Hydroxide, $Ba(OH)_2.8H_2O$.—When barium monoxide is treated with water, the hydroxide is formed with evolution of heat according to the following reaction:

$$BaO + H_2O = Ba(OH)_2.$$

If just enough water is added to form the compound, the result is a white powder, which at a low red heat melts to an oily liquid, that solidifies on cooling to a crystalline mass. Commercially the hydroxide is made by heating a mixture of ground barytes and coke in an electric furnace:

$$(1)\ 4BaSO_4 + 4C = 3BaSO_4 + BaS + 4CO.$$
$$(2)\ 3BaSO_4 + BaS = 4BaO + 4SO_2.$$

The flux is leached with hot water, barium hydroxide and hydrosulphide are obtained. The former crystallizes from the solution ($Ba(OH)_2.8H_2O$), while the latter remains in the mother liquor. For experimental purposes barium hydroxide may be prepared by pouring a hot concentrated solution of barium chloride in the same of sodium hydroxide; on cooling, barium hydroxide separates:

$$BaCl_2 + 2NaOH = Ba(OH)_2 + 2NaCl.$$

These crystals, on exposure to the air, form a white powder with a loss of seven molecules of water. Barium hydroxide absorbs carbon dioxide readily from the air with formation of the carbonate. It is soluble in 20 p. of water at 15° (*baryta water*) and 3 p. of boiling water. Barium hydroxide solution is a useful reagent (see U. S. P. Reagent) for carbon dioxide, owing to the formation of insoluble barium carbonate.

OXYGEN SALTS OF BARIUM AND THE HALOGENS

Barium Chlorate, $Ba(ClO_3)_2$, is prepared by saturating aqueous chloric acid with barium carbonate, or by electrolysis of the chloride as given under potassium chlorate. It crystallizes in monoclinic prisms, and is easily soluble in water. It is used in fireworks, producing a bright green flame.

Barium Iodate, $Ba(IO_3)_2$, is obtained in the preparation of barium iodide, separating from the solution containing the iodide because of its insolubility. It may be prepared extemporaneously by interaction between potassium iodate and barium chloride; barium iodate separates, since it requires about 3000 parts of water to dissolve it; it is soluble in 600 parts of boiling water. Its chief use is for the preparation of iodic acid.

BARIUM AND SULPHUR

Barium Monosulphide, BaS, is formed when an intimate mixture of 100 parts barium sulphate, 25 parts of coal, and 20 parts of common salt is made into a plastic mass with water, dried, and heated for several hours to whiteness:

$$BaSO_4 + C_4 = 4CO + BaS.$$

Properties.—Barium monosulphide is a reddish-white, or, from the presence of coal, a grayish-white, mass, which in the presence of water is decomposed into barium hydroxide and barium sulphydrate, which are dissolved. When a mixture of 5 parts of the barium monosulphide and 1 part of sulphur is boiled with water and allowed to evaporate in a vacuum, colorless crystals separate, having the formula $BaS.6H_2O$.

Barium Sulphydrate, $Ba(SH)_2$, is prepared by passing hydrogen sulphide into a solution of barium hydroxide until saturated; by evaporating in a vacuum it crystallizes in white, four-sided prisms.

These compounds are used in medicine as depilatories and in the manufacture of luminous or phosphorescent paints.

OXYGEN SALTS OF BARIUM

Barium Sulphate, $BaSO_4$, *Heavy Spar, Barytes.*—This is the most abundant native compound of barium, and on that account it furnishes the starting-point in the preparation of the other barium compounds.

It is a by-product in the manufacture of hydrogen peroxide.

Barium sulphate is prepared by precipitating any soluble barium salt with dilute sulphuric acid. That made in this manner is extensively used as a pigment in water-colors under the name of *blanc fixé* or *permanent white.*

Properties.—The precipitate is a heavy, fine, white powder of specific gravity of 4.53. It is almost absolutely insoluble in water, since 1 part requires 430,000 parts of water to dissolve it. In the freshly precipitated state it is soluble in concentrated sulphuric acid, but is precipitated on dilution with water.

Barium sulphate is decomposed by fusing with three to four times its weight of sodium carbonate, by which barium carbonate and sodium sulphate result; the latter can be removed by solution in water.

In order to precipitate barium sulphate in an impalpable powder, the solution of barium chloride, having a specific gravity of 1.19, is treated in the cold with dilute sulphuric acid having a specific gravity of 1.245; the resulting precipitate is collected, washed with cold water, and sent into commerce in the moist state. This compound is not only used as an unalterable paint base, but also for giving weight and finish to cards and paper. The finely-powdered mineral is sometimes employed to mix with white lead in the manufacture of the cheaper paints, but, on account of its crystalline character, it does not possess the covering power of the pure lead compound.

Barium sulphate is administered internally in large doses when preparing X- or Roentgen-ray photographs. It should form a fine, white, inodorous, tasteless and relatively light powder, insoluble in acids, alkalies, and be free from all traces of soluble barium salts. The following tests should always be applied:

Boil 10 gm. with a mixture of 10 mils of acetic acid (1.064 sp. gr.) and 90 mils of water, filter, evaporate 50 mils on a water-bath to dryness. Treat the residue with 20 mils of water, filter until perfectly clear, add a few drops of dilute sulphuric acid, and after half an hour no separation of barium sulphate should take place (barium carbonate). Boil 2 gm. with 10 mils of nitric acid (1.15 sp. gr.), filter, add to the filtrate ammonium molybdate, T.S., no yellow precipitate should form within half an hour (barium phosphate). Boil 10 gm. of barium sulphate for Roentgen-ray work with 50 mils of water containing 1 mil of HCl (U. S. P.), cool and filter; the clear filtrate shows no spectral line for barium.

Barium Nitrate, $Ba(NO_3)_2$.—Nitric acid is saturated with barium carbonate or sulphide in order to obtain this salt, or by mixing hot concentrated solutions of barium chloride and sodium nitrate, whereby barium nitrate is precipitated. As thus prepared it forms permanent, colorless, anhydrous, octahedral crystals. It is soluble in 10 parts of water at 25°, and in 3 parts of boiling water; insoluble in alcohol. When heated to redness it is converted into barium oxide, the source for barium peroxide.

Barium nitrate is used as a reagent (see U. S. P. Reagent), also for the preparation of the oxide, in smokeless gunpowder and in the preparation of green colored fires. The following formula will produce a satisfactory color: Potassium chlorate, 50 parts; barium nitrate, 25 parts; sugar or shellac, 25 parts. Each ingredient to be pulverized separately, and then all carefully mixed and run through a sieve. Sulphur is a frequent constituent of colored fires, and may be used in place of the sugar or shellac, but it renders the fires more liable to inflame spontaneously.

Barium Carbonate, $BaCO_3$.—This compound occurs native as witherite, or it may be prepared by adding sodium carbonate to a soluble salt of barium or by passing carbon dioxide into a solution of barium sulphide made from the native sulphate:

$$Ba(SH)_2 + Ba(OH)_2 + 2CO_2 = 2H_2S + 2BaCO_3.$$

The sulphur compounds may be removed by boiling the precipitate with $Ba(OH)_2$. The native salt occurs in glistening, rhombic crystals, but the precipitated compound is a white powder. It is soluble in 14,000 parts of cold water, and in 15,400 parts at 100°.

When heated, away from contact with carbon dioxide, barium carbonate loses carbon dioxide only in the flame of the oxyhydrogen lamp. The decomposition takes place more readily and at a lower temperature in the presence of carbon, or when steam is passed over it.

CHAPTER III

THE MAGNESIUM GROUP

MAGNESIUM

Symbol, Mg. *Atomic Weight,* 24.32. *Valence,* II.

History.—Attention was first directed to the magnesium salts about the close of the seventeenth century by Grew, a physician of London. He found a peculiar salt in the mineral spring at Epsom, which salt soon became celebrated for its medicinal virtues. The metal was first isolated by Davy, in 1808, although he did not obtain it in a pure condition. Bussy was the first to obtain a tangible quantity of the metal, which he accomplished by fusing the chloride with potassium.

Occurrence.—The metal is not found in the uncombined state in nature. Its compounds, however, are almost as widely distributed as those of calcium, although not in such large quantities. The principal minerals containing it are ***magnesite,*** $MgCO_3$; ***dolomite,*** $MgCa(CO_3)_2$; ***kieserite,*** $MgSO_4.H_2O$; ***carnallite,*** a chloride of magnesium and potassium, KCl, $MgCl_2.6H_2O$; and the following silicates: ***talc,*** $3MgO.4SiO_2.H_2O$; ***meerschaum,*** $2MgO.3SiO_2.2H_2O$; and ***serpentine asbestos,*** $3MgO.2SiO_2.2H_2O$. Magnesium salts are found in plants, in which they may to a certain extent replace the salts of calcium. As phosphate, magnesium is found in the bones and urine of animals.

Isolation.—Magnesium is now usually prepared by the electrolysis of the fused double chloride; that is, carnallite ($MgCl_2.KCl$) to which some fluorspar or sodium chloride is added as a flux. The vessel in which the decomposition is effected is made of especially prepared cast-steel, which acts as the negative pole at which the magnesium is liberated; the positive pole is made of gas-carbon. In order to prevent the oxidation of the metal, a stream of hydrogen or nitrogen is led through the vessel during the operation.

The metal may also be prepared by the reduction of fused magnesium chloride with sodium or aluminum.

The metal is furnished usually either in form of powder ("flash-powder") or ribbon.

Magnesium unites directly with nitrogen at 670° to magnesium nitride.

Properties.—Magnesium is a silver-white, highly lustrous metal, having a specific gravity of 1.75. It is unchangeable in dry air, but in the presence of moisture it gradually becomes covered with a film of oxide. When heated without access of air, magnesium melts at about 650° and boils at 1120°. Heated in the air it ignites, and burns with a blinding white light which is especially rich in actinic rays. Water is decomposed by magnesium but slightly at or above 100°, with evolution of hydrogen and the formation of magnesium oxide.

Uses.—On account of the comparatively low ignition-point (800°), high heat of combustion (134,000 cal.), and relatively low heat of vaporization of magnesium and the actinic activity of the magnesium light, it is useful in photography, and enters into the composition of the numerous " flash-light " powders and illuminants employed for military purposes. Previous to the development of electric lighting it was used in making strong lights for signalling purposes. It is used in pyrotechny. Bengal fires are made as follows: Red—1 part of pulverized shellac, 5 parts of dried strontium nitrate, 2.5 parts of powdered magnesium. Green—1 part of pulverized shellac, 6 parts of dried barium nitrate, 2.5 parts of powdered magnesium. An alloy of magnesium (10 per cent.) with aluminum is known as " magnalium " and is of a silver-white appearance, very light, fuses at 633°, and is used in aviation machines. Magnesium also has some use in the laboratory, where, on account of its freedom from arsenic, it may replace zinc in Marsh's test. In metallurgy magnesium is employed for scavenging alloys; that is, for removing oxides of other metals, as aluminum, nickel, copper, brass, bronze, etc. Magnesium reduces many metallic oxides to their metals, as boric oxide, silica, etc.

MAGNESIUM AND THE HALOGENS

Magnesium Chloride, $MgCl_2.6H_2O$.—Sea water and most mineral waters contain magnesium chloride. In the solid state it is found abundantly as carnallite, $KCl,MgCl_2.6H_2O$, at Stassfurt; also in a number of the double salts in that locality. It may be prepared by dissolving magnesite in hydrochloric acid; but, since it is a by-product of not much value in the preparation of potassium chloride from carnallite, it is usually derived from this source.

Properties.—Magnesium chloride occurs in colorless, very deliquescent, monoclinic crystals. It cannot be deprived of its water of crystallization by heat, since, when heated, it decomposes with evolution of hydrochloric acid and formation of magnesium oxychloride, $MgCl.OH$. This decomposition may be prevented by adding 3 parts of ammonium chloride for every part of magnesia. A double salt, $MgCl_2.2NH_4Cl$, forms, which may be evaporated to dryness without decomposition.

The anhydrous salt is obtained by heating the double chloride, $MgCl_2.NH_4Cl.6H_2O$, until a crystalline mass, which fuses at 708°, forms; this distills at red heat; or it may be prepared by drying the crystallized chloride in a stream of hydrochloric acid gas.

Anhydrous magnesium chloride occurs in transparent, laminated, pearly plates, which dissolve in water with the evolution of heat. It possesses a bitter, saline taste, and is readily soluble in water. With magnesium oxide it forms an oxychloride which is insoluble in water. Water containing magnesium chloride cannot be used in boilers owing to its liberation of hydrochloric acid which attacks the iron.

Uses.—Magnesium chloride is used in the preparation of a cement prepared by mixing magnesium oxide and chloride with infusorial earth or sawdust and sufficient water to form a paste. It is also used as a finisher for cotton and woolen textiles.

Magnesium Ammonium Chloride, $MgCl_2.NH_4Cl.6H_2O$, is a double salt which is usually prepared by evaporating a solution of 3 parts of ammonium chloride with one part of magnesium chloride. The addition of ammonia water does not precipitate the magnesium.

Magnesium Oxychloride.—When an aqueous solution of magnesium chloride of 1.16 to 1.26 specific gravity is mixed with freshly-prepared magnesium oxide, the mass after some time hardens sufficiently to be capable of taking a high polish. It has a composition represented by the formula $Mg_{11}Cl_2(OH)_{20}.4H_2O$. On exposure to the air for some time it absorbs carbon dioxide. Another oxychloride is formed when magnesium sulphate, containing ammonium hydroxide and chloride, is exposed to the air for some time: the crystalline precipitate, which is deposited, has the composition $Mg_2Cl(OH)_3.4H_2O$.

Magnesium Bromide, $MgBr_2.6H_2O$, occurs in sea water and in a number of salt springs. It is this salt more than any other that is the source of bromine. It may be prepared by heating magnesium in bromine vapor or dissolving freshly precipitated magnesium hydroxide in hydrobromic acid and evaporating over sulphuric acid.

The anhydrous salt forms in solid, white, crystalline masses, which are very deliquescent, and become hot in contact with water. When the salt contains water of crystallization, it loses hydrobromic acid on the application of heat, leaving a residue of magnesium oxybromide.

Magnesium Iodide, $MgI_2.8H_2O$, occurs associated with the bromide in sea water. It may be prepared by adding iodine to an excess of magnesium powder suspended in water, digesting, filtering, and evaporating over sulphuric acid. It forms very deliquescent, hydrated crystals, which readily decompose with liberation of iodine.

Magnesium Nitride, Mg_3N_2.—Obtained as a yellow powder when magnesium is heated in an atmosphere of nitrogen or a current of ammonia:

$$Mg_3 + 2NH_3 = Mg_3N_2 + 3H_2.$$

When magnesium is heated in a current of air at 670°, a mixture of oxide and nitride forms.

When the nitride is boiled with water, ammonia is given off:

$$Mg_3N_2 + 3H_2O = 2NH_3 + 3MgO.$$

When heated in a current of CO, cyanogen is obtained:

$$Mg_3N_2 + 3CO = 3MgO + 2CN + C.$$

MAGNESIUM AND OXYGEN

Magnesium Oxide, MgO. **Magnesii Oxidum,** U.S.P.—Black, in 1755, appears to have been the first to prepare this oxide. He noted its solubility in diluted sulphuric acid, which served to distinguish it from lime.

Occurrence.—Magnesium oxide is found native in the rare mineral *periclase,* found near Naples.

Preparation.—Magnesia is prepared on a large scale by heating the carbonate, $(MgCO_3)_4Mg(OH)_2.5H_2O = 5MgO + 6H_2O + 4CO_2$. When the light carbonate is ignited, the light or calcined magnesia, *magnesia usta,* results. When a denser carbonate is used, the result is heavy magnesia, **Magnesii Oxidum Ponderosum,** U.S.P.

The operation is conducted in iron or earthenware crucibles; at 300° to 350° the decomposition readily takes place, and it is known to be complete when a small quantity, taken from the middle of the vessel with an iron spoon, cooled and mixed with water, gives no effervescence with dilute hydrochloric acid.

Probably the most important feature in the successful manufacture of this compound is that of avoiding too high a temperature. In order to prevent parts of the powder from becoming too hot it should be stirred frequently, or it has been recommended to perform the ignition in shallow pans, so that the depth of the carbonate does not exceed 2 to 3 inches. Much also depends upon the purity and physical condition of the carbonate employed.

Properties.—Official " light " or " heavy " magnesia, which after ignition contains not less than 96 per cent. of MgO and not more than 2 per cent. of CaO, occurs as a loose, white, odorless powder; possessing an earthy but not saline taste. It is almost insoluble in water (1 to 55,000), insoluble in alcohol, but readily soluble in dilute acids without effervescence. Being a weak base, magnesium readily forms insoluble basic (oxy) salts with acids. When mixed with water magnesium oxide forms the hydroxide $Mg(OH)_2$.

The presence of ammonium salts materially increases its solubility in water. In moist air it readily absorbs moisture and carbon dioxide, becoming converted into a basic carbonate.

Magnesia is not visibly affected by any temperature below that of the oxyhydrogen flame, but it will, at lower temperatures, become more dense and crystalline. When heated with distilled water it does not yield more than 2 per cent. of soluble salts (U.S.P.). The heavy magnesia is a denser and finer powder, but in most other characters resembles the light compound.

Magnesium Hydroxide, $Mg(OH)_2$, occurs in nature as the mineral brucite. It may be prepared by allowing magnesium oxide which has not been overcalcined to stand in contact with water, or more quickly by heating the same compound with water to 150°. Sodium or potassium hydroxide precipitates magnesium hydroxide from solutions of the salts.

Magnesium hydroxide is a white, nearly insoluble powder. It is easily soluble in solutions of ammonium salts. Magnesium salts are not precipitated by the reagents for the heavy metals, as ammonium hydroxide or hydrosulphide, when ammonium salts as NH_4Cl are present due to the formation of complex magnesium ammonium compounds. At 100° magnesium hydroxide is not affected, but when the temperature approaches redness it is easily converted into oxide. It is sufficiently soluble in water to impart an alkaline reaction.

Magma Magnesiæ, U. S. P. Milk of Magnesia.—A suspension of magnesium hydroxide in water, obtained by interaction between magnesium carbonate, 125 gm., and a solution of sodium hydroxide, 80 gm. This mixture yields not less than 6.5 per cent. nor more than 7.5 per cent. of $Mg(OH)_2$.

SALTS OF MAGNESIUM

Magnesium Sulphite, $MgSO_3.6H_2O$, may be made by adding sulphurous acid in excess to a mixture of 8 parts of magnesium oxide in 16 parts of water.

Properties.—Magnesium sulphite is a white, crystalline powder, becoming oxidized on exposure to air, odorless, having a slightly bitter, somewhat sulphurous taste, and a neutral or slightly alkaline reaction. It is soluble in 20 parts of water at 15°, and in 19 parts of boiling water; insoluble in alcohol. When heated to 200° the salt loses its water of crystallization, amounting to 50.9 per cent., and is converted into magnesia and anhydrous magnesium sulphate.

Magnesium Sulphate, $MgSO_4.7H_2O$. **Magnesii Sulphas,** U.S.P.—Epsom salt became known about the end of the seventeenth century, because of its valuable purgative qualities, and was designated on the continent of Europe as bitter salt and *Sal Anglicum.*

Occurrence.—Magnesium sulphate occurs in many mineral waters, the most notable being those of Pullna and Seidlitz, in Bohemia, of Epsom, in England, of Friedrichshall, in Germany, and Hunyadi Janos, in Hungary. Under the name of *kieserite,* $MgSO_4.H_2O$, magnesium sulphate is found at Stassfurt. The upper layer of this salt deposit, known as *Abraumsalz,* is a mixture of magnesium and potassium salts, chiefly carnallite, kainite, and kieserite.

Preparation.—Formerly much magnesium sulphate was obtained by the concentration of natural bitter waters. At the present time large quantities are obtained as a by-product in the manufacture of carbon dioxide for use in mineral waters. Magnesite is used to furnish this gas, and sulphuric acid is used to effect its liberation, as follows:

$$\underset{\text{Magnesite.}}{MgCO_3} + \underset{\substack{\text{Sulphuric}\\\text{Acid.}}}{H_2SO_4} = \underset{\substack{\text{Magnesium}\\\text{Sulphate.}}}{MgSO_4} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O.}$$

After the escape of carbon dioxide, the residue is dissolved in hot water, neutralized with magnesite, some ammonium sulphide added, and the mixture allowed to stand for some time in order to separate iron; finally, the clear liquid is concentrated and allowed to crystallize. The *Abraumsalz* is also employed as a source of magnesium sulphate. This salt is usually suspended in baskets over open evaporators, so that it is brought in contact with the ascending steam; by this means the very soluble magnesium and potassium chlorides are dissolved, while the kieserite remains behind. Kieserite is not easily dissolved by water, but on contact with steam it disintegrates and is converted into Epsom salt, containing 7 molecules of water; in this form it is dissolved and recrystallized.

Properties.—Magnesium sulphate, "which contains not less than 48.59 nor more than 53.45 per cent. of the anhydrous salt," crystallizes from water in colorless, rhombic prisms, or in small acicular crystals; the latter form is obtained by allowing the crystallization to take place from hot concentrated solutions. The salt is without odor, and has a cooling, saline, bitter taste; the crystals slowly effloresce in dry air. It is soluble in 1 part of water at 25°, and in 0.2 part of boiling water; insoluble in alcohol. When heated to 52° the salt loses 1 molecule of water; from this temperature up to 132° it loses 5 additional molecules, and at somewhat above 200° the remaining seventh molecule of water is removed and the salt becomes anhydrous. The aqueous solution is neutral to litmus.

One molecule of water of crystallization (above 200°) of $MgSO_4.H_2O.$-$6H_2O$ is readily replaced by sulphates of the alkali metals, yielding double isomorphous salts of the general formula $MgSO_4.MeSO_4.6H_2O$, as $MgSO_4.$-$K_2SO_4.6H_2O$; $MgSO_4(NH_4)_2SO_4.6H_2O$, etc. This may be extended to such other isomorphous sulphates as $NiSO_4.7H_2O$, $CoSO_4.7H_2O$, and $ZnSO_4.7H_2O$, which form similar double salts with the alkali sulphates.

When anhydrous magnesium sulphate is dissolved in hot concentrated sulphuric acid, six-sided tabular crystals separate on cooling, which have the composition $MgSO_4.H_2SO_4$.

Uses.—Magnesium sulphate is used in medicine as an active cathartic. It also has some use in dyeing and calico printing as a finisher. When this salt is used with aniline colors, the finished goods are found to withstand the action of soap.

Magnesium Nitrate, $Mg(NO_3)_2.6H_2O$, is prepared by neutralizing nitric acid with magnesium carbonate. It forms deliquescent monoclinic prisms or acicular crystals. From hot solutions it separates with 2 molecules of water of crystallization. The crystals are soluble in 0.5 part of water at 15°, and in 9 parts of alcohol.

Normal Magnesium Phosphate, $Mg_3(PO_4)_2$, is found in bones, in the seeds of many plants, and in a number of minerals. It is precipitated when a solution of trisodium orthophosphate is added to one of magnesium sulphate. It is soluble in about 5000 parts of water.

Magnesium Hydrogen Phosphate, $MgHPO_4$, is formed when a solution of ordinary sodium phosphate, Na_2HPO_4, is added to one of magnesium sulphate. On standing in contact with water, this precipitate crystallizes with 7 molecules of water. One part of this crystalline precipitate is soluble in 322 parts of water. If the above precipitation takes place in presence of ammonia and an ammonium salt, the insoluble $Mg(NH_4)PO_4.6H_2O$ forms.

Ammonium Magnesium Phosphate, $Mg(NH_4)PO_4.6H_2O$.—This salt frequently separates from alkaline urine, and forms the triple phosphate calculi. It is formed when ammonium chloride followed by ammonium hydroxide is added to a solution of a magnesium salt followed by a solution of sodium phosphate (Na_2HPO_4). The crystals which are thus produced are transparent, quadratic prisms, soluble in 15,000 parts of water at 15° and in 44,000 parts of ammoniacal water. At 100° five molecules of water are given off without loss of ammonia, and at higher temperatures the remainder of the water and the ammonia escape, leaving magnesium pyrophosphate, $Mg_2P_2O_7$. Magnesium as well as phosphorus is determined quantitatively in this form.

Magnesium Arsenate and *Magnesium Ammonium Arsenate* ($MgNH_4AsO_4.6H_2O$) are similar in their method of preparation and properties to the corresponding phosphates.

Magnesium Borate.—When solutions of borax and magnesium sulphate are mixed in the cold, no precipitation takes place, but on long boiling a precipitate forms having the composition $Mg(BO_2)_2.2Mg(OH)_2.7H_2O$. This compound has had some use as an antiseptic.

Magnesium Carbonate, $MgCO_3$.—This is the normal magnesium carbonate, and is found abundantly in nature as magnesite. In pharmacy and medicine we are concerned chiefly with the artificially prepared or basic magnesium carbonate, **Magnesii Carbonas,** U.S.P. The official salt is a mixture of hydrated carbonate and hydroxide, corresponding to not less than 39.2 per cent. of MgO containing not more than 0.8 per cent. CaO. This compound became known as a valuable medicinal agent about the beginning of the eighteenth century, under the name of *magnesia alba.*

Preparation.—The *light* carbonate may be prepared by precipitating magnesium sulphate with sodium carbonate and boiling the mixture, a slight excess of the sulphate being used. The precipitate is collected on a muslin strainer and washed with hot water until the washings cease to give a reaction with barium chloride for sulphuric acid. The *heavy* carbonate of magnesia is prepared as above, finally evaporating the resulting mixture to dryness. The dry residue is then washed thoroughly with hot water until all sodium sulphate is removed. The product is a dense powder. The reaction which takes place in these processes is as follows:

$$\underset{\substack{\text{Magnesium}\\\text{Sulphate.}}}{5MgSO_4} + \underset{\substack{\text{Sodium}\\\text{Carbonate.}}}{5Na_2CO_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Magnesium Carbonate.}}{(MgCO_3)_4,Mg(OH)_2.5H_2O} + \underset{\substack{\text{Sodium}\\\text{Sulphate.}}}{5Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{CO_2}.$$

The method of Pattinson consists in gently igniting dolomite, a magnesium and calcium carbonate, whereby magnesium oxide forms and the calcium remains as carbonate, then treating the product with water and carbon dioxide under a pressure of 5 to 6 atmospheres. The magnesium carbonate passes into solution as bicarbonate much more readily than the calcium carbonate. The clear solution is separated from the precipitate of the latter, and on heating deposits a precipitate of the official carbonate, with evolution of some carbon dioxide, which may be used again.

Properties.—The official magnesium carbonate comes into commerce in loose, white, easily-pulverized masses, or more usually as a fine, white, amorphous powder, without odor, having an earthy taste, and permanent in the air. It dissolves in about 2500 parts of cold water and about 9000 parts of hot water, and imparts to the solution an alkaline reaction; alcohol exerts no solvent action upon it. Dilute acids dissolve it with active effervescence, and without leaving any residue. When boiled with distilled water, magnesium carbonate does not yield more than 1 per cent. of soluble salts.

Solutions of ammonium salts have considerable solvent action on magnesium carbonate, and in the presence of ammonium chloride no precipitation will occur after the addition of ammonium carbonate.

On the application of heat, water is first given off, and at 300° the decomposition of the carbonate is complete, magnesium oxide remaining.

When the official magnesium carbonate is shaken with water until a uniform mixture results, and carbon dioxide is passed in, there results a clear solution of *acid magnesium carbonate,* $MgH_2(CO_3)_2$, which has not been separated in the solid state. This solution, on exposure to the air and warming to 50°, deposits crystals of the neutral carbonate with 3 molecules of water, $MgCO_3.3H_2O$, or at a low temperature $MgCO_3.5H_2O$ separates. Under ordinary atmospheric pressure 1 part of magnesium carbonate requires about 761 parts of carbonated water to dissolve it, under 3 atmospheres of pressure the solubility is 1 to 134, and at 6 atmospheres it is 1 to 76 of the carbonated water.

Uses.—Magnesium carbonate is used in medicine as an antacid, and in the presence of acids becomes cathartic in its action.

GLUCINUM (BERYLLIUM) (Gl)

Symbol, Gl. *Atomic Weight,* 9.1. *Valence,* II.

Occurrence.—Glucinum occurs in nature in a few rare minerals, its name being derived from γλυκυς = *sweet,* referring to the sweet taste of its salts. Beryl is a silicate of glucinum and aluminum, $3BeSiO_3,Al_2(SiO_3)_3$, which occurs in beautiful hexagonal crystals of a green color; the transparent, green-colored varieties are known as emerald (which owes its color to the presence of a trace of chromium), and those of a bluish-green tint (due to FeO) are termed aquamarine. Phenacite is a glucinum silicate of the composition Be_2SiO_4, and chrysoberyl is a glucinum aluminate, $BeO.Al_2O_3$.

Isolation.—Metallic glucinum is prepared by electrolysis of the fused double fluoride $NaF.BeF_2$.

Properties.—Glucinum is a silver-white, lustrous metal; malleable, and having the specific gravity of 1.84. It is soluble in acids (excepting dilute HNO_3) and dilute alkalies and does not decompose water.

Glucinum Chloride, $GlCl_2$, is obtained in the anhydrous condition by passing chlorine over a heated mixture of GlO and charcoal. It is easily fusible and volatile, and may be obtained with 4 molecules of water of crystallization from aqueous solution.

Glucinum Oxide and Hydroxide, GlO, yields with acid salts having a sweet taste. The solutions of these salts form precipitates of the hydroxide, $Gl(OH)_2$, on the addition of sodium or potassium hydroxide; this hydroxide is distinguished from that of magnesium by being soluble in excess of the reagent, and from the hydroxide of aluminum by its solubility in excess of alkali carbonate. The hydroxide behaves as a weak acid towards strong bases, like aluminum. When heated, glucinum hydroxide yields GlO.

Glucinum Sulphate, $GlSO_4.4H_2O$, separates from hot, neutral concentrated solutions, while $GlSO_4.7H_2O$ crystallizes from acid solution; it is isomorphous with magnesium sulphate. The double salt $GlSO_4.K_2SO_4.3H_2O$ is but slightly soluble.

Glucinum Nitrate, $Gl(NO_3)_2.3H_2O$, is an extremely deliquescent salt, easily soluble in alcohol.

Glucinum Carbonate, $GlCO_3$.—This is soluble in water and readily gives off CO_2.

ZINC

Symbol, Zn. *Atomic Weight,* 65.37. *Valence,* II.

History.—Paracelsus in the sixteenth century first recognized zinc as a metal. It was known, however, long before that certain ores of zinc known as *cadmia* would, when smelted with copper ores, furnish a yellow metal (brass). Works for the preparation of metallic zinc were first established in the year 1743, at Bristol, England.

Occurrence.—Zinc occurs chiefly as a sulphide or *zinc blende* (ZnS), as carbonate or *smithsonite* ($ZnCO_3$), as a mixture of carbonate and silicate ($2ZnO.SiO_2.H_2O$) or *calamine.* The most noted European localities are Belgium, Silesia, Saxony, and England. In the United States fully half the zinc is produced in Missouri, although there are important deposits in New Jersey, Virginia, Wisconsin, Kansas, Arkansas and Montana.

In the United States there are two ores peculiar to the localities named and are not found abroad—namely, the native oxide, called red oxide, or *zincite,* and a mixture of zinc oxide with manganese and iron oxide, known as *franklinite.* Both of these minerals occur at Franklin and Mine Hill, New Jersey.

Metallurgy.—Zinc ores are first roasted to remove carbon dioxide and water in the case of smithsonite or calamine, and in the blende to convert the sulphide into oxide. The roasted ore is then reduced by heating to redness in fireclay retorts with charcoal; the zinc, which boils at about 920°, distils over.

Modern methods consist in making an intimate mixture of the pulverized roasted ore with powdered coal; this is introduced into long, cylindrical clay retorts placed horizontally in rows slightly tipped toward the front. These are heated to 1200° to 1300° by means of natural or process gas; as soon as the CO gas becomes luminous, long receivers (alembics) are attached to the ends of the retorts for condensation of the metal. Zinc powder or dust appears first, followed by the molten metal. This "zinc dust" is largely employed as a reducing agent in organic synthesis.

Commercial zinc often contains as impurities lead, cadmium, copper, silver, carbon, iron, arsenic, antimony, and sulphur. It, therefore, requires further purification. This is accomplished by melting in a small reverberatory furnace with an inclined hearth at a temperature somewhat above its melting-point; the Pb and Fe collect on the bottom, while the other impurities collect on the surface. Zinc purified in this manner is usually remelted and cast into rods, rolled into thin sheets, or granulated by pouring into cold water, in which form it is known as "mossy" zinc. In the United States it is customary to prepare pure (arsenic free) zinc from such ores as are free from foreign metals. Zinc is marketed in plates or ingots. Arsenic may be removed from impure zinc by adding 0.2 per cent. of sodium to the fused metal, whereby a sodium zinc arsenate rises to the surface, which may be removed by skimming.

Electrolytic zinc of high purity is also produced.

Properties.—Zinc is a bluish-white metal, with a luster which is almost insignificant when compared with that of some other metals. When cast it exhibits a tabular structure. Its specific gravity ranges from 6.9, when it is cast, to 7.2, when it is rolled. It is very ductile, considering its hardness. Its malleability is considerable when pure, but in the impure condition it is quite brittle.

When heated to 100° and not above 150°, its malleability and ductility are materially increased; above 200° it becomes sufficiently brittle to be powdered in an iron mortar. Zinc melts at 418° to 419°, and at 918° it boils. Above this temperature zinc burns with a greenish-yellow flame, yielding a light white powder of zinc oxide. It is official under the name of **Zincum**, and this metal dissolves in dilute hydrochloric or sulphuric acid with evolution of hydrogen, and leaves a slight residue. "When 1 gm. of zinc is dissolved in 25 mils of diluted sulphuric acid the liberated hydrogen does not discolor a strip of paper moistened with lead acetate, T.S. (sulphur), or with silver nitrate, T.S. (As, Sb, P)." The purest metal, owing to the practical absence of foreign metals, more especially iron, reacts so slowly with diluted sulphuric acid that it is useless for the generation of hydrogen. An active reaction with the evolution of a steady current of this gas may be brought about by the addition of a little platinic chloride or copper sulphate or stannous chloride solution, which establishes galvanic action.

Zinc is not readily affected by dry air; in damp air it becomes coated with a thin film of oxide and carbonate, which prevents further action. For this reason zinc is used as a protective coating on iron (*galvanized iron*).

Sodium or potassium hydroxide dissolves zinc with evolution of hydrogen and formation of sodium and potassium zincate:

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

Zinc, such as is used as a reagent in arsenic testing, should be in mossy or globular (shot) form, the latter being known as No. 7 shot zinc. The "mossy" zinc is made by dropping the molten metal into warm water. Very pure arsenic-free zinc will dissolve very slowly in diluted sulphuric acid. Rapid solution (gas evolution) indicates presence of much iron or added copper. The presence of much over 0.08 per cent. Fe as well as platinic chloride tends to retain some of the arsenic in the metal. Diluted sulphuric acid is used in the U.S.P. test for arsenic because it can be readily obtained free from this impurity, while the purest reagent hydrochloric acid (when kept in glass containers) always responds to the tests for arsenic.

Uses.—Zinc is used in the manufacture of brass and galvanized iron in the form of wire, nails, and sheets. It is also employed in desilvering lead and in battery construction.

ZINC AND THE HALOGENS

Zinc Chloride, $ZnCl_2$. **Zinci Chloridum,** U.S.P., which contains not less than 95 per cent. of $ZnCl_2$, is obtained by evaporating a solution of zinc chloride.

Liquor Zinci Chloridi, U.S.P., is prepared by dissolving the metal in hydrochloric acid to saturation; a small quantity of nitric acid is then added to oxidize the iron present as impurity, and the solution evaporated to a dry mass at a temperature not exceeding 115°. The residue is dissolved in water and allowed to stand in contact with zinc carbonate for 24 hours (to remove Fe as hydrated oxide); the clear, supernatant liquid is then drained off and brought to a strength of 50 per cent.

Since zinc oxide is to be had in commerce of great purity and at a reasonable price, this solution can be economically prepared by saturating the acid with oxide as follows:

$$\underset{\substack{\text{Zinc}\\\text{Oxide.}}}{ZnO} + \underset{\substack{\text{Hydrochloric}\\\text{Acid.}}}{2HCl} = \underset{\substack{\text{Zinc}\\\text{Chloride.}}}{ZnCl_2} + \underset{\text{Water.}}{H_2O.}$$

The dilute solution of zinc chloride may be filtered through paper, but when more concentrated it should be filtered through asbestos, or allowed to stand until clear and then decanted.

In order to obtain the dry salt the solution is evaporated in a porcelain dish on a sand-bath with constant stirring until brought to dryness. Some oxychloride (ZnOH.Cl) is formed during the evaporation, or larger quantities if overheated, which may be avoided by the cautious addition of hydrochloric acid from time to time. The presence of the basic salt (oxychloride) may be detected by mixing equal volumes of an aqueous solution of the salt (1 in 20) with alcohol, when a lesser or greater degree of turbidity results, according to the quantity present (see U.S.P. limit).

Properties.—Zinc chloride is found in commerce as a white, granular powder, or in irregular, porcelain-like masses, or it may be obtained moulded into sticks. It is odorless, intensely caustic, and, very deliquescent; soluble in 0.25 part of water and about 1.3 parts of alcohol at 25°. When heated to 115° the salt fuses to a clear liquid, and at a higher temperature it is volatilized with some decomposition, leaving a residue of oxychloride and oxide. Zinc chloride distils at about 600°.

The official salt forms a clear solution with water, from which on prolonged boiling a basic salt is deposited. The syrupy solution, on the addition of a few drops of hydrochloric acid, deposits octahedral crystals, containing one molecule of water of crystallization. The official solution has a specific gravity of 1.548 at 25°, and reacts acid with litmus paper.

The concentrated, aqueous solution dissolves paper and cotton, while the oxychloride dissolves wool and silk, hence the former cannot be filtered through paper. A concentrated solution of zinc chloride dissolves zinc oxide, forming zinc oxychloride ($Zn(OH)Cl$), which, if sufficient oxide has been added, hardens quickly. This forms the base of dental enamel filling.

Uses.—Zinc chloride in solution is largely used as a caustic and, when diluted, as an antiseptic and disinfectant. It enters into the composition of some embalming fluids, and constitutes Burnett's disinfecting liquid. A solution of 100 parts of zinc chloride in 12 parts of water, saturated with 6 parts of potassium iodide, and then as much iodine added as the solution will dissolve, furnishes a valuable microscopic reagent for cellulose, with which it gives a blue color. A commercial solution of calamine, zinc blende, or the impure metal in hydrochloric acid, is used to impregnate wood to effect its preservation.

Zinc Bromide, $ZnBr_2$.—This is prepared by interaction between zinc and bromine in the presence of water as detailed under zinc iodide.

Properties.—Zinc bromide occurs as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is a very deliquescent salt, readily soluble in water and alcohol.

Zinc Iodide, ZnI_2.—Prepared by a method similar to that employed in making ferrous iodide, in which powdered iodine is added to an excess of granulated zinc in the presence of water. The mixture is gently warmed until the color of iodine has disappeared and the solution has become quite concentrated, the clear solution of zinc bromide is drained off and evaporated at a low temperature and finally over sulphuric acid.

Properties.—Zinc iodide occurs as a white, granular powder, odorless, and having a sharp, saline, and metallic taste. It is very deliquescent, and, when exposed to light and air, it becomes brown, owing to gradual decomposition into iodine and zinc oxide. Zinc iodide is very soluble in water, alcohol and ether.

ZINC AND OXYGEN

Zinc Oxide, ZnO. **Zinci Oxidum,** U.S.P.—Zincite, or red oxide of zinc, associated with oxides of manganese and iron, occurs with other zinc minerals at Mine Hill, New Jersey.

Zinc oxide is prepared on a large scale by distilling the metal in earthenware retorts, through which a current of air is drawn, and conducting the vapors into large chambers. The product is the commercial zinc white; cadmium must be absent, since it dissolves the oxide. For pharmaceutical purposes a heavy oxide is prepared by heating the basic carbonate to low redness, when the following reaction takes place:

$$\underset{\text{Basic Zinc Carbonate.}}{2ZnCO_3.3Zn(OH)_2} = \underset{\substack{\text{Zinc}\\\text{Oxide.}}}{5ZnO} + \underset{\substack{\text{Carbon}\\\text{Dioxide.}}}{2CO_2} + \underset{\text{Water.}}{3H_2O.}$$

The oxide was formerly known as *Lana Philosophica, Nihilum Album,* and *Nix Alba.* Commercially it is known as *zinc white* or *Chinese white.*

Properties.—Zinc oxide is a white, amorphous powder, without odor or taste. It is insoluble in water or alcohol, but is soluble, without effervescence, in dilute acids; it is also soluble in ammonia water and in solution of ammonium carbonate. It turns yellow when heated, but recovers its whiteness on cooling. On exposure to the air it gradually but slowly absorbs carbon dioxide.

Uses.—Zinc oxide, when ground with oil, is extensively used as a paint. It has the advantage of not darkening in the presence of sulphur compounds, and the disadvantage of possessing less covering power than white lead when used as paint. Lithopone, a mixture of zinc sulphide and barium sulphate, is generally preferred to the oxide because it possesses the advantages and none of the disadvantages of zinc oxide. Zinc oxide is used in making glass for physical purposes, such as thermometers, since the glass has a high resistance to tension, compression, and chemical action. It is one of the most economical and satisfactory compounds from which to prepare the various salts of zinc, and is considerably used in medicine.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white precipitate when sodium or potassium hydroxide is added to a solution of zinc sulphate. It is readily soluble in excess of the reagent as well as ammonia, forming zincates, as $Zn(ONa)_2$.

When the above zincate solution is boiled the hydroxide is precipitated. Zinc hydroxide deports itself as a weak acid in the presence of alcohol, forming ZnO_2 anions and H_2 cations.

On immersing a strip of zinc in ammonia water the hydroxide is slowly deposited in the form of rhombic prisms. Ammonia water does not precipitate zinc hydroxide from solutions containing ammonium salts, owing to the formation of double salts like those of magnesium.

Zinc Dioxide or Peroxide, ZnO_2.—A mixture of zinc dioxide and zinc oxide or hydroxide containing not less than 45 per cent. of the dioxide, which may be obtained by interaction between barium dioxide and zinc sulphate, and is known under the commercial name of *Zinc Peroxide.* It contains from 7.4 to 10 per cent. of available oxygen. Zinc peroxide is a yellowish-white, voluminous, inodorous powder, insoluble in water, but on longer contact is gradually decomposed into oxygen and zinc hydroxide. It dissolves in dilute acids with formation of hydrogen peroxide.

OXYGEN SALTS OF ZINC

Zinc Sulphate, $ZnSO_4.7H_2O$. **Zinci Sulphas,** U.S.P.—Under the name of *white vitriol* this salt was known in the fifteenth century. It was prepared by lixiviation of zinc blende which has been roasted at low red heat ($ZnS + 2O_2 = ZnSO_4$), a process which is used on a large scale at the present time.

The sulphate is also made by dissolving the metal or zinc white in dilute sulphuric acid, and purifying by recrystallization.

Properties.—Zinc sulphate, containing 7 molecules of water of crystallization, occurs in colorless, transparent, rhombic crystals, without odor, and with an astringent, metallic taste. The crystals effloresce in dry air. The salt is soluble in 0.6 part of water at 25° and in 0.25 part of boiling water, also soluble in 2.5 parts of glycerin.

Zinc sulphate is isomorphous with and closely resembles magnesium sulphate, differing physically, however, in that it effloresces when exposed.

It melts in its water of crystallization when rapidly heated, and may be partly decomposed, losing H_2O and H_2SO_4 at higher temperatures. On applying heat gradually, 5 molecules of water are driven off at 50° (31.3 per cent.) without melting. At 100° the sixth is lost, and at 110°, in a current of dry air, the salt becomes anhydrous. It loses 6 molecules of water in a vacuum. Monoclinic crystals, containing only 6 molecules of water, may be obtained by having crystallization take place from concentrated solutions and above 40°. A salt having the composition $ZnSO_4.H_2O$ may also be obtained from the hot, concentrated solution. Like magnesium sulphate, one H_2O may be replaced by alkali sulphates, forming such double salts as $ZnSO_4.K_2SO_4.6H_2O$. The aqueous solution of zinc sulphate has an acid reaction. Basic salts may be obtained by boiling concentrated solutions of zinc sulphate with metallic zinc or with zinc oxide.

Uses.—Zinc sulphate is used in medicine; in very small doses as a tonic and astringent; in larger doses as an emetic. It has the property, common to all the other zinc salts, of acting as an irritant poison in large doses. This salt is also used as a wood and hide preservative, for rendering fabrics fire-proof, and also as a disinfectant.

Zinc Nitrate, $Zn(NO_3)_2.6H_2O$, forms deliquescent crystals when 1 part of zinc oxide is dissolved in 6.5 parts of nitric acid of 25 per cent. strength. The process by which the metal is dissolved in nitric acid is not employed, since a part of the acid is decomposed and lost in the reaction. The crystals of zinc nitrate form colorless, striated, four-sided prisms, very soluble in water and in alcohol. When heated, the salt loses nitric acid and becomes converted into a basic nitrate.

Zinc Phosphate, $Zn_3(PO_4)_2.4H_2O$, is obtained as a white, nearly insoluble precipitate, by the addition of sodium phosphate solution to a solution of zinc sulphate:

$$2Na_2HPO_4 + 3ZnSO_4 = Zn_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4.$$

This precipitate is gelatinous when first formed, but becomes crystalline on standing.

Zinc Carbonate. **Zinci Carbonas Præcipitatus,** U.S.P.—This compound is officially defined as "an impalpable powder, of somewhat variable chemical composition, corresponding to not less than 68 per cent. of ZnO." The true carbonate, $ZnCO_3$, occurs native as zinc-spar, in hexagonal prisms, and massive as smithsonite, hardly to be distinguished from calamine. It may be prepared by precipitating a solution of zinc sulphate in the cold with a solution of acid potassium carbonate in excess:

$$ZnSO_4 + 2KHCO_3 = ZnCO_3 + K_2SO_4 + H_2O + CO_2.$$

The precipitate, when ammonium carbonate is used, is soluble in excess of the precipitant.

The official basic carbonate is not of constant composition, but is generally expressed as consisting of 2 molecules of normal zinc carbonate and 3 molecules of zinc hydroxide, $2ZnCO_3.3Zn(OH)_2$.

To prepare it, 1 part of sodium carbonate is dissolved in 10 parts of water and heated to the boiling point; to it is then added, in a thin stream so as not to interfere with the boiling, a solution of 1 part of zinc sulphate in 10 parts of water. The proportions should be such that, after all the zinc solution has been added, the mixture has a slight alkaline reaction. The following expresses the reaction which occurs:

$$5ZnSO_4.7H_2O + 5Na_2CO_3.10H_2O = 2ZnCO_3.3Zn(OH)_2 + 5Na_2SO_4 + 3CO_2 + 82H_2O.$$

The precipitate is first washed with hot water by decantation, then collected on a filter and further washed with hot water until the washings cease to react with barium chloride.

Properties.—Basic zinc carbonate is an impalpable, amorphous powder, permanent in the air, and practically insoluble in water or alcohol; dilute acids, ammonia water, and solution of ammonium carbonate dissolve it freely. It is also soluble in water containing carbon dioxide. At about 300° the salt loses water and carbon dioxide, and is converted into zinc oxide, which is yellow while hot, but becomes white when cold.

Zinc Sulphide, ZnS.—Zinc blende is found native in crystals, belonging to the regular system. The color varies from a light brown to a deep black, depending on the amount of iron present.

When hydrogen sulphide is passed into a neutral solution of a zinc salt, the sulphide is formed as a white, amorphous precipitate. It is used as a pigment (lithopone) mixed with barium sulphate, and is made by mixing barium sulphide with a solution of zinc sulphate.

Zinc sulphide is soluble in the dilute mineral acids, but insoluble in acetic acid.

Zinc Permanganate, $Zn(MnO_4)_2.6H_2O$.—Prepared like other permanganates. It occurs in dark brown, lustrous, deliquescent crystals, soluble in 3 parts of water. This salt gives up oxygen more readily than the potassium salt. Used in medicine like potassium permanganate, but is more astringent.

Zinc Phosphide, Zn_3P_2, is obtained as a gray mass by heating powdered zinc in the vapor of phosphorus. It should be preserved in small, glass-stoppered vials. Zinc phosphide is a gritty powder of a dark-gray color, or crystalline fragments of a dark, metallic luster, and having a faint odor and taste of phosphorus. In contact with the air it slowly emits phosphorous vapor.

Uses.—Zinc phosphide is employed in medicine. Its physiological properties so closely resemble those of phosphorus that it is used as a convenient method of administering that element.

CADMIUM

Symbol, Cd. *Atomic Weight,* 112.4. *Valence,* II.

History.—Cadmium was discovered in 1817 by Stromeyer of Göttingen. Hermann of Schönebeck discovered it independently and at about the same time.

Occurrence.—Cadmium is found in small quantity in a number of zinc ores, and chiefly as sulphide. The fibrous zinc blende found at Przibram, Bohemia, contains from 2 to 3 per cent. of cadmium. The rare mineral greenockite consists almost entirely of cadmium sulphide. It is found at Bishoptown, in Scotland, near Friedensville, in Pennsylvania, and at Granby and Joplin, Missouri. The presence of cadmium is indicated by the appearance of a brown flame at the orifice of the retort just before the characteristic zinc flame appears in the distillation of zinc.

Metallurgy.—In the preparation of zinc from ores which contain cadmium the latter metal distils first, and by saving this first portion, mixing it with coal and distilling it at the lowest possible temperature, a distillate is obtained very rich in cadmium, while the zinc remains behind, the boiling point of cadmium being 766°, while that of zinc is 918°. The cadmium is finally separated from the zinc by dissolving in hydrochloric acid, having the latter in slight excess, and passing in hydrogen sulphide; the cadmium sulphide is precipitated, while the zinc remains in solution in the presence of acid. The cadmium sulphide is dissolved in hot concentrated hydrochloric acid and the metal precipitated as carbonate by an excess of a solution of ammonium carbonate, by which means the copper and arsenic are retained in solution. The cadmium carbonate is washed, dried, and converted by heat into cadmium oxide, which, on distillation with coal, yields the metal.

Properties.—Cadmium is usually found in commerce in sticks. It is a white, lustrous metal, with a fibrous fracture. When pure it is malleable and ductile. Its specific gravity is 8.6. It melts at 321°, and boils at 766°. When heated in the air it burns, giving off a brown vapor. Most of the acids dissolve it readily. Its salts are colorless. In many of their properties the salts of cadmium are identical with those of zinc.

COMPOUNDS OF CADMIUM

Cadmium Chloride, $CdCl_2.2H_2O$, *Cadmium Bromide,* $CdBr_2.4H_2O$, and *Cadmium Iodide,* CdI_2, are colorless, soluble salts, which are prepared similarly to the corresponding zinc salts. The chloride is made by dissolving the metal or oxide in hydrochloric acid, while the bromide and iodide are prepared by digesting the metal with bromine and iodine respectively in the presence of water. These salts are readily soluble in alcohol and water, but not deliquescent. Cadmium potassium iodide (U. S. P. reagent), made by mixing equal weights of cadmium and potassium iodides, is a useful reagent for alkaloids. Cadmium iodide has some use in photography. The chloride and iodide are used as U. S. P. reagents.

Cadmium Oxide, CdO, forms as a brown, infusible, amorphous powder, when cadmium is burned in the air, or by ignition of the carbonate or nitrate.

Cadmium Hydroxide, $Cd(OH)_2$, is prepared by precipitation of a soluble cadmium salt, by potassium or sodium hydroxide. It forms, when collected and dried, a white, amorphous powder, which at 300° loses water and is converted into oxide.

Cadmium Sulphate, $CdSO_4$.—This salt was official in the Pharmacopœia of 1870, but since that time it and the other salts of cadmium have practically ceased to have any use in medicine. To prepare this salt, 10 parts of cadmium in small pieces are placed in a porcelain dish with 10 parts of pure sulphuric acid and 40 parts of water. The mixture is warmed until the solution is effected, and the solution is filtered and evaporated to crystallize. On account of the slowness with which sulphuric acid acts on cadmium, the metal is sometimes first dissolved in nitric acid, and the hydroxide is precipitated from the resulting nitrate with sodium hydroxide, and is then dissolved in diluted sulphuric acid.

Properties.—Cadmium sulphate crystallizes in large, colorless, monoclinic crystals, having the composition $3CdSO_4.8H_2O$. It is permanent in the air, easily soluble in water, and the aqueous solution has an acid reaction. The sulphates of the alkalies and of the alkaline earths yield with cadmium sulphate well-crystallized double salts similar to those of zinc and magnesium. It has been used as an astringent in diseases of the eye.

Cadmium Nitrate, $Cd(NO_3)_2.4H_2O$, is obtained by dissolving the metal in nitric acid. It crystallizes in fibrous needles, which are very deliquescent and are, therefore, very soluble in water; soluble also in alcohol.

Cadmium Carbonate.—A basic salt is obtained by precipitating a solution of cadmium sulphate with sodium carbonate. It has a variable composition, and in other respects resembles the corresponding zinc salt.

Cadmium Sulphide, CdS, is obtained as a yellow powder, insoluble in hydrochloric acid. It is used as a pigment under the names of *King's yellow* and *jaune brilliant.*

CHAPTER IV

THE SILVER GROUP

SILVER (Argentum)

Symbol, Ag. *Atomic Weight,* 107.88. *Valence,* I.

History.—Silver was one of the earliest known metals. It was the *Luna* or *Diana* of the alchemists.

Occurrence.—Native silver is found to some extent; large masses have been found in Mexico, Peru, Australia, and in western United States. In the Lake Superior district it occurs associated with copper, but not alloyed with it, which points to the fact that deposition has taken place from solution. In combination silver occurs most abundantly as sulphide, termed *argentite,* or *silver glance* (Ag_2S), which is also associated with the sulphides of lead, antimony, and iron. Silver chloride (*horn silver*) is found around Great Salt Lake, Utah, also in Chile and Peru. Small quantities of silver occur in nearly all lead ores, and although the amount appears to be small, nevertheless the quantity extracted from this source is very considerable. Silver occurs in sea water, and in the ash of some land plants.

Metallurgy.—Metallic silver is extracted from its ores by several different processes, depending largely upon local conditions, the most important of which are: (1) *The Cupellation Process,* (2) *The Amalgamation Process,* (3) *Cyanide Process.*

(1) *The Cupellation Process* is based on the property of lead dissolving silver from various ores, from which solution (metallic) the lead is readily removed, since silver, unlike most other metals, is not oxidizable. Lead ores generally contain some silver, and if sufficiently rich in silver it is cupelled at once, but oftener it is necessary first to remove the large excess of lead; this is accomplished by the Pattinson process, which consists in melting the lead in an iron vessel and allowing it to cool slowly. Crystals of pure lead first separate (as long as it contains less than 2.5 per cent. of Ag), which are constantly removed with perforated ladles; this is continued until but one-third of the metal in the pot remains. If then it is sufficiently rich in silver it is removed and cupelled. This consists in injecting a blast of air into a cupel,* which oxidizes the lead to litharge (PbO). This fuses and can be drawn from the surface; when nearly all of the lead has thus been removed, leaving the bright surface of the silver exposed, the last portions of the lead are absorbed by the porous lining of the cupel. The small quantities of other metals (Cu, Fe, Zn, Bi, etc.) are finally removed by cupelling in a smaller furnace with a strong air blast, whereby they are oxidized to form a slag with the addition of some bone-ash.

(2) *Wet Amalgamation Processes.*—These are based on property of mercury amalgamating with or dissolving silver from the ores under proper conditions.

(*a*) European Amalgamation Process.—The ground ore (containing S, Fe, Cu), mixed with sodium chloride, is roasted in a furnace, whereby sulphates and oxides are formed and the silver converted into chloride. This mass is rotated in barrels with water and iron, whereby the following reaction takes place: $2AgCl + Fe = FeCl_2 + 2Ag$. To this mass mercury is added, and the rotation con-

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* A reverberatory furnace, the bottom of which is depressed and lined with bone-ash or a calcareous marl (a kind of clay).

tinued until all of the silver has been dissolved by the mercury. The latter is drawn off and distilled, leaving the silver behind.

(*b*) American Amalgamation Process.—The Patio process is employed in hot climates, as Mexico and South America, where no artificial heat is used. This is essentially the same as the Washoe process used in Nevada, excepting that prolonged maceration replaces heating as used in the latter, which is as follows:

The ore is finely ground and placed in heated pans with copper sulphate, salt, and water, where it is further subjected to a grinding process, during which the sulphides, arsenides, and antimonides of silver are converted into chloride. The iron that is present reduces the silver chloride to metallic silver, which amalgamates with mercury now added. The amalgam is drawn off and distilled.

(3) *Cyanide Process.*—The finely pulverized sulphide ore is allowed to stand for some time mixed with a dilute solution (0.1 to 0.4 per cent.) of sodium cyanide, whereby the double cyanide of silver and sodium forms according to the equation:

$$Ag_2S + 4NaCN = 2AgNa(CN)_2 + Na_2S$$

To prevent the sodium sulphide from reacting with the silver to form silver sulphide, air is blown into the solution which oxidizes the former to sodium sulphate. The silver is recovered from the double cyanide solution by electrolysis.

Preparation of Pure Silver.—The metal obtained by the above processes is still contaminated with copper, lead, and iron, sometimes also with gold and platinum. To effect its purification, it is dissolved in nitric acid, which leaves gold undissolved, and from this filtered solution the silver is precipitated with hydrochloric acid. The silver chloride is then fused with sodium or potassium carbonate and saltpetre as follows:

Five p. of the dried chloride are well mixed with 2 p. of potassium carbonate and 1 p. of the nitrate, and the mixture added in small portions to a red-hot, unglazed crucible, stirring the mass with a clay pipe stem. Continue heating a while, and then cool. The silver collects on the bottom of the crucible.

$$4AgCl + 2K_2CO_3 + 2KNO_3 = 4KCl + 2KNO_2 + 2CO_2 + 2O_2 + 2Ag_2.$$

Properties.—Silver is a pure white, lustrous metal, capable of taking a high polish. In some conditions—for instance, that in which it is obtained from some organic silver salts—it has a white, porcelain-like color, owing to the roughness of its surface, and is devoid of luster.

Of all the metals, silver is the best conductor of heat and electricity. In hardness it stands between copper and gold. In malleability and ductility it is inferior only to gold; it has been beaten into leaf 0.00025 millimeter in thickness, and drawn into wire of such fineness that 180 meters weigh 0.1 gramme. In very thin films, as when deposited on glass from solution, it transmits blue light. The specific gravity of silver is from 10.4 to 10.6.

Silver fuses at a temperature of 960° C., and boils at 1955°. When melted in air, pure silver absorbs 20 times its volume of oxygen, which passes off again at the moment of solidification; this is sometimes accompanied with the projection of small particles of the metal, and is termed the *spitting of silver.*

When exposed to the atmosphere or to water, silver remains unchanged, but in the presence of a small quantity of ozone it becomes coated with a layer of peroxide. The darkening, which sometimes takes place when silver is exposed to the air, is due to the presence of small quantities of hydrogen sulphide.

Nitric acid is the best solvent of silver. The compact metal is only slightly attacked by hydrochloric or dilute sulphuric acid, even at the boiling temperature. Hydriodic acid dissolves the finely divided metal.

Hot concentrated sulphuric acid dissolves silver with evolution of sulphur dioxide and formation of silver sulphate.

The alkalies have little or no action on silver; potassium or sodium hydroxide may be fused with it, and fused potassium nitrate has but little action upon it. The halogens act readily at ordinary temperature.

Besides the compact metallic silver, we can obtain *molecular silver* as a fine powder by reducing freshly precipitated silver chloride with formaldehyde in the presence of potassium carbonate, and *colloidal silver* by adding a solution of the nitrate to a concentrated solution of sodium silicate containing formaldehyde, or by passing an electric current between silver electrodes in water. It dissolves in water, forming a red solution, from which it may be precipitated by means of alcohol. This when collected and washed will yield with water a colloidal solution. Both forms are converted into ordinary silver by fusion. See Colloids, p. 151.

Uses.—The pure metal is used to prepare the salts of silver, and in the manufacture of certain utensils for pharmaceutical and chemical purposes, as crucibles, dishes, wire, foil, etc. For many of the purposes to which silver is applied it is too soft to resist wear, and in order to increase its hardness it is alloyed with copper in various proportions. In the United States, France, Germany, and Austria the proportion of copper is 10 per cent., and such an alloy is used in those countries for coinage. In England the proportion employed is 7.5 per cent. of copper.

The term *fineness* applied to silver indicates the parts per thousand of pure silver in the alloy; for instance, in this country silver coin is spoken of as "900 fine"; that is, 90 per cent. silver and 10 per cent. copper.

Electroplating.—This is a process in which a thin layer of silver is deposited on metallic surfaces by electrolysis. The object to be coated must have a conducting surface, and is made the negative pole; a bar of silver acts as the positive pole. These electrodes are placed in a solution of silver cyanide in an excess of sodium cyanide. If the object to be coated is properly cleaned, the silver will be deposited on it as a coherent layer; at the same time cyanogen is liberated at the positive pole and dissolves the silver, thereby keeping the silvering solution of constant strength.

The silvering solution used in electroplating is made by dissolving 1 part of silver nitrate in 50 parts of distilled water and mixing with a solution of 5 parts of sodium cyanide in 20 parts of distilled water.

Silvering on Glass.—When alkaline solutions of silver salts are mixed with certain organic compounds, like grape-sugar, Rochelle salt, etc., the silver is deposited on the surface of the vessel in which it is contained as a thin, coherent film. The following process will yield satisfactory results if the glass be first thoroughly cleaned with alkali, and then washed with distilled water:

Dissolve 7.8 grammes of silver nitrate in 60 mils of water and divide the solution in two equal portions. Dissolve, also, 3.11 grammes of Rochelle salt in 1180 mils of water, and heat the solution to the boiling point. Add to it gradually (so as not to stop the ebullition) one of the portions of silver solution, boil some 10 minutes longer, cool, and decant the clear liquid. To the other half of the silver solution add just sufficient ammonia water to dissolve the precipitate which is first formed, or only leave a faint cloudiness; then add 360 mils of water and filter. Equal portions of these two solutions, when mixed and poured on glass, will deposit a brilliant coating of silver in about 10 minutes, according to the temperature of the room. The coating of silver should then be well washed, dried, and varnished. The coating may be made more adherent by rinsing with a weak solution of potassium-mercuric cyanide, which serves as an amalgamating agent. Or to a 10 per cent. solution of silver nitrate add sufficient ammonia water to redissolve the precipitate formed, and to this add 1 per cent. of formaldehyde, pouring at once upon the clean glass surface, which is set aside in a warm place.

SILVER AND THE HALOGENS

Silver Chloride, $AgCl$, is found native as ceragyrite, or horn silver. It occurs in crystals of the regular system or in pearl-gray, translucent, wax-like masses. Sea water contains a small quantity of silver chloride.

Preparation.—Pure silver chloride is prepared by precipitating a solution of silver nitrate with pure hydrochloric acid. The precipitate is of a more or less curdy consistence, but boiling or long standing causes it to become more granular; it is collected and washed until the washings cease to have an acid reaction. The whole process should be conducted with exclusion of light to avoid darkening due to the formation of the subchloride Ag_2Cl. This will not take place in the presence of chlorine, nor will dry $AgCl$ darken.

Properties.—The artificially prepared salt is a white, amorphous, insoluble powder. The insolubility in water and dilute acids is so complete as to make the chloride the best salt by which to determine silver quantitatively. When freshly prepared, it is readily soluble in ammonium hydroxide, in solutions of sodium thiosulphate and potassium cyanide:

$$AgCl + 2NH_3 = Ag(NH_3)_2Cl.$$
$$AgCl + 2KCN = AgCN.KCN + KCl.$$
$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl.$$

On the application of heat, silver chloride melts between 450° and 460° to a thick, yellow liquid, which becomes a tough, solid mass on cooling.

When exposed to light the moist salt rapidly darkens, with loss of chlorine. Dry silver chloride absorbs at ordinary temperatures 19 per cent. of its weight of gaseous ammonia, forming the ammonio-silver chloride, $AgCl,3NH_3$, a white compound, which at 37.7° gives off the ammonia.

Use.—Silver chloride finds some use in photography.

Silver Bromide, AgBr, occurs native as bromargyrite in Mexico and Chili. The bromide is prepared similarly to the chloride, by precipitating silver nitrate with hydrobromic acid or potassium bromide. It has a faint yellow color, and possesses many of the properties of the chloride. Silver bromide fuses between 526° and 556°. It is not easily soluble in ammonium hydroxide, and the dry bromide does not absorb ammonia. Silver bromide melts at 420°. The freshly precipitated salt is soluble in solutions of sodium thiosulphate and alkali cyanides. Silver bromide is largely used in photography, being more sensitive to light than silver chloride.

Silver Iodide, AgI.—This salt occurs native as the mineral iodargyrite, in Mexico, Chili, Spain, and Arizona, in the form of thin, slightly elastic, hexagonal tables.

Preparation.—Silver iodide may be prepared in a variety of ways, by direct union of the elements, and by dissolving silver in hydriodic acid, but it is most readily and economically obtained by adding a solution of potassium iodide to one of silver nitrate, collecting, washing, and drying the precipitate without exposure to light. It should be preserved in dark amber-colored vials.

Properties.—Silver iodide is a heavy, yellowish, amorphous powder, without odor or taste. It is insoluble in water, dilute acids (excepting hot HI), or solution of ammonium carbonate; soluble in 2500 parts of stronger ammonia water. It is dissolved by an aqueous solution of potassium cyanide, and but slightly by sodium thiosulphate and by a concentrated solution of potassium iodide.

On application of heat, silver iodide melts at 427° to a dark-red liquid, which, on cooling, congeals to a soft, yellow, translucent mass. The dry precipitated compound absorbs 12.68 per cent. of ammonia gas, forming the white compound $AgI,2NH_3$, which on exposure to air gives off ammonia and becomes yellow.

Like the chloride and bromide, silver iodide has considerable use in photography. It also has some use in medicine.

Silver Fluoride, AgF, is obtained by dissolving silver oxide or carbonate in hydrofluoric acid. It is a deliquescent salt, soluble in one-half its weight of water.

SILVER AND OXYGEN

Silver Oxide, Ag_2O. *Argentic Oxide,* **Argenti Oxidum,** U.S.P.—A solution of 10 parts of silver nitrate in 100 parts of water is treated with solution of sodium hydroxide so long as a precipitate is formed:

$$2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O.$$

The precipitate is first washed by decantation, then on a filter, until the washings cease to give reaction for nitric acid, and finally dried in the dark at ordinary temperatures. The U.S.P. silver oxide contains not less than 99.6 per cent. of Ag_2O.

Properties.—Silver oxide is a heavy, dark-brownish-black powder. It is slightly soluble in water, to which it imparts an alkaline reaction, insoluble in alcohol, and completely soluble in nitric and sulphuric acid without effervescence. When heated to 250° or 300° it is decomposed into metallic silver and oxygen.

In the freshly precipitated, moist condition silver oxide is more active than the same compound after it has been dried and then moistened. In the freshly precipitated state it decomposes soluble chlorides, precipitates oxides from many metallic salts, and absorbs carbon dioxide from the air.

Silver oxide should not be triturated with antimony sulphide, arsenic sulphide, precipitated sulphur, amorphous phosphorus, tannin, or other easily oxidizable substances, since such mixtures readily inflame. Silver oxide is soluble in concentrated solution of ammonia, from which upon evaporation or on diluting with alcohol or water, black crystals of silver nitride, Ag_3N (Berthollet's fulminating silver) separate; these on drying become very explosive; for this reason the precaution should be observed not to bring dry silver oxide in contact with ammonia.

Silver oxide has some use in medicine, but its greatest value is as a laboratory reagent, where it is employed in the freshly precipitated condition.

Silver Peroxide, Ag_2O_2, is obtained by electrolysis of the nitrate in solution separating at the positive platinum pole. It is a more powerful oxidizer than silver oxide and detonates with sulphur or phosphorus; decomposes at 110°.

OXYGEN SALTS OF SILVER

Silver Chlorate, $AgClO_3$, is prepared by dissolving silver oxide in chloric acid. It forms small, quadratic crystals, soluble in 10 parts of water.

Silver Bromate, $AgBrO_3$, and *Silver Iodate,* $AgIO_3$, are difficultly soluble white, crystalline precipitates, obtained by treating solution of silver nitrate with potassium bromate or iodate.

Silver Sulphite, Ag_2SO_3, is obtained as a white, curdy precipitate when sulphurous acid is added to a solution of silver nitrate.

Silver Sulphate, Ag_2SO_4, is prepared by dissolving silver in concentrated sulphuric acid, or by adding sulphuric acid to an alcoholic solution of silver nitrate.

It forms in small, lustrous, rhombic crystals, which are isomorphous with anhydrous sodium sulphate. It is soluble in 200 parts of cold water and in 70 parts of boiling water; insoluble in alcohol. Silver sulphate fuses at 654°.

Silver sulphate is obtained in considerable quantities in the commercial separation of silver from gold by means of sulphuric acid.

Acid Silver Sulphate, $AgHSO_4$, is formed by dissolving silver sulphate in hot, concentrated sulphuric acid, and allowing the solution to cool.

Silver Pyrosulphate, $Ag_2S_2O_7$, results when silver sulphate is heated with sulphur trioxide.

Silver Nitrite, $AgNO_2$.—On mixing warm, concentrated solutions of 16 parts of silver nitrate and 10 parts of potassium nitrite, a crystalline precipitate of silver nitrite results. Soluble in 300 parts of cold and partly decomposed by boiling water. $2AgNO_2 = AgNO_3 + Ag + NO$.

Silver Nitrate, $AgNO_3$. **Argenti Nitras,** U.S.P.—This salt was first obtained in the crystalline form by Geber, in the eighth century. It came into medical use in the seventeenth century, under the names of *magisterium argenti, crystalli dianæ,* and, when cast into sticks, as *lapis infernalis* and *lunar caustic.*

A pure silver should be selected for the preparation of the nitrate. In a capacious porcelain dish 3 parts of metallic silver are mixed with 10 parts of nitric acid (containing 25 per cent. HNO_3), and the mixture warmed until the reaction begins. In case the silver is finely divided, the action is sufficiently active without warming, and may have to be controlled by the addition of a little cold water:

$$3Ag + 4HNO_3 = 3AgNO_3 + 2H_2O + NO.$$

A funnel should be inverted over the liquid in the dish and when the action ceases, the silver being dissolved, the sides of the funnel are rinsed down with distilled water; the solution is filtered through glass wool, if necessary, and evaporated on a sand-bath to dryness. The temperature is then raised so as to melt the salt and expel the excess of acid. When it contains copper nitrate the heating should be continued somewhat longer, to convert the copper into its insoluble oxide, as follows:

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

The reaction is known to be ended when there is no further evolution of oxides of nitrogen, and the mass becomes dark or black through the formation of copper oxide.

The fused mass is dissolved in double its weight of water, filtered through a small, well-washed filter, and set aside to crystallize; dust and light should be excluded as far as possible during the operation. In case lunar caustic is wanted, the fused silver nitrate is treated with a few drops of nitric acid to oxidize any nitrite, and after a few moments more heating is poured into polished silver moulds such as are used in the preparation of sticks of sodium or potassium hydroxide.

Properties.—Silver nitrate, which must be not less than 99.8 per cent. pure (U.S.P.), occurs in colorless, transparent, tabular, rhombic crystals, permanent in the air, but becoming gray or grayish-black on exposure to light in the presence of organic matter.

The salt is soluble in 0.4 part of water at 25°, and in 0.1 part of boiling water; also soluble in 30 parts of cold and in 6.5 parts of boiling alcohol; slightly soluble in ether.

On the application of heat, the salt melts at about 200° without decomposition, and on cooling forms a white, crystalline mass. If kept for some time at or slightly above 210° it begins to decompose with formation of silver oxide and silver nitrite. At a red heat decomposition takes place, nitrous fumes, nitrogen, and oxygen being evolved and metallic silver remaining. The aqueous solution of silver nitrate is neutral to litmus.

Solution of ammonia added to a solution of silver nitrate at first produces a precipitate which in the presence of a larger amount of the reagent dissolves; if this solution then be allowed to evaporate, rhombic, prismatic crystals separate, having the composition $AgNO_3$, $2NH_3$. When heated above 100° they melt, evolving nitrogen and ammonia, leaving a residue of ammonium nitrate and a mirror of metallic silver. Silver nitrate forms crystalline double salts, as $AgNO_3.KNO_3$ and $AgNO_3.NH_4NO_3$.

Uses.—Silver nitrate is largely used as a laboratory reagent and in photography. It also has considerable use in medicine as a caustic. When in contact with organic substances and exposed to light, a black deposit of metallic silver is produced.

For external use, **Argenti Nitras Fusus,** U.S.P., which contains not less than 94.5 per cent of $AgNO_3$, is used. The fused nitrate, or *lunar caustic,* contains a small quantity of silver chloride in order to toughen it; this is accomplished by adding to 100 grams of the salt 4 grams of hydrochloric acid, melting the mixture at as low a temperature as possible, and pouring into suitable moulds. The diluted silver nitrate, or *mitigated caustic,* formerly official, is made by melting at the lowest possible temperature 30 grams of silver nitrate and 60 grams of potassium nitrate, and casting in suitable moulds.

Silver Phosphate, Ag_3PO_4, is obtained when the normal sodium phosphate or the disodium hydrogen phosphate is added to a solution of silver nitrate. It is a yellow, amorphous compound, insoluble in water.

Compounds of silver with pyrophosphoric acid and with metaphosphoric acid are also known.

Silver Carbonate, Ag_2CO_3, is obtained by adding sodium carbonate to silver nitrate solution, collecting and washing the precipitate. It is a yellow, amorphous powder, insoluble in water.

Silver Sulphide, Ag_2S, is found native as argentite or vitreous silver, in grayish-black crystals of the regular system. It can be obtained artificially by igniting silver chloride in a current of hydrogen sulphide.

Much of the so-called *oxidized silver* is coated with a thin layer of sulphide, obtained by immersing silver in a solution of potassium sulphide. A more permanent effect is obtained by coating the silver with platinic chloride solution.

Colloidal Silver, that is metallic silver in a very fine state of subdivision which forms with water mixtures resembling solutions. Such solutions are not precipitated by the ordinary reagents for silver salts. Such colloidal solutions may be mixed with various organic liquids or injected into the circulatory system without precipitation or causing irritation. They possess the antiseptic properties of the silver salts. Collargol is a colloidal silver containing a small percentage of albumin which prevents its precipitation by acids or salts. Electrargol is a colloidal suspension of silver containing a small percentage of sodium arabate. Cargentos is a colloidal silver oxide with a small quantity of modified casein as a protective colloid (see Colloids, page 151).

GOLD (Aurum)

Symbol, Au. *Atomic Weight,* 197.2. *Valence,* I, III.

History.—Gold has been known from the earliest times. On account of its scarcity, its color, and its stability in contact with air, resistance to acids, extreme malleability and ductility, high gravity and fusing-point, it early became of the highest intrinsic value as a metal.

Occurrence.—Gold is very widely distributed in nature, but always in small quantities. A yield of 10 grammes per ton is considered a paying ore in some localities. It is ordinarily found in the free or uncombined state.

The native deposits are usually in veins of quartz, although the usual source of the metal is in alluvial soils and sands of rivers in small scales or nuggets resulting from the disintegration of primitive rocks in which it was imbedded. Minute quantities are present in sea water.

Gold occurs frequently mixed with silver, also copper, iron, and platinum.

The principal localities in which gold is found in sufficient quantity to extract are the gold-fields of western United States, Alaska, Australia, Siberia, Transylvania, Brazil, New Zealand, and South Africa.

Metallurgy.—Gold was formerly chiefly obtained from alluvial sands, either by *pan* or *cradle washing*. In the former, the sand is shaken with water in a pan or bowl, and, owing to the high gravity of the gold, it settles to the bottom while the sand may be poured off with the water. In the cradle process, an inclined wooden trough mounted on rockers was used, at the lower end a small opening for the outflow of water and sand. In the upper end the auriferous sand with water was introduced, while the gold settled along the bottom.

The usual methods of recovering gold are the amalgamation or cyanide or chlorination processes.

The *amalgamation* process is best adapted for recovering gold from such ores as hold the free metal. For other ores the cyanide process is preferred. In the former case the ore is stamped to a fine powder and then washed through a fine screen, over slanting sheets of copper which have been coated with mercury or silver amalgam. The fine particles of gold and silver which wash over these plates readily amalgamate with the mercury, while the quartz and other metals with impurities pass on. After a time the amalgam is scraped off and the mercury removed by distillation.

The *cyanide* process consists in leaching the finely comminuted ore with a very dilute solution of alkali cyanide, which, in the presence of oxygen from the air, reacts with the gold to form a soluble double cyanide of gold and alkali. $2Au + 4KCN + O_2 + 2H_2O = 2AuCN.KCN + 2KOH + H_2O_2$ $2Au + 4KCN + H_2O_2 = 2AuCN.KCN + 2KOH$. The gold is precipitated from the solution by means of metallic zinc or aluminum, or by electrolysis. The details of the process require modification for the various ores.

The *chlorination* process, applicable to low-grade ores, consists in rotating the roasted and crushed ore in closed vessels with water while introducing chlorine. The gold is dissolved as a chloride, which is afterwards precipitated from its solution through the addition of ferrous sulphate or electrolytically.

Gold obtained by the above processes usually contains silver, copper, and sometimes platinum. When the proportion of gold does not exceed 33 per cent. the silver of the alloy may be dissolved by nitric acid of specific gravity 1.320; this was formerly known as *quartation,* because this alloy must not contain over 25 per cent. gold in order that the silver be dissolved by the acid. When the gold in the alloy exceeds 33 per cent. it is fused with sufficient silver to reduce it to that proportion, when the silver can be removed by nitric acid. Sulphuric acid is used in the same way to dissolve the silver from the gold.

When a sample of gold does not contain more than 10 per cent. of silver the Miller process as is used in Australia may be employed; the gold alloy is fused in a clay crucible, which has been glazed on the inside with borax, and a stream of chlorine is passed into the molten metal; silver chloride forms and rises to the top, a layer of borax prevents it from volatilizing; the chlorides of zinc, bismuth, arsenic, and antimony, when present, are volatilized. A final purification is sometimes given to the gold, after removal of the silver, by dissolving it in nitrohydrochloric acid, evaporating on a water-bath to a syrupy consistence, mixing this with some twenty times its volume of water, filtering, and treating the filtrate with a solution of ferrous chloride, when metallic gold is precipitated.

Oxalic acid or ferrous sulphate may be used to effect this precipitation of the gold. The Moebiu process is an economical electrolytic method adapted for silver which contains little gold. The electrolytic bath consists of a weak solution of silver nitrate with nitric acid (1 per cent.). As anode the silver containing the gold is used, which is enclosed in a cotton sack, while the cathode is a silver plate. All the metals of the anode, except the gold, which remains in the sack, dissolve, while all of the silver collects on the cathode.

Properties.—In the compact state gold has a characteristic yellow color, a peculiar luster, and is capable of a high polish. In the precipitated condition it is a brown powder. The native gold occurs in small cubical or octahedral crystals, and sometimes in other forms of the regular system. It is the most malleable and ductile of the metals; in very thin leaves it transmits green light. When pure it is nearly as soft as lead. The specific gravity at 15° varies, according to its mode of preparation or treatment, from 19.26 to 19.55. On the application of heat it melts at 1062.4° to a bluish-green liquid.

Gold is obtained in a soluble, red, colloidal form by reducing a faintly alkaline dilute solution of gold chloride, or a dilute gold solution containing a little sodium silicate, with formaldehyde. A blue colloidal solution is obtained by the reduction of a neutral solution of gold chloride (1 to 10,000) by means of a solution of hydrazine hydrate (1 to 2000).

Gold is not affected at any temperature by air, oxygen, or water. It is not dissolved by any of the acids singly, unless it be selenic acid. It is dissolved by nitrohydrochloric acid, free chlorine, and bromine, and in a lesser degree by iodine. It is also attacked by the fused alkalies and fused potassium nitrate.

Uses.—Gold is used for coinage, for jewelry, and for gilding; gold leaf is employed in the latter process, while the finely precipitated gold is used in the decoration of glass and porcelain. Gilding is oftener accomplished now by electrolytic deposition; solutions of gold chloride and potassium cyanide constitute the bath, and a piece of gold plate is employed as the positive pole.

Alloys.—Pure gold is too soft for most purposes, and is therefore alloyed with silver or copper; the latter metal gives it a reddish color. When pure it is designated as 24-carat, or 1000 fine. In England the coinage is 22-carat. equivalent to a fineness of 916.66; in most other European countries and in the United States it is 21.6-carat, or 900 fine.

Alloys for jewelry contain both silver and copper; that of 14-carat is, perhaps, used the most extensively. Gold is soldered by means of an alloy of silver, gold, and copper.

GOLD AND THE HALOGENS.

The halogen elements combine with gold in two proportions, in which the metal exhibits valence of I and III; for example, $AuCl$ and $AuCl_3$.

Aurous Chloride, $AuCl$, *Gold Monochloride,* is obtained as a yellow powder by carefully heating auric chloride to 185°; it is decomposed at higher temperatures into gold and chlorine. When warmed with water it decomposes into the metal and auric chloride.

$$3AuCl = AuCl_3 + 2Au.$$

Aurous Bromide, $AuBr$, and *Aurous Iodide,* AuI, are obtained by interaction between auric chloride and potassium iodide or bromide solutions.

$$AuCl_3 + 3KI = 3KCl + AuI + I_2.$$

Auric Chloride, $AuCl_3$. *Gold Trichloride.*—This forms a red-brown hygroscopic mass obtained through the action of chlorine on gold leaf at about 200°. It is soluble in alcohol, ether, and water. What is commercially known as gold chloride is the compound obtained by dissolving gold in nitromuriatic acid.

Chlor-auric Acid, $AuCl_3,HCl.4H_2O$, is one of the double compounds with hydrochloric acid. If a solution of gold in nitromuriatic acid be evaporated to dryness, auric chloride is not obtained, owing to its decomposition into aurous chloride and chlorine. If the solution be concentrated and allowed to crystallize, a compound of auric chloride and hydrochloric acid forms, namely, chlor-auric acid, $AuCl_3.HCl.4H_2O$, commercially known as auric chloric (gold chloride).

$$2Au + 8HCl + 2HNO_3 = 2AuCl_3.HCl + 2NO + 4H_2O.$$

This forms reddish-yellow to yellow needle to scale-like hygroscopic crystals, readily soluble in water, alcohol, and ether. When heated they fuse, decomposing into hydrochloric acid, chlorine, auric and aurous chlorides, and finally into aurous chloride and gold. Chlor-auric acid is employed as an alkaloidal reagent, since it forms insoluble double salts with these bases in which the hydrochloride of the alkaloid takes the place of the alkali chloride as in ammonium chlor-aurate, $AuCl_3.NH_4Cl.x H_2O$.

This compound forms a series of salts termed *chlor-aurates,* which may simply be considered as double compounds of auric chloride with a molecular equivalent weight of the alkali chloride; the best known of these is *sodium chlor-aurate,* or *gold* and *sodium chloride.*

The **Auri et Sodii Chloridum,** U.S.P., is a mixture prepared by rubbing together equal parts of anhydrous gold chloride and sodium chloride. Theoretically it contains 32 per cent. of metallic gold, although the official requirements are that it shall contain not less than 30 per cent. of this metal.

The true gold and sodium chloride double salt has the formula $AuCl_3$, $NaCl.2H_2O$, and contains 49.5 per cent. of metallic gold. It occurs in orange-yellow, rhombic tables or prisms, is deliquescent, and when exposed to a red heat decomposes, leaving a residue of metallic gold.

This compound is used in photography, for gilding, and to some extent in medicine.

The proportions for its preparation are 10 parts of gold to 13 parts of 25 per cent. nitric acid and 32 parts of 25 per cent. hydrochloric acid. The syrupy solution of chlor-auric acid is treated with a solution of 4 parts of pure sodium chloride in 20 parts of water, and the resulting mixture evaporated until a pellicle forms; further evaporation being completed at ordinary temperatures over calcium oxide.

Auric Bromide, $AuBr_3$ (Gold Tribromide), *Auric Dibromide,* $AuBr_2$, and *Auric Iodide,* AuI_3, are known.

GOLD AND OXYGEN

Since gold cannot be oxidized directly, these compounds are obtained by indirect means.

Aurous Oxide, Au_2O, is a dark-violet powder, obtained by treating aurous chloride with potassium hydroxide in the cold. This breaks up into its elements at 250°.

Auric Oxide, Au_2O_3, is a dark-brown powder, formed by heating auric hydroxide to 100°. At 250° it decomposes it into gold and oxygen.

Auric Hydroxide, $Au(OH)_3$, *Auric Acid.*—This compound is best prepared by heating a solution of auric chloride with magnesia, and washing the precipitate with dilute nitric acid. When freshly prepared it is a yellowish-brown precipitate, which on drying becomes a brown powder. Auric hydroxide is acid-forming, and its salts are termed aurates. When it is treated with an excess of ammonia water a green to brown powder is formed, known as *fulminating gold.* In the dry state this ammonia compound explodes violently, either by percussion or on heating.

CHAPTER V

THE COPPER AND MERCURY GROUP

COPPER

Symbol, Cu. *Atomic Weight,* 63.57. *Valence,* I and II.

History.—Copper, because of its rather abundant occurrence in the metallic state, was probably the first metal used by man. It formed the material for tools and weapons before the metallurgical processes necessary to produce iron were known. Originally copper was found in the island of Cyprus, hence the application of the Latin title, *cuprum.*

Occurrence.—Abundant deposits of native copper occur in Michigan, in what is known as the Lake Superior district, and of sulphide and carbonate ores in Montana, Arizona and Canada. Valuable ores of copper are found in Siberia, Spain, Chile, Peru and Australia. The United States furnishes the greater portion of the world's supply. One of the most abundant ores of copper is cuprous oxide (*cuprite*), Cu_2O, or red copper ore; cupric oxide, CuO, is found more rarely. The sulphide, or copper glance, Cu_2S, as well as copper pyrites, a double sulphide of copper and iron, $Cu_2S.Fe_2S_3$, are widely distributed. Smaller quantities occur as *malachite,* $CuCO_3.3Cu(OH)_2$, and *azurite,* $CuCO_3$, $Cu(OH)_2$, both being basic carbonates.

Metallurgy.—The method of obtaining copper from its ores depends on whether the ore is an oxide or sulphide. If an oxide or carbonate, the ore is simply heated with charcoal or other fuel, with, perhaps, the addition of some flux rich in silica. This process is much employed in the United States. Usually, however, the ore is a sulphide mixed with iron sulphide, lead, antimony, and silver; often not more than 5 per cent. of copper is present. The ore is first roasted on the floor of a reverberatory furnace, the air-supply being controlled so that it is possible to convert the copper pyrites into a mixture of copper sulphide and ferrous oxide. Through the addition of a silicious flux the iron forms a silicate while the cuprous sulphide collects in the basin of the furnace and is known as coarse metal. This operation of fusing with a flux is repeated until the iron is entirely removed, and a mixture of cuprous oxide and sulphide remains, the reactions being:

$$(1)\ Cu_2S.Fe_2S_3 + 4O_2 = Cu_2S + 2FeO + 3SO_2.$$
$$(2)\ Cu_2S + 2FeO + 2SiO_2 = Cu_2S + 2FeO.SiO_2.$$
$$(3)\ Cu_2S + 3O = Cu_2O + SO_2.$$

On roasting this mixture the following reaction takes place:

$$\underset{\text{Cuprous Oxide.}}{2Cu_2O} + \underset{\text{Cuprous Sulphide.}}{Cu_2S} = \underset{\text{Copper.}}{6Cu} + \underset{\text{Sulphur Dioxide.}}{SO_2.}$$

The copper thus obtained still contains as chief impurities lead, antimony, arsenic, and occasionally other metals, which are removed by another treatment in a current of air; the impurities, with some of the copper, form a slag with the silicious material of the hearth and are removed. This slag is known as refinery slag, and is used as a flux during the earlier treatments of the ore. The metal still contains some cuprous oxide, which renders it brittle, so it must be subjected to a refining process which is known as *poling,* because it consists in melting the copper with coal, and stirring the melted mass with an oak or birch pole; the gases evolved complete the deoxidation of the metal; the latter is then run into ingots.

Considerable quantities of copper are now obtained by extracting in the wet way. The residue from the burning of iron pyrites, in the manufacture of sulphuric acid, contains about 3 per cent. of copper. This is recovered by roasting the residue with 12 to 15 per cent. of common salt, the reaction being essentially

$$CuO + SO_2 + O + 2NaCl = CuCl_2 + Na_2SO_4.$$

On leaching this mass with water, the whole of the copper is obtained as cupric chloride, and is precipitated from the solution by the addition of scrap-iron.

Low-grade copper ores (so-called porphory ores) are also worked by "flotation," depending on the fact that in the presence of oil and other frothing agents the metallic sulphides float when air bubbles are produced in a thin mixture of ore and water, while the gangue goes to the bottom.

The most recent process of copper refining is that in which electrolysis is employed, by which any silver or gold present may be recovered, as well as removing the remaining traces of foreign metals. The anodes consist of the cast impure copper ingots, while the cathodes are thin sheets of electrolytic copper upon which the copper dissolved from the anodes is deposited. The electrolyte is a 20 per cent. solution of copper sulphate in dilute sulphuric acid. From the anode slimes silver, gold, platinum, selenium, and tellurium are recovered.

Properties.—Copper is a lustrous, malleable, and ductile metal, with a peculiar reddish color, and capable of taking a high polish. Its specific gravity is about 8.9, and it melts at 1083°. In malleability and heat conductivity copper is exceeded only by gold and silver, while it is the best conductor for the electric current.

In dry air copper undergoes no change, but in the presence of moisture it becomes covered with a greenish layer of basic copper carbonate, which protects it from further rusting. When heated in air or oxygen the metal becomes black on the surface, owing to the formation of a thin layer of oxide.

With exclusion of air, copper is not soluble in diluted acids;

however, by means of heat and excess of air it is even soluble in dilute acetic acid. Copper is soluble in many saline solutions and also ammonia water if shaken with air or oxygen, forming an intense blue solution of hydroxyammoniate of copper. Under these conditions a solution of sodium chloride yields copper oxychloride, $CuCl_2.3CuO.4H_2O$. Concentrated nitric and hot sulphuric acids dissolve copper according to the following reactions:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$
$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Diluted hydrochloric and cold concentrated sulphuric acids are without action. Copper is precipitated from solutions of its salts by iron, magnesium and other metals.

Uses.—Owing to its ductility, strength, high heat and electric conductivity, comparative resistance to chemicals, and ease with which it can be worked into a great variety of forms, copper is extensively employed in the arts and manufactures. The alloys of copper are of great industrial and commercial importance.

Alloys of Copper.—The most important alloys of copper are those it forms with zinc and tin.

Brass is composed of about 70 per cent. copper and 30 per cent. zinc, with sometimes 2 or 3 per cent. of tin. By increasing or decreasing the proportion of zinc a lighter or darker colored, harder or softer brass is obtained. Brass is superior to copper because it does not tarnish so readily, it has a more pleasing color, is harder, has a lower melting point, and when cast does not blister.

The following are the percentages in some of the other important alloys of copper:

	Copper	Tin	Lead
Bell metal	78	22	..
Gun metal	90	10	..
Art bronze	90.1	6.6	3.3

	Cu	Tin	Lead	Zinc	Nickel
German silver	50	...	...	25	25
Speculum metal	66.6	33.4	...	...	...
Aluminum bronze	90	Aluminum 10			

COPPER AND THE HALOGENS

Copper forms two classes of compounds, one the "ous" in which Cu deports itself as a monad, while in the "ic" it is a dyad. The cuprous salts are insoluble in water and the Cu ion is colorless. The more important cupric compounds are usually soluble, imparting to water a green or blue color, while the anhydrous salts are colorless. The Cu "ic" ion is blue.

Cuprous Chloride, CuCl, or Cu_2Cl_2, is formed by dissolving cuprous oxide in hydrochloric acid, taking care to exclude air. It is probably most readily prepared by boiling cupric chloride with copper turnings, with the addition of a little platinic chloride to establish galvanic action. On pouring the clear solution into water, which has been heated to expel air, cuprous chloride separates as a white precipitate.

Properties.—Cuprous chloride is a white, crystalline powder, soluble in solution of ammonia, forming a colorless solution which becomes blue on absorption of oxygen from the air. Cuprous chloride may be recrystallized from hot, concentrated hydrochloric acid; it is insoluble in water, but, left in contact with air, the solution takes on a green color, due to the formation of copper oxychloride.

On the application of heat, cuprous chloride melts at 430°, and on cooling it forms a solid crystalline mass. Near 1000° it is volatilized.

The solution of cuprous chloride in hydrochloric acid and in ammonia readily absorbs carbon monoxide and a number of compounds of the acetylene series; it is, therefore, a valuable reagent in gas analysis.

Cupric Chloride, $CuCl_2.2H_2O$, is prepared by dissolving 1 part of cupric oxide in 4 parts of 25 per cent. hydrochloric acid. The solution is filtered, concentrated on a water-bath, and crystallized.

Properties.—Cupric chloride occurs in blue, rhombic crystals, which deliquesce on exposure to damp air. It is readily soluble in water and in alcohol, and somewhat soluble in ether. The aqueous solution of the salt is green when concentrated, since there is only a very slight dissociation, and blue when dilute, owing to presence of blue $Cu^{\cdot\cdot}$ ions.

At 100° the crystals begin to lose their water of crystallization, and at 500° the salt melts; when heated to redness it is decomposed into cuprous chloride and chlorine.

The anhydrous cupric chloride, which is yellow, readily absorbs ammonia, a blue powder having the composition $CuCl_2,6NH_3$ being formed. The solution of the salt in strong aqueous ammonia deposits octahedral crystals of the composition $CuCl_2,4NH_3.H_2O$. Both of the above compounds are changed at 150° into a green powder, having the composition $CuCl_2,2NH_3$.

When cupric chloride solution is digested with cupric hydroxide, or when potassium hydroxide is added to a cupric chloride solution, there is formed an oxychloride having the composition $CuCl_2.3CuO.4H_2O$, and known as atacamite.

Cuprous Bromide, CuBr, and *Cupric Bromide*, $CuBr_2$, are prepared like the corresponding chlorides, and resemble them in appearance and properties. The anhydrous cupric bromide occurs in lustrous crystals resembling iodine.

Cuprous Iodide, CuI, is the only stable compound of copper and iodine; it is a white, permanent, insoluble powder, which is prepared by adding potassium iodide to copper sulphate in the presence of sulphurous acid or ferrous sulphate:

$$2CuSO_4 + 2KI + 2FeSO_4 = 2CuI + K_2SO_4 + Fe_2(SO_4)_3.$$

Cupric Iodide is unstable, dissociating in water into $I_2 + CuI$.

If a solution of an iodide be added to a solution of copper sulphate without the use of a reducing agent, cuprous iodide and iodine are precipitated.

$$2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4.$$

The halogen salts of copper color the flame blue. Cupric salts give a chocolate colored precipitate of copper ferrocyanide upon the addition of potassium ferrocyanide.

COPPER AND OXYGEN

Cuprous Oxide, Cu_2O.—This compound is found native as cuprite, or red copper ore, in regular octahedrons or compact crystalline masses. It is readily prepared by fusing cuprous chloride with anhydrous sodium carbonate, or by heating Fehling's Solution with grape sugar. It is a red powder, wholly insoluble in water, but soluble in solution of ammonia. It is used for coloring glass red.

Cupric Oxide, CuO, occurs native as black oxide of copper or melaconite in dark, earthy masses, or rarely in cubes. It is artificially prepared by heating to redness copper nitrate ($Cu(NO_3)_2 = 2NO_2 + O + CuO$) or hydroxide, or by heating metallic copper to redness with access of air.

Properties.—Cupric oxide is a fine, amorphous, brownish-black powder; sometimes it is found in scales. It is insoluble in water, but easily dissolves in acids with the formation of cupric salts; it is also soluble in solution of ammonia by aid of ammonium chloride, giving a blue solution.

When heated in the presence of hydrogen, carbon monoxide, marsh-gas, and many other organic substances, cupric oxide readily gives up its oxygen and is reduced to metallic copper. On account of this property it is employed in organic ultimate analysis.

When fused with glass it imparts to the latter a light-green color.

Cuprous Hydroxide, Cu(OH), having this formula, is not known, but a compound derived from it, having the composition $4Cu_2O.H_2O$, is made by pouring a solution of cuprous chloride into a cold solution of sodium hydroxide. It is a bright yellow precipitate. It readily passes into cuprous oxide on the application of a gentle heat, and on exposure to air becomes blue by oxidation.

Cupric Hydroxide, $Cu(OH)_2$, is readily obtained as a light-blue, bulky precipitate, when a solution of copper sulphate is treated in the cold with excess of sodium hydroxide. When dried and ignited, it is converted into CuO. A solution of the freshly precipitated hydroxide in NH_4OH is called Schweitzer's reagent, which is employed as a solvent for cellulose.

At least two other oxides of copper are known—namely, Cu_4O, copper tetroxide, and copper superoxide or dioxide, $CuO_2.H_2O$.

OXYGEN SALTS OF COPPER

Cuprous Sulphate, Cu_2SO_4, may be prepared by the action of ethyl sulphate on cuprous oxide at 160°:

$$Cu_2O + (C_2H_5)_2SO_4 = Cu_2SO_4 + (C_2H_5)_2O$$

In contact with water it quickly decomposes with evolution of heat, as follows: $Cu_2SO_4 = CuSO_4 + Cu$.

Cupric Sulphate, $CuSO_4.5H_2O$. **Cupri Sulphas,** U.S.P., Blue Vitriol. —Most readily prepared by dissolving copper in hot sulphuric acid. Dilute sulphuric acid may be employed if a free access of air is secured.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O.$$

The clear solution is decanted and allowed to crystallize, and these crystals are further purified by recrystallization. Copper sulphate is a by-product in several metallurgical operations, so that its preparation is usually carried on in conjunction with them. For example, through the roasting of copper pyrites ($Cu_2S.Fe_2S_3$) with a plentiful supply of air, both are partly converted into sulphates, $Cu_2S.Fe_2S_3 + 8O_2 = 2FeSO_4 + 2CuSO_4$. The ferrous sulphate, which decomposes at a lower temperature than the copper sulphate, forms ferric oxide ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$). On treatment with water the copper sulphate is removed. Another source consists in gently roasting copper pyrites, when the following reaction takes place:

$$Cu_2S + 5O = CuSO_4 + CuO.$$

This mixture is then treated with so much sulphuric acid as is necessary to convert the oxide into sulphate.

Large quantities of copper sulphate are obtained in the refining of silver when this metal contains copper and gold. Silver and copper sulphates are formed, and from their solution the silver is precipitated by suspending in the liquid strips of copper. Commercial copper sulphate frequently contains small quantities of iron and zinc salts. *Double vitriol* consists of the sulphates of copper and iron, which, being isomorphous, crystallize together.

Properties.—Copper sulphate occurs in large, transparent, deep blue triclinic crystals, odorless, of a nauseous, metallic taste; slowly efflorescent in dry air. It is soluble in 2.5 parts of water at 25°, and in 0.5 part of boiling water; soluble in 500 parts of alcohol. When heated to 30° the salt loses 2 of its 5 molecules of water (14.43 per cent.), and is converted into a pale blue, amorphous powder. Two more molecules of water are lost at 100°, while the fifth is retained until 200° is reached, when a white, anhydrous powder remains (63.9 per cent. of the original weight). At a still higher temperature sulphur dioxide and oxygen are given off, and a residue of black cupric oxide remains.

$$CuSO_4 = CuO + SO_2 + O.$$

The aqueous solution reacts acid with litmus paper.

Copper sulphate in a crystallized, anhydrous condition may be obtained by acting on copper in closed vessels with concentrated sulphuric acid. The salt in the anhydrous as well as in the hydrated condition has a strong affinity for hydrochloric acid, forming cupric chloride with liberation of sulphuric acid; on account of this property, anhydrous copper sulphate is used in separating hydrogen chloride from mixtures with other gases.

Copper sulphate is used in the manufacture of colors for calico-printing, as a mordant, in electroplating and electrotyping; it also is extensively employed in some galvanic batteries. When mixed in solution with slaked lime, copper hydroxide forms; this mixture is used in spraying over grape vines to destroy phylloxera.

Copper Ammonium Sulphate, $CuSO_4,4NH_3.H_2O$.—Several deep blue colored compounds of copper and ammonium sulphate exist. One, having the above formula, is produced when an excess of concentrated ammonia water is triturated with copper sulphate. It was official in the Pharmacopœia of 1870, and was prepared in the solid state by rubbing together, in a mortar, copper sulphate and ammonium carbonate, and drying the product between folds of bibulous paper. It occurs as a deep-blue, crystalline powder, which on heating to 150° is transformed into $CuSO_4.2NH_3$. Anhydrous copper sulphate absorbs gaseous ammonia with great avidity, forming the compound $CuSO_4,5NH_3$.

Copper Nitrate, $Cu(NO_3)_2.3H_2O$, *Cupric Nitrate,* is prepared by treating, in a capacious flask, 1 part copper turnings with 11 parts of 25 per cent. nitric acid. The mixture is carefully warmed until the reaction begins, which then continues quietly without further application of heat:

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

The solution is diluted with water, filtered, and then evaporated until a pellicle forms, when it is set aside to crystallize. If the solution is crystallized below 26° a $Cu(NO_3)_2.6H_2O$ forms.

Properties.—Copper nitrate occurs in deep-blue, prismatic crystals;

it possesses a sharp metallic taste, and is easily soluble in water and alcohol. Like the sulphate, this salt forms an ammonia compound, having in this case the formula $Cu(NO_3)\ ,4NH_3$.

Copper nitrate is used in dyeing and in calico-printing; it is also a convenient compound from which to prepare pure copper oxide.

$$Cu(NO_3)_2 + \text{heat} = 2NO_2 + O + CuO.$$

Cuprous Cyanide, $CuCN$.—Through interaction between solutions of copper sulphate and potassium cyanide, cuprous cyanide first forms, which at once dissolves in an excess of KCN, forming the colorless double salt $Cu(CN)KCN$. The very stable complex ion $Cu(CN)'_2$, which is formed, does not respond to the usual copper tests.

Copper Arsenate, $Cu_3(AsO_4)_2.4H_2O$, is formed as an amorphous precipitate by warming equivalent quantities of copper nitrate and calcium arsenate with a little water to 60°. By varying the proportions of the above salts compounds of different composition may be obtained.

Copper Arsenite, $CuHAsO_3$, is known as *Scheele's green*, or *Swedish green*, and is obtained by mixing solutions of copper sulphate and potassium arsenite. *Paris green* is an aceto-arsenite of copper, and will be considered later.

Copper Borate of variable composition is obtained by mixing solutions of copper sulphate and borax.

Copper Silicate, $CuSiO_3$, is found in nature with variable amounts of water. It may be obtained as a blue-green precipitate by mixing solutions of copper sulphate and sodium silicate.

Copper Carbonate.—The normal salt, $CuCO_3$, is not known, but a compound having the composition $CuCO_3,3Cu(OH)_2$, is found in nature as the mineral malachite. Azurite, $CuCO_3.Cu(OH)_2$, occurs with malachite and other copper ores.

Malachite occurs in the Urals, at Cornwall, England, and in various parts of the United States. It is susceptible of a high polish, and is on this account much used for making vases, ornamental table tops, and jewelry.

Azurite is sometimes known as blue malachite, and is employed in the same manner as the green variety.

When cold solutions of copper sulphate and sodium carbonate are mixed, a blue precipitate forms having the composition $CuCO_3.Cu(OH)_2.H_2O$, which, on standing, becomes green, and has the same composition as malachite.

The term *verdigris*, or copper rust, is sometimes applied to the compound formed on copper when it is exposed to the joint action of air and water, and which has the same composition as malachite. The basic acetate of copper is usually considered to be verdigris.

Copper Hydride, Cuprous Hydride, CuH.—Obtained as a brown precipitate when copper sulphate is heated with hypophosphorous acid. When heated to over 60° it decomposes into Cu and H.

Copper Phosphate, $Cu_3(PO_4)_2.3H_2O$, is formed when copper carbonate is dissolved in dilute phosphoric acid; on warming the solution to 70° the salt is deposited as a bluish-green, insoluble precipitate. Various compounds of copper and phosphoric acid are found in nature.

COPPER AND SULPHUR

Cuprous Sulphide, Cu_2S, occurs native as the mineral *chalcocite*. It is formed when copper and sulphur are fused together.

Cupric Sulphide, CuS, when found in nature as the mineral *corellite*, is also known as indigo copper. It is formed as a black precipitate when hydrogen sulphide is passed into solution of copper sulphate. In moist state it is slowly converted into the sulphate, while if heated in a current of hydrogen it is transformed into cuprous sulphide and sulphur.

MERCURY (Hydrargyrum)

Symbol, Hg. *Atomic Weight*, 200.6. *Valence*, I and II.

History.—Mercury, or quicksilver, was known to the ancients, but at a more recent period than gold and silver. It was first mentioned in the writings of Aristotle, 400 B.C., and in those of Theophrastus, 300 B.C. The latter described it as liquid silver, and gave a method for the preparation of it from cinnabar. The symbol is derived from the Greek name *hydrargyrum* (ὕδωρ, water, and ἄργυρος, silver).

Occurrence.—Mercury is found native in minute globules disseminated through its ores. The most abundant ore is cinnabar, or mercuric sulphide, HgS. This is found at Idria, in Austria-Hungary; at Almaden, in Spain; in California, Nevada, and Texas, in the United States; in Mexico, New South Wales, China, and Japan. The chief sources of supply are the mines of Idria, Almaden, and California.

Metallurgy.—The chief ore of mercury being the sulphide, it is simply necessary to heat this ore to a temperature above 360° with excess of air in order to decompose it into the metal and sulphur dioxide, as follows:

$$HgS + O_2 = Hg + SO_2.$$

The vapors are passed through a series of stone chambers, the last one of which is so arranged that water trickles down and meets the ascending column of vapor. The mercury collects under the water. This process is employed at Idria, while at Almaden the vapors are conducted through a long series of vessels known as *aludels*, shown in Fig. 110. The combination of the mercury and sulphur is more easily destroyed in the presence of iron or lime, so that one of these is sometimes heated with the ore. When lime is employed the reaction is as follows:

FIG. 110.

Aludels.

$$4HgS + 4CaO = 4Hg + CaSO_4 + 3CaS.$$

In the United States these furnaces are usually so constructed as to be worked continuously, while in the older localities it is customary to allow the furnace to cool after each charge of about 50 tons has been heated; this is usually accomplished in one day, and then four or five days are required for the cooling before another charge can be filled in. Mercury prepared in this manner is marketed in iron bottles holding 75 pounds. It contains mechanical impurities, chiefly iron oxide, as well as small amounts of other metals, as lead, silver, tin, bismuth, copper, and zinc, and must be purified by first pressing through chamois, and then by distilling from iron retorts. The metallic impurities may also be removed by treatment with dilute nitric acid (equal parts of 25 per cent. HNO_3 and water); this is best accomplished by spraying the metal into the acid by pressing through chamois, then agitating frequently for 24 hours, after which it is well washed with water and dried with filter-paper.

Properties.—At ordinary temperatures mercury is a liquid, silver-white, lustrous metal. When cooled to —38.8° it forms, with considerable contraction, a malleable, ductile, and crystalline solid. Its specific gravity at 25° is 13.573.

Mercury is insoluble in water and the other usual solvents. It is not dissolved by hydrochloric acid or sulphuric acid at ordinary temperature, but when boiled with the latter it slowly dissolves with evolution of sulphur dioxide. Nitric acid, when concentrated, dissolves it rapidly. If an excess of nitric acid is used, mercuric nitrate is formed, $3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O$. If mercury be in excess, mercurous nitrate results, $6Hg + 8HNO_3 = 6HgNO_3 + 2NO + 4H_2O$. Nitro-hydrochloric acid dissolves mercury, forming mercuric chloride. The halogens react direct with mercury to form its halides, while with sulphur mercury forms a sulphide.

At ordinary temperatures mercury volatilizes slowly, and when heat is applied this progresses rapidly, until at about 358° the metal boils, and is completely dissipated (if pure), yielding a colorless and very poisonous vapor. The U.S.P. permits a non-volatile residue of not more than 0.02 per cent. The vapor has a density of 99.4 ($H = 1$), hence its molecule would weigh 198.8. According to the molecular weight determinations of many of the volatile mercury compounds, this same number also represents the atomic weight, hence the molecular weight and atomic weights of mercury are alike.

Pure mercury may be agitated with pure air or oxygen without undergoing change, but when other metals are present it becomes grayish in color, owing to the formation of a covering of oxidation products of these metals. A globule of the metal when placed on clean white paper should be spherical and roll about freely and leave no streaks, as it does when foreign metals are present. When heated to just below its boiling-point, mercury is slowly converted into red mercuric oxide, which at a still higher temperature again breaks up into its constituents.

When mercury is rubbed or agitated with fat, chalk, honey, glycerol, viscid substances, as well as certain liquids, as oil of turpentine or acetic acid, it is reduced to a very finely-divided condition, when it is said to be "extinguished" or "deadened." In this condition it becomes an active medicinal agent for both internal and external use.

Uses.—Besides its medicinal use, mercury is employed in the metallurgy of silver and gold, and has many uses in the laboratory, especially in making barometers and thermometers.

Amalgams.—The alloys of mercury with other metals are known as amalgams. This property of dissolving other metals, which is possessed by mercury, has been likened to the solvent action of water, but in the case of the metals it is much easier to demonstrate the formation of a definite compound; thus, for instance, the compounds of mercury and silver have the composition $AgHg$ and Ag_2Hg_3. Potassium, sodium, zinc, cadmium, tin, lead, gold, silver, etc., dissolve readily in mercury, and in the case of potassium and sodium, with considerable evolution of heat. An amalgam of 1 part of sodium in 100 parts of mercury is viscid; with 80 parts of mercury, pasty; with 30 parts, hard. This amalgam is employed as a reducing-agent, for when brought into contact with water, *nascent* hydrogen is evolved. Attention has been called to the use of mercury in the amalgamation process of gold extraction. An amalgam with silver is used in dentistry. The old method of silvering mirrors consisted in applying an amalgam of tin and mercury. This method has been largely replaced by the deposition of a very thin layer of silver from its solution by means of reducing agents.

Compounds.—Mercury forms two classes of compounds: mercuric, which in solution yield bivalent Hg˙˙ ions, while in the mercurous state the mercury atoms are mono-valent, sometimes expressed in bivalent grouping as —Hg—Hg—. The salts of mercury are more or less poisonous, depending upon their solubility, hence the mercuric compounds are sometimes termed "corrosive," while those of the "ous" class, "mild"; thus corrosive chloride and mild chloride of mercury are synonyms for mercuric and mercurous chlorides.

Reactions of Mercuric Salts.—Generally the mercuric salts are soluble in water or alcohol and are poisonous.

Alkali hydroxides precipitate yellow mercuric oxide.

$$HgCl_2 + 2KOH = HgO + 2KCl + H_2O.$$

Ammonia water gives a precipitate of mercuri-ammonium chloride (white precipitate).

$$HgCl_2 + 2NH_4OH = NH_4Cl + HgNH_2Cl + 2H_2O.$$

Alkali iodides yield red mercuric iodide, which is soluble in an excess of the precipitant, forming a colorless solution of a double salt of the alkali and mercuric iodides known as Mayer's reagent for alkaloids.

$$HgCl_2 + 2KI = 2KCl + HgI_2.$$
$$HgI_2 + KI = HgI_2.KI.$$

Hydrogen sulphide or ammonium sulphide precipitates black mercuric sulphide.

$$HgCl_2 + H_2S = HgS + 2HCl.$$

Stannous chloride reduces mercuric solutions to mercurous, with an excess of the reagent, to metallic mercury.

$$2HgCl_2 + SnCl_2 = SnCl_4 + 2HgCl.$$
$$2HgCl + SnCl_2 = SnCl_4 + 2Hg.$$

Sulphurous as well as hypophosphorus acids reduce mercuric salts to mercurous.

$$2HgCl_2 + H_2SO_3 + H_2O = 2HgCl + 2HCl + H_2SO_4.$$
$$4HgCl_2 + HPH_2O_2 + 2H_2O = 4HgCl + H_3PO_4 + 4HCl.$$

Reactions of Mercurous Salts.—Generally the mercurous salts are insoluble in water and alcohol, hence relatively non-poisonous.

Alkali hydroxides precipitate black mercurous oxide.

$$2HgNO_3 + 2KOH = 2KNO_3 + Hg_2O + H_2O.$$

Ammonia water precipitates a black mixture of a mercuric-ammonium compound and metallic mercury.

$$2HgNO_3 + 2NH_4OH = NH_4NO_3 + HgNH_2NO_3 + Hg + 2H_2O.$$

Ammonia water with calomel' produces black mercurous-ammonium chloride (black wash).

$$2HgCl + 2NH_4OH = NH_2Hg_2Cl + NH_4Cl + 2H_2O.$$

Soluble chlorides or hydrochloric acid yield mercurous chloride.

$$2HgNO_3 + 2HCl = 2HgCl + 2HNO_3.$$

Alkali iodides precipitate yellow to yellowish-green mercurous iodide which is soluble in an excess of the precipitant forming a double salt with precipitation of a portion of the mercury.

$$2HgNO_3 + 2KI = 2KNO_3 + 2HgI.$$
$$2HgI + 2KI = HgI_2.2KI + Hg.$$

Stannous chloride reduces mercurous salts to metallic mercury.

$$2HgCl + SnCl_2 = SnCl_4 + 2Hg.$$

MERCURY AND THE HALOGENS

Mercurous Chloride, HgCl (Hg_2Cl_2), *Calomel.* **Hydrargyri Chloridum Mite,** U.S.P.—The mineral *horn-quicksilver,* found native in various parts of the world, has the same composition as calomel.

Preparation.—When hydrochloric acid or a soluble chloride is added to a solution of mercurous nitrate, calomel is precipitated. The same result may be attained by passing sulphur dioxide into a solution of mercuric chloride. The product thus obtained is not satisfactory for medicinal use, owing to its coarse crystalline structure, hence before it can be used it must be subjected to a process of levigation, whereby it is reduced to an impalpable powder. The salt is, therefore, usually prepared by sublimation. This is accomplished by heating a mixture of 36 parts of sulphuric acid with 24 parts of mercury, until the latter is dissolved and a dry salt remains. The mercuric sulphate thus formed is rubbed with 24 parts of mercury until the globules disappear, and then with 18 parts of common salt. The mixture is then sublimed in such a manner as to rapidly condense the vapor and form a very fine amorphous product. This is in some cases accomplished by forcing a jet of steam into the condenser with the vapor of the calomel, and in other cases by a current of cold air in like manner. The reactions involved are as follows:

$$(a)\ \underset{\text{Mercury.}}{Hg} + \underset{\text{Sulphuric Acid.}}{2H_2SO_4} = \underset{\text{Mercuric Sulphate}}{HgSO_4} + \underset{\text{Sulphur Dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O.}$$

$$\underset{\text{Mercuric Sulphate.}}{HgSO_4} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercurous Sulphate.}}{Hg_2SO_4.}$$

$$(b)\ \underset{\text{Mercurous Sulphate.}}{Hg_2SO_4} + \underset{\text{Sodium Chloride.}}{2NaCl} = \underset{\text{Mercurous Chloride.}}{2HgCl} + \underset{\text{Sodium Sulphate.}}{Na_2SO_4.}$$

The same results may be obtained by using 4 p. of mercuric chloride instead of the sulphate, rubbing it with 3 p. of mercury and subliming.

In both cases the product is washed well with warm water to remove any traces of mercuric chloride, since the latter is soluble in that liquid. The washing is known to be complete when the addition of ammonia to the wash-water causes no further turbidity.

Properties.—Calomel is "a white, impalpable powder, becoming yellowish-white on being triturated with strong pressure, and showing only small, isolated crystals under a magnifying power of one hundred diameters. It is odorless and tasteless, and permanent in the air." It is "insoluble in water, alcohol, or ether, and also cold dilute acids."

On the application of heat calomel is volatilized without melting, leaving not more than 0.1 per cent. of residue (U.S.P.). Through prolonged exposure to strong light, calomel undergoes a slight decomposition into mercuric chloride and metallic mercury, taking on a gray color. Some organic substances, including sugar, when mixed with calomel and kept in a moist place, cause a similar appreciable change. On the other hand, milk sugar possesses no influence. Boiling with water or alcohol causes decomposition, $2HgCl = Hg + HgCl_2$. The same is true of the alkali chlorides. The halogens convert calomel into mercuric halides. Alkali iodides form mercurous iodide, soluble in excess, yielding potassio-mercuric iodide. One of its most characteristic reactions is that of blackening on the addition of lime water or solution of ammonia or alkali carbonates or of the caustic alkalies or alkaline earth oxides in the presence of water. In presence of an excess of lime water, calomel is converted into black mercurous oxide, known as *black wash,* the reaction being $2HgCl + Ca(OH)_2 = Hg_2O + CaCl_2 + H_2O$. With ammonia water, $2HgCl + 2NH_4OH = Hg_2NH_2Cl + NH_4Cl + 2H_2O$. Alkali bicarbonates or carbonates of the alkaline earths do not react with calomel when cold, excepting ammonium carbonate, which reacts the same as ammonia water. When concentrated hydrochloric acid is boiled with calomel, the latter is converted into mercuric chloride and mercury. Hot nitric acid converts it into mercuric chloride and nitrate, and hot sulphuric acid decomposes it, with evolution of sulphur dioxide and formation of mercuric chloride and sulphate. Vapor density determinations indicate the molecular weight formula $HgCl$ at higher, and Hg_2Cl_2 at ordinary temperatures.

Uses.—The chief use of calomel is in medicine.

Mercuric Chloride, $HgCl_2$, *Corrosive Sublimate. Mercury Bichloride.* **Hydrargyri Chloridum Corrosivum,** U.S.P.—This salt was described by Geber in the eighth century. It may be prepared in a small way by dissolving with the aid of heat 10 parts of mercuric oxide in 14 parts of 25 per cent. hydrochloric acid, previously diluted with 28 parts of water:

$$HgO + 2HCl = HgCl_2 + H_2O.$$

The method usually employed on a large scale consists in heating 2 parts of mercury and 3 parts of sulphuric acid, until dry:

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

The dried mercuric sulphate is intimately mixed with half its weight of common salt and a little manganese dioxide to prevent formation of mercurous salts.

The dry mixture is then sublimed into large earthenware vessels. The reaction which takes place in the sublimation is as follows:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

Mercuric chloride is also prepared by passing chlorine over heated metallic mercury, and condensing the vapors in earthenware vessels.

Properties.—Sublimed corrosive sublimate "occurs as heavy, colorless, rhombic crystals, or crystalline masses, or as a white powder, odorless, permanent in the air." When rubbed in a mortar it yields a pure white powder; calomel becomes yellow when so treated.

Corrosive sublimate is soluble in 13.5 parts of water at 25°, and in 2.1 parts of boiling water; in 3.8 parts of cold and 1.6 parts of boiling alcohol; it is also dissolved by 22 parts of ether and by 12 parts of glycerol. Ether extracts mercuric chloride to the extent of 69 per cent. from aqueous solutions; this is prevented by the presence of alkali chlorides or hydrochloric acid.

On the application of heat the salt fuses at 265° to a colorless liquid, which at about 300° volatilizes in dense white vapors, leaving not more than 0.1 per cent. of residue. The aqueous solution reddens litmus paper, but becomes neutral on the addition of alkali chlorides, due to the formation of soluble double salts such as $HgCl_2.NaCl$ or $HgCl_2.2NaCl$.

These, when in solution, contain Hg, Na, and Cl ions, hence react like other mercury salts. Dilute solutions of mercuric chloride in distilled water frequently deposit, on long standing in glass containers, an insoluble basic chloride. This is due to reaction with traces of alkali taken up from the glass by the water.

Some mercuric chloride is volatilized when boiled with water, also when heated dry at moderate temperatures it volatilizes slowly.

Sulphuric acid dissolves mercuric chloride without decomposition. Hydrochloric acid combines with it, forming the crystalline compounds $HgCl_2.HCl$ and $2(HgCl_2).HCl$, which lose HCl upon exposure.

Mercuric chloride forms a number of basic chlorides; for instance, when the aqueous solution is boiled with mercuric oxide and the solution is cooled to 60°, basic chlorides separate; the clear solution when poured off from these yields, on further cooling, a compound having the composition $2HgCl_2.3HgO$.

Mercuric chloride forms a number of double chlorides with the alkali metal chlorides; these double chlorides are more soluble than the mercuric salt. When an aqueous solution containing equal weights of mercuric chloride and ammonium chloride is evaporated a residue is obtained, which was formerly known as *sal alembroth*, and has the composition $2NH_4Cl,HgCl_2.H_2O$. This is a powerful antiseptic, not so irritating as the mercuric salt alone.

When mercuric chloride solution is added to ammonia water, *white precipitate* results (page 435). Most metals reduce mercuric chloride with precipitation of mercury or mercurous chloride. Hypophosphorous or sulphurous acid reduces sublimate to calomel when cold and to metallic mercury when heated. Similar in action are many organic bodies, as sugar, formates and tartrates, cotton, heat and light facilitating. Solutions of albumin precipitate with mercuric chloride. Alkali and alkaline earth hydroxides precipitate from solutions of mercuric chloride the yellow hydroxide. With alkali bicarbonates, a dioxychloride ($HgCl_2 + 2HgO$) or tetraoxychloride ($HgCl_2 + 4HgO$) precipitates, or a solution of trioxychloride ($HgCl_2 + 3HgO$) forms, according to the quantity of bicarbonate employed.

Uses.—Mercuric chloride is a valuable agent from which to prepare the other salts of mercury. It also has extended use in medicine, especially as an antiseptic. Internally it acts as a powerful poison, except in very small doses. The common antidote is egg albumin.

Mercurous Bromide, $HgBr(Hg_2Br_2)$, may be prepared by adding hydrobromic acid or sodium bromide to a solution of mercurous nitrate; in this form it bears a close resemblance to calomel.

Mercuric Bromide, $HgBr_2$ (U. S. P. Reagent), is obtained by treating mercury under water with an excess of bromine; it crystallizes from water in glistening scales, and from alcohol in rhombic needles. It is readily soluble in about 200 parts of water at 25° and in 25 parts of boiling water. Soluble in alcohol and in ether. It is used in preparing mercuric bromide Test Paper for arsenic tests.

Mercurous Iodide, $HgI(Hg_2I_2)$. **Hydrargyri Iodidum Flavum**, U.S.P.—This form of mercurous iodide has replaced the green variety which was official in the earlier Pharmacopœias, and was prepared by triturating in a mortar 40 parts of mercury with 2 or 3 parts of alcohol and 25.5 parts of iodine added in small portions at a time, finally adding sufficient hot alcohol to form a thin paste, and after transferring to a filter, the precipitate was washed with alcohol for the removal of traces of mercuric iodide. The yellow iodide is usually prepared by precipitating a solution of mercurous nitrate with one of potassium iodide, avoiding an excess of the latter.

$$Hg_2(NO_3)_2 + 2KI = 2HgI + 2KNO_3.$$

The precipitate is directed to be washed with alcohol to remove the last traces of mercuric salt, then dried at not above 30°. It should be kept in dark amber-colored vials, with the least possible exposure to light.

Properties.—The official salt is a bright yellow, amorphous powder, odorless and tasteless. Being unstable, especially on exposure to light, it becomes darker in proportion as it undergoes decomposition into metallic mercury and mercuric iodide. The green mercurous iodide owes its color to the presence of metallic mercury. A similar decomposition takes place when mercurous iodide is treated with an excess of potassium iodide; the mercuric iodide formed dissolves and metallic mercury precipitates $2HgI + 2KI = HgI_2.2KI + Hg$. Caustic alkalies react as with calomel, while ammonia water, when heated with mercurous iodide, decomposes it into the mercuric salt and mercury; if the ammonia be added in excess a double salt is formed, $HgI_2.NH_3$.

Mercurous iodide is nearly insoluble in water, and entirely insoluble in alcohol or ether.

"When slowly and moderately heated, it assumes an orange and then a red color, becoming yellow on cooling." This is due to a change in its molecular state of subdivision. "When quickly and strongly heated, it is at first partially decomposed into mercury and mercuric iodide, and finally is volatilized, leaving not more than 0.2 per cent. of residue."

$$2HgI = HgI_2 + Hg.$$

Mercuric Iodide, HgI_2. **Hydrargyri Iodidum Rubrum,** U.S.P.—This salt is prepared by dissolving mercuric chloride, 40 parts, and potassium iodide, 50 parts, each in a sufficient quantity of water, and pouring the two solutions simultaneously and in a thin stream, with active stirring, into 2000 parts of distilled water:

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

The precipitate is well washed, dried in the dark between folds of filter paper at a temperature not exceeding 70°. The product should be kept excluded from the light. Mercuric iodide may also be prepared by rubbing in a mortar 20 parts of mercury, moistened with 2 or 3 parts of alcohol, and 25.5 parts of iodine, until a uniform product is obtained.

Properties.—Mercuric iodide is a scarlet-red, amorphous powder without odor or taste. It is almost insoluble in water; soluble in 115 parts of alcohol at 25°, and in 20 parts of boiling alcohol. Also soluble in ether, chloroform, acetone, carbon disulphide, acetic, hydrochloric and hydriodic acids and hot solutions of the soluble chlorides and iodides as well as glycerol, fats, and fatty oils. Solubility in the latter bodies is aided by alkali iodides. Since the salt is soluble in solutions of potassium iodide or mercuric chloride, it is important in its preparation that the proportion of these two salts be properly adjusted.

When heated to about 150° the salt becomes yellow, assuming, after cooling, its red color again. At 238° the salt fuses and at higher temperature it volatilizes, leaving a residue of not more than 0.2 per cent. (U.S.P.). The vapors are colorless and condense to yellow crystals.

Insoluble mercuric iodide dissolves in alkali iodide solutions to form complex or double salts; for example, with potassium iodide a potassio-mercuric iodide ($HgI_2.2KI$), which, unlike mercuric salts, is not precipitated by alkali hydroxides.* A solution of this double salt is known as *Mayer's reagent,* which forms insoluble compounds with the alkaloids.

If this Mayer's solution be mixed with an excess of potassium hydroxide, *Nessler's* solution is formed, which is a very sensitive reagent for minute quantities of ammonia, producing from an orange coloration to a brown precipitate of oxy-dimercuric-ammonium iodide, according to the percentage of ammonia present.

$$2(HgI_2.2KI) + NH_3 + 3KOH = O{:}Hg_2{:}NH_2I + 7KI + 2H_2O.$$

Mercurous Fluoride, HgF, is formed by digesting calomel with silver fluoride; it forms in small, yellow crystals, soluble in water.

Mercuric Fluoride, $HgF_2.2H_2O$, forms as a white, crystalline mass when mercuric chloride is treated with an excess of hydrofluoric acid.

Mercuric Cyanide, $Hg(CN)_2$.—Obtained by dissolving mercuric oxide in hydrocyanic acid. This salt dissociates but little, hence is not affected by the addition of alkali hydroxides. When heated, mercuric cyanide decomposes into mercury and cyanogen. Mercuric cyanide forms colorless, translucent crystals soluble in 12 p. of cold and 3 p. of boiling water and 12 p. of alcohol.

MERCURY AND OXYGEN

Mercurous Oxide, Hg_2O, is obtained by precipitating a solution of a mercurous salt with sodium hydroxide: $2HgNO_3 + 2NaOH = 2NaNO_3 + Hg_2O + H_2O$. The product is an odorless and tasteless brownish-black powder, insoluble in water, and readily decomposed at 100° or by light into mercuric oxide and mercury.

Mercuric Oxide, HgO.—The Pharmacopœia recognizes two varieties of mercuric oxide, the yellow, **Hydrargyri Oxidum Flavum,** and the red, **Hydrargyri Oxidum Rubrum.** The yellow variety is prepared by pouring a solution of 100 grams of mercuric chloride in 1000 mils of water into a solution of 40 grams of sodium hydroxide (90 per cent. strength) in 1000 mils of water. If the quantity of alkali be insufficient or the alkali be added to the mercuric solution a reddish-yellow mercuric oxychloride forms (see page 430).

The precipitate is well washed, and dried at a temperature below 30° without exposure to light. Chemically, the yellow oxide is more

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* Such a complex salt solution does not contain Hg ions, but HgI_4 ions, which deport themselves differently from the former. Complex salt solutions contain compound ions which react with other reagents quite differently from the simple ions usually present.

active than the red oxide. The difference in color is due to the finer degree of subdivision of the former.

The red mercuric oxide, or *red precipitate,* is prepared by dissolving 10 parts of mercury in 30 parts of nitric acid (25 per cent.), evaporating to dryness, and then heating on a sandbath so long as yellowish vapors escape. The product obtained is a basic mercuric nitrate. This basic salt is then triturated with 10 parts of mercury until the particles of the latter cease to be visible; the result is a basic mercurous nitrate, which is heated as long as acid fumes are evolved, whereby mercuric oxide is obtained.

$$Hg(NO_3)_2.HgO + Hg = 2HgNO_3.HgO.$$
$$2HgNO_3.HgO = 3HgO + 2NO_2.$$

Properties.—The yellow oxide is officially described as "a light orange-yellow, amorphous, heavy, impalpable powder," while the red oxide is stated to consist of "heavy, orange-red, crystalline scales, or a crystalline powder, becoming more yellow the finer it is divided." Both varieties are odorless, with a metallic taste, and permanent in the air. The yellow oxide darkens on exposure to light. Both are almost insoluble in water, insoluble in alcohol, but readily and completely soluble in dilute hydrochloric or nitric acid, forming colorless solutions. On the application of heat both oxides become darker in color, the yellow becoming of a reddish color, and at a low red heat they are completely dissipated into oxygen and mercury, leaving not more than 0.2 per cent. of residue (U.S.P.). When boiled with stronger ammonia water a yellow solution of di-hydroxy-dimercuro-ammonium hydroxide forms, $(HO.Hg)_2NH_2.OH$ (*Millon's base*).

Uses.—The oxides of mercury are used in the preparation of some of the mercurial salts, and in medicine for external use. The yellow oxide, because of its amorphous nature, is the only kind employed in diseases of the eye, usually in form of **Unguentum Hydrargyri Oxidi Flavi.**

Mercurous Chlorate, $HgClO_3$, is formed when mercurous oxide is dissolved in chloric acid, and the solution evaporated at ordinary temperatures over sulphuric acid. It is deposited in rhombic prisms which decompose at 250°, and when heated with organic matter deflagrate violently.

Mercuric Chlorate, $Hg(ClO_3)_2.2H_2O$.—This salt is obtained by dissolving mercuric oxide in warm chloric acid. It crystallizes on cooling in small, rhombic pyramids.

Mercurous Sulphate, Hg_2SO_4, is precipitated as a white powder on adding dilute sulphuric acid to a solution of mercurous nitrate. It is a white, crystalline powder, slightly soluble in water, and decomposes on heating into $Hg + O_2 + SO_2$.

Mercuric Sulphate, $HgSO_4$.—This salt is obtained as a white, crystalline mass by heating mercury with an excess of sulphuric acid. The solution in sulphuric acid is assisted by the addition of nitric acid. When gently warmed, mercuric sulphate becomes yellow, then red, and at a stronger heat is decomposed into mercury, oxygen, sulphur dioxide, and mercurous sulphate. When mercuric sulphate is mixed with an excess of water a basic salt $(HgSO_4.2HgO)$ called Turpeth Mineral (Hydrargyri Subsulphas Flavus) is formed.

This subsulphate is a heavy, lemon-yellow powder, odorless, and almost tasteless; permanent in the air. Soluble in 2000 parts of water at 15°, and in 600 parts of boiling water; readily soluble in nitric or hydrochloric acid. On the application of heat the salt turns red, becoming yellow again on cooling. At higher temperatures it is decomposed and volatilized without leaving any residue.

Mercurous Nitrate, $HgNO_3.H_2O$, is prepared by acting on an excess of mercury in the cold with dilute nitric acid. One part of mercury is covered in a beaker with 1.5 parts of nitric acid (25 per cent.) and set aside in a cool place for several days:

$$6Hg + 8HNO_3 = 6Hg(NO_3) + 4H_2O + 2NO.$$

The solution is allowed to evaporate until crystals form, when it is warmed and filtered through asbestos to remove the undissolved mercury. The filtrate yields the pure crystals on cooling.

Properties.—The white or colorless salt readily loses its water of crystallization. When heated, mercurous nitrate fuses at 70° with decomposition; at higher temperature it breaks up into mercuric oxide and nitric oxide. It is soluble in warm water, yielding an acid solution. In the presence of an excess of water it is hydrolyzed (becoming turbid) into a basic salt of variable composition, usually $Hg_2OH.NO_3$, the solution being clarified by the addition of a few drops of nitric acid. Mercurous nitrate dissolves only in dilute nitric acid without decomposition.

The absence of any mercuric salt may be determined by triturating with an excess of common salt and water, filtering and adding stannous chloride. Any mercuric salt that may be present is dissolved by the sodium chloride solution and precipitated by the $SnCl_2$.

Uses.—Mercurous nitrate has some use in the laboratory as a reagent, and especially for the detection of protein substances. When used in this way it is known as *Millon's reagent,* and is prepared by dissolving 1 part of mercury in 1 part of cooled, fuming nitric acid, and adding 2 parts of distilled water. The U. S. P. Mercurous Nitrate T.S. is prepared by mixing 10 gm. of mercury with 5 mils of nitric acid (U. S. P.) and 5 mils of distilled water; after standing 24 hours, the crystals are separated and dissolved in 100 mils of distilled water. This solution should be kept in contact with a small quantity of mercury.

Mercuric Nitrate, $Hg(NO_3)_2$.—Prepared by dissolving mercury in an excess of nitric acid by aid of heat, $3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 4H_2O + NO_2$, until a portion of the solution on diluting with water ceases to precipitate upon the addition of a solution of sodium chloride. The salt crystallizes readily from concentrated solutions. When the salt is added to water a yellow basic nitrate, $(HgNO_3)_2.2HgO$, forms, which further decomposes to HgO on boiling. In former editions of the U. S. Pharmacopœia a Liquor Hydrargyri Nitratis was recognized which was made by dissolving 40 grams of red mercuric oxide in a mixture of 45 grams of nitric acid and 15 grams of distilled water. This solution is now used as a U.S.P. test solution.

The solution of mercuric nitrate when mixed with fat, or lard oil, forms an important official ointment under the name of **Unguentum Hydrargyri Nitratis.**

Mercuric Cyanate, $Hg(OCN)_2$, is obtained as a white, crystalline precipitate by adding a solution of potassium cyanate to one of mercuric chloride.

Mercuric Thiocyanate, $Hg(SCN)_2$, is prepared by precipitating a mercuric salt with potassium thiocyanate. This compound is used in the preparation of the so-called Pharaoh's serpents. The powder is made into a plastic mass with gum and water, and then formed into cones or cylinders. These, when once ignited, burn with a bluish flame, and yield a bulky vermiform of mellone.

MERCURY AND SULPHUR

Mercuric Sulphide, HgS.—This compound is found in two forms, according to its method of preparation. The amorphous, unstable, black variety is produced by precipitating mercuric salts with hydrogen sulphide. Treatment with alkali polysulphides or sublimation converts it into the red variety. The crystalline, red variety is formed by sublimation of the black compound. The red is also found in nature as *cinnabar.* It occurs in red, hexagonal prisms or in crystalline masses. The black variety was formerly known as *Ethiops mineral.* Mercuric sulphide is the most insoluble compound of mercury, dissolving only in nitro-hydrochloric acid to form mercuric chloride with separation of sulphur.

Vermilion is a very finely divided red sulphide prepared, usually, by subliming a mixture of 8 parts of sulphur and 42 parts of mercury.

Uses.—Mercuric sulphide was formerly used in medicine, but at the present time it is rarely employed. Vermilion and cinnabar are much used in paints.

MERCURY AMMONIUM COMPOUNDS

Mercurous Ammonium Chloride, $NH_3.HgCl$.—When calomel is subjected to the action of dry ammonia a black compound of the above composition is formed. It is readily decomposed on heating, or by exposure to the air.

Dimercurous Ammonium Chloride, NH_2Hg_2Cl.—This compound is formed when calomel is treated with aqueous ammonia.

When mercurous nitrate is used instead of the chloride, a compound of somewhat variable composition is formed, having, presumably, the formula $NH_2Hg_2NO_3$. This was the *mercurius solubilis Hahnemannii.* It is readily decomposed on exposure to light.

Mercuric Ammonium Chloride, NH_2HgCl. **Hydrargyrum Ammoniatum,** U.S.P. *White Precipitate.*—This compound is prepared by pouring a cooled solution of 100 grams of mercuric chloride in 2000 mils of warm water, into 150 mils of ammonia water (10 per cent.), keeping the latter in excess.

$$HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O.$$

The precipitate is collected, washed well with cold water, and dried between the folds of bibulous paper at a temperature not exceeding 30°. Light should be excluded as much as possible during the process.

Properties.—White precipitate occurs in " white, pulverulent pieces, or a white, amorphous powder, without odor, and having an earthy, afterwards styptic and metallic taste. Permanent in the air." It contains not less than 78 nor more than 80 per cent. of metallic mercury and is insoluble in water and in alcohol. By prolonged washing it is converted into a basic compound and becomes yellowish in color.

$$2NH_2HgCl + H_2O = NH_4Cl + (NH_2HgCl).HgO.$$

Warm hydrochloric, nitric, or acetic acid readily dissolves it. The salt is readily soluble in cold solution of ammonium carbonate, and in warm solution of sodium thiosulphate with evolution of ammonia, $HgNH_2Cl + Na_2S_2O_3 + H_2O = NH_3 + NaOH + NaHgClS_2O_3$. When this solution is heated, red mercuric sulphide separates.

$$NaHgClS_2O_3 + H_2O = NaCl + HgS + H_2SO_4.$$

When boiled with caustic alkalies ammonia is evolved and mercuric oxide forms, $NH_2HgCl + KOH = NH_3 + HgO + KCl$.

On the application of heat white precipitate is decomposed without fusion, $6HgNH_2Cl = 6HgCl + 4NH_3 + N_2$, and at a higher temperature it yields a sublimate of calomel, $3HgNH_2Cl = 3HgCl + N + 2NH_3$.

Uses.—White precipitate is used for external application in skin diseases.

Other compounds of mercuric ammonium chloride are known. The most important is the *Mercuric diammonium chloride,* $(NH_3)_2HgCl$, also known as *fusible white precipitate.* It may be obtained by adding 20 parts of yellow mercuric oxide to a boiling solution of 100 parts of ammonium chloride in 350 parts of water. On cooling, crystals of the above composition separate. Towards solvents this compound behaves similarly to the preceding one, but on the application of heat it readily fuses with evolution of nitrogen and ammonia.

CHAPTER VI

ALUMINUM AND THE RARE EARTHS

ALUMINUM

Symbol, Al. *Atomic Weight,* 27.1. *Valence,* III.

History.—Alumina, the oxide of the metal, has long been known. It was formerly regarded as identical with lime; it was shown to be distinct from that substance by Marggraff in 1754. The metal was first obtained by Wöhler in 1827 through the reduction of aluminum chloride with sodium.

Occurrence.—The most abundant sources of aluminum are the oxide and its hydrates and the silicates. The oxide is found native as corundum, of which the finely-crystallized varieties constitute the gems sapphire and ruby, colored blue or red through the presence of traces of metallic oxides, while the granular impure variety is known as emery. Of the hydrates, the monohydrate, $Al_2O_3.H_2O$, is the mineral *diaspore,* the dihydrate is found admixed with ferric oxide in *bauxite,* $Al_2O_3.2H_2O$, and the trihydrate, $Al_2O_3.3H_2O$, as the mineral *gibbsite.* Of these the second is by far the most important, and is now mined both in France and in this country, in Georgia and Alabama, as the chief material for the preparation of alumina in the production of the metal and for the manufacture of alum. A double fluoride of aluminum and sodium, $3NaF.AlF_3$, is also found in Greenland as the mineral cryolite; a basic sulphate is found as alunite or alum stone, $Al_2(SO_4)_3.4Al(OH)_3.K_2SO_4$, and lastly numerous silicates are found in the various clays, of which kaolin or porcelain clay is the purest. Where combined with potassium silicate it forms feldspar, $K_2O.Al_2O_3.6SiO_2$.

Extraction.—The first working process for the manufacture of aluminum is due to Deville, who developed and improved Wöhler's method, using the double chloride of aluminum and sodium, which he caused to react with metallic sodium, according to the reaction:

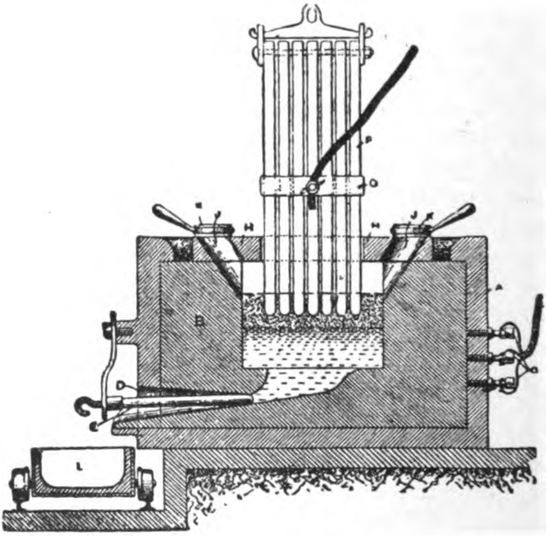
$$2(AlCl_3.NaCl) + 6Na = Al_2 + 8NaCl.$$

This process, elaborated on in 1855, remained the sole one for its manufacture for thirty years. It was an expensive method, however, in that it involved the use of the costly metal sodium and because the reaction was not capable of being made a continuous one. With the advent of cheaper sodium as made by the Castner process (see page 340) the price of aluminum as made by the Deville process was greatly reduced, but it finally was displaced by electrolytic methods.

In 1885 the Cowles Bros.' patent for the reduction of alumina (in the form of corundum) by carbon at the temperature of the electric arc was made public. This process was not so much adapted for the production of pure aluminum as for the formation of aluminum alloys, as aluminum bronzes (copper and aluminum). Two purely electrolytic processes have since been introduced —the Héroult process in 1887 and that of Hall in 1889, and these now practically monopolize the manufacture of the pure metal. Both methods, which differ somewhat in the form of plant employed, are based on the electrolysis of a solution of alumina (bauxite) in molten cryolite. Since alumina melts at about 2010°, a lower melting solvent as cryolite (1000°) is used. As the electrolysis proceeds fresh charges of alumina are added, about 20 parts for each 100 parts of solvent. The current used for each cell is 10,000 ampères at 5.5 volts. The Héroult cell is illustrated in Fig. 111. The positive electrode here is a bundle of carbon plates, and is suspended in the molten bath, while the negative electrode is of metal, and is introduced from below, where the metal may also be drawn off. The Hall cell consists of rectangular iron pots lined with carbon which serve as cathodes, while large graphite rods suspended in the bath form the anodes. The metal made by this process is very pure, running over 99 per cent., the chief impurities being iron and silicon.

Properties.—Aluminum is a bluish-white metal of high luster, and a specific gravity of about 2.6. It is a little softer than silver, but its ductility allows it to be drawn, punched, or spun into almost any form. It fuses at 658°, being intermediate between zinc and silver. It is practically non-tarnishable in the air, either dry or moist, and hydrogen sulphide has no action upon it because it becomes covered with a thin layer of adherent oxide. It is not acted upon by water at any temperature. Diluted sulphuric acid acts very slowly, while the concentrated acid attacks the metal with evolution of sulphur dioxide. Either diluted or concentrated phosphoric acid dissolves aluminum with evolution of hydrogen. Nitric acid reacts extremely slowly, especially the more concentrated acid.

FIG. 111.



Héroult process for aluminum.

$$Al + 4HNO_3 = Al(NO_3)_3 + 2H_2O + NO.$$

Hydrochloric acid, both dilute and concentrated, dissolves it rapidly with evolution of hydrogen. Solutions of the alkali hydroxides also attack it rapidly, dissolving it with evolution of hydrogen and the formation of an alkaline aluminate.

$$Al_2 + 2KOH + 2H_2O = 2KAlO_2 + 3H_2.$$

With ammonia water or the alkali carbonates the products are aluminum hydroxide and hydrogen.

Aluminum filings amalgamate superficially with mercury, forming an active reducing agent which when in contact with water evolves hydrogen.

An *aluminum amalgam* is obtained by treating aluminum filings with a (0.5 per cent.) solution of mercuric chloride; this is a very active neutral reducing agent, giving off hydrogen when in contact with water, leaving aluminum hydroxide.

Aluminum leaf has replaced silver leaf to some extent. Its chief impurities are iron and silicon.

Uses.—Aluminum is used in large and increasing amounts for fancy and useful articles as well as in the automobile industry because of the two qualities of lightness and freedom from tarnish. It is peculiarly adapted for culinary vessels, as the effect of vegetable juices and acids upon it has been shown to be less than upon tin and copper. One objectionable feature to this use is the difficulty encountered in soldering, the only recourse being autogenous soldering (by fusion of edges). Other important uses of aluminum are in the form of foil, replacing tin-foil and *thermite* (see below). The alloys of aluminum, however, from a commercial point of view, form its most important applications. Of these, first in importance are the alloys of copper, known as aluminum bronzes, of golden color, and composed of 90–95 per cent. copper and 5–10 per cent. aluminum. These alloys are superior to brass in tensile strength and elasticity, hence are valuable for physical instruments. The addition of a very small amount of aluminum to other metals seems, in many cases, to allow of superior castings being made. Thus, from 0.02 to 0.04 per cent. of aluminum added to steel greatly improves it; 0.01 per cent. of aluminum added to zinc makes the molten metal thinner, and reduces the amount of oxidation that takes place in the galvanizing process. The aluminum scale beams now made, which combine rigidity with lightness, contain 3 per cent. of silver and 2 per cent. of copper.

Magnalium is an alloy of aluminum with from 1 to 2 per cent. of magnesium and a little copper, nickel and tin; it is used for scientific apparatus, cooking vessels, optical mirrors, etc.

Finely divided aluminum readily burns to Al_2O_3, liberating an extraordinary amount of heat; this has been utilized by H. Goldschmidt in "*Thermite*" to attain temperatures of over 2000°, whereby many metallic oxides are reduced to free metals. Thermite is a mixture of equal parts of iron oxide and finely divided aluminum, which is ignited by means of magnesium powder and barium peroxide. By means of this thermite wrought and cast iron objects may be welded. More recently a powdered alloy of aluminum and calcium is employed.

ALUMINUM AND THE HALOGENS

Since aluminum hydroxide is a very weak base, all the salts of aluminum dissociate hydrolytically in solutions, hence possess an acid reaction. This hydrolysis is slight in the salts of the strong acids and considerable in the salts of the weak acids.

Aluminum Chloride, $AlCl_3$.—The chloride is obtained by heating aluminum metal in a current of chlorine or of hydrogen chloride; in the latter case hydrogen is liberated and aluminum chloride sublimes as a white crystalline mass. It may also be obtained by heating a mixture of aluminum oxide (or clay or bauxite) in a current of chlorine and sulphur monochloride, condensing the vapors in a receiver.

$$4Al_2O_3 + 3S_2Cl_2 + 9Cl_2 = 8AlCl_3 + 6SO_2.$$

Aluminum chloride forms a very deliquescent white crystalline powder, which, through the moisture of the air, decomposes as follows: $AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl$. This same decomposition takes place when the salt is dissolved in water; hence aluminum chloride cannot be prepared from aqueous solution by evaporation, owing to the formation of a basic salt. Aluminum chloride sublimes at 183°. If alumina (Al_2O_3) be dissolved in HCl and evaporated, a salt of the composition $AlCl_3.6H_2O$ is obtained, which on heating decomposes into Al_2O_3, HCl, and H_2O. Aluminum chloride forms double salts with the alkali and alkaline earth chlorides, as for example: $AlCl_3.NaCl$. Also such compounds as $AlCl_3.PCl_5$. The sublimed aluminum chloride is employed as catalytic agent in the Friedel-Crafts reaction.

Aluminum Fluoride, AlF_3, is formed by passing hydrogen fluoride over alumina heated to redness. A double fluoride of aluminum and sodium, occurring native in Greenland as *cryolite,* $AlF_3.3NaF$, is important in the aluminum industry. Cryolite is also the raw material for the manufacture of sodium carbonate (see p. 359) and of alum.

ALUMINUM AND OXYGEN

Aluminum Oxide (Alumina), Al_2O_3, is found native as corundum, ruby and sapphire, and emery. Obtained artificially by igniting the hydroxide, it forms a white, amorphous powder, which is insoluble in water, and fuses only at very high temperatures. Rubies and sapphires are made artificially by heating alumina calcined at 1000° with chromic oxide or lead oxide in an oxyhydrogen flame at about 1900°. Electrolytic oxygen and hydrogen are necessary because of the very high purity of these gases. Commercially alumina is now prepared from bauxite, either by the action of sulphuric acid or of sodium carbonate, the former process dissolving out the alumina from the impurities, and the latter making a sodium aluminate which is soluble. This solution upon standing for 5 or 6 days undergoes dissociation with precipitation of alumina.

Aluminum Hydroxide, $Al(OH)_3$.—This occurs native in mineral forms as *diaspore* ($Al_2O_3.H_2O$), *bauxite* ($Al_2O_3.2H_2O$), and *hydrargillite* ($Al_2O_3.3H_2O$). It is precipitated as a gelatinous mass from solutions of aluminum salts by the addition of ammonia, ammonium sulphide, an alkali hydroxide or carbonate. The aluminum carbonate or sulphide formed is immediately hydrolyzed by the water to hydroxide with evolution of CO_2 or H_2S.

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 3CO_2.$$
$$Al_2(SO_4)_3 + 6NH_4HS + 6H_2O = 2Al(OH)_3 + 3(NH_4)_2SO_4 + 6H_2S.$$

Alumini Hydroxidum, U.S.P.—In the official process sodium carbonate and alum solutions are used, and after straining, the precipitate is washed thoroughly with hot water to remove the alkali sulphates.

$$2AlK(SO_4)_2.12H_2O + 6NH_4OH = 2Al(OH)_3 + K_2SO_4 + 3(NH_4)_2SO_4 + 24H_2O.$$

When freshly precipitated it is a white, gelatinous precipitate. When dried at a temperature not exceeding 40° it can be reduced to a uniformly fine white powder, which is insoluble in water or alcohol, but completely soluble in hydrochloric or sulphuric acid, and also in potassium or sodium hydroxide solutions.

Aluminum hydroxide is insoluble in an excess of ammonia water. When heated to redness, the hydroxide loses about 34 per cent. of its weight, forming the oxide Al_2O_3.

Gelatinous aluminum hydroxide, owing to its colloidal character, possesses the property of precipitating many dyestuffs from their solutions, forming insoluble colored compounds (*lakes*) with them. Hence the importance of aluminum compounds as mordants in dyeing. Aluminum acetate, also sodium aluminate, is used in this connection, so when the mordanted goods are steamed, the acetic acid passes off, leaving the aluminum hydroxide upon the fiber. Fabrics are rendered waterproof by impregnating with aluminum hydroxide by means of the acetate. This destroys the capillarity of the fibers.

Aluminum hydroxide possesses feebly basic as well as acid properties, hence is able to form salts with strong acids as well as bases, $2Al(OH)_3 + 3H_2SO_4 = Al_2(SO_4)_3 + 6H_2O$. The freshly precipitated hydroxide dissolves in sodium or potassium hydroxide, yielding *aluminates*, $Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$. Of these sodium aluminate, $NaAlO_2$, is the best known, playing an important part in the "cryolite process" for making sodium carbonate (see p. 359). Similar aluminates occur in nature as minerals, as *spinel*, or magnesium aluminate, $Mg(AlO_2)_2$, and *chrysoberyl*, or beryllium aluminate, $Gl(AlO_2)_2$.

OXYGEN SALTS OF ALUMINUM

Aluminum Sulphate, $Al_2(SO_4)_3 + 18H_2O$.—This salt, which also crystallizes with 16 molecules of water, forms white crystalline masses, inodorous, of a sweetish astringent taste. It is soluble in less than its weight of water at 20°. Aluminum sulphate may be prepared by dissolving the hydroxide, or, preferably, commercially, any pure clay free from iron, in sulphuric acid, the clay being used in excess in order to avoid solution of the silica. The sulphate obtained is known commercially as *alum cake*. When once contaminated with iron, which is difficult to remove, alum cake cannot be used as a mordant in dyeing.

Aluminum sulphate unites with alkali sulphates to form a class of well-characterized and crystallizable isomorphous double sulphates, which are known by the general name of *Alums*. In a still wider sense, the term is applied to the whole class of double sulphates, in which we have a sesquisulphate, an alkali sulphate, and 12 molecules of water crystallizing together in the regular system as octahedra or cubes. Their constitution is represented by the general formula $\begin{array}{l} R''' = SO_4 \\ R' \diagdown SO_4 \end{array} + 12H_2O$. R′ may be represented by either K, Na, Rb, Cs, NH_4, and R‴, by trivalent Al, Fe, Cr, V, Mn, Co, etc.

Alumen, U.S.P.—Both potassium and ammonium alum are official.

Aluminum and Potassium Sulphate, Potash Alum, $AlK(SO_4)_2.12H_2O$, is manufactured either from alum shale or alunite $[K(AlO)_3(SO_4)_2.3H_2O]$, bauxite $[Al_2O_3.2H_2O]$, or cryolite $[3NaF.AlF_3]$. The alunite or alum stone is roasted at 500° and then weathered, whereby the pyrite present is oxidized to ferrous sulphate and sulphuric acid. These react with the aluminum oxide to form the sulphate. The mass is then leached, and after concentration of the solution the iron sulphate is removed from the aluminum sulphate by fractional crystallization.

Alum may be prepared from bauxite by treatment with 50 per cent. sulphuric acid. To the aluminum sulphate prepared by either of these methods the necessary quantity of potassium sulphate is added. Or aluminum hydroxide is prepared, as described under that heading, then dissolved in diluted sulphuric acid and mixed with an alkali sulphate.

Alum is prepared from cryolite by calcining with limestone, whereby calcium fluoride, sodium aluminate, and carbon dioxide result. On leaching with water, the sodium aluminate dissolves, which on treating with CO_2 deposits hydrated alumina; this is dissolved in sulphuric acid and the necessary alkali sulphate added.

Both alums form large, colorless, octahedral crystals, having a sweetish but strongly astringent taste. On exposure to the air the crystals of potash alum are liable to absorb ammonia and acquire a whitish coating of a basic salt. Potash-alum is soluble in 7.2 parts of water at 25° and 0.3 parts of boiling water, and insoluble in alcohol. When heated to 92.5° either potash or ammonia alum fuses in its crystal water; heated slowly to 200° it loses all its water of crystallization and leaves *dried alum* (**Alumen Exsiccatum,** U.S.P.), which retains all the chemical characters of the crystallized alum.

Aluminum and Ammonium Sulphate (Ammonia Alum), $AlNH_4(SO_4)_2 + 12H_2O$, crystallizes in the same octahedral forms as potash alum, and possesses very similar properties, but is slightly less soluble in water. It is prepared by adding ammonium sulphate to aluminum sulphate.

Aluminum Silicates.—A large number of silicates found native are double silicates of aluminum and other bases. By the decomposition of these *in situ* pure aluminum silicates are often formed. Thus, one of the most abundant minerals is feldspar [K_2O.(or Na_2O)$Al_2O_3.6SiO_2$], a double silicate of aluminum and potassium (*orthoclase*) or sodium (*albite*). Its gradual decomposition through weathering, with the elimination of the alkali, gives rise to the large deposits of kaolin or porcelain clay ($Al_2O_3.2SiO_2 + 2H_2O$), a very pure aluminum silicate. The common clays, impure aluminum silicates, found so abundantly, have resulted either from similar decomposition of aluminum silicate minerals or from their gradual comminution and deposit by aqueous agency.

Pottery and Ceramics.—The most important utilization of the clays is in the manufacture of the various grades of pottery and earthenware.

We may distinguish between the *infusible* clays, of which kaolin or "China clay" is an example, and *fusible* clays, of which the common clays for earthenware manufacture afford examples. To these may be added the colored clays used for the brick and terra-cotta industry. The difference in chemical character of these three groups may be seen from the subjoined type analyses:

	Kaolin.	Fusible Clay.	Brickmaker's Clay.
Silica	46.31 per cent.	66.38	49.44
Alumina	39.91 per cent.	26.08	34.26
Magnesia	0.44 per cent.	trace	1.94
Lime	0.43 per cent.	0.84	1.48
Ferrous oxide	0.27 per cent.	1.26	7.74
Water	12.69 per cent.	5.14	5.14
	100.05	99.70	100.00

From kaolin, to which has been added some powdered quartz and a so-called flux, usually feldspar, is made porcelain. Berlin hard porcelain consists of a mixture of kaolin 55 parts, quartz 22.5 parts, and feldspar 22.5 parts. The materials are thoroughly admixed in a finely ground and levigated condition with the aid of water, and after the articles are shaped on the potter's wheel or by hand they are dried and burned in the pottery kiln. The baked ware is known as "porcelain biscuit," and is then to be given a glaze. This is a mixture of silicate of alumina and alkalies, and is applied in a thin cream, dried on, and then burned again in the kiln at a temperature sufficient to cause uniform fusion on the surface. The hard porcelains which are intended to resist great heat are so made that the hard glaze is fired at about 1400° in one operation. Such ware is used for laboratory utensils, such as crucibles, dishes, etc. Another variety, or soft porcelain especially adapted for ornamental coloration, consists in first forming a vitreous mass from an alkali-earth silicate, which is covered with a lead glaze similar to flint glass composed of a mixture of sand, potassium nitrate, sodium chloride, sodium carbonate, gypsum, and alum. This is fired at a lower temperature.

Enamels, used for covering iron vessels, are applied by first coating with a glaze, consisting of a mixture of quartz, feldspar, borax, sodium carbonate, sodium fluosilicate, saltpetre, nickel and copper oxides with kaolin. This fusible enamel is covered with a white opaque enamel, likewise baked on, consisting of a mixture of quartz, feldspar, borax, cryolite, and saltpetre.

Stoneware utensils are extensively employed in the chemical industry for a great variety of purposes. They have a semi-vitrified surface which must withstand as much as possible the erosive action of various chemicals. The composition of the clay used is from 60 to 70 per cent. of SiO_2, 20 to 25 per cent. of

Al_2O_3, 0.5 to 1.5 per cent. of CaO and MgO, 1.5 to 3.5 per cent. of K_2O and Na_2O with Fe_2O_3 and moisture. The clay is mixed with alkali silicates, feldspar, and quartz, which serve as fluxes, and after moulding the ware is baked in kilns. To obtain a surface glaze moist sodium chloride is thrown into the furnace; through the high temperature with steam this decomposes into HCl and NaOH. The latter unites with the silica of the ware to form a fusible alkali-aluminum silicate, which covers the surface with the desired glaze.

Fire clay for firebricks contains about 45 per cent. of silica, 35 per cent. of Al_2O_3, with less than 1 per cent. of calcium and magnesium oxides and alkali.

Cements.—The natural clay limestones and artificial mixtures of similar composition are used in the manufacture of hydraulic mortars or cements. Common or Roman cements are prepared by burning natural calcareous clays or cement-rock at a temperature short of that required to cause the sintering of the mass. Portland cement, an artificial product, is made from mixtures of limestone and clay or natural cement-rock, of such composition that when burned the product will contain from 55 to 60 per cent. of lime, from 22 to 25 per cent. of silica, and about 7 per cent. of alumina. This variety is also burned until the mass is sintered together. It is then ground, allowed several months to season, and packed in barrels. These cements are essentially basic silicates of lime and alumina, and they " set " by virtue of their power of absorbing and combining with water, forming an artificial stone.

Ultramarine is a blue coloring matter, consisting of silica, alumina, soda, and sulphur, first found in the rare and costly mineral *lapis lazuli,* but since 1828 made artificially. A mixture of kaolin, charcoal, sulphur, and dried sodium carbonate is heated to redness in closed fire-clay crucibles, and the green mass thus formed is ground to powder and then gently roasted in thin layers with flowers of sulphur until the required blue shade is obtained. Part of the sodium in ultramarine is combined as a double silicate with alumina, and part is present as sulphide. Hence, when ultramarine is heated with hydrochloric or other acids, hydrogen sulphide is evolved and the blue color is destroyed.

Violet and red ultramarines are also prepared at present by conducting dry hydrochloric acid gas and air over common ultramarine at 100°–150°.

RARE EARTHS AND METALS

In some minerals which were formerly considered rare, like cerite, gadolinite, allanite, monazite, and samarskite, occur a number of metals, the oxides of which are very analogous to alumina in chemical characters. The chief source for these so-called rare earths is *monazite* sand, of which large deposits occur in Brazil and North Carolina. The composition of monazite sand varies according to the localities where it is found; that from near the sea coast contains from 5 to 7 per cent. of thoria, while the inland deposits contain from 4 to 5.5 per cent. The sand contains about 30 per cent. of cerium oxide, from 4 to 7 per cent. of thorium oxide, about 30 per cent. of lanthanum oxide, 24 to 30 per cent. of phosphoric acid, with small and variable percentages of alumina, yttria, calcium and iron oxides with silica, and 3 per cent. of titanic acid.

These elements are trivalent and form oxides of the general formula Me_2O_3; the hydroxides form white amorphous precipitates, which do not dissolve in alkali hydroxides; with alkali sulphates they form double salts and with hydrochloric, nitric, and oxalic acids crystalline salts.

Scandium (Sc = 44.1) is contained in euxenite and wolframite. Its oxide, Sc_2O_3, is a white, infusible powder like magnesia. It forms a hydroxide ($Sc(OH)_3$, and a double sulphate, $K_3Sc(SO_4)_3$, which is, however, not an alum and is insoluble in potassium sulphate solution. It is interesting as having been discovered since the announcement of the periodic system theory, and as filling a place pointed out in that system by its author Mendeléeff.

Yttrium (Yt = 89) is mostly obtained from gadolinite. It forms a potassium double sulphate, soluble in potassium sulphate solution, and thus separable from cerium, lanthanum, and didymium.

Lanthanum (La = 139) has been obtained by the electrolysis of its chloride as a white metal, malleable and ductile, and with a specific gravity of 6.16. Its oxide is a white, infusible powder, while its hydroxide is strongly basic and forms salts. It possesses pyrophoric properties like cerium.

Ytterbium (*Neoytterbium*) (Yb = 172) is obtained from the so-called erbium earths by fractional decomposition of the mixed nitrates by heating. Its oxide, Yb_2O_3, is a white, infusible powder, of specific gravity 9.17.

Cerium (Ce = 140.25), the most abundant of the rare earths, occurs in the mineral cerite and in monazite sand. The metal has been obtained by the electrolysis of the chloride. It is very similar to lanthanum, but burns more readily. Its specific gravity is 7; in appearance the metal resembles iron, but is soft like lead and through superficial oxidation becomes yellow. When the metal is filed a shower of sparks is produced (pyrophoric), hence is useful in making mechanical ignition boxes in which an alloy of cerium with 30 per cent. of iron is used. Cerium forms two oxides, cerous Ce_2O_3 and ceric CeO_2. The salts of the sesquioxide are colorless, while those obtained from the dioxide are yellow or brown.

Cerium Oxalate, $Ce(C_2O_4)_3$ (**Cerii Oxalas,** U.S.P.), "forms a fine, white or slightly pink powder, without odor or taste, and permanent in the air. Insoluble in water, alcohol, ether, or in solutions of potassium or sodium hydroxide; insoluble in cold but soluble in hot diluted sulphuric or hydrochloric acid. When heated to redness it is decomposed, leaving a residue of reddish-brown ceric and other rare earth oxides constituting not less than 47 per cent. of the salt." This official cerium oxalate is, however, not pure, but is "a mixture of the oxalates of cerium, didymium, and lanthanum, and other associated elements." Cerium oxalate is useful to allay vomiting.

The *Welsbach burner* or lamp consists of a Bunsen burner and a conoidal gauze or mantle. The Bunsen burner is attached to the usual outlet for gas. The mantle consists of a cone-shaped fabric of artificial silk, which is impregnated with a concentrated solution of thorium nitrate containing from 1 to 2 per cent. of cerium oxide. This is then dried and ignited, leaving a skeleton of the oxides, which is then immersed in a solution of collodion and dried. This mantle is supported above the burner in such a way that it is heated to whiteness by the non-luminous flame of the burner. The light emitted is brilliantly white, owing to the incandescence of the oxides of thorium and cerium. Thorium oxide emits a bluish-white, while cerium a reddish-white, light.

Neodymium (Nd = 144.3.)—This closely resembles praseodymium, but forms red colored salts.

Praseodymium (Pr = 140.6).—The salts are of a green color.

Samarium (Sm = 150.4) was discovered in samarskite. It is very similar to didymium. Its salts are yellow.

Erbium (Er = 167.7).—Found in certain titanium minerals; its salts are pink and have a sweet, astringent taste.

Terbium (Tb = 159.2).—The existence of this element was foretold in 1843. It occurs in samarskite.

Three rare heavy metals also form a sub-group belonging in the same group of the periodic system as aluminum—viz., gallium, indium, and thallium. They occur in various zinc blendes, also in American zinc ores.

Gallium (Ga = 69.9) was discovered in zinc-blende in 1875 by means of the spectroscope. It also exactly corresponded with one of the hypothetical elements indicated as possible by Mendeléeff in his periodic system. It has been obtained by the electrolysis of an ammoniacal solution of its sulphate as a white, hard metal of sp. gr. 5.9, with the low melting point of 30° C. Gallium does not react with water, is but slightly affected by HNO_3, and dissolves in HCl and alkalies. It forms a true alum, $Ga(NH_4)(SO_4)_2.12H_2O$.

Indium (In = 114.8) was discovered in 1863 by the aid of spectrum analysis in zinc-blendes from Freiberg. It is a silvery-white, soft, and tenacious metal of sp. gr. 7.4. It fuses at 176°, and when heated burns with a blue flame. It forms a true alum with ammonium sulphate.

Thallium (Tl = 204) is rather widely distributed in nature, being found in traces with potassium in carnallite, in mineral springs, and in some pyrites and zinc-blendes. It was discovered in the chamber sludge of the sulphuric-acid works by means of the spectroscope. It is a white metal, as soft as sodium, and with a sp. gr. 11.8. It fuses at 290°, and oxidizes rapidly in moist air. It burns with a beautiful green flame, in which the spectrum shows an intense green line, whence the name, from θαλλος, green. It forms two series of salts, thallous, derived from Tl_2O, and thallic, derived from Tl_2O_3.

CHAPTER VII

THE TIN GROUP (II and IV)

Germanium, Tin, and **Lead,** with **Carbon** and **Silicon,** form a group in which the elements exhibit a bivalency forming oxides of the type MeO; these possess basic characters, increasing with the atomic weights. The higher dioxides of the tetravalent elements exhibit decided acidic characters which decrease with the rise in atomic weight. The halogen compounds, MeX_4, excepting CX_4, are decomposed by water. A sub-group related to these includes Titanium, Zirconium, and Thorium.

GERMANIUM

Symbol, Ge. *Atomic Weight,* 72.5. *Valence,* II and IV.

This extremely rare element was discovered in 1886 by Winkler in *argyrodite* ($GeS_2.3Ag_2S$), a silver ore mined at Freiberg, Saxony.

Upon discovery it was found to possess the exact characteristics of the hypothetical eka-silicon, whose properties Mendeléeff, by the aid of his "Periodic Law," had predicted in 1871.

Germanium may be obtained through the reduction of the powdered mineral, which contains about 7 per cent. of the element, with charcoal in a current of hydrogen.

Properties.—Germanium is a white, brittle, crystalline metal, stable in air, with a specific gravity of 5.47, and fusing at about 900°. Heated on charcoal it melts to a metallic globule, and, like antimony, burns with a white smoke and produces a white incrustation, both due to the formation of germanic oxide, GeO_2.

Hydrochloric acid fails to dissolve the metal, which is readily soluble in nitrohydrochloric and also in concentrated sulphuric acid, forming soluble salts. Nitric acid converts it, like tin, into white hydrated germanic oxide, GeO_2, while concentrated solution of potassium hydroxide is without action. Zinc slowly deposits the metal from its solutions.

COMPOUNDS OF GERMANIUM

Like most of the members of the tin group to which this metal, through many of its properties, is related, germanium forms two series of compounds—viz., derivatives of GeO, unstable *germanous,* and those of GeO_2, the stable *germanic* compounds.

Germanous Chloride, $GeCl_2$, is little known. Germanic chloride, $GeCl_4$, obtained through direct action of chlorine on the metal, forms a fuming liquid which boils at 87°, which with water yields the *hydroxide* $Ge(OH)_4$. When heated in a current of hydrochloric acid, *germanium chloroform,* $GeHCl_3$, is obtained, which boils at 72°.

Germanous Oxide, GeO, a gray-black powder, is obtained by decomposing germanous chloride with potassium hydroxide. In hydrochloric acid solution it acts as an active reducing agent.

Germanic Oxide, GeO_2, a white powder, is prepared by treating the metal with nitric acid or by roasting the sulphide or hydroxide.

Germanic Sulphide, GeS_2, is obtained as a white precipitate through the action of hydrogen sulphide upon a strong hydrochloric acid solution of the dioxide. Soluble in alkalies and alkali sulphides, forming sulpho-salts.

TIN (Stannum)

Symbol, Sn. *Atomic Weight,* 119. *Valence,* II and IV.

For many ages antecedent to any progress in the working of iron, tin was known, and was employed in the production of bronze.

The Cassiterides, or "tin islands," spoken of by Herodotus, are supposed to have been the British Isles, from whence, after Cæsar's conquest, tin was carried to Rome.

Occurrence.—The most important ore of tin is the mineral *cassiterite,* or tin-stone, SnO_2.

It is usually accompanied by arsenopyrite (FeAsS) and pyrites (FeS_2). Besides the mines of Cornwall, England, those in Malacca, Banca, and Pulo Brani, near Singapore, are important, the last-named being the largest; the ore is known as *straits-tin.* Extensive mines are being developed in Australia. Tin is also found in Saxony, Bohemia, Mexico, Bolivia, South Dakota, and South Carolina.

Metallurgy.—When present in large quantity, the ore is picked out from the rock by hand; but, ordinarily, after stamping the rock to a coarse powder, the quartz and other minerals are washed away by a stream of water.

The ore is then roasted to expel sulphur and arsenic, while the iron present is converted into a light porous oxide, and the copper into the sulphate, the latter two being then removed by washing. The washed mass is mixed with powdered anthracite coal, and a little lime or fluorspar for the purpose of forming a slag, and then reduced on the hearth of a reverberatory furnace.

The impure metal obtained is cast into ingots, which are subjected to a well-regulated heat, by which means the tin is made to melt and run off, leaving behind a less fusible alloy of some tin with any iron or copper present.

The final purification is effected by agitating the molten metal. The lighter impurities rise to the surface and are skimmed off, the heavier settle to the bottom of the vessel, and from these the tin is ladled off into ingot moulds.

Practically all of the tin from scrap tin plate is now recovered, either electrolytically, in which the compressed scrap serves as anode and sheet iron the cathode in the presence of 10 per cent. solutions of caustic soda and sodium chloride. Sodium stannate, which forms at the anode, is reduced by hydrogen to spongy tin at the cathode. Or the scrap tin is treated under the Goldschmidt patents with dry chlorine, which leaves the iron and converts the tin into stannic chloride.

Properties.—Tin is dimorphous, crystallizing in forms belonging to the isometric and the quadratic systems. It has a white, lustrous appearance, is a good conductor of heat and electricity, and, on account of the friction of its crystalline particles, it emits, when bent, a cracking sound, designated as the "cry of tin."

It is softer than zinc, but harder than lead, with the exception of which its ductility is lowest of all the metals in common use, while in malleability it is surpassed by gold, silver, and copper only.

At 100° its ductility is increased, and it may be drawn into wire; at 200° it becomes brittle, and may be powdered; and at 232° it melts.

The specific gravity of the metal is 7.3 (13°). Tin is not affected by air or water at ordinary temperatures. If heated strongly, tin burns with an intense white light to its oxide, SnO_2. Cold dilute nitric acid dissolves tin to form stannous nitrate ($4Sn + 10HNO_3 = 4Sn(NO_3)_2 + NH_4NO_3 + 3H_2O$), while concentrated nitric acid oxidizes tin to metastannic acid ($3Sn + 4HNO_3 + H_2O = 3H_2SnO_3 + 4NO$), a white powder. In this respect tin differs from all other metals except antimony. Hydrochloric acid dissolves it with evolution of hydrogen and formation of chloride, while strong hot concentrated solutions of the alkalies act in a like manner with the production of metastannates, $Sn + 2KOH + H_2O = K_2SnO_3 + 2H_2$.

Tin is not affected by weak (organic) acids and alkalies.

Uses.—Pure metallic tin in the granulated or mossy state is directed by the United States Pharmacopœia to be used for the preparation of fresh stannous chloride as a reagent. The best tin, hammered to the proper thinness, constitutes *tin-foil,* but ordinary " tin-foil " consists largely of lead. Owing to its resistance to many chemical solutions, tin is used for tinning iron and copper vessels.

Tinned-plate is sheet-iron superficially coated with the metal in which the iron plate, previously washed in alkali and then HCl, is then dipped into molten tin. Terne-plate is iron coated with an alloy of tin and lead. Pins are made of brass wire coated in the same manner.

Alloys of Tin.—Tin forms with lead the useful alloys *pewter* and *solder,* with antimony and copper *britannia metal,* and with copper *gun-metal, bronze, bell-metal, speculum-metal,* and *phosphor-bronze,* the latter owing its hardness and elasticity to several per cent. of tin introduced as phosphide.

The so-called *fusible metals* are alloys which contain tin as their most important constituent. *Tin-mercury-amalgam* is largely used for silvering mirrors.

Tin forms two classes of derivatives, divalent or *stannous* and tetravalent or *stannic* compounds; the oxide of the latter is an acid (anhydride). The stannous salts pass readily into the " ic " state, hence are active reducing agents.

TIN AND THE HALOGENS

Stannous Chloride, $SnCl_2 + 2H_2O$.—The anhydrous salt may be obtained as a gray, fatty-looking substance by heating tin in hydrochloric acid gas. The hydrous chloride, $SnCl_2 + 2H_2O$, which is better known, is prepared by dissolving the metal in hot hydrochloric acid. Upon evaporating the solution and cooling the salt separates as colorless prismatic needles, which readily dissolve, when freshly made, in alcohol and small quantities of water. Upon exposure to the air or mixing with large volumes of water, stannous oxy- or basic chloride [$3SnCl_2 + O + H_2O = 2Sn(OH)Cl + SnCl_4$] forms, which requires the addition of a little hydrochloric acid for clear solution. Such acidified solutions when exposed change gradually to stannic chloride; to prevent this, some metallic tin should be added to the solution. At 100° the crystals part with their water. Under the name of *tin-salts* stannous chloride finds extensive application as a mordant in dyeing and in calico-printing. It is a strong reducing agent; for example, mercuric chloride is reduced to mercurous chloride, and when the stannous chloride is in excess the latter is reduced to mercury.

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl$$
$$2HgCl + SnCl_2 = SnCl_4 + Hg_2.$$

Stannic Chloride, $SnCl_4$, is made by conducting chlorine into a retort in which is placed stannous chloride, tin-foil, or fused tin. Stannic chloride is chiefly prepared by the Goldschmidt process by treating tin-plate scrap with dry chlorine. Thus obtained, it constitutes a colorless or yellowish fuming liquid, having a specific gravity of 2.23 at 15° C., and a boiling point of 114°. If to this liquid one-third of its weight of water be added, the latter combines with the stannic chloride, and a crystalline mass, known as *butter of tin,* $SnCl_4.3H_2O$, is obtained. With an excess of water stannic hydroxide precipitates, $SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl$. By dissolving the metal in a mixture of hydrochloric and nitric acid by the aid of heat, such a hydrous compound having the composition $SnCl_4 + 5H_2O$ is obtained. This last is the one best known, and is a valuable mordant for madder-red colors. With alkali chlorides stannic chloride forms crystalline double salts, as $SnCl_4.2KCl$; $SnCl_4.2NH_4Cl$, the latter being the "*Prime salt*" used as mordant in dyeing and in weighting silks. Stannous and stannic bromides, iodides, and fluorides are known.

TIN AND OXYGEN

Stannous Oxide, SnO, remains when stannous oxalate is ignited out of contact of air, or when stannous hydroxide is heated in a current of carbon dioxide. When heated in contact with air, stannous oxide is converted into stannic oxide.

It is a white or brown powder, soluble in acids and concentrated solutions of the alkalies.

Stannous Hydroxide, $Sn(OH)_2$, forms as a white precipitate upon the addition of an alkali hydroxide or carbonate to a solution of stannous chloride. Soluble in an excess of caustic potash or soda (to form *stannites,* $Sn(ONa)_2$), but insoluble in ammonia.

Stannic Oxide, SnO_2, occurs native as tin-stone or cassiterite. Artificially it is produced as a fine white powder by strongly heating tin or stannous oxide in free access of air. It is then known as "putty powder," and is used as a polishing agent. Ignition of stannic hydroxide, obtained by precipitation, and of metastannic acid, obtained when tin is treated with nitric acid, also yields it. Stannic acid is not easily attacked by concentrated acids. When fused with alkalies, soluble alkali stannates are produced.

Stannic Hydroxide, Stannic Acid, $SnO(OH)_2$, is obtained when a solution of stannic chloride is treated with an alkaline hydroxide, or when a solution of a stannate is carefully precipitated by an acid. The stannic hydroxide exhibits acid properties, reddening blue litmus paper. It dissolves readily in acids, forming stannic salts, and in alkali hydroxides, forming *stannates* (Na_2SnO_3).

Metastannic hydroxide or acid (H_2SnO_3) results when hot nitric acid acts on tin. It is distinguished from stannic acid by being altogether insoluble in nitric acid. Metastannic acid dissolves in caustic alkalies, forming metastannates, solutions of which readily pass into the more complex form of $Me_2Sn_5O_{11}.4H_2O$.

TYPICAL REACTIONS OF STANNOUS SALTS

(1) Hydrogen sulphide or alkali sulphides precipitate brown stannous sulphide, soluble in alkali polysulphides, forming sulphostannates. $SnS + Na_2S_2 = Na_2SnS_3$.

(2) Solutions of alkali hydroxides and carbonates precipitate stannous hydroxide. $SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2NaCl + CO_2$. Soluble in acids and alkali hydroxides (stannites); the latter undergo decomposition in aqueous solution when heated or on standing. $2Sn(ONa)_2 + H_2O = SnO(ONa)_2 + Sn + 2NaOH$.

(3) Stannous chloride reduces solutions of several metals, as mercuric, ferric, cupric or gold chlorides, also permanganates and dichromates. The detection of arsenic by Bettendorff's reagent is based on its reduction according to the equation:

$$3SnCl_2 + 2AsCl_3 = 3SnCl_4 + As_2.$$

TYPICAL REACTIONS OF STANNIC SALTS

(1) Hydrogen sulphide and soluble alkali sulphides precipitate yellow stannic sulphide, soluble in alkali hydroxides and sulphides, forming sulphostannates. $3SnS_2 + 6KOH = 2K_2SnS_3 + K_2SnO_3 + 3H_2O$. $SnS_2 + K_2S = K_2SnS_3$.

(2) Solutions of alkali hydroxides and carbonates precipitate stannic hydroxide, soluble in excess of the former, forming stannates.

$$Sn(OH)_4 + 2KOH = K_2SnO_3 + 3H_2O.$$

OXYGEN SALTS OF TIN

By far the most important compound of this class is sodium stannate, $Na_2SnO_3 + 3H_2O$. It is prepared either by fusing the stannic oxide with alkali, or the metal with alkali and sodium nitrate, or by dissolving the hydrated oxide in a solution of a caustic alkali. Under the name of "preparing salts" it is extensively employed in calico-printing. The salt forms hexagonal crystals. The stannates of the alkali metals are soluble, those of the earthy and heavy metals insoluble in water, and may be prepared by precipitation of the soluble stannates. The metastannates of the alkali metals are also used in dyeing. Stannous nitrate, stannous sulphate, stannic nitrate, and stannic sulphate are all known. The salts of tin possess an unpleasant metallic taste and an acid reaction.

TIN AND SULPHUR

Stannous Sulphide, SnS, is obtained by heating together the metal and sulphur, or by precipitating a solution of stannous chloride with hydrogen sulphide. When obtained by the first process it is a lead-gray, tough, crystalline mass; from the second method of preparation it forms a brown precipitate, which becomes black on drying. It is soluble in alkali polysulphides, forming alkali sulphostannates.

$$SnS + K_2S_2 = K_2SnS_3, \text{ or}$$
$$SnS + (NH_4)_2S + S = (NH_4)_2SnS_3.$$

Stannic Sulphide, SnS_2.—This well-known compound is usually obtained by heating together tin-amalgam, sulphur, and sal-ammoniac, whereby it is obtained in gold-colored, translucent scales. It is used largely for bronzing articles of gypsum and wood, and is known as "mosaic gold." It is also obtained as a yellow amorphous powder on passing hydrogen sulphide into the acid solution of a stannic salt.

LEAD (Plumbum)

Symbol, Pb. *Atomic Weight,* 207.10. *Valence,* II and IV.

History.—Lead has been known from the earliest times; its extraction from ores and use in making water-pipes was described by Pliny. Lead was designated *Saturn* by the alchemists.

Occurrence.—By far the most abundant and important ore of lead is the sulphide or *galena,* PbS; this is very widely distributed, usually occurring with quartz, fluorspar, calcspar, and heavy spar. The most important deposits in England are those of Cornwall and Cumberland. In the United States there are two localities which furnish the chief supply of lead—the Rocky Mountain district, in which the lead is a by-product in the metallurgy of silver, and the Mississippi Valley district, in which galena is worked for lead alone. The ores are known respectively as argentiferous and non-argentiferous, the former furnishing by far the greater proportion of lead. *Cerussite* or native carbonate, $PbCO_3$, and *anglesite* or native sulphate, $PbSO_4$, are ores of minor importance when compared with galena.

Metallurgy.—Lead is almost exclusively prepared from galena. In case the ore is nearly free from other metallic sulphides and silica, it is roasted in a reverberatory furnace, whereby a part of the sulphide is converted into oxide and sulphate; air is then excluded, the temperature is increased, when the following reactions take place with formation of metallic lead:

$$PbS + 2PbO = 3Pb + SO_2.$$
$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

This is known as the *air reduction process,* and is conducted in a furnace as shown in Fig. 112. The furnaces are constructed to hold 20 tons of ore, which is introduced at T, and evenly spread over the hearth, through openings at O; the hearth is hollowed out at B, so as to allow the metal to collect, and from which it can be drawn out by a tap-hole into an iron pot. When the ore is impure, charcoal is used to assist in the reduction. Small quantities of other metals are removed by melting the lead, and subjecting it to the oxidizing action of a current of air in a reverberatory furnace. The impurities oxidize first, rise to the surface, and are removed as slag.

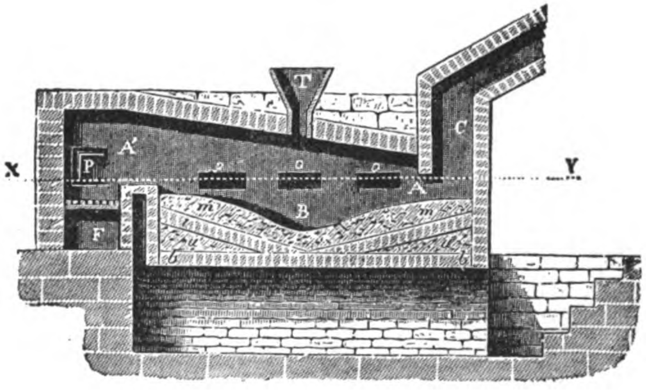
When argentiferous lead ores are worked the process becomes modified according to the richness of the ore in silver, or the lead is further treated.

If silver predominates, the ore is oxidized and cupelled as described under that metal. It is much oftener the case that the lead predominates, when Pattinson's process of desilverization is employed. This consists in cooling the melted metal, when pure lead first crystallizes out and is removed by perforated ladles. In this way a metal very rich in silver is obtained, which is cupelled for the removal of the lead from the silver.

Parke's process for desilvering lead is based on the fact that melted lead dissolves but little zinc, and that zinc alloys readily with silver, so that by adding a certain proportion of zinc to the argentiferous lead an alloy of zinc and silver is formed, which rises to the top and solidifies. It is then removed by ladling, the zinc removed by mixing with carbon and distilling. What lead remains with the silver is removed by cupelling.

Properties.—Lead is a bluish-gray, lustrous metal; it is soft and malleable, but is not capable of being drawn into wire. It is easily cut with a knife, and when drawn over white paper leaves a gray streak. Lead has a specific gravity of 11.37, melts at 327°, and quickly becomes covered with a layer of oxide which protects it from further atmospheric oxidation; at red heat it vaporizes slowly, and when heated to whiteness distils. Melted lead crystallizes, when cooled slowly, in regular octahedrons.

FIG. 112.



Lead furnace.

Distilled water, free from dissolved gases, exerts little if any solvent action upon lead. Rain water, which contains oxygen, carbon dioxide and traces of ammonia, forms a basic lead carbonate ($PbCO_3.Pb(OH)_2$) which is slightly soluble in water charged with these gases. The film of oxide which forms upon the surface of lead is insoluble in natural waters containing soluble carbonates and sulphates, hence hard waters may be carried through lead pipes without danger of contamination. For carbonated water (soda water) blocked tin pipes (lead covered with tin) are used. Concentrated hydrochloric or sulphuric acid attacks lead but slightly when cold. It is soluble in boiling concentrated or diluted hydrochloric acid, lead chloride being formed. With hot concentrated sulphuric acid lead sulphate forms over the surface of the metal (see lead chamber acid). Lead is readily attacked by nitric acid with the formation of lead nitrate and oxides of nitrogen. In the presence of air (O_2), lead acetate is formed upon treatment with acetic acid (see white lead).

Uses.—Because of its relative resistance to the corrosive action of air, water, and acids, lead is extensively employed industrially for evaporating pans, pipes, retorts, lining of chambers, etc.; in such instances joints are made by autogenous welding (lead burning) and not by soldering. Bullets and shot are made of lead; the latter contain one-half per cent. of arsenic in order to give them a spherical form.

Storage Batteries.—Spongy lead and lead peroxide form the active elements of the storage battery described on page 75. The chemical reactions involved in their charging (energy consuming) and discharging (liberated energy) may be described as follows: leaden grids, used in pairs, the openings of which are filled with a paste of diluted sulphuric acid and red lead (or litharge), and dried. These are immersed in diluted sulphuric acid, which serves as the exciting fluid. Each plate is connected with a dynamo current, the negative terminal of which is connected with the intended negative plate and the positive with the intended positive plate. The $H^{\cdot}$ ions of the bath (acidulated water undergoing electrolysis) are attracted to the plate with the negative charge, causing liberation of the SO''_4 ions and formation of spongy lead; that is, the lead sulphate is reduced by the hydrogen to spongy lead.

$$PbSO_4 + 2H^{\cdot} \longrightarrow Pb + 2H^{:} + SO''_4.$$

At the same time, the SO''_4 ions are attracted to the positive charged plate, forming lead persulphate with the lead sulphate, thus:

$$SO''_4 + PbSO_4 \longrightarrow Pb(SO_4)_2.$$

This lead persulphate hydrolyzes immediately when the plates are discharging, forming lead peroxide: $Pb(SO_4)_2 + 2H_2O \longrightarrow PbO_2 + 2H_2SO_4$. Hence it is customary to consider this as a PbO_2 plate.

In the reaction involved in the discharge of the battery plates immersed in dilute sulphuric acid, the SO''_4 ions migrate toward the plate containing the spongy lead, converting this into $PbSO_4$ and imparting a negative charge, thus $SO''_4 + Pb \longrightarrow PbSO_4$. Simultaneously the $H^{\cdot}$ ions migrate towards the other plate of PbO_2, reducing this to lead monoxide, imparting a positive charge, thus: $2H^{\cdot} + PbO_2 \longrightarrow H_2O + PbO$. During the discharge there is a loss in free sulphuric acid and consequent decrease in specific gravity of the exciting fluid, due to its combination with the lead.

The chemical changes involved in the charge and discharge may be summarized thus: $\overset{\text{charge}}{2PbSO_4 + 2H_2O} \rightleftarrows \overset{\text{discharge}}{Pb + 2H_2SO_4 + PbO_2}$.

Alloys of Lead.—Lead enters largely into the composition of a number of useful alloys. *Type-metal* is composed of 2 parts lead, 1 part each of antimony and tin. *Solder* consists of 1 part lead and 2 parts tin; a common variety is made of equal parts of these two metals.

Babbitt metal for antifriction bearings consists of nearly equal amounts of lead and tin with smaller amounts of antimony and a trace of copper.

LEAD AND OXYGEN

Lead forms five compounds with oxygen, viz.: Pb_2O, PbO, Pb_2O_3, Pb_3O_4, and PbO_2.

Lead Suboxide, Pb_2O.—This compound is formed on the surface of melted lead when the temperature is not too high. It may be prepared by heating lead oxalate in an atmosphere free from oxygen and at a temperature below 300°,

$2PbC_2O_4 = Pb_2O + CO + 3CO_2$. It is a black, velvety powder, which yields salts and metallic lead with acids.

Lead Monoxide, PbO. **Plumbi Oxidum,** U.S.P. *Litharge*.—There are two varieties of lead oxide in commerce—namely, ***massicot,*** which is yellow in color and prepared by the prolonged heating of lead at a moderate temperature, and *litharge,* which is obtained when massicot is melted (850°) or lead has been heated at a much higher temperature, and is a by-product in the desilverization of lead ores. Litharge obtained at a temperature sufficiently high to fuse it solidifies in shining, scaly masses, which are sometimes of a yellowish color, but oftener inclining to red, due to the presence of some red oxide. From 1 to 3 per cent. of finely subdivided lead is also frequently present.

Properties.—The official oxide is "a heavy, yellowish, or reddish-yellow powder, or minute scales, without odor or taste. On exposure to the air it slowly absorbs moisture and carbon dioxide." It is almost insoluble in water, but when left in contact with it imparts to it an alkaline reaction. Litharge is a strong base and is soluble in acetic and dilute nitric acids, also in solutions of sodium and potassium hydroxides, forming plumbites (K_2PbO_2). Litharge should not be fused in clay or porcelain crucibles, since it unites with the silica to form a readily fusible lead silicate.

On the application of heat lead oxide assumes a brownish-red color, and at a red heat it fuses, becoming yellow on cooling. When heated before the blow-pipe on charcoal it yields metallic lead.

Uses.—Litharge is used in the manufacture of flint glass, and is a constituent of the glaze used for earthenware. It is used in preparing various lead compounds, especially **Emplastrum Plumbi,** U.S.P.

Lead Sesquioxide, Pb_2O_3, is formed as a reddish-yellow powder when a cold solution of lead peroxide in sodium hydroxide is mixed with a solution of sodium hypochlorite. This oxide is a lead salt of the acid H_2PbO_3($PbPbO_3$), and since it is decomposed by dilute nitric acid into PbO_2 (the anhydride of H_2PbO_3) and lead nitrate, it may therefore be considered to be a mixture of Pb and PbO_2.

Red Lead or Minium, Pb_3O_4.—Obtained by heating litharge in a reverberatory furnace at about 450°, whereby oxygen is absorbed. It may also be obtained by heating litharge with sodium nitrate in an oxidizing flame or heating a mixture of lead sulphate, sodium nitrate, and carbonate. Minium is of a bright red color and consists of a mixture of 2PbO and PbO_2. This may be proven by treatment with diluted nitric acid, which dissolves the PbO, leaving undissolved the brown PbO_2. When heated, red lead becomes a dark brown, but on cooling it regains its red color. When added to hydrochloric acid, chlorine is evolved, $Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O$. Red lead is used in paints, glass, and match manufacture.

Lead Dioxide or *Peroxide,* PbO_2.—This is also known as *puce-colored lead oxide.* It is obtained by passing chlorine into an alkaline solution of a lead salt:

$$2PbCl_2 + 2KOH + 2H_2O + 2Cl_2 = 2PbO_2 + 2KCl + 6HCl.$$

Also through action of alkali peroxides upon a solution of lead plumbate. The peroxide may be prepared electrolytically from a solution of lead nitrate, separating at the anode. It is also readily obtained by treating red lead with diluted nitric acid.

Lead peroxide is a dark-brown, amorphous powder, which is readily decomposed by heat into lead monoxide and oxygen. The U. S. P. reagent assays

90 per cent. peroxide. It partakes of the nature of an acid anhydride, the salts being called plumbates, *ortho*, $Me^{I}_4PbO_4$, and *meta*, $Me^{I}_2PbO_3$, which with an excess of water break up into the alkali hydroxide and lead peroxide. When heated, this compound gives up half of its oxygen, hence is an active oxidizing agent. With hydrochloric acid, chlorine is evolved, $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$. With oxalic acid the reaction is as follows: $PbO_2 + 2COOH = PbO + 2CO_2 + H_2O$.

Lead peroxide is employed as an oxidizing agent in analytic work; also it forms the active plate of storage batteries.

Lead Hydroxide, $Pb(OH)_2$, Plumbous Hydroxide, is obtained as a voluminous white precipitate upon adding a solution of an alkali hydroxide to a solution of a lead salt until of an alkaline reaction, $Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$. This precipitate is insoluble in ammonia, but soluble in an excess of caustic alkali, forming plumbites, $Pb(ONa)_2$ or $Pb(OK)_2$. Lead hydroxide is slightly soluble in water; it is formed through the action of water containing dissolved oxygen on lead. Lead hydroxide when heated yields yellow PbO.

LEAD AND THE HALOGENS

Lead Chloride, $PbCl_2$.—A white, crystalline powder obtained usually by precipitation, through the addition of hydrochloric acid, or a concentrated solution of sodium chloride to a concentrated solution of a lead salt. It is almost insoluble in cold, but soluble in 30 parts of boiling water, crystallizing in anhydrous needles. Lead chloride unites with lead oxide to form basic salts, oxychlorides; the same being obtained on heating ammonium chloride with litharge. These basic salts are used as yellow pigments.

Lead Bromide, $PbBr_2$, is obtained by treating a soluble lead salt with solution of potassium bromide. In many respects it resembles the chloride.

LEAD IODIDE, PbI_2.

Preparation.—One part of lead nitrate in 20 parts of water is poured, with constant stirring, into 1 part of potassium iodide in 10 parts of water.

The resulting precipitate is collected on a filter, washed well with cold water, and carefully dried. Instead of the lead nitrate, one may use 9 parts of lead acetate in 90 parts of water acidified with a little acetic acid, and 8 parts of potassium iodide in 80 of water.

Properties.—Lead iodide is a heavy, bright yellow powder, without odor or taste; soluble in about 1300 parts of water at 25° and in 200 parts of boiling water, separating from the latter solution in brilliant, golden-yellow spangles or crystalline laminæ. Very slightly soluble in alcohol, but soluble, without color, in solutions of the fixed alkalies, in concentrated solutions of the acetates of the alkalies, of potassium iodide, and of sodium thiosulphate, and in a hot solution of ammonium chloride. When moderately heated, the salt fuses to a thick, reddish-brown liquid, which congeals, on cooling, to a yellow, crystalline mass. At a higher temperature it is decomposed, with the evolution of vapors of iodine, leaving a lemon-yellow residue of lead oxy-iodide.

Uses.—The principal use of lead iodide is in medicine, where it is employed externally in the form of an ointment.

Lead Fluoride, PbF_2, is precipitated as a white insoluble powder when hydrofluoric acid is added to a soluble salt of lead.

OXYGEN SALTS OF LEAD

Lead Sulphate, $PbSO_4$, is found in nature as *lead vitriol* or *anglesite*, in transparent rhombic crystals, isomorphous with those of strontium and barium sulphate. It is formed as a white, heavy, insoluble crystalline mass on adding sulphuric acid or a soluble sulphate to a soluble lead salt. Lead sulphate is slightly soluble in sulphuric acid and in concentrated solutions of the caustic alkalies; upon diluting the former, lead sulphate again precipitates. Lead sulphate is soluble in ammonium tartrate containing an excess of ammonia, also soluble in solutions of sodium thiosulphate or ammonium acetate. When heated with sodium carbonate, lead carbonate and sodium sulphate are formed.

LEAD NITRATE, $Pb(NO_3)_2$.

Preparation.—This salt is prepared by adding, in small portions at a time, 10 parts of lead oxide to 23 parts of nitric acid (25 per cent.), previously mixed with an equal weight of water and warmed:

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

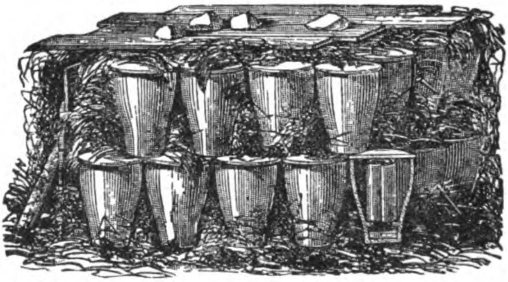
The solution is filtered, and, after the addition of a few drops of nitric acid, is set aside to crystallize.

Properties.—Lead nitrate crystallizes in colorless octahedral crystals, isomorphous with the nitrates of barium and strontium. When these crystals separate from hot solutions they are white and opaque, but if formed by the spontaneous evaporation of cold solutions they are transparent. The salt is soluble in 1.85 parts of water at 25° C. and in 0.75 part of boiling water; almost insoluble in alcohol. On the application of heat nitrogen dioxide and oxygen are evolved and a residue of lead oxide remains. $2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$.

Uses.—Lead nitrate is used in the manufacture of mordants for dyeing and calico-printing, in the manufacture of lead chromate, matches, fireworks, and as a reagent in the U. S. P.

Lead Carbonate, $PbCO_3$.—The normal lead carbonate is found in nature as the mineral *cerussite*, or it may be artificially prepared by precipitating a solution of lead acetate with one of ammonium carbonate, or by passing carbon dioxide through the former solution. This compound is not much used.

FIG. 113.



Dutch process for making white lead.

Basic Lead Carbonate, $(PbCO_3)_2Pb(OH)_2$. *White Lead.*—This compound was known to the ancients. The commercial white lead varies in chemical composition and covering power according to the method and conditions of preparation, consisting in some instances of almost pure carbonate, while in most others a variable mixture of from one to three molecules of lead carbonate to one of lead hydroxide. The hydroxide serves to form an insoluble soap with linseed oil when used as a paint.

Preparation.—White lead is manufactured on a large scale by several processes, in which lead acetate serves as a catalyzer in accelerating the combination of lead carbonate and oxide.

1. *The Dutch Process* is the oldest, and is still in use, being often referred to as the "corrosion process." It consists in placing coils or buckles of lead in earthenware pots, in the bottom of which is a small quantity of vinegar or crude pyroligneous acid. The lead is placed on projections in the pots so as not to come in direct contact with the liquid; the walls of the pots are perforated just above the vinegar, so as to allow a free circulation of air and gas. A number of the pots are placed together, as shown in Fig. 113, and after covering each with a wooden plate they are surrounded with horse manure or spent tan-bark. The fermentation of the manure or tan causes the requisite elevation of temperature to vaporize some of the acetic acid of the vinegar,

which "corrodes" the lead with the formation of basic lead acetate. This is slowly converted into carbonate by the carbon dioxide which results from the fermentation. After some weeks the lead will be found wholly converted into basic carbonate.

2. In the *English Method* sheet-lead is melted on the hearth of a reverberatory furnace so as to convert it into oxide, and this, in turn, is intimately mixed with a small quantity of solution of lead acetate. The resulting mass is placed in a series of closed troughs communicating with one another, and so arranged as to admit the passage of a current of carbon dioxide. This gas is obtained by the combustion of coke in a furnace provided with a blast to give impulse to the gas.

3. The *German* or *Chamber* process involves the action of acetic acid and carbon dioxide vapors with steam on lead plates hung or placed on horizontal gratings in closed chambers, the temperature being maintained at about 60°. A basic acetate is formed on the plates, which is converted into a basic carbonate by coke furnace gases containing carbon dioxide.

4. The *French Method* consists in dissolving an excess of lead or lead oxide in acetic acid, so as to form basic lead acetate, and then passing carbon dioxide into this solution, by which means two molecules of lead oxide are converted into basic carbonate, while neutral acetate of lead remains. This is again converted into basic acetate, which is, in turn, decomposed by more carbon dioxide.

Many more processes have been patented and worked in a small way in the production of white lead, but it is probable that in this country, as well as in most foreign countries, the Dutch process is given the preference.

The product of all the foregoing processes is finely ground with water, well washed to remove lead acetate, and finally dried.

Properties.—Basic lead carbonate is a heavy, white, amorphous, inodorous and tasteless powder, permanent in the air. It is insoluble in water, soluble in acetic and diluted nitric acid; sulphuric and hydrochloric acid convert basic lead carbonate into their respective insoluble salts. When heated to 200° basic lead carbonate turns yellow without charring, giving off its carbon dioxide, leaving a residue of oxide.

Uses.—White lead is frequently mixed with gypsum, and with barium sulphate or heavy spar, which diminishes its covering power as a paint. *Hamburg white* is a mixture of 1 part white lead and 2 parts barium sulphate. *Dutch white* contains 3 parts of the barium sulphate to 1 part of white lead. The amount of barium or calcium salt is readily determined by treating the powder with warm acetic or dilute nitric acid, which will dissolve only the lead salt. Lead sulphate is sometimes used as an adulterant.

Paint is chiefly made by grinding white lead with oil, and then thinning with linseed oil or oil of turpentine, according to the use to which it is to be applied. Lead paint, when exposed for some time to the action of hydrogen sulphide, turns yellow, then brown, and finally black.

LEAD AND SULPHUR

Lead Sulphide, PbS, is very widely distributed in nature as the most important lead ore, called *galena*, which occurs in cubes of a gray metallic luster. It may be artificially prepared by passing hydrogen sulphide into a solution of lead acetate. It is a black, insoluble powder, which is scarcely dissolved by hydrochloric acid, but converted by hot concentrated nitric acid into lead sulphate. At a red heat it melts, and it may be sublimed in a current of carbon dioxide or hydrogen. Lead sulphide is used in the glazing of certain kinds of pottery-ware.

TITANIUM, ZIRCONIUM, THORIUM

These elements present analogies to the carbon silicon group parallel to the relationship of Ca, Sr, Ba to Mg and Be. They are tetravalent. Titanium and Zirconium form acid oxides, while Thorium yields only a basic oxide.

TITANIUM

Symbol, Ti. *Atomic Weight,* 48.1. *Valence,* IV.

Occurrence.—Titanium occurs as oxide, TiO_2, under the names of *rutile, anastase,* and *brookite,* and in titanates such as $CaTiO_3$ and $FeTiO_3$.

Metallurgy and Properties.—The metal is a gray, metallic powder or steel-like mass which melts at 1795°. It burns when heated in the air, and is dissolved by dilute hydrochloric or sulphuric acid with evolution of hydrogen. Titanium, because of its affinity for oxygen and nitrogen when heated, is used for toughening steel. It is obtained by heating the oxide with powdered aluminum.

COMPOUNDS OF TITANIUM

Titanium Cnloride, $TiCl_4$, and *Titanium Fluoride,* TiF_4, are known. The latter forms compounds like K_2TiF_6, analogous to the silico-fluoride of potassium, K_2SiF_6.

Titanium is one of the elements that combine directly with nitrogen to form the *nitride* TiN.

Titanic Acid, H_4TiO_4, is obtained as a white, amorphous powder on adding ammonium hydroxide to the hydrochloric acid solution of the titanates. It readily loses 1 molecule of H_2O, and becomes $TiO(OH)_2$, analogous to $CO(OH)_2$.

Titanium Dioxide (acid anhydride), TiO_2, is abundantly found in nature. It is a white powder which becomes yellow on heating, almost insoluble in the acids, and forms titanates on fusion with the alkalies.

ZIRCONIUM

Symbol, Zr. *Atomic Weight,* 90.6. *Valence,* IV.

Zirconium is relatively rare, being generally found as the silicate $ZrSiO_4$, called *Zircon.* The metal can be obtained as an amorphous gray powder or in crystalline metallic leaflets.

Zirconic Acid or *Hydroxide,* $Zr(OH)_4$, is precipitated from acid solutions by ammonia water as a white, voluminous precipitate, which, on ignition, leaves

Zirconium Dioxide, ZrO_2.—Both this oxide and the hydroxide dissolve when warmed with sulphuric acid, forming $Zr(SO_4)_2$, which may be crystallized from water.

THORIUM

Symbol, Th. *Atomic Weight,* 232.4. *Valence,* IV.

Thorium was first obtained by Berzelius from the Norwegian mineral *thorite* ($ThO_2.SiO_2$) in 1828. At present the chief source of thorium is monazite sand, which occurs in extensive deposits in Brazil and North and South Carolina (see page 444). This sand consists chiefly of the phosphates of the rare earths, cerium, lanthanum, yttrium, præsodymium, and neodymium, with variable amounts of thorium. After washing, the sand yields from 5 to 7 per cent. of ThO_2. The impurities present are iron oxide, lime, alumina, and silica. For isolation of the thoria, several methods are employed, in one of which the pulverized sand is heated with twice its weight of sulphuric acid; after cooling, the mass is treated with water, which dissolves the thorium and other rare-earths present, as sulphates and phosphates. If this solution be partially neutralized with magnesium oxide, thorium is precipitated in the first fraction. Further purification may be effected by precipitating as oxalate from its solution in moderately concentrated nitric acid, since thorium oxalate is the least soluble of all rare-earth oxalates in acids. The same is true of the phosphates, that of thorium being the most insoluble in dilute acids. The metal is obtained by heating thorium tetrachloride with Na in a vacuum. It has a gravity of 12.1, fuses above 1700°, is soft and ductile, and is very slowly attacked by acids excepting aqua regia.

Thorium Hydroxide, $Th(OH)_4$.—This forms a gelatinous precipitate when ammonia water is added to a solution of a soluble thorium salt. When the hydroxide is heated to redness, thorium oxide, ThO_2, results. The oxide and hydroxide are the most basic of this group, forming salts with acids, but not with alkalies.

Thorium Chloride, $ThCl_4$.—Prepared by heating a mixture of thorium oxide and charcoal in a current of chlorine or by heating the oxide in a current of carbon tetrachloride vapor. $ThO_2 + 2CCl_4 = ThCl_4 + 2COCl_2$. The salt forms white crystals, soluble in water, from which it crystallizes as $ThCl_4.8H_2O$.

Thorium Sulphate, $Th(SO_4)_2.9H_2O$.—Very slightly soluble in water and insoluble in dilute acids.

Thorium Nitrate, $Th(NO_3)_4.12H_2O$, when crystallized from cold solutions; from hot solution, the salt crystallizes with $6H_2O$. Hygroscopic white crystals readily soluble in water and alcohol. When heated, thorium nitrate yields thorium oxide. This salt is used in the preparation of Welsbach mantles.

Thorium belongs to the radio-active elements (page 472). Precipitation of thorium hydroxide from a solution of its salt removes most of its radio-activity. The filtrate, which now possesses the greater part of the emanating power of the original solution of the salt, on evaporation to dryness and ignition to remove the ammonia salts, leaves a radio-active slight residue, which is called *Thorium X*. This radioactivity is of but short duration. If thorium hydroxide be dissolved in an excess of ammonia, a small insoluble fraction remains behind; if this be dissolved in HCl and a little $ZrCl_4$ added and then ammonia water, *Mesothorium* I is precipitated, while *Mesothorium* II remains in solution. Mesothorium I is rayless and identical chemically with radium. Hence all radium obtained from uranium minerals containing thorium contains mesothorium; also all mesothorium preparations contain the radium present in the mineral from which they are obtained. Mesothorium II emits gamma and beta rays.

BISMUTH

Symbol, Bi. *Atomic Weight,* 208. *Valence,* III and V.

Bismuth Group.—Bismuth is a member of the fifth periodic group which includes Vanadium, Niobium, and Tantalum, as well as the electronegative elements N, P, As and Sb. The latter four elements form gaseous hydrides, acid-forming oxides, and belong to the non-metals, while the former do not form hydrides, and the oxides are basic, especially those of bismuth.

History.—Probably bismuth was first distinctly recognized in 1450 by Basil Valentine, who attempted to classify it with other metals. In the following century, Paracelsus classed it among the *semi-metals,* but it was afterwards proposed as a true metal by Agricola. Although clearly described by the last author, bismuth was subsequently confounded with other metals, especially with antimony and zinc, until 1739, when Pott contributed to the more accurate knowledge of the element. The name is derived from the German, *Wismuth.*

Occurrence.—The sources of bismuth are not numerous. Both the metal and its ores are generally disseminated through rock, the chief deposits occurring in Saxony, Bohemia, Bolivia, Colorado, Utah, Mexico, and Australia. The chief source at present is Bolivia.

In addition to the free metal, it is found as *bismuth-ochre,* Bi_2O_8, and associated with many of the heavy metals, as copper, iron, lead, nickel, cobalt, and silver with arsenic, sulphur, and selenium. The South American bismuth is usually quite pure and free from arsenic.

Metallurgy.—The process of obtaining the metal usually applied in the past consisted in heating the ore in iron tubes inclined in such a way that the easily fusible metal could run off into proper receptacles. This method extracted only that part of the bismuth which existed in the free state.

At present the ores are roasted to expel most of the sulphur, and part of the arsenic then fused in small furnaces with iron and coal to remove sulphur, and reduce the ore, and slag to facilitate the operation. The molten mass so obtained is allowed to stand, when a separation into two layers occurs, the lower being nearly pure bismuth. When the upper layer, which consists of the cobalt-speiss, iron, nickel, silver, and lead, has hardened, the still liquid bismuth is transferred to ingot moulds.

When the metal occurs in ores of lead and silver, it is extracted from the slag, in which it collects in quantity from 5 to 20 per cent., by nitrohydrochloric acid, and subsequently precipitated as basic chloride by water, or as metal by means of iron. In all such cases it is finally reduced by soda-ash and coal.

Bismuth is generally sent into commerce in ingots which weigh from 10 to 12 kilograms.

Properties.—Bismuth is isomorphous with arsenic and antimony, resembling the latter in general appearance, but may be distinguished by its roseate reflex. It possesses a highly crystalline structure and is very brittle. When melted and allowed to cool, the metal expands quite notably.

Bismuth is the most diamagnetic of all known bodies, a good conductor of electricity, but a poor conductor of heat. It combines directly with the halogens and sulphur, and has a specific gravity of 9.83.

It melts at about 268° and at a white heat (about 1420°) may be distilled in hydrogen. It is permanent in air at ordinary temperatures, but when heated before the blowpipe on charcoal yields bismuth trioxide as a brown incrustation, which becomes yellow on cooling.

Hydrochloric acid does not dissolve the metal, but it is soluble in nitrohydrochloric acid, nitric acid, and in hot concentrated sulphuric acid. Bismuth combines readily with the halogens. When nitric acid of specific gravity 1.2 is employed, the presence of larger quantities of arsenic may be detected by the white deposit of insoluble bismuth arsenate.

The soluble salts of bismuth when diluted with large volumes of water precipitate as basic salts similar to those of antimony.

Commercial bismuth, the Bolivian being the purest, contains small amounts of such impurities as arsenic, iron, lead, silver, copper, etc.; these are removed in the preliminary precipitations necessary in the preparation of its various basic salts.

Uses.—The insoluble (basic) salts of bismuth, more especially the subnitrate and subcarbonate, are extensively employed in medicine. The soluble salts are toxic. Metallic bismuth is a valuable constituent in various alloys.

Alloys.—The presence of bismuth materially lowers the fusing point of alloys, and on that account, as also because of its property of expanding when fused and allowed to cool, alloys containing it are specially adapted for type-metal, for taking the impression of wood-cuts, and for stereotyping. For making readily *fusible alloys* suitable for fusible valves, plugs, and wires, the following mixtures are used: *Wood's metal*, consisting of 15 parts of bismuth, 8 parts of lead, 4 parts of zinc, and 3 parts of cadmium, which melts at 68°, while *Rose's metal*, containing 1 part of tin, 1 part of lead, and 2 parts of bismuth, has a fusing point of 94°. In connection with antimony, bismuth is employed in the construction of thermo-electric piles.

Bismuth forms two classes of compounds, one containing the trivalent $Bi^{\prime\prime\prime}$ ion, while the other consists of the monovalent *bismuthyl* BiO group characteristic of the basic subsalts.

BISMUTH AND THE HALOGENS

Bismuth Trichloride, $BiCl_3$, is obtained when bismuth is heated in dry chlorine, or by dissolving bismuth in nitrohydrochloric acid, evaporating the solution, and distilling the residue.

It is a white, deliquescent mass, melting between 225 and 230° and boiling at 447°, known as *bismuth butter*. It is soluble in alcohol, and by the addition of much water is changed to insoluble, white basic bismuth chloride (oxychloride), known as *pearl white*, $6BiOCl.Aq$, which is usually prepared by pouring a solution of bismuth trinitrate into water containing sodium chloride, collecting and washing.

Bismuth trichloride forms double chlorides with the alkali metals; for example, $BiCl_3.2KCl$.

Bismuth Tri-iodide, BiI_3, results from the direct combination of its constituent elements when the same are fused together, but it may be more conveniently prepared by precipitation of a solution of bismuth nitrate by potassium iodide. So obtained, it is a brown-red powder which fuses at 439°.

Bismuth Oxy-iodide, BiOI.—This compound is produced by heating for one hour upon a bath of boiling water a mixture of bismuth subnitrate 10 parts, potassium iodide 4 parts, and water 50 parts, stirring until the product assumes a uniform brick-red color; it is then washed free from soluble alkali and dried at low temperature.

Bismuth Tribromide, $BiBr_3$, forms yellow crystals.

BISMUTH AND OXYGEN

Bismuth Trioxide, Bi_2O_3, the most important of this class of compounds, occurs naturally as *bismuth-ochre*. It may be prepared by heating bismuth or its carbonate, nitrate, or hydroxide, and usually occurs as a yellow, fusible powder, or as small needles of the same color.

$$4Bi(NO_3)_3 = 2Bi_2O_3 + 12NO_2 + 3O_2.$$
$$2Bi(OH)_3 = Bi_2O_3 + 3H_2O.$$

It is insoluble in water, and constitutes a stronger base than antimony trioxide. Strong acids dissolve it to form corresponding salts of bismuth.

Bismuth trioxide is employed in the manufacture of optical glass, to which it imparts greater hardness and higher refractive power than is obtained by the use of lead.

Bismuth Dioxide, BiO_2, and *Bismuth Pentoxide*, Bi_2O_5, are known.

Bismuth Hydroxides.—When a solution of a bismuth salt is added to an excess of a solution of an alkali hydroxide the *ortho* or *trihydroxide*, $Bi(OH)_3$, is produced. This is insoluble in alkalies and deports itself like a base; upon heating to 100° the *meta* or *bismuthyl* hydroxide, BiO.OH, is obtained, the hydroxyl group of which is replaceable by acid rests. Most of the basic bismuth salts are theoretically derivable from this hydroxide.

Magma Bismuthi, U.S.P.—Milk of Bismuth, "a thick, white opaque liquid containing bismuth hydroxide and bismuth subcarbonate in suspension in water. It is neutral to litmus and phenolphthalein." Bismuth magma yields not less than 5.6 per cent. nor more than 6.2 per cent. of Bi_2O_3. This is prepared by pouring a dilute solution of bismuth nitrate into a diluted solution of ammonia water containing a little ammonium carbonate. The presence of the basic bismuth carbonate serves to overcome the translucency of the suspended bismuth hydroxide.

OXYGEN SALTS OF BISMUTH

Bismuth Nitrate, $Bi(NO_3)_3.5H_2O$, is obtained by gradually adding to 5 parts of nitric acid of specific gravity 1.2, contained in a capacious flask, and previously heated to from 75° to 90°, 1 part of bismuth. A strong reaction ensues, the metal is dissolved, and nitrogen dioxide is liberated. On account of this gas changing in the air to noxious nitrogen tetroxide, the operation is best conducted in a place capable of ventilation. After the bismuth has dissolved, the solution is heated to boiling to remove the excess of nitric acid, then cooled, and any precipitated bismuth arsenate removed by filtration through asbestos wool; the filtrate, after evaporating to a weight corresponding to about 3 times that of the metal taken, is set aside for crystallization. This salt is sometimes called *tri* or *neutral* nitrate to distinguish it from the basic nitrates.

$$2Bi + 8HNO_3 = 2Bi(NO_3)_3 + 4H_2O + 2NO.$$

Bismuth nitrate forms colorless, transparent, triclinic prisms which melt at 78° in their water of crystallization, and by continued heating at 80° lose water and nitric acid, and are changed to a white basic nitrate. It dissolves in a small quantity of water to form a strongly caustic liquid, from which upon the further addition of water white basic or sub-nitrate is precipitated in which the proportion of the nitric acid radicle is much decreased. Bismuth nitrate dissolves readily in glycerin; this solution (1:5) may be diluted with water without precipitation taking place.

Basic Bismuth Nitrate. **Bismuthi Subnitras,** U.S.P.—This compound was introduced into the practice of medicine by Odier in 1786.

It is a white powder, of somewhat varying chemical composition, odorless and almost tasteless, and permanent in the air. Almost insoluble in water, and insoluble in alcohol, but readily soluble in nitric or hydrochloric acid. When heated to 120° C., the salt loses water (between 3 and 5 per cent. of its weight); and when subsequently heated to redness it evolves vapors of oxides of nitrogen, leaving not less than 79 per cent. of its weight of a yellow residue (Bi_2O_3), which is soluble in nitric or hydrochloric acid, and blackened by hydrogen sulphide. When brought in contact with moistened blue litmus paper, the salt shows a slightly acid reaction.

The composition of the salt depends upon the quantity and temperature of the water employed in precipitating and washing, also the temperature at which the drying is conducted. At lower temperatures salts approximating $Bi(OH)_2NO_3$ and $BiONO_3(OH)_2$ exist, which, upon drying, lose water, yielding a variable mixture consisting chiefly of $BiO.NO_3$ and $BiO.OH$, which, upon ignition, leaves from 80 to 82 per cent. of oxide.

Bismuth subnitrate may be prepared by adding slowly nitric acid to the metal, mixed with some water, in slight excess of that necessary for solution.

After removing the excess of acid and nitrogen dioxide by boiling, the solution is diluted with water until it becomes opalescent; it is then allowed to stand for the precipitation of any bismuth arsenate. To the clear decanted solution, a solution of caustic alkali is added until almost neutral, whereby the basic nitrate precipitates; this is thoroughly washed by decantation to remove all traces of alkali nitrate. The moist mass is then dried at a moderate temperature. From the filtrate the remaining traces of bismuth may be recovered as basic carbonate or as hydroxide by the addition of an excess of sodium carbonate or of ammonia water respectively.

Uses.—Besides its use in medicine, bismuth subnitrate is extensively employed in cosmetics under the name of *flake-white,* and in the preparation of a colorless, iridescent glaze for porcelain and in glass staining.

Bismuth subnitrate, like the other basic salts employed internally, is tested for the presence of arsenic by means of the Bettendorff test; since in the arsenic tests (U.S.P. or Marsh-Berzelius), based on the formation of arsine, metallic bismuth is precipitated over the zinc, through the reducing action of the nascent hydrogen, which stops the further generation of gas. If the bismuth salt be boiled with a caustic alkali and the bismuth oxide removed by filtration, the filtrate, after acidifying, may then be tested in the usual manner for arsenic.

Basic Bismuth Carbonate. **Bismuthi Subcarbonas,** U.S.P., obtained by dissolving the subnitrate in dilute nitric acid and pouring into a cold solution of an alkali carbonate, is "a white or pale yellowish-white powder, of somewhat varying chemical composition, odorless and tasteless, and permanent in the air. Insoluble in water or alcohol, but completely soluble in nitric or hydrochloric acid, with copious effervescence. When heated to redness the salt loses water and carbon dioxide, and leaves not less than 90 per cent. of a yellow residue (Bi_2O_3) which is soluble in nitric or hydrochloric acid, and blackened by hydrogen sulphide."

Another basic carbonate is found native in small quantity as a yellow amorphous mass. Neutral bismuth carbonate is not known. The official salt is usually assigned the formula $(BiO)_2CO_3.H_2O$.

Bismuth Sulphate, $Bi_2(SO_4)_3$.—An amorphous white powder obtained by heating the metal with concentrated sulphuric acid. With water it forms a basic sulphate, $Bi_2(OH)_4SO_4$.

Bismuth Trisulphide, Bi_2S_3, occurs native as bismuth glance in dark gray lustrous prisms. It is also obtained by heating bismuth with sulphur or as a brown precipitate by passing hydrogen sulphide into an aqueous solution of a bismuth salt. This sulphide is soluble in warm dilute nitric acid and insoluble in alkalies and alkali sulphides.

VANADIUM GROUP

The rare elements, vanadium, niobium, and tantalum, are related to nitrogen and phosphorus in that their highest oxidation products are pentavalent and possess acidic characters. Their halogen salts are volatile and their sulphates form alums. As metals they are similar to chromium, iron, and tungsten.

VANADIUM

Symbol, V. *Atomic Weight,* 51. *Valence,* III and V.

Vanadium occurs as the vanadate of lead, iron, and copper in Cheshire, England, Mexico, Colorado, and Chile, and as sulphide in Peru. In the United States it is found especially as the important mineral carustite in Colorado (see Radium). It is obtained 97 per cent. pure as a gray-colored metallic powder by the reduction of the oxide with carbon. With oxygen it forms five oxides corresponding to the oxides of nitrogen. The first three, or lowest of these, act as basic oxides, and the two highest act as acid-forming oxides.

Vanadium Pentoxide, V_2O_5, or vanadic anhydride, is a brown mass obtained by heating ammonium-meta-vanadate. It dissolves in the alkalies with a red color, forming the normal *vanadates.* The free ortho- acid, H_3VO_4, is not known, but salts, such as Na_3VO_4, exist. The ***metavanadic acid,*** HVO_3, forms a fine yellow pigment sometimes termed "vanadium bronze." The most important salt of this acid is ***ammonium metavanadate,*** NH_4VO_3. The solution of this salt becomes deep black when treated with tincture of galls. As the solutions containing this highest oxide of vanadium are reduced they show very characteristic changes of color; thus, vanadic salts are yellow; hypovanadic salts blue; vanadous salts green; and hypovanadous salts lavender colored.

Vanadium shows a greater range of valency than other members of this group, forming four chlorides, VCl_4, VCl_3, VCl_2, and VCl, and an oxychloride. $VOCl_3$.

Certain vanadium salts are used in cotton printing (aniline black), since they readily undergo reduction. The metal is chiefly used in high-grade steels, rendering them tougher, hard and more resistive to vibrations.

NIOBIUM (or Columbium)

Symbol, Nb (or Cb). *Atomic Weight,* 93.5. *Valence,* III and V.

Niobium, as it was named by Rose, or Columbium, as it was first named by Hatchett, is a very rare metal found in columbite and tantalite and other rare minerals. Niobium has been obtained as a steel-gray crust of sp. gr. 12.7 and melts at 1950°. Its most important compound is H_3NbO_4, forming salts known as ***niobates.***

TANTALUM

Symbol, Ta. *Atomic Weight,* 181.5 *Valence,* III and V.

Tantalum accompanies niobium in the minerals above named, also in tantalite, $Fe(TaO_3)_2$. It has been obtained as an iron-gray powder of sp. gr. 16.6, melting at 2910°. Its most important compounds are the pentoxide, Ta_2O_5, tantalic acid, H_3TaO_4, and meta-tantalic acid, $HTaO_3$. With halogens it forms pentavalent compounds.

Tantalum resists the action of acids, aqua regia, and alkalies, hence can readily replace platinum for electrodes.

Tantalum filaments are used in incandescent electric lights because of high fusing-point stability and great light emissive power.

CHAPTER VIII

THE CHROMIUM GROUP

THIS embraces the elements Chromium, Molybdenum, Tungsten, and Uranium (Cr, Mo, W, and U), which belong under group (VI) of the Periodic System. Their analogies to the sulphur compounds are exemplified in the valencies of the elements, their higher oxides (acid anhydrides), as CrO_3, MoO_3, WO_3, and UO_3, and salts which correspond with those of sulphuric acid and its polyacids. The sesqui-oxides (as Cr_2O_3) are basic.

CHROMIUM

Symbol, Cr. *Atomic Weight,* 52. *Valence,* II, III, and VI.

Chromium was discovered by Vauquelin in 1797. It derives its name from χρῶμα = color, alluding to the variety of colors of its compounds. Klaproth, independently, and about the same time, made the same discovery. Both chemists first observed it in the mineral *crocoite,* a lead chromate.

Chromium occurs chiefly as chrome iron ore, or *chromite,* FeO, Cr_2O_3. This is found in the United States, Scandinavia, Canada, Rhodesia, and the Urals.

Metallurgy.—Chromium is obtained by the alumino-thermic process of Goldschmidt, in which chromium oxide is reduced with aluminum filings.

$$Cr_2O_3 + Al_2 = Al_2O_3 + Cr_2.$$

Properties.—Chromium is a light-gray, crystalline, non-magnetic powder or a steel-gray lustrous metallic solid of sp. gr. 6.8, fusing at 1520° C. It is not oxidized in the air. Hydrochloric acid dissolves the metal rapidly when not prepared by the Goldschmidt process, with evolution of hydrogen; diluted sulphuric acid, when hot, behaves in a similar manner, but concentrated nitric acid does not attack it; like iron, it becomes "passive."* When prepared by the Goldschmidt method chromium is "passive" and is not attacked by acids.

Chromium is either bivalent in "chromous" compounds or tri- to hexa-valent in "chromic" compounds, and sometimes appears to be heptavalent.

The chromous compounds are less stable and obtained through reduction of the chromic; they readily absorb oxygen and pass over into the "ic" state, hence must be preserved away from the air. For the preparation of chromous salts, chromous acetate may be used. This may be prepared by pouring a concentrated solution of chromous chloride into one of sodium acetate. Chromic salts are green or violet, while the alkali chromates are yellow.

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* The following metals may, under conditions, assume a passive state: Fe, Ni, Co, Cr, Mo, W, V, Ru.

Uses.—Chromium is employed to impart hardness to steel (chrome-steel), and its ore is used in furnace lining in iron metallurgy.

CHROMIUM AND THE HALOGENS

Chromous Chloride, $CrCl_2$.—This is obtained through solution of chromium in hydrochloric acid, or the reduction of chromic chloride by nascent hydrogen. It forms a white crystalline powder, which dissolves in water, forming a blue solution; this solution rapidly absorbs oxygen, changing to green, and acts as a powerful reducing agent.

Chromic Chloride, $CrCl_3$.—Prepared by heating chromium or a mixture of chromic oxide and charcoal in a current of chlorine. It sublimes in reddish-violet, lustrous scales, which are nearly insoluble in water, but readily dissolve in that liquid with a green color in the presence of a trace of chromous chloride. Chromic chloride may be obtained in solution by dissolving chromic hydroxide in hydrochloric acid; by concentrating this solution very slowly, easily soluble crystals, having the composition $CrCl_3.12H_2O$, separate. These salts are used as mordants.

Chromous Bromide, $CrBr_2$, and *Chromic Bromide,* $CrBr_3$, are prepared like the corresponding chlorides.

CHROMIUM AND OXYGEN

Chromous Oxide, CrO.—This oxide is not known in the anhydrous state, but *chromous hydroxide,* $Cr(OH)_2$, is easily formed by precipitating chromous chloride with potassium hydroxide; it forms a yellow precipitate, which is oxidized immediately through contact with air.

Chromium Sesquioxide, Cr_2O_3, *Chromic Oxide,* occurs native, mixed with clay, as *chrome-ochre.* It may be prepared by heating chromic anhydride or ammonium dichromate to redness.

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2.$$

It is a dark-green, amorphous powder, which is insoluble in water; also insoluble in acids after ignition.

Chromic oxide is used in the preparation of colored glass, enamels, and porcelain, to which it imparts a beautiful green tint. It is known in commerce as *chrome green. Guignet's green* is obtained by fusing a mixture of potassium dichromate (1 part) and boric acid (3 parts), and extracting with water.

Chromic Hydroxide, $Cr(OH)_3$, is formed as a voluminous bluish-green precipitate, when ammonia water is added to a solution of chromic salt. This precipitate is considered by some as the *hydrogel of chromic oxide,* $Cr_2O_3.nH_2O$, is soluble in an excess of sodium hydroxide, and upon boiling deposits chromic hydroxide.

Chromic hydroxide deports itself as a feeble acid towards strong alkalies, dissolving in these to form alkali chromates. With other metals it forms salts most of which are derived from CrO.OH. Towards strong acids chromic hydroxide is a weak base; it does not form salts with weak acids as sulphurous and carbonic acid. When heated strongly the hydroxide is converted into the sesquioxide and water; at higher temperature the oxide ignites, leaving a dark-green powder which is insoluble in acids.

Perchromic Acid, $H_2Cr_2O_8$(?).—Assumed to be produced upon treating a chromate or dichromate with sulphuric acid followed by hydrogen peroxide, whereby a blue solution is obtained, soluble in ether. A dry compound has not been isolated. This reaction serves as a very sensitive test for either chromium or hydrogen peroxide (page 206).

Chromium Trioxide, CrO_3. **Chromii Trioxidum,** U.S.P. *Chromic Anhydride, Chromic Acid.*—This compound was first prepared in 1797 by Vauquelin. It is obtained by adding to 1 volume of a saturated solution of potassium bichromate 1½ volumes of concentrated sulphuric acid:

$$K_2Cr_2O_7 + 2H_2SO_4 = 2CrO_3 + 2KHSO_4 + H_2O.$$

By cooling, the oxide separates in acicular crystals; these are drained by vacuum suction through a porous alundum cup, removing the adhering sulphuric acid and potassium bisulphate by moistening repeatedly with nitric acid (1.46 sp. gr.) and again draining by suction. Finally the crystals are dried at a temperature sufficiently high (60 to 80° C.) to remove the adhering nitric acid.

Properties.—Chromium trioxide occurs in lustrous, dark-red, acicular crystals or rhombic prisms. The crystals are very soluble in water (1 in 0.6) and deliquescent in moist air. The scarlet-red crystals usually contain sulphuric acid, while those that are free from this substance are darker, with a brownish-red color and a steel-blue luster. On account of its energetic oxidizing action, the anhydride should not be brought in contact with the usual organic solvents, as they are liable to be inflamed, thereby leaving a residue of chromic oxide (Cr_2O_3). It must be preserved in glass-stoppered bottles, and not brought in contact with such substances as cork, tannin, sugar, alcohol, etc. Glacial acetic acid, benzol, and absolute ether dissolve chromium trioxide. "When chromium trioxide is heated, its color darkens, and finally becomes black, but is restored on cooling. At 192° to 193° it fuses to a reddish-brown liquid, which, on cooling, forms a dark-red, brittle mass (often enclosing cavities filled with crystals), furnishing a scarlet powder." After protracted heating at 250° it is entirely decomposed into chromic oxide, Cr_2O_3, and oxygen. Heated with sulphuric acid, chromic anhydride gives off oxygen and is converted into chromium sulphate, $2CrO_3 + 3H_2SO_4 = 3O + Cr_2(SO_4)_3 + 3H_2O$. Hydrochloric acid (25 per cent.) when heated with chromic anhydride converts the latter into the green chloride with evolution of chlorine, $CrO_3 + 6HCl = 3Cl + CrCl_3 + 3H_2O$. Concentrated hydrochloric acid converts the anhydride into chromium oxychloride (CrO_2Cl_2).

Uses.—Chromium trioxide is employed medicinally as a caustic, in dilute solution (1 to 100) for hardening tissues in microscopic preparations, and more extensively as an oxidizing agent in the laboratory, owing to the readiness with which it gives off oxygen, forming a lower oxide. Such substances as sulphurous acid, hydrogen sulphide, arsenous oxide, phosphorus, ferrous salts, stannous chloride, zinc, alcohol, oxalic acid, sugar, etc., readily reduce chromic anhydride to the green oxide while undergoing oxidation themselves.

Chromium Oxychloride, Chromyl Chloride, CrO_2Cl_2, is obtained by introducing a fused mixture of 10 parts of common salt and 17 parts of potassium dichromate in small pieces into a retort with 40 parts of concentrated sulphuric acid.

$$K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = K_2SO_4 + 2Na_2SO_4 + 3H_2O + 2CrO_2Cl_2.$$

The retort must be connected with a well-cooled receiver, as the reaction proceeds without the aid of heat, a dark-red liquid distilling over. It has a specific gravity of 1.92 at 25°, and boils at 118°. Chromyl chloride in its relationship to CrO_3 recalls that exhibited between sulphuryl chloride, SO_2Cl_2 and SO_3.

CHROMIC ACID AND CHROMATES

The analogy between the compounds of chromium and sulphur is especially noticeable among their acid anhydrides and salts; for example, CrO_3 and SO_3, the chromates and sulphates, the (pyro or) dichromates and pyrosulphates which are isomorphous. Sulphuric acid (H_2SO_4) is a stable compound, while chromic acid (H_2CrO_4) has not been isolated. The chromates are yellow, while the dichromates are reddish. The ready solubility of the insoluble chromates of barium, lead, and silver in mineral acids indicates the weak acidic properties of this acid. Upon the addition of an acid to chromates they are transformed into dichromates:

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

Chromic Acid, H_2CrO_4.—The aqueous solution of chromic anhydride is assumed to be represented by this formula. This solution upon evaporation yields the anhydride. Chromic acid (H_2CrO_4) exists only in the form of its salts.

Potassium Chromate, K_2CrO_4. *Neutral* or *Yellow Potassium Chromate.* U.S.P. Reagent.—In order to prepare this salt, 2 parts of potassium dichromate are dissolved in 4 parts of hot water; to the resulting solution about 1 part of potassium carbonate is added, or such an amount as will produce a slightly alkaline reaction:

$$K_2Cr_2O_7 + K_2CO_3 = 2K_2CrO_4 + CO_2.$$

After filtering the yellow solution and concentrating, yellow crystals separate. Commercially, the alkali chromates are prepared by roasting in a reverberatory furnace chrome iron ore with an alkali carbonate and lime.

$$2(FeO.Cr_2O_3) + 4Na_2CO_3 + 4CaO + 7O = Fe_2O_3 + 4CaCO_3 + 4NA_2CrO_4.$$

The mass of calcium and sodium chromates is heated with more sodium carbonate, which precipitates the calcium as carbonate. This is filtered off with the iron oxide. The sodium chromate, which is hygroscopic and not readily crystallizable, is converted into its dichromate by the addition of sulphuric acid. This is then converted into the corresponding potassium dichromate by interaction with a concentrated solution of potassium chloride, whereby sodium chloride settles as a crystalline precipitate and the dichromate crystallizes on lead rods suspended in the solution. From the dichromate the normal chromate is prepared by addition of potassium carbonate, as already described.

Properties.—Potassium chromate occurs in permanent, yellow, rhombic crystals, which are isomorphous with potassium sulphate. No acid salt is known. The salt is soluble in 1.6 parts of water, forming a yellow solution which has a weak alkaline reaction towards litmus paper. It is insoluble in alcohol. The aqueous solution is colored red on the addition of acids, owing to the formation of the dichromate.

POTASSIUM DICHROMATE, POTASSIUM BICHROMATE, $K_2Cr_2O_7$.

Preparation.—This salt is made from chrome iron ore, as described under potassium chromate, by roasting chrome iron ore with soda and lime. The resulting chromate, after dissolving in water, is acidified with sulphuric acid to convert it into a dichromate.

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

The sodium dichromate is then converted into its corresponding potassium salt by interaction with potassium chloride. Purification of potassium bichromate is readily effected by recrystallization.

The dichromates are analogous to the pyrosulphates in that they represent a combination of their respective acids and acid anhydrides. Thus pyrosulphuric acid may be obtained by dissolving sulphuric anhydride in sulphuric acid ($H_2SO_4.SO_3$ or $H_2S_2O_7$). If to a solution of a neutral chromate, chromic anhydride be added, a bichromate is obtained, thus, $K_2CrO_4 + CrO_3 = K_2Cr_2O_7$. The above equation may be divided into two stages as follows:

$$(a)\ Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + H_2CrO_4\ (\text{or } CrO_3 + H_2O)$$
$$(b)\ Na_2CrO_4 + H_2CrO_4\ (\text{or } CrO_3 + H_2O) = Na_2Cr_2O_7 + H_2O.$$

Potassium dichromate crystallizes in red, anhydrous, triclinic prisms or four-sided tables. It is permanent in the air, odorless, and has a bitter, metallic taste. The salt is soluble in 10 parts of cold water, in 1.5 parts of boiling water, but insoluble in alcohol. The aqueous solution is acid to litmus paper. On the application of heat it fuses at about 400° and then decomposes as follows:

$$2K_2Cr_2O_7 = K_2CrO_4 + Cr_2O_3 + 3O.$$

In sulphuric acid solution it is a powerful oxidizing agent, undergoing reduction to green chromous compounds, thus:

$$K_2Cr_2O_7 + 4H_2SO_4 = Cr_2(SO_4)_3.K_2SO_4\ (\text{or } 2KCr(SO_4)_2) + 3O + 4H_2O,$$

chrome alum being one of the products of the reaction. If a dichromate be heated with hydrochloric acid, chlorine is evolved:

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

Uses.—Potassium dichromate is rarely employed in medicine. It is, however, extensively used in the dyeing, tanning, and photographic industries and as a chemical reagent. (See U. S. P., p. 544.)

Sodium Chromate, Na_2CrO_4, and *Dichromate,* $Na_2Cr_2O_7$, are prepared as outlined under potassium chromate. The sodium salt occurs in deliquescent crystals, which are used in many technical processes as well as the source of various other chromium compounds, especially the pigments, in place of potassium dichromate, because of cheapness and more ready solubility in cold water.

Barium Chromate, $BaCrO_4$, is a yellow powder, insoluble in water and in acetic acid. It is obtained by precipitation of a soluble barium salt with potassium chromate or dichromate. Under the name of *yellow ultramarine* it is used as a pigment.

Lead Chromate, $PbCrO_4$.—There are at least three commercial substances which belong under this title—namely, the neutral chromate or *chrome yellow,* basic chromate, or *chrome red,* and *chrome orange,* which is a mixture of the two.

Chrome yellow is prepared by precipitating a solution of potassium chromate with a solution of lead acetate. The precipitate is often mixed with gypsum or barium sulphate in order to obtain the lighter chrome colors. Another process consists in digesting lead sulphate, which is a by-product in calico-printing and dyeing, with a solution of potassium chromate. The depth of shade depends upon the amount of unchanged lead sulphate. It is stated that a beautiful chrome yellow may also be obtained by digesting 100 parts of freshly precipitated lead chloride with 47 parts of potassium dichromate.

Chromic red is a basic lead chromate having the composition $PbCrO_4\text{-}Pb(OH)_2$. It is sometimes known as *Austrian cinnabar.* In order to obtain it the yellow chromate is boiled with a solution of potassium hydroxide, or a better quality is made by fusing together equal parts of sodium and potassium nitrates, and adding to the fused mass, in small quantities at a time, the yellow chromate. After cooling, the insoluble chrome red is well washed and dried. The different shades of this compound appear to be due to the size of the crystalline particles, as may be shown by separately rubbing a number of samples to a uniform powder.

A large number of other chromates are known, and may in most cases be prepared by precipitating a soluble salt of the metal with sodium dichromate.

OXYGEN SALTS OF CHROMIUM

Chromous Sulphate, $CrSO_4.7H_2O$, is prepared by cooling a solution of chromous acetate in dilute sulphuric acid, whereby crystals of the above composition separate. It is also obtained when metallic chromium is dissolved in dilute sulphuric acid.

Chromous sulphate occurs in bluish crystals, which are isomorphous with magnesium sulphate.

Chromic Sulphate, $Cr_2(SO_4)_3.15H_2O$.—This compound is prepared by dissolving chromic hydroxide in the necessary quantity of dilute sulphuric acid. The crystals may be obtained by careful evaporation or by the addition of alcohol. The solution is green when heated to 80°, but becomes violet on cooling, and deposits crystals of a violet color.

Chromium and Potassium Sulphate, $KCr(SO_4)_2.12H_2O$, *Chrome Alum.*—This salt is obtained by dissolving in water molecular proportions of chromic sulphate and potassium sulphate and carefully evaporating. The violet-red solution yields dark crystals of the same color as the solution from which they separate, having the above composition. It may also be prepared by adding to an aqueous solution of potassium dichromate the necessary quantity of sulphuric acid and passing in sulphurous oxide.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = 2KCr(SO_4)_2 + H_2O.$$

When the solution is heated it turns green, and crystals cannot be obtained from it, but by long standing, cold, it acquires the violet-red color and will then crystallize.

Other alums of chromium may be obtained by the substitution of the sulphates of ammonium or sodium for potassium.

Chrome alum is used as a mordant in dyeing, and to some extent in the manufacture of leather.

MOLYBDENUM, TUNGSTEN, URANIUM

In addition to chromium, in this group we have the rarer elements molybdenum, tungsten, and uranium.

These elements possess many points of resemblance to the sulphur group of non-metals. The members have an equivalence II, IV, VI, and some of them more rarely VIII.

Molybdenum, Mo. *Atomic Weight,* 96.—This element occurs in Bohemia, Italy, and the United States, chiefly as *molybdenite,* MoS_2, and as *wulfenite,* a lead molybdate, $PbMoO_4$. The name molybdenum (*μολυβδος* = lead-like) was chosen because of the resemblance of molybdenite to black lead.

Molybdenum tends to form polyacids, and with oxygen a number of oxides.

Molybdenum is prepared by heating the chloride or oxide to a high temperature in a current of hydrogen or roasting the oxide with charcoal in the electric furnace. It is a silver-white, nearly infusible metal, harder than topaz, and having a specific gravity of 9, melting at about 2450°(±30°). It is permanent in the air, unless heated, when it is slowly converted into the trioxide. Hydrochloric, hydrofluoric, and dilute sulphuric acids do not dissolve it, but it is readily attacked by nitric and nitro-hydrochloric and sulphuric acids.

Molybdenum Trioxide, Molybdic Anhydride, MoO_3, is the final product of the oxidation of the metal and is the most important of all oxides. It forms a white, glassy, crystalline powder usually obtained by either roasting molybdenite in the air or evaporating the same with nitric acid. It is insoluble in water and acids, but dissolves in sodium hydroxide or ammonia water. Molybdic anhydride forms polyacid salts, as $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, etc. The best known of these is ammonium molybdate, or heptamolybdate $(NH_4)_6Mo_7O_{24}.4H_2O$. The other oxides are prepared from this by various processes of reduction. They are MoO_2, Mo_2O_3, and MoO.

Molybdic Acid, H_2MoO_4, is obtained in shining white crystalline scales when a molybdate solution is decomposed by a strong acid. Molybdates are obtained by fusing molybdenum trioxide with alkali hydroxides or carbonates.

Ammonium Molybdate, or Heptamolybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, is formed by dissolving molybdenum trioxide in solution of ammonia, and precipitating the salt formed by the addition of alcohol. A solution of this salt in an excess of nitric acid is used as a reagent for phosphoric acid. When the reagent is warmed with phosphoric acid or its salts, acidified with nitric acid, a yellow precipitate of ammonium phosphomolybdate [$(NH_4)_3PO_4.12MoO_3.6H_2O$] is obtained. This is insoluble in nitric acid, but readily soluble in ammonia water.

Phosphomolybdic Acid is prepared by the union of phosphoric and molybdic acids. The one with the highest molybdenum content, obtained by evaporating an aqueous solution of these two acids, has the composition $2H_3PO_4.24MoO_3.58H_2O$. It occurs in yellow crystals, and loses water at 140°.

Ammonium Phosphomolybdate, $(NH_4)_3PO_4.12(MoO_3).6H_2O$, is the compound which is formed when ammonium molybdate in the presence of nitric acid is added to phosphoric acid or a phosphate, and represents the form in which phosphoric acid is usually determined quantitatively.

Tungsten (Wolfram), W, *Atomic Weight,* 184, is found in nature as *wolframite,* an iron and manganese tungstate, $FeWO_4$, and as *schleelite* or calcium tungstate, $CaWO_4$. Like molybdenum, it forms a great number of compounds, and as *tungstic acid* combines with bases to form a great variety of salts.

The free metal now obtained by the Goldschmidt process by reducing tungstic acid with powdered aluminum, is very hard, malleable and lustrous, melting at about 3080°, and has a specific gravity of 20. It resists the action of most chemical reagents, but is readily soluble in a mixture of HF and HNO_3, and dissolves in fused nitrates and caustic potash, hydrogen being given off. In the colloidal solid state it is now employed in the manufacture of filaments for incandescent lamps. Tungsten is largely employed in place of platinum for electric contact points. The presence of a small percentage of tungsten in steel imparts great hardness (tungsten steel).

Tungsten Trioxide, WO_3.—This is the most important oxide, also known as tungstic anhydride, prepared by decomposing hot concentrated solutions of tungstates with an excess of nitric acid. It is insoluble in water and acids, but soluble in alkalies. The yellow tungstic acid [$WO(OH_4)$] is precipitated on addition of an acid to the cold solution of a tungstate.

Tungstic Acid, $WO(OH)_4$, forms a variety of polyacids (complex tungstic acids), and, like molybdenum, forms complex compounds with phosphoric, arsenic, and antimonic acids. Among these is *Phospho-tungstic acid,* $H_3PO_4.12WO_3$ x H_2O, which is used as an alkaloidal reagent because of the insolubility of its salts with alkaloids.

Sodium Tungstate, $Na_2WO_4.2H_2O$.—Prepared by fusing wolframite with Na_2CO_3 and extracting with water. This salt is used as a mordant in calico-printing as well as a fire-proofing material for fabrics, and as a chemical reagent.

Tests. A yellow precipitate of WO_3 is produced by the addition of stannous chloride to a tungstate solution. If hydrochloric acid be added and warmed, a blue solution (W_2O_5) results.

Uranium, U, *Atomic Weight,* 238.5, occurs in nature chiefly as the mineral *uranite,* or *pitch-blende,* U_3O_8, deposits of which are found in Bohemia, Saxony, Cornwall, England, North Carolina, and German East Africa. Another ore is *carnotite* (uranium potassium vanadate), found in Colorado. Thorianite contains about 60 per cent. of ThO_2 and from 10 to 20 per cent. of uranium. Metallic uranium is prepared by reducing UCl_4 with sodium. It forms a white malleable metal of sp. gr. 18.6, dissolving in acids with evolution of H. At 170° uranium ignites and at 1000° in an atmosphere of nitrogen it forms uranium nitride. Like iron, uranium forms two series of salts, uranous (UX_4), and uranic (UX_6), corresponding with the oxides UO_2 and UO_3.

Radio activity was first discovered in uranium salts, and because of the constancy of its radiation a thin film of the black oxide, U_3O_8, was first employed in the standardization and calibration of electroscopes and such other instruments employed in radio-active work.

Uranous Oxide, UO_2, a basic oxide, termed *uranyl,* is prepared by reducing the trioxide with hydrogen. Salts of this oxide, as *uranous chloride,* UCl_4, and hydroxide, $U(OH)_4$, are not common, and, like the ferrous salts, are active reducing agents and are readily oxidized in the air.

The uranous salts are usually green.

Uranic Oxide, UO_3, or trioxide, possesses both basic and acid properties and is obtained by heating uranyl nitrate, $UO_2(NO_3)_2$, to 250°. This oxide, like CrO_3, forms salts with the alkalies, known as uranates, analogous to the dichromates, $Na_2U_2O_7$. Pitch-blende or the common black oxide, U_3O_8, prepared by heating the other oxides in air, is a compound of uranous and uranic oxides ($UO_2 + 2UO_3$).

Uranyl Compounds.—These are the most common of this group and yellow in color. They contain the bivalent group UO_2 derived from the higher oxide UO_3; thus $UO_3 + 2HCl = H_2O + UO_2Cl_2$, *uranyl chloride*. *Uranyl nitrate*, $UO_2(NO_3)_2.6H_2O$, and *Uranyl acetate*, $UO_2(C_2H_3O_2)_2.2H_2O$, are the best known salts of uranium, which show a yellow-green fluorescence. Both are used as laboratory reagents and in photography. Through the action of light in contact with organic matter, they are reduced to uranous salts.

Uranyl salts impart to glass, when fused with it, a greenish-yellow fluorescence. Both uranyl nitrate and acetate are used in the volumetric determination of phosphoric acid, whereby uranyl phosphate precipitates.

$$UO_2(NO_3)_2 + Na_2HPO_4 = UO_2.HPO_4 + 2NaNO_3.$$

Chlorine unites with uranium to form three compounds, UCl_3, UCl_4, and UCl_5. The *pentachloride* is obtained by passing Cl over a red-hot mixture of uranium oxide and carbon. This breaks up readily into chlorine and *uranium tetrachloride*, which in turn, when reduced in a current of hydrogen, yields *uranium chloride*, UCl_3.

RADIO-ACTIVITY

Many years ago Crookes made the discovery that when an electric discharge was passed through a vacuum-tube (known as Crookes' tube), a marked fluorescence was produced where the rays (cathode) impinged on its walls. These rays were different from light, in that they could be deviated from their straight course by means of a magnet, also they would turn vanes of mica suspended in the tube, and in addition possessed properties now recognized as those of the X-ray discovered by Roentgen in 1895. These rays did not illuminate like light rays, but caused such substances as barium or magnesium-platino-cyanide or calcium tungstate to fluoresce. They affected the photographic plate and ionized air and other gases, rendering them for the time being partial conductors of electricity, thus discharging a charged electroscope.

In view of the foregoing, Becquerel investigated the fluorescent properties of pitch-blende (U_3O_8), which he found to emit rays propagated in straight lines and acted on the photographic plate when wrapped in black paper. Madame Curie found further that these rays caused platino-cyanides to fluoresce and gases to become ionized. In addition it was observed that the radiation of the pitch-blende was 4.5 times as powerful as that of the metal uranium, although only 50 per cent. of the latter was present. Hence it followed that the pitch-blende must contain one or more new bodies having a stronger radiating power than uranium. This was measured by the conductivity of a layer of air exposed to these rays. These observations of Mme. Curie led to the discovery of the new radio-elements called Radium, Polonium, and Actinium. Radium was found to be one million times more active than uranium. Later a number of radio-active elements were discovered in thorium obtained from monazite sand.

The radio-elements, of which about 30 are known, are unstable and undergo a constant spontaneous disintegration of their atoms at a definite rate and in a definite manner, accompanied by expulsion of three types of radiations, known in order of their penetrative powers and other characteristics as alpha, beta, and gamma rays. *Alpha* rays, which are the most predominant, consist of electro-positively charged particles of atomic size (of helium), which are expelled with a velocity of about one-twentieth of that of light; they are the most energetic in ionizing air, while possessing the most feeble penetrating powers; aluminum foil 0.1 mm. thick or a sheet of paper stops their passage. When a screen covered with zinc sulphide is held in the path of alpha rays, through their individual impacts, separate minute flashes of light may be observed and the actual number of alpha particles expelled in a given time from a radio-active substance may be counted.

Beta rays consist of expelled " electrons "; that is, atoms of negative electricity (not atoms of matter), which represent about $^1/_{2000}$ of the mass of an atom of hydrogen and move with a velocity of from $^1/_{25}$ of, to that of light. These beta rays are identical in type with the cathode rays and possess penetrating powers, passing through thin plates of metals (1 cm. aluminum) and other substances with almost the same velocity as that of light. Beta rays are the most active of all in their action on the photographic plate. Screens of the platino-cyanides fluoresce when subjected to either beta or gamma radiation.

Gamma rays, which form but a small part of the total radiation, usually accompany beta rays; they possess properties similar to X-rays, being electrically neutral and made up of one negative and one positive electron. The gamma rays pass through great thicknesses of metal without complete absorption. The alpha and beta rays are deviated from their path in a magnetic field, while the gamma rays are not affected. The gamma rays are the most useful therapeutically.

The radio-elements, being unstable, are constantly undergoing spontaneous changes accompanied by expulsion of " rays " from their atoms with the production of a new type of radio-active atoms. These in turn again undergo similar changes with formation of other new atoms, and so successive series of changes take place. Evidences point to the production of about 30 new types of radio-active matter by series of successive changes from thorium and uranium. The ultimate result of this successive disintegration-process from radium or thorium is helium or some other inactive gas of lower atomic weight. According to the preceding, *Radio-activity* represents the spontaneous changes of certain elements accompanied by the emission of alpha, beta and gamma radiations. Aqueous solutions of radium salts continuously give off radium emanations, all of which are expelled through boiling. These can be collected, determined quantitatively, dissolved in water for internal or external use or used in free state for inhalation. Radium and its emanations find varied applications in medicine.

Determination of Radio-activity.—The measurement of the radio-activity of radium or its preparations is based on the property of ionizing gases. When such a preparation is brought near to a charged gold-leaf electroscope, the air becomes ionized and thereby an electric conductor discharging the electroscope and causing the leaf to move. From the rate of this movement in a calibrated apparatus, the measure of radio-activity is obtained. The radium content is determined either (1) through the measurement of its gamma rays or (2) through its emanation. According to method 1, the rate of discharge of an electroscope by means of gamma rays which have passed through a sheet of lead 1 cm. in thickness is determined. This gives the number of milligrams of radium present in the sample. Method 2 is generally used for solutions containing radium, which are compared by means of an emanation-electroscope with the emanation from a standard radium solution. The following *units* of measurement are in use, methods 1 and 2 express the actual radium content in radium preparations, while methods 3 and 4 express the radium *emanation* content or rather emanation concentration. (1) Milligrams or fractions thereof of radium (Ra) present. (2) Micrograms (0.001 milligrams) or fractions thereof of radium (Ra) present. (3) Curies or microcuries (0.001 milligram) or fractions thereof. The curie represents the maximum quantity of emanation given off by one gram of radium (Ra). (4) **Maché units.** One micro-curie (0.001 milligram) is equivalent to 2,700 Maché units.

Structure of the Atom.—Since the discovery of the radio-active properties of matter the old theories of the existence of the chemical atom have gradually given way to the modern hypothesis of electrons. That the elements radium, thorium, and uranium undergo spontaneous decomposition points to the fact that their atoms must possess complex structures. These are made up of electrically charged particles called electrons, which are approximately 2000 times smaller than the old hydrogen atom. They consist of a central core or nucleus, positively charged and surrounded by concentric layers of negative electrons, the outer ones of which are more mobile, that is, less strongly held than the inner layers. The positive charge of the nucleus is equal to the sum of the negative charges of the electrons surrounding it. The nucleus may carry a positive charge yet contain negative electrons within. These electrons of the outer layers, being more mobile, arrange themselves readily according to the influence of forces exerted by other atoms, some becoming detached and transferred to other atoms. Valency is considered by some to represent the number of electrons which are readily detachable. The chemical and radio-active properties reside chiefly in the nuclear (positive) charge, the magnitude of which varies with each element. The mass of the atom is approximately proportional to the nucleus charge. It may be noted that the nuclear charge of an atom of an element may be calculated through the determination of the power of the element to scatter gamma or X-rays; this charge is equal to about one-half of the atomic weight.

Radio-active Elements.—In the full accepted understanding of the term, there are but two (parent) radio-active elements, namely, uranium and thorium, with the highest atomic weights of 238.5 and 232.4 respectively. Next in order are bismuth (208) and lead (207); in between these two pairs of elements a group of about 30 new elements has been discovered (see below). These form distinctive types, each of which is endowed with definite and characteristic kinds of radio-activity. All these are obtained from minerals containing uranium (pitch-blende or carnotite) or thorium (monazite sand). Chief among the disintegration-derivatives of uranium are *radium, ionium,* and *polonium,* with actinium and its derivatives in a subsidiary series; thorium yields meso-thorium, radio-thorium, thorium, etc. These constitute two groups or disintegration-series in which each parent member disintegrates with the re-formation of a new product; this in turn repeats the same phenomenon.* The average life of the different members varies; thus in Ra and Ac no diminution of radio-activity after isolation has been noted; with other radio-elements it requires a period of years, while the majority are quite short-lived, lasting in some instances from a few months to days, while in others it is a matter of hours or even minutes. In addition to *radiations* given off by the elements Th, Ra, Ac, Ur, Po, the first three produce radio-active gases or *emanations,* which give off rays similar to those from other elements, and may be separated by passing a current of air over the substance or through aqueous solutions of their salts. These emanations or transformation-products which retain their radio-activity only for variable but short periods of time resemble chemically the inert elementary gases of the argon group; they impart (induce) radio-activity by contact with solids; this imparted activity is also very transient and may be regarded as a transformation-product of the radium emanation.

The radio-elemental atom is indistinguishable from the ordinary atom up to the time of its disintegration. After this the new atom formed retains its ordinary atomic characters until a new disintegration takes place. In cases of atomic disintegration accompanied by alpha radiation (which carries two atomic charges of positive electricity), the atom loses part of its mass, which is forcibly ejected as a separate atom; thus helium was discovered (spectroscopically) as consisting of alpha positively charged particles expelled from radium. All the atoms of any radio-element do not disintegrate at the same instant; the radiation is discontinuous, as shown by the action of alpha rays on the phosphorescent screen of zinc sulphide (spinthariscope).

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*THE RADIO ELEMENTS
In Order of their Degradation

	Period of life				Period of life
Thorium	**4 x 10^{10} years**	**Uranium**			**8 x 10^{9} years**
Mesothorium I	7.9 years	Uranium X	35.5 days	Polonium	202 days
Mesothorium II	8.9 hours	Ionium	5 x 10^{4} years	Actinium	(?)
Radiothorium	2.9 years	Radium	2500 years	Radioactinium	28 days
Thorium X	5.3 days	Niton	5.5 days	Actinium X	15 days
Thorium Emanation	76 seconds	Radium A	4.3 minutes	Actinium Emanation	5.6 seconds
Thorium A	0.2 seconds	Radium B	38.5 minutes	Actinium A	0.003 second
Thorium B	15 hours	Radium C	28.1 minutes	Actinium B	52 minutes
Thorium C	79 minutes	Radium C_2	1.9 minutes	Actinium C	3 minutes
Thorium D	4.5 minutes	Radium D	24 years?	Actinium D	7.4 minutes
		Radium E	7.2 days		

Radium, Ra.—Atomic weight 226.4. This, first of this group to be discovered and by Mme. Curie in 1898, is found associated with uranium and also present in many natural mineral springs. The European source is from the Bohemian pitch-blende, while in the United States it is prepared from carnotite (potassium-uranium vanadate), which is found in Colorado and Utah. Radium may be separated from the ores by converting the insoluble sulphates present into carbonates by boiling with an excess of sodium carbonate, washing out the soluble sulphates, then dissolving the carbonate in hydrochloric acid, which takes up alkaline earths (with Ra) as chlorides. The radium with barium is then precipitated from these either as a sulphate or as a chloride, the chlorides of Pb, Fe, Ca, etc., remaining in solution. The radium is then separated from the barium by fractional precipitation. Radium closely resembles barium in its analytic reactions, its sulphate being less soluble than that of barium. It may be separated from barium by the fractional crystallization of its halogen salts, preferably the bromide, which is less soluble. All radium compounds are luminous; they also excite or cause certain other substances to fluoresce, such as the alkaline earth-platino-cyanides, calcium tungstate, uranyl sulphate, and diamonds. About 1 part of radium is present in ten millions of pitch-blende. The radio-activity of pure radium bromide is about one million times that of the mineral. The average life period of radium is about 2500 years, and radium is the fourth phase in the slow transformation of uranium, which occupies thousands of years, thus $Ur \rightarrow Ur\ X \rightarrow Io \rightarrow Ra$. Aside from the products of its disintegration, radium-radio-activity consists of alpha rays and a feeble beta radiation. In solution its first disintegration-product (Ra emanation) escapes readily, while in the solid state, as a salt, retention is more or less complete, especially so when sealed in glass containers. The spectrum of this emanation indicates that it is related to xenon and has been named Niton.

Actinium, Ac.—A ray-less element which occurs with the rare-earth metals, especially lanthanum separated from pitch-blende. Its first disintegration-product is radio-actinium, which has a duration of 28 days.

Ionium, Io.—An intermediate product between Ur X and Ra; that is, radium is the disintegration-product of Io. Chemically, ionium is closely allied to thorium and cannot be completely separated from it.

Niton, Nt.—A radium emanation which occurs in all radium minerals and in the atmosphere in minute amounts. Niton is obtained by heating radium salts to about 800°. Through constant emission of energy, niton slowly decomposes CO_2, CO, NH_3, HCl and H_2O and also oxidizes wet mercury and turns white glass violet.

Polonium (Radium F).—Chemically this is closely related to bismuth, accompanying this metal in working pitch-blende for radium.

Radium E is its parent, and an element related to lead is its disintegration-product.

MANGANESE

Symbol, Mn. *Atomic Weight,* 54.93. *Valence,* II, III, IV, VI, and VII.

Manganese, a member of Group VII of the Periodic System, exhibits certain analogies on the one hand with chlorine of the same group, while on the other it is closely related with the iron group (Fe, Co, Ni) of the same period. For instance, $KMnO_4$ and $KClO_4$ are isomorphous; Mn_2O_7 and Cl_2O_7 are analogous, possessing heptad valencies. In its physical and chemical properties Mn shows strong resemblances to Fe and Cr.

History.—The ore called pyrolusite, or black oxide of manganese, was used in the decolorization of glass and was known to the early chemists, by whom it was confounded with magnetic iron oxide or magnetite.

In 1774 Scheele proved that pyrolusite contained a new element and Galm was the first to isolate the metal.

Occurrence.—Manganese occurs in nature frequently associated with iron. It exists free to a small extent in meteoric iron.

The most widely occurring ores are the oxides, of which the most important is manganese dioxide, or *pyrolusite,* MnO_2. Besides this it is found as sesquioxide, or *braunite,* Mn_2O_3, as hydrated sesquioxide, or *manganite,* $Mn_2O_3 + H_2O$, as mangano-manganic oxide, or *hausmannite,* Mn_3O_4, as carbonate, or *manganese-spar,* $MnCO_3$, as sulphide, or *manganese-blende,* MnS, in many silicious minerals, in some mineral waters, and in plant and animal organisms, which derive it from the soil.

Metallurgy.—The metal cannot be obtained from its oxides by reduction with hydrogen. The purest manganese is obtained by the method of Goldschmidt, through reduction of manganese dioxide with finely divided aluminum.

Properties.—This element is a very difficultly fusible (m. p. 1245°), very hard, brittle, lustrous metal, which has much the appearance of white cast-iron. It has a specific gravity of from 6.8 to 8. It possesses a very great affinity for oxygen, with which it combines in moist air at ordinary temperatures. Cast-manganese containing iron is, however, unalterable in the air. In fine powder it decomposes boiling water. The metal is easily soluble in diluted acids with the liberation of hydrogen, forming manganous salts.

Uses.—In the pure state it has little use, but as alloys with iron in *spiegeleisen* or ferro-manganese for the production of steel, and with copper and zinc for the preparation of manganese-bronze, it is extensively employed.

Alloys.—Manganese readily alloys with several metals, among which are *ferro-manganese, ferro-silicon-manganese, manganese bronze, manganese German silver,* etc. Spiegeleisen that contains 25 per cent. and upward of manganese attains a granular structure, and is known as *ferro-manganese*. These materials are used in white cast-iron, the color of which is due to this ingredient. Manganese German silver, an alloy of ferro-manganese, copper, and zinc, closely resembles *German silver*. *Manganese-bronze* contains 15 parts of copper, 4 parts of manganese, and 1 part of zinc. When these alloys have a manganese content of 3 to 8 per cent. they are soft and ductile, but by 12 or 15 per cent. they are rendered hard and brittle.

MANGANESE AND THE HALOGENS

Manganous Chloride, $MnCl_2.4H_2O$.—This is obtained as a side product in the preparation of chlorine from manganese dioxide and hydrochloric acid. In the residual liquid it is mixed with iron, from which to separate it the filtered liquid is evaporated to dryness to expel free acid, the residue treated with water, and the resulting solution heated with an excess of manganous carbonate, which precipitates the iron as oxide. After filtration the solution is evaporated and allowed to crystallize. The manganous carbonate required for the operation is previously prepared from some of the same solution by precipitation with sodium carbonate. Should lead and copper be present, they are precipitated by hydrogen sulphide after the iron has been separated and before the solution is concentrated for crystallization. It is a pink, deliquescent salt.

Manganese trichloride, $MnCl_3$, and *Manganese Tetrachloride*, $MnCl_4$, have never been isolated, for they readily decompose, giving chlorine and manganous chloride.

Manganous Bromide, $MnBr_2.4H_2O$, and *Manganous Iodide*, $MnI_2.4H_2O$, are pink, deliquescent salts obtained by dissolving manganous carbonate in hydrobromic or hydriodic acid and then crystallizing.

MANGANESE AND OXYGEN

Manganese forms a series of oxides, MnO, Mn_2O_3, Mn_3O_4, **MnO_2**, MnO_3, and **Mn_2O_7**. MnO and Mn_2O_3 are basic, while MnO_3 and Mn_2O_7 are acid anhydrides.

Manganous Oxide, MnO, is obtained as a green powder by heating manganous carbonate, or an oxide of manganese that is richer in oxygen (Mn_3O_4 or MnO_2), in a stream of hydrogen. It is a strong base, and dissolves easily in acids with the formation of manganous salts.

Manganous Hydroxide, $Mn(OH)_2$.—Manganous oxide forms a hydroxide of an unstable character, as a white, flocculent precipitate when a solution of a manganous salt is treated with potassium or sodium hydroxide. It is insoluble in excess of either precipitant, but is soluble in ammonium hydroxide. It soon acquires in the air a brown color, due to partial change first to $Mn(OH)_2$ and finally to Mn_2O_3, which is insoluble in all the alkali hydroxides.

Manganic Oxide, Manganese Sesquioxide, Mn_2O_3, occurs in nature as braunite crystallized in brown-black, lustrous, very hard, obtuse quadratic pyramids. It is usually prepared (and of the same color) by careful ignition of manganous hydroxide, manganese dioxide, or manganic nitrate. It is a very weak base, in consequence of which it combines with acids only with difficulty to form manganic salts.

Hot hydrochloric acid effects solution, with liberation of chlorine and production of manganous chloride $MnCl_2$.

Manganic Hydroxide, $MnO.(OH)_2$ or $MnO_2 + H_2O$.—This compound results from the oxidation of manganous hydroxide, in moist air. It is soluble in hot nitric acid, forming manganous nitrate and manganese dioxide; $2MnO.(OH)_2 + 2HNO_3 = Mn(NO_3)_2 + MnO_2 + 2H_2O$. Warmed with sulphuric acid it dissolves to manganic sulphate, $Mn_2(SO_4)_3$, with no evolution of oxygen. It is used in the preparation of varnishes.

Manganous-manganic Oxide, or *Trimanganic tetroxide*, Mn_3O_4, occurs native as *hausmannite* in brown-black quadratic pyramids. It results upon the continued ignition of the oxides of manganese, of the hydroxides, and of the carbonates with access of air. With evolution of chlorine it dissolves in hydrochloric acid to yield manganous chloride.

Manganese Trioxide, MnO_3, and *Permanganic Anhydride*, Mn_2O_7, see page 80.

Manganese Dioxide, or *Peroxide*, MnO_2, **Mangani Dioxidum Præcipi-**

tatum, U.S.P.—This most important of manganese ores was known and used in the middle ages. It is often called black oxide of manganese or pyrolusite. The largest deposits are in the Russian Caucasus, Chile, Cuba, Germany, Spain, and in the United States in Virginia, Arkansas, and Colorado. It crystallizes in steel-gray, more or less lustrous, rhombic masses, which usually enter commerce in a compact or striated state. The dioxide can be artificially prepared by carefully heating manganous oxide with potassium chlorate, or by repeated treatment of manganous oxide with hot concentrated nitric acid, or by heating the nitrate, or, best, when a manganous hydroxide is formed, by the action of ammonium hydroxide upon a solution of manganous sulphate; this is oxidized as formed by the addition of hydrogen dioxide solution. The result is a manganic hydroxide, which when dried should contain not less than 80 per cent. of manganese dioxide (U.S.P. IX).

Upon paper or porcelain manganese dioxide gives a gray-black streak, and when crushed a graphite-colored powder. The other oxides give brown stains and powders. Manganese dioxide is not attacked by nitric acid or dilute sulphuric acid except in the presence of oxidizable bodies, when solution takes place. When heated with strong sulphuric acid to 110° it forms manganic sulphate, $2MnO_2 + 3H_2SO_4 = Mn_2(SO_4)_3 + 3H_2O + O$, while at the boiling-point of sulphuric acid manganous sulphate results, $Mn_2(SO_4)_3 = 2MnSO_4 + SO_3 + O$. This mixture is frequently used as an oxidizing agent. In the presence of easily oxidizable organic substances, such as sugar or oxalic acid, manganese dioxide dissolves in dilute sulphuric acid with liberation of oxygen, which acts upon the organic matter present as an oxidizing agent.

Hydrochloric acid yields with the dioxide chlorine and manganous chloride.

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

At a low red heat it gives off one-fourth of its oxygen and changes to sesquioxide, while at white heat it gives up one-third, and passes into manganous-manganic oxide, Mn_3O_4. The pyrolusite of commerce is not pure, but contains, besides other oxides of manganese, variable quantities of calcium carbonate and sulphate, silica, and iron oxides. When heated with alkalies, maganese dioxide forms salts known as manganites. The acid corresponding to these compounds is not known in the free state.

Uses.—Manganese dioxide serves for the preparation of other manganese compounds, of oxygen, of chlorine, and for the decolorization of glass, in which it corrects the green color imparted by the iron oxide derived from the sand used. Aside from the last use, it is employed to give an amethyst color to glass. Pyrolusite is the chief source of metallic manganese.

Salts of Manganic and Permanganic Acid.—These acids are well known in form of their salts, manganates having the formula $X'_2\ MnO_4$, and permanganates $X'\ MnO_4$. If any oxide or salt of manganese be fused with an alkali hydroxide or carbonate, with or without an oxidizing agent (KNO_3 or $KClO_3$), a green mass is produced, $MnO_2 + 2KOH + O = K_2MnO_4 + H_2O$. This when dissolved in water gives a green solution of an alkali *manganate*, isomorphous with the same chromate or sulphate. Solutions of alkali manganates when treated with CO_2, chlorine, acids or ozone, yield *permanganates*. Thus:

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3.$$
$$K_2MnO_4 + Cl = KMnO_4 + KCl.$$
$$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O.$$

Manganic Anhydride, **Manganese Trioxide**, MnO_3, may be prepared in small quantities by slowly adding a solution of potassium manganate in conc. sulphuric acid to anhydrous Na_2CO_3 contained in a special form of apparatus; the pink sublimate formed is collected on a cool surface. It forms a red amorphous mass which with water yields *manganic acid* (H_2MnO_4), which rapidly decomposes to oxygen, MnO_2, and permanganic acid.

Permanganic Anhydride, Mn_2O_7.—This is a dark, oily liquid produced by the decomposition of a permanganate with conc. sulphuric acid, $2KMnO_4 + 2H_2SO_4 = 2KHSO_4 + Mn_2O_7 + H_2O$. The compound is unstable, decomposing with explosion when heated. With water *permanganic acid* ($HMnO_4$) is produced. Manganese heptoxide is a powerful oxidizing agent, detonating with oxidizable substances. Permanganic acid is only known in solution as a deep red liquid.

Potassium Manganate, K_2MnO_4.—This compound is made by evaporating 500 parts of potash lye of specific gravity 1.44 in a bright iron kettle to about one-third its weight, and adding to the fused potassium hydroxide so obtained 180 parts of manganese dioxide and 105 parts of potassium chlorate, separately powdered and previously mixed. The mass is then dried with constant stirring to a stiff consistency, and then heated in a Hessian crucible to low redness until a small quantity taken out and put into water almost completely dissolves with an intense green color:

$$3MnO_2 + 6KOH + KClO_3 = 3K_2MnO_4 + KCl + 3H_2O.$$

The heating of the mixture must not be carried to full fusion, or decomposition of the manganate will ensue. When the reaction has been shown to be complete, the mass is poured out on an iron plate, and, when cold, is broken and extracted with water. The solution is filtered through asbestos, and then evaporated in a rarefied atmosphere, whereby the salt is obtained in dark-green, almost black crystals.

For technical purposes it may also be prepared by fusing solid potassium hydroxide, 2 parts, with finely powdered manganese dioxide, 2 parts, with or without the addition of potassium nitrate, 1 part. If air is excluded a temperature of about 150° suffices, but if air is admitted or an oxidizing agent (as $KClO_3$) is used, a higher temperature is necessary. When no oxidizing agent is used, some of the manganese sesquioxide is formed.

$$3MnO_2 + 2KOH = K_2MnO_4 + Mn_2O_3 + H_2O.$$

The crystals of this compound are isomorphous with those of potassium sulphate. They dissolve in water with a dark-green color. When allowed to stand, the color of this solution gradually passes through blue into violet, on account of the formation of potassium permanganate. This change is hastened by heat and by the action of ozone, nitric acid, chlorine, bromine, and carbon dioxide.

Because of these changes in color early chemists called the salt *chameleon mineral,* although the name has also been applied to the permanganate.

Organic substances, sulphur dioxide, and other reducing bodies decolorize a solution of potassium manganate by taking up its oxygen. For this reason its solutions should not be filtered through paper.

By substituting the corresponding sodium compounds in relative proportion, green crystallized sodium manganate, $Na_2MnO_4 + 10H_2O$, can be obtained by the method employed for the potassium salt.

Barium Manganate, $BaMnO_4$, is easily produced by roasting a mixture of 1 part of powdered manganese dioxide with 4 parts of barium nitrate, and rapidly lixiviating the green mass. It is an emerald-green, crystalline, insoluble powder, sometimes called *barium green.*

Potassium Permanganate, $KMnO_4$. **Potassii Permanganas, U.S.P.**—To prepare this salt the green, fused mass obtained in making potassium manganate is treated with twice its weight of hot water. After stirring, the mixture is allowed to settle, and the clear, green solution produced is poured off. The sediment is washed with more water by affusion and decantation after subsidence. The mixed clear solutions are warmed in a water-bath, at which temperature a current of carbon dioxide is conducted into the liquid until a pure red-violet color has been acquired:

$$3K_2MnO_4 + 2CO_2 = 2KMnO_4 + MnO_2 + 2K_2CO_3.$$

The manganate can also be converted into permanganate by thoroughly boiling the solution, potassium hydroxide resulting as one of the products of the change:

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH.$$

In both cases a precipitate of hydrated manganese dioxide [$MnO(OH)_2$] is produced.

After standing, the clear solution is siphoned off, and the last turbid portion is filtered through glass wool. Care having been taken to exclude dust, the liquid is evaporated until a pellicle forms on the surface, and then it is allowed to cool. The crystals which separate are collected and placed to drain away from contact with organic matter. The salt may be obtained in a crude state by evaporating the solution at once to dryness. It forms metallic, lustrous, almost black, rhombic prisms, which are permanent in the air. These are soluble in 13.5 parts of water at 25°, and 3.5 parts of boiling water. The solution gradually undergoes change in the presence of traces of organic matter with separation of manganese dioxide. Potassium permanganate is a powerful oxidizing agent, hence should not be mixed with organic or other readily oxidizable substances in the dry state. In the neutral solution two molecules of the salt give up *three* atoms of oxygen, with the production of a brown, flocculent precipitate of a hydrated dioxide.

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO_2.H_2O + 3O.$$

In acid solution two molecules give up *five* atoms, and if sufficient of the oxidizable matter is present, a clear and colorless solution results. Since potassium permanganate solution is employed in volumetric analysis it is important that the solutions being titrated remain clear, hence sulphuric acid is always added to the solution of the substance.

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O.$$
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2.$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

On account of the ease with which they yield their oxygen, both manganate and permanganate are employed as disinfectants: foul-smelling gases or substances are rendered entirely odorless by contact with these compounds. Its use in the quantitative analysis of iron and of organic matter in potable waters depends upon this same feature. Chlorine is liberated by the action of hydrochloric acid on potassium permanganate.

$$2KMnO_4 + 16HCl = 2KCl + 5Cl_2 + 2MnCl_2 + 8H_2O.$$

When heated to about 240° it decomposes into oxygen, potassium manganate, and manganese dioxide.

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

In alkaline solution permanganates are reduced to manganate by small quantities of such reducing agents as alcohol, sodium thiosulphate, hydrogen sulphide, etc., in neutral solution or more active reduction induced by heating, hydrated manganese dioxide is precipitated.

Sodium Permanganate ($NaMnO_4.3H_2O$), Calcium, Barium, and Zinc Permanganates are used as disinfectants and otherwise in medicine.

MANGANESE AND SULPHUR

Two sulphides of manganese are found native. Manganese monosulphide, MnS, occurs as *manganese-blende* in black, cubic crystals, and manganese disulphide, MnS_2, as *hauerite* in red-brown crystals of the same system.

The former sulphide may be prepared as a green powder by heating manganese sesquioxide in a stream of hydrogen sulphide, or by precipitating a solution of a manganous salt with an alkali sulphide, whereby a flesh-pink precipitate of a hydrated sulphide is produced. Upon exposure to air, this takes up oxygen and assumes a brown color.

OXYGEN SALTS OF MANGANESE

Manganous Sulphate, $MnSO_4.4H_2O$.—Usually prepared by heating a paste of manganese dioxide with conc. sulphuric acid to redness, whereby any ferric sulphate present is decomposed to oxide. The mass is then extracted with water, manganese carbonate added to precipitate any remaining iron, filtered, and evaporated to crystallization.

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$
$$Fe_2(SO_4)_3 + 3MnCO_3 = Fe_2O_3 + 3MnSO_4 + 3CO_2.$$

Lead and copper are removed by saturating the liquid with hydrogen sulphide previous to evaporation, while zinc is separated by the same reagent, but in the presence of sodium acetate and acetic acid.

Manganese sulphate forms pale, rose-colored crystals which are somewhat efflorescent. It crystallizes with $7H_2O$ when evaporated and crystallized below 8°, being isomorphous with ferrous sulphate. Between 8° and 27° manganese sulphate crystallizes with $5H_2O$, isomorphous with copper sulphate, and between 25° and 30° with $4H_2O$, which represents the commercial salt. When the solution is evaporated at a temperature above 30° an almost colorless, difficultly soluble, crystalline powder of still lower percentage of water separates.

Manganese sulphate is soluble in about 1.5 p. of water. With the sulphates of potassium and sodium it forms double salts. Manganous sulphate is used in medicine, usually in conjunction with iron.

Manganic Sulphate, $Mn_2(SO_4)_3$, is a dark-green, deliquescent powder which results from the action of concentrated sulphuric acid on manganese sesquioxide at 138°.

Manganese alums $[R'Mn(SO_4)_2.12H_2O]$ crystallize in octahedra obtained by mixing alkali sulphates with manganic sulphate.

Manganous Nitrate, $Mn(NO_3)_2.6H_2O$, separates in deliquescent crystals when manganese carbonate is added to nitric acid and the solution is evaporated.

Manganous Phosphate, $Mn_3(PO_4)_2.7H_2O$, is produced as a white precipitate by the addition of sodium phosphate to a solution of manganous sulphate.

Manganous Hypophosphite, $Mn(PH_2O_2)_2 + H_2O$, is a pink, crystalline powder, odorless, nearly tasteless; permanent in the air. It is soluble in 6.6 parts of water at 25° C.; almost insoluble in alcohol.

Manganese Borate is formed when a solution of a manganous salt is precipitated by sodium borate. The white precipitate becomes brownish upon drying.

Manganous Carbide, Mn_3C. Obtained by heating Mn_3O_4 with charcoal in an electric furnace. It is decomposed by water, yielding hydrogen and methane; $Mn_3C + 6H_2O = CH_4 + H_2 + 3Mn(OH)_2$.

Manganous Carbonate, $MnCO_3$.—Manganese-spar, the native form of this compound, occurs in red, hexagonal crystals, which are contaminated with iron and other carbonates. The artificial white salt is prepared by adding a slight excess of sodium carbonate to a solution of manganous sulphate. Upon drying it undergoes some decomposition and becomes darker on account of the sesquioxide formed. When ignited it loses carbon dioxide and leaves manganous-manganic oxide.

CHAPTER IX

THE IRON GROUP

This eighth group of the Periodic System, which includes iron, nickel, and cobalt, is distinguished because of the magnetic properties of its members. The highest oxides of iron and the lowest oxides of nickel and cobalt are the most stable.

IRON

Symbol, Fe. *Atomic Weight,* 55.84. *Valence,* II and III.

History.—The discovery of iron antedates the earliest historical times, as it was known to the ancient Egyptians and Assyrians, and is mentioned in the Pentateuch. The earliest form was undoubtedly malleable iron, prepared direct from the ore by smelting with charcoal. Steel was also known to the ancient Greeks, and is described by Homer, the Chalybes, a tribe on the coast of the Black Sea, being famed for its production. The manufacture of cast-iron by the blast-furnace process appears to date from the end of the fifteenth century.

Occurrence.—Iron rarely occurs as *native metal,* but such as is found occurs in form of meteorites (meteoric iron) which have fallen upon the earth. It is present in stars and the sun. These meteorites contain from 4 to 10 per cent. of nickel, with some Co, Cr, Mn, Cu, Sn, C, P, and S.

Iron ores are very abundant on the earth, the most important being:

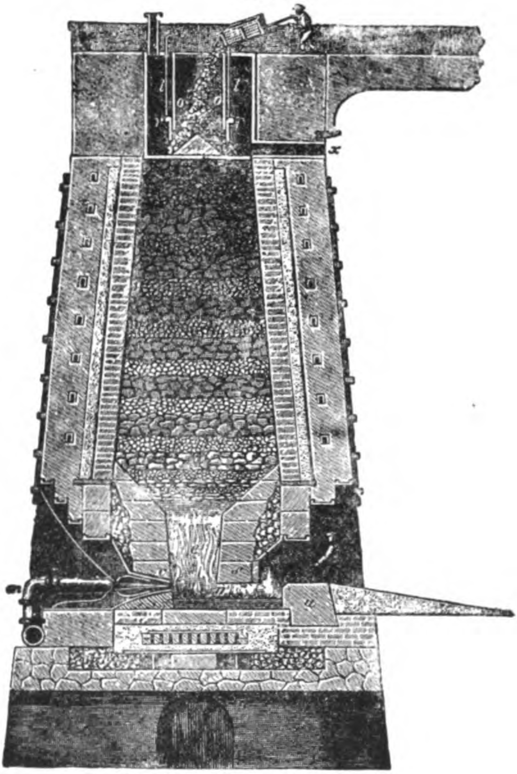
Magnetite—Ferroso-ferric oxide—Fe_3O_4.
Red Hæmatite, Specular Iron } Ferric Oxide—Fe_2O_3.
Brown Hæmatite—Hydrated Ferric Oxide—$2Fe_2O_3.2H_2O$.
Spathic Iron Ore or Siderite—Ferrous Carbonate—$FeCo_3$.

The ferric sulphide (FeS_2), which occurs so abundantly under the name of *pyrite,* is not used as a source of iron, although valuable for the manufacture of sulphuric acid.

Metallurgy.—The extraction of iron from its ores depends on the reducing action of carbon at high temperatures. $Fe_2O_3 + 2C = 2Fe + CO + CO_2$. The liberated iron, while very hot, takes up some of the carbon and fuses, forming *cast-iron,* while the remainder of the carbon passes off as CO and CO_2. The impurities, liberated during the smelting, form readily fusible slags through the use of fluxes. According to the carbon content and its form of combination as well as different physical properties, commercial irons are classified by the International Commission as follows:

- **Cast or Pig Iron**
  Carbon 2.3 to 5 per cent.
  Non-malleable
  Non-weldable
  Readily fusible
  - *Gray Cast Iron* greater portion of its carbon in uncombined (graphitic) form. Its smaller portion chemically combined.
  - *White Cast Iron* contains 3 to 5 per cent. of carbon chemically combined as carbide (FeC_4, FeC_3, Fe_3C_2) and 0.2 to 0.5 per cent. of graphitic carbon.
- **Malleable Iron**
  Carbon 0.02 to 2.3 per cent. Fuses with difficulty
  - Fused Iron C = 0.05 to 2.3 per cent.
    - If tempered = *Cast Steel* Bessemer and open-hearth steel C = 0.5 to 2.3 per cent.
    - If non-tempered = *Cementation* or *Puddled steel.* C = 0.2 to 0.5 per cent.
  - Unfused or welded Iron C = 0.02 to 0.5 per cent.
    - If tempered, *cementation* or *puddled steel.* C = 0.2 to 0.5 per cent.
    - If non-tempered, *wrought iron* combined C = 0.02 to 0.2 per cent.

FIG. 114.

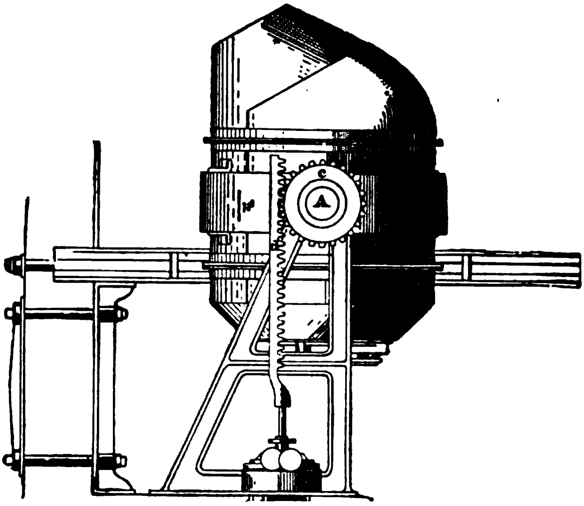


Sectional view of blast-furnace.

Cast- or Pig-Iron.—Pig-iron is the direct product of the blast furnace, varying in composition according to the nature of the ore and operation of the furnace. The ores selected, containing from 30 to 60 per cent. of iron, are mixed with coke and limestone (flux) in the blast furnace, the materials being stratified alternately. In order to attain a sufficiently high temperature, a blast of air at about 800° is blown in near the bottom of the furnace under a pressure of about 15 pounds per square inch. The temperature of the furnace rises gradually to about 1600°

in the hottest parts. The lower layer of coke exposed to the air blast burns to carbon dioxide, which is reduced to carbon monoxide on passing upwards through the layers of hot coke, and this reducing gas meeting the layer of highly heated ferric oxide (ore) reduces it to metal, carbon dioxide being formed. This, in turn, meeting the next layer of heated fuel, is changed to monoxide, which again acts as a reducing agent. The clay (aluminum silicate) present in the ore, being infusible at this temperature, unites with the limestone ($CaCO_3$), which in the meantime has been ignited to lime (CaO), to form a readily fusible glass or *slag*. The molten iron settles to the bottom of the furnace because of its higher gravity, while the lighter slag remains floating upon its surface, and is periodically drawn off at a somewhat higher level than the opening through which the molten iron is run. When in fused condition iron dissolves some carbon, part of which is present as iron carbide, and part remains in uncombined (graphitic) state. Other foreign elements present are silicon, manganese, phosphorus, and sulphur. The latter two render the iron brittle. The properties of the cast-iron will vary according to the nature of the ore and furnace conditions. *White cast-iron* contains nearly all of its carbon in combined state as carbide, while in the *gray cast-iron* it is present uncombined.

FIG. 115.



Bessemer converter.

Spiegeleisen is pig-iron containing from 5 to 20 per cent. of manganese. This is used in making steel.

Ferromanganese is pig containing from 25 to 85 per cent. of manganese. These are used in making hard and soft steels.

Cast-iron has a crystalline, granular structure on a fractured surface, is very hard and brittle, and melts at from 1150° to 1200°. Its carbon content varies from 2.5 to 5 per cent. Its specific gravity is about 7.1.

Wrought-iron.—This is the purest variety of manufactured iron made by burning out as much of the carbon (below 0.5 per cent.), silicon, manganese, phosphorus, and sulphur as possible in reverberatory furnaces lined with hematite or magnetite. It fuses at about 1500°. Owing to its low per cent. of carbon, wrought iron cannot be hardened.

Steel in chemical composition stands intermediate between cast-iron and wrought-iron, containing from 0.2 to about 1.5 per cent. of carbon, 0.02 to 0.25 per cent. of silicon and small percentage of manganese. Steel is distinguished by acquiring a temper, losing its elasticity, and becoming hard when heated to 900° and quickly cooled in water or oil. Special steels of variable degrees of hardness, elasticity and brittleness are produced through the removal of harmful elements with occluded gases; adding other elements to form isomorphous solutions with iron; altering the ratio of carbon to iron with form of combination; and tempering. Steel is made from iron by the following processes:

Cementation Process.—In this the bars of wrought-iron cut in short lengths are packed with fine charcoal in fire-clay chests or "troughs," and heated to about 1100° for from 4 to 8 days. When heated with charcoal at a white heat, from which it absorbs the proper percentage of carbon, and cast into ingots, it is known as *crucible steel,* which is the hardest and finest variety, and is used for edged tools and temper steel.

Bessemer Process.—In this we start with cast-iron, of which some 4 to 10 tons are melted in one charge in a pear-shaped vessel known as the "converter," and a blast of air at a pressure of 20 to 30 pounds per square inch is blown through holes in the bottom of this vessel and the molten metal until the necessary amount of carbon has been burned out. The Bessemer converter is shown in Fig. 115 in general view. The converter, which is lined with fire-brick, is first heated to a bright red heat and put into a horizontal position. The pig-iron is then run in from a cupola, or it may be direct from the blast-furnace, and the blast turned on when the converter is swung back into a vertical position. The reaction lasts some 20 minutes, and is known to be complete by the change in the appearance of the flame that issues from the mouth of the converter. In this time the carbon of the cast-iron is almost entirely burned out, leaving what might be called a wrought-iron. The converter is, therefore, returned to the horizontal position, the blast is shut off, and a certain quantity (some 7 per cent.) of spiegeleisen, rich in carbon and manganese, is added to the charge, which gives to the thus purified iron the quantity of carbon necessary for its transformation into steel, while the manganese reduces any oxide of iron that has formed in the molten mass. The presence of phosphorus in more than the most minute quantity is very injurious to the quality of steel, and in making steel by the original Bessemer process it was necessary to select pig-iron containing the least of this element. A modification of the process was therefore made in order to enable good steel to be made from pig-iron containing larger quantities of phosphorus. This modification is known as the *basic* Bessemer process, and consists in lining the converter with fire-brick made from a mixture of lime and magnesia, obtained by calcining dolomite. These bases absorb the phosphorus with the production of phosphates of calcium and magnesium, and, after use, the so-called basic brick containing these substances are sold to the fertilizer industry.

Siemens-Martin or "open-hearth" process. In this is taken either a mixture of pig-iron and ore, which is heated with a reverberatory flame, as in the puddling process, or bars of wrought-iron are heated with the pig-iron. In this process old iron and steel scrap may be used. Steel can be obtained directly from the ore, using a mixture of 20 per cent. of the latter with 20 per cent. of scrap iron and 60 per cent. of cast-iron.

Steel contains from 0.5 to 2.3 per cent. of carbon, all of which is chemically combined with the iron. Its specific gravity is 7.6–8.0. It has a fine-grained structure and melts at from 1300° to 1800°. If cooled rapidly it becomes hard and brittle; if cooled slowly it is soft and may be forged and welded. Steel is tempered by reheating to temperatures varying from 220° to 320°, according to the use intended, and then allowing it to cool slowly. It thus acquires elasticity combined with hardness, due to its carbon content. (See page 485.)

Manganese, chromium, nickel, tungsten, molybdenum, etc., are used to produce *special alloy steels* noted for hardness, toughness, strength, resistance to shock, etc. Very pure refined steel is also obtained in the electric furnace, which entirely eliminates many of the ordinary impurities like phosphorus and sulphur.

Vanadium and chromium increase resistance to fracture and tension. Tungsten (rapid tool) steel retains its hardness at high temperatures. Silicon renders steel very hard and brittle.

Acid Resisting Alloys.—All kinds and forms of vessels possessing acid resisting properties are in great demand in industrial plants. Various iron-silicon alloys have been introduced under special trade names, their chief qualities being resistance to acids, alkalies, and other corrosive fluids. Among the silicon iron alloys are Duriron, Tantiron, and Ferrosilicon.

Physical Properties.—Pure iron may be obtained by the electrolysis of solutions of iron salts or by reduction of pure iron oxide in a current of hydrogen. When reduced at low temperature the iron becomes pyrophoric.* In the chemically pure state, iron is of a silver-white appearance, of sp. gr. 7.86, and melts at from 1505° to 1520° (according to different authorities), expanding on solidification. In this state it is too soft for commercial purposes and becomes valuable only when small quantities of such elements as C, Si, Mn, etc., are present.

A pure form of commercial iron is " piano-wire " or any non-elastic bright fine wire recognized by the Pharmacopœia as **Ferrum.** A much less pure form of iron in a finely divided state is *reduced iron* (**Ferrum Reductum**). This should be prepared by the reduction of pure ferric oxide by means of hydrogen. The commercial article contains about 90 per cent. of metallic iron with variable percentages of ferrous, ferric, and ferroso-ferric oxides, with traçes of sulphide.

Chemical Properties.—Dry air or water, free from carbon dioxide, does not affect iron, while moisture with carbon dioxide causes rusting, due to formation of hydrated ferric oxide ($2Fe_2O_3.3H_2O$). When heated in the air iron becomes covered with a layer of scales (Fe_3O_4); this same oxide (*ferro-ferric*) forms when steam is passed over red-hot iron, hydrogen being formed at the same time. Concentrated sulphuric and nitric acid are without action upon iron at ordinary temperatures, although when diluted they dissolve it rapidly, the former yielding hydrogen and the latter NO. When iron is immersed in concentrated nitric acid (sp. gr. 1.45) no reaction takes place; if this be then immersed into diluted nitric acid it is not attacked. The iron has entered a *passive state,* its surface having become covered with a layer of magnetic oxide which protects it from further action of acids. The following metals may assume a passive state: Fe, Ni, Co, Cr, Mo, W, and V.

COMPOUNDS OF IRON

Iron forms two well-defined series of compounds: the *ferrous,* which contains a divalent Fe'', and *ferric,* with a trivalent Fe'''. The ferrous compounds are usually of a green color and act as reducing agents, while the ferric are brown to red and serve as oxidizers.

Ferrous compounds are obtained by treating iron with acids or an electro-negative element, excluding air or oxidizing substances as much as possible. They may also be obtained through the reduction of ferric salts. Ferric compounds are obtained by oxidizing ferrous salts.

IRON AND THE HALOGENS

Ferrous Chloride, $FeCl_2.4H_2O$.—This is obtained by the action of diluted hydrochloric acid on an excess of iron yielding a green colored solution and green monoclinic crystals which readily oxidize in the air. An anhydrous salt is also obtained by passing hydrochloric acid over heated iron, and sublimes in white leaflets. With alkali chlorides it forms double salts of the type, $FeCl_2.2KCl.2H_2O$.

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* Lead tartrate or citrate, when ignited away from the air, or some other metals when reduced to a similar fine state of subdivision will inflame spontaneously in the air. Such substances are termed "*pyrophoric.*"

Ferric Chloride, $FeCl_3$. **Ferri Chloridum**, U.S.P.—The official salt, prepared by oxidizing a solution of ferrous chloride with nitric acid. $6FeCl_2 + 6HCl + 2HNO_3 = 6FeCl_3 + 2NO + 4H_2O$, and evaporating, crystallizes indistinctly in orange-yellow masses, which are "odorless or having a faint odor of hydrochloric acid and a strongly styptic taste." It contains not less than 20 per cent. of Fe and is very deliquescent in moist air. Very soluble in water and alcohol. It melts at about 35.5°, forming a reddish-brown liquid. When strongly heated it is decomposed, hydrochloric acid and water escaping, leaving a residue of ferric oxide. An aqueous solution of ferric chloride is official (**Liquor Ferri Chloridi**, U.S.P.), containing not less than 10 nor more than 11 per cent. of metallic iron. It is also official as tincture (**Tinctura Ferri Chloridi**, U.S.P.), containing about 13 per cent. of $FeCl_3$, corresponding to not less than 4.48 per cent. of Fe. When exposed to light some ferrous chloride forms, due to the reducing action of the alcohol present.

Ferrous Bromide, $FeBr_2$.—This may be obtained by action of bromine on iron in the presence of water which crystallizes with $6H_2O$ in bluish-green, rhombic tablets, or anhydrous as a yellowish crystalline mass.

Ferric Bromide, $FeBr_3$, may be obtained in the form of dark-red crystals by heating iron in an excess of bromine vapor. It is deliquescent, and its solution dissolves ferric hydroxide readily with formation of soluble oxybromides.

Ferrous Iodide, $FeI_2.5H_2O$, is readily obtained by adding iodine to an excess of iron wire or clean filings in the presence of water. Should the reaction become too violent, the mixture must be cooled in order to avoid the loss of iodine. The reaction is complete when the solution assumes a greenish tint. This solution, unless kept in contact with clean iron, readily oxidizes on exposure to the air with separation of iodine. As a dry salt it is best protected from oxidation by mixing with sugar of milk, evaporating, reducing to powder, and keeping in a well-stoppered bottle.

Syrupus Ferri Iodidi.—A syrup containing not less than 4.75 per cent. nor more than 5.25 per cent. of FeI_2. Since the solution as well as the syrup of this salt tends to become discolored on standing, the Pharmacopœia directs the addition of diluted hypophosphorous acid. The reactions involved are as follows:

$$FeI_2 + 2H_2O + O = Fe(OH)_3 + I + HI.$$
$$HPH_2O_2 + 2I_2 + 2H_2O = H_3PO_4 + 4HI.$$

Ferroso-ferric Iodide, Fe_3I_8. A compound stable only in solution, prepared by adding 1 part of iodine to a filtered solution of ferrous iodide (Fe 1 p. + I 4 p.). It is used in reaction with the alkali carbonates for the preparation of their iodides.

IRON AND OXYGEN

Ferrous Oxide, FeO, is obtained as a black powder either by reducing ferric oxide with carbon monoxide, $Fe_2O_3 + CO = CO_2 + 2FeO$, or by heating ferric oxide to 300° in a current of dry hydrogen. It readily oxidizes, and when prepared by this latter method becomes incandescent on exposure to the air, so rapid is the oxidation.

Ferrous Hydroxide, $Fe(OH)_2$, is precipitated from solutions of ferrous compounds by the alkali hydroxides as a greenish-white precipitate. It soon absorbs oxygen, and changes first to a dirty green (hydrated ferroso-ferric oxide) and then to the reddish-brown ferric hydroxide.

Ferric Oxide, Iron Sesquioxide, Fe_2O_3, is found abundantly in nature as red hematite or specular iron. Artificially it is prepared by igniting the hydroxide or ferrous sulphate ($2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$), whereby a dark-red powder is obtained; that from the latter was formerly known as *colcothar* or *caput mortuum.* Natural red ochres, which consist of clay containing ferric oxide, on ignition yield red pigments. Soft deposits of hematite when dried are sold as Indian red and Venetian red, etc. Like alumina, ferric oxide is a weak base, yet it assumes the part of an acid towards strong bases (see *ferrates*).

Ferric Hydroxide, $Fe(OH)_3$, is formed when a solution of a ferric salt is added to an excess of an alkali hydroxide. It appears as "brownish-red magma, wholly soluble in hydrochloric acid without effervescence." On boiling it becomes more compact, gives up water, and is converted into the basic hydroxide $Fe_2O(OH)_4$ (or $Fe_2O_3 + 2H_2O$). The same change takes place gradually by the prolonged contact of the precipitated hydroxide with water. Freshly precipitated ferric hydroxide is soluble in solution of ferric chloride with dark-red color, owing to the formation of a basic chloride. If this solution be allowed to dialyze we can obtain a liquid containing 98.5 per cent. of ferric hydroxide in colloidal solution and 1.5 per cent. of hydrochloric acid. This solution is known as "Dialyzed Iron."

Freshly precipitated ferric hydroxide readily dissolves in various organic acids, as citric, or tartaric, or their acid salts; such solutions when evaporated and spread on glass plates form the "scale" salts of iron.

Freshly precipitated ferric hydroxide is employed as an antidote to arsenical poisoning. **Ferri Hydroxidum cum Magnesii Oxido,** U.S.P., is the official antidote prepared by mixing the solution of ferric sulphate (U.S.P.) with hydrated magnesium oxide.

$$Fe_2(SO_4)_3 + 3Mg(OH)_2 = 2Fe(OH)_3 + 3MgSO_4.$$

Ferroso-ferric Oxide, or *Black Oxide of Iron,* Fe_3O_4 (or $FeO.Fe_2O_3$).—This combination of the two oxides of iron is found abundantly in nature as magnetite or magnetic iron ore. It is also formed when iron is quickly burned in oxygen or when steam is passed over ignited iron. The iron scale that forms when wrought-iron is heated in the air is a varying mixture of ferrous and ferric oxides.

A similar combination of ferric oxide with other protoxides replacing the FeO occurs in nature as the mineral *Franklinite* (containing zinc oxide with ferric oxide), while in *Chromite* (or chromic iron) we find chromium sesquioxide with ferrous oxide in combination.

Ferric Acid, H_2FeO_4.—When iron filings are fused with an alkali nitrate, a cherry-red fused mass of ***potassium ferrate,*** K_2FeO_4, is obtained. This compound may be obtained in crystals isomorphous with potassium chromate and sulphate. It is, however, unstable and soon decomposes with separation of ferric hydroxide. The free acid, H_2FeO_4, has not been obtained.

OXYGEN SALTS OF IRON

Ferrous Sulphate, $FeSO_4.7H_2O$ (**Ferri Sulphas,** U.S.P.), has long been known under the name of *green vitriol* or *copperas.* It is obtained by dissolving iron in diluted sulphuric acid. It is also prepared industrially by partly roasting iron pyrites (FeS_2) and exposing the product (FeS) to moist air until oxidation takes place; this when leached yields a solution of ferrous and ferric sulphates and sulphuric acid, which when allowed to stand in contact with scrap iron undergoes reduction to ferrous sulphate, the reaction being:

$$FeS_2 + H_2O + 7O = FeSO_4 + H_2SO_4.$$

Various metallurgical processes, the "pickle liquors" of foundries where castings are cleaned, yield ferrous sulphate. Ferrous sulphate is largely used in the preparation of other iron salts, as ferric sulphate and ferric hydroxide, from which the various iron scale salts are made.

It forms green, monoclinic crystals, without odor, and with a saline, styptic taste; efflorescent in dry air. In moist air the crystals rapidly absorb oxygen and become coated with a brownish-yellow crust of basic ferric sulphate.

$$3FeSO_4 + O + H_2O = Fe_2(SO_4)_3.Fe(OH)_2.$$

It is soluble in 1.4 parts of cold and 0.4 part of boiling water, insoluble in alcohol. The aqueous solution of the salt has an acid reaction. When slowly heated to 115° the salt loses 6 molecules of water and the seventh only at 300°. The official dried ferrous sulphate (**Ferri Sulphas Exsiccatus,** U.S.P.) contains not less than 80 per cent. of the anhydrous salt and forms a grayish-white powder. The official granulated salt (**Ferri Sulphas Granulatus,** U.S.P.) has the same composition as the crystals, being obtained through rapidly stirring a concentrated solution of the salt while cooling, then removing the adhering mother liquor by means of alcohol.

Ferrous sulphate, like magnesium sulphate, forms crystallizable double salts with alkali sulphates, in which one molecule of water of crystallization (lost at 300°) is replaced by an alkali sulphate, as ferrous ammonium sulphate, $FeSO_4, (NH_4)_2SO_4.6H_2O$. As these double salts are more stable than the ferrous sulphate by itself and oxidize only slowly in the air, they are often used in volumetric analysis and in such instances when a *ferrous* salt free from *ferric* is desired.

Ferric Sulphate, $Fe_2(SO_4)_3$, forms a white mass which gradually dissolves in water with a reddish-brown color. It is prepared by oxidizing a solution of ferrous sulphate, containing some sulphuric acid, by means of nitric acid.

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

The solution is official as **Liquor Ferri Tersulphatis,** U.S.P., which contains not less than 9.5 per cent. nor more than 10.5 per cent. of Fe. Ferric sulphate unites with alkali sulphates to form iron alums in which Fe''' replaces Al''' of the various alums. For example, ammonium iron alum $Fe''' NH'_4(SO_4)_2.12H_2O$; in potassium iron alum K replaces the NH_4.

A basic or subsulphate of iron is also official in solution as **Liquor Ferri Subsulphatis,** U.S.P., known commonly as *Monsel's Solution,* which contains not less than 13 per cent. nor more than 14 per cent. of Fe. In its preparation the ferrous sulphate taken is converted into ferric sulphate at the expense of the nitric acid added; but the sulphuric acid mixed with the nitric is in quantity insufficient to form the normal salt. The formula of this salt is variable and uncertain, but usually given as $Fe_2(SO_4)_3.5Fe_2O_3.H_2O$.

Ferric Nitrate, $Fe(NO_3)_3$, is formed when iron is dissolved in nitric acid. It crystallizes either with 12 molecules of water in cubes or with 18 molecules in monoclinic crystals, both forms being colorless and deliquescent.

Ferrous Phosphate. $Fe_3(PO_4)_2$, is obtained as a white amorphous powder by precipitating a solution of ferrous sulphate with a mixture of sodium acetate and phosphate, the acetate being used to neutralize the sulphuric acid liberated in the reaction. $3FeSO_4 + 2Na_2HPO_4 = Fe_3(PO_4)_2 + 2Na_2SO_4 + H_2SO_4$. $H_2SO_4 + 2NaC_2H_3O_2 = Na_2SO_4 + 2HC_2H_3O_2$.

Ferric Phosphate, $FePO_4$, is obtained as a white precipitate on adding sodium phosphate to ferric solutions. It is present in the official scale preparation **Ferri Phosphas,** U.S.P., the salt being rendered soluble by the addition of sodium citrate.

Ferric Pyrophosphate, $Fe_4(P_2O_7)_3$, is prepared by interaction between ferric solutions and sodium pyrophosphate.

Ferrous Carbonate, $FeCO_3$, occurs in nature as the mineral *siderite* or *spathic iron.* It is artificially obtained by adding a hot solution of ferrous sulphate to a solution of sodium bicarbonate, washing with hot water. Hot water is employed to prevent any dissolved air (present in cold water) from oxidizing the ferrous iron. To prevent a too rapid oxidation when dry, sugar is added to the precipitated magma before drying, as in the official preparation, **Ferri Carbonas Saccharatus,** U.S.P. Ferrous carbonate is soluble in water containing dissolved carbon dioxide, forming a bicarbonate $[Fe(CO_3H)_2]$, and hence is present in the natural chalybeate mineral waters. When such a water is exposed to the air, loss of carbonic acid gas takes place with precipitation of ferric hydroxide.

Iron Carbonyls.—These are formed when carbon monoxide or gases containing the same are passed over finely divided iron (by hydrogen) at 80°, or when the gas under pressure is in contact with the metal. Iron tetra and penta carbonyl ($Fe(CO)_5$) are formed which may be condensed by sufficient cooling to amber-colored liquids. The penta carbonyl boils at 102.5°; at 216° it is decomposed into Fe and CO.

Potassium Ferrocyanide and *Ferricyanide* are described later under the cyanogen compounds in Part IV.

The organic salts of iron, such as the Tartrate and Citrate, etc., are also noted in Part IV.

IRON AND SULPHUR

Ferrous Sulphide, FeS, is obtained artificially by fusing together iron and sulphur or holding roll sulphur against a bar of red hot iron. It forms a dark-gray or black metallic mass, which finds extended use in the chemical laboratory as a source of hydrogen sulphide gas. Ferrous sulphide is also precipitated as a black precipitate by the addition of alkali sulphides to ferrous solutions directly and to ferric solutions after previous reduction of the iron salt to the ferrous state.

Ferric Sulphide, FeS_2, occurs abundantly in nature as *pyrites*, a mineral used on a large scale in the manufacture of sulphuric acid and green vitriol. This disulphide is distinguished from FeS by its insolubility in HCl.

NICKEL

Symbol, Ni. *Atomic Weight*, 58.68. *Valence*, II and III

Nickel and cobalt are two similar metals which are also allied to iron (ferrous). They are silver-like in color when polished, magnetic, of high melting-point, nearly the same atomic weight, and similar in their compounds.

History.—The ore called copper-nickel (nicolite) was known as early as 1694 to resemble copper in appearance without containing that metal. In 1751 Cronstedt demonstrated that it contained a foreign element, to which he proposed to give the name of nickel.

Occurrence.—The most important sources of nickel at present are the mines of New Caledonia and Sudbury, Ontario. The ore worked in New Caledonia is the hydrated silicate of nickel and magnesia known as *garnierite* (or *genthite*), $2(NiMg)_5Si_4O_{13}.3H_2O$, while that of Canada is a *nickeliferous pyrrhotite* (magnetic pyrites), $(NiFe)S_2$, containing from 3 to 8 per cent. of nickel. The Saxon and Bohemian ores contain CO, As, S, and Fe, among which are *Kupfer nickel* or *nicolite*, NiAs; *nickel glance*, $NiAs_2.NiS_2$; and *nickel blende*, NiS.

Metallurgy and Properties.—Such nickel ores as contain sulphur or arsenic are first subjected to a roasting process to remove the arsenic and convert the iron and copper sulphides to oxides. This is then smelted with salt cake (Na_2SO_4) and coke or calcium sulphide (alkali waste), the former being reduced to Na_2S, which dissolves copper and iron sulphides but not nickel sulphide, which settles to the bottom with the Cu_2S and FeS on top. The NiS is again roasted with $NaNO_3$ or blown in Bessemer converters to NiO, which is reduced to metal by means of charcoal. In the Mond process, the Bessemerized matte (blown in Bessemer converters), containing 80 per cent. of nickel, is crushed and treated at 100° with a current of carbon monoxide or furnace gases, whereby a volatile nickel tetracarbonyl ($Ni(CO)_4$) is formed, which is passed into a tower heated to 180°, when pure nickel is deposited.

Nickel is a lustrous white metal with a steel-gray tinge. Its specific gravity is 8.9, and it fuses at 1452°. When pure it is malleable and can be welded. The cast-nickel formerly obtained from arsenide and sulphide ores did not possess these properties, owing to the combined carbon, which made it like cast-iron. In 1879 Fleitmann discovered that the addition of ⅛ of 1 per cent. of magnesium rendered the nickel malleable and more fusible. Since then it has been found that manganese in amount from 2 to 5 per cent. would accomplish the same result. Nickel is unaffected by the air and dissolves very slowly in hydrochloric and sulphuric acids, but readily so in nitric acid. Commercial nickel contains about 1 per cent of Fe, Cu, and Si.

Uses of the Metal.—Nickel is largely employed in alloys; with copper it forms a white, hard alloy of high electric resistance. In nickel coinage 75 per cent. of copper and 25 per cent. of nickel is used. German silver, which is employed in electrical resistances, is brass (Cu 50 p., Zn 25 p.) to which from 10 to 30 per cent. of nickel has been added. The addition of 3 to 5 per cent. of nickel to steel imparts hardness, strength, and elasticity. Monel metal, an alloy of nickel 70 and copper 30 parts, which is made by the direct reduction of copper-nickel matte, possesses hardness and resistive properties towards acids, the atmosphere, and salt water. Alloys of steel with 25 to 50 per cent. of nickel possess a very low coefficient of thermal expansion, hence can be sealed, as wire, into glass, thereby replacing platinum. In the form of wire nickel steel has many applications, including resistance wire, as a substitute for German silver, wire cables for mines, torpedo defense netting, electric lamp wire, and in the mounting of lenses, mirrors, etc., and for balances for clocks, rules, measuring rods, pendulum rods, thermostats, rheostats, circuit breakers, etc. It is also used extensively for fine springs and fine tools. Nickel-plating has also been an important utilization of the metal, as the coating, if well deposited, undergoes scarcely any oxidation, and takes a high polish. The solution from which the plating is done is always that of the nickel-ammonium sulphate.

Nickel Compounds.—Nickel, like iron, forms two well-defined series of salts: the *nickelous* compounds, in which it has the valence two, and the *nickelic*, with a valence of three. The former series appear to be the more stable.

Nickelous Chloride, $NiCl_2.6H_2O$, forms green monoclinic prisms, soluble in water and alcohol, prepared by dissolving nickel in aqua regia or nickelous oxide in hydrochloric acid.

Nickelous Cyanide, $Ni(CN)_2$, is an apple-green precipitate obtained by interaction between an alkali cyanide and a nickel salt; it is easily soluble in excess of potassium cyanide, with the formation of a crystalline double salt, $Ni(CN)_2.2KCN$. This salt is easily decomposed by dilute acids, and therefore is not analogous to the ferrocyanides and cobalticyanides.

Nickelous Oxide, NiO, occurs sparingly in nature as the mineral *bunsenite*, and may be obtained artificially by igniting the hydroxide, carbonate, or nitrate. It forms a green, crystalline powder.

Nickelous Hydroxide, $Ni(OH)_2$, is precipitated when alkalies are added to nickelous solutions, as a bright-green precipitate. It dissolves in ammonia water with a blue color, and separates as a green, crystalline powder on boiling the ammoniacal solution.

Nickelous Sulphate, $NiSO_4.7H_2O$.—This salt crystallizes from aqueous solutions in green, rhombic crystals, isomorphous with magnesium sulphate. From solutions containing an excess of acid there separate at ordinary temperatures $NiSO_4.6H_2O$, in bluish-green, quadratic pyramids, and at 50°–70° green, monoclinic crystals of the same composition. The double sulphate which forms green crystals and is prepared by mixing solutions of ammonium and nickel sulphates acidified with sulphuric acid, is used for nickel-plating; its formula is $NiSO_4.(NH_4)_2SO_4.6H_2O$.

Nickelous Sulphide, NiS.—The sulphide is found in nature as *millerite*, of brass-yellow color. Obtained by precipitation by alkali sulphides in nickelous solutions, it is black.

Nickelic Oxide, Ni_2O_3, is a black powder obtained by gentle ignition of the nitrate or carbonate in air. It behaves like a peroxide, as it dissolves in sulphuric or nitric acid with evolution of oxygen, and in hydrochloric acid with evolution of chlorine. When strongly heated it forms nickelous oxide. $2Ni_2O_3 = 4NiO + O_2$.

Nickelic Hydroxide, $Ni(OH)_3$.—If chlorine be passed through the nickelous hydroxide suspended in water, this higher compound is obtained. $3Ni(OH)_2 + Cl_2 = 2Ni(OH)_3 + NiCl_2$. It is also formed as a black precipitate when the solution of a nickelous salt is warmed with an alkaline hypochlorite.

Nickel Tetracarbonyl, $Ni(CO)_4$.—A colorless liquid boiling at 43°, prepared by passing dry CO over finely divided nickel and condensing the gas by a mixture of ice and salt. When vaporized and heated from 150 to 200°, it decomposes into nickel and carbon monoxide.

COBALT

Symbol, Co. *Atomic Weight*, 58.97. *Valence*, II and III.

History.—Certain ores containing cobalt were known to impart a blue color to glass when smelted with it, and in these Brandt, in 1735, pointed out the presence of a peculiar metal to which he gave the name of ***kobalt-rex***.

Occurrence.—Cobalt occurs, less abundantly than nickel, as a sulpho-arsenide in *cobalt-glance*, $CoAs_2.CoS_2$, and as an arsenide in *smaltine*, $CoAs_2$. These are found in Canada and New Caledonia, frequently accompanied by nickel.

Metallurgy and Properties of the Metal.—The method of extraction from the ores is the same as nickel. When necessary to separate the cobalt from nickel the former is precipitated from the solution of both by means of potassium nitrite as potassium cobaltic nitrite or bleaching powder as cobaltic hydroxide. The metal is obtained by heating cobalt oxide with charcoal.

Cobalt is a slightly reddish-white metal, harder than iron, melts at about 1490°, and of specific gravity 8.9. It is attracted by magnets, but in a lesser degree than iron. It is slowly attacked by sulphuric and hydrochloric acids, more readily by nitric acid. Cobalt is somewhat used for plating upon other metals like nickel, but most of it is made into the oxide for use in the manufacture of the pigment *smalt*.

Compounds of Cobalt.—Two well-defined series of compounds are formed: the *cobaltous* and the *cobaltic*, corresponding to the ferrous and the ferric. The former of these possesses a reddish color when in the hydrated state, but becomes blue when made anhydrous.

Cobaltous Chloride, $CoCl_2.6H_2O$, is obtained by the solution of cobaltous oxide in hydrochloric acid. It forms red, prismatic crystals which when dried become blue; they dissolve in water, yielding a pale pinkish solution. This is well known as the basis of "sympathetic inks"; these leave upon paper almost invisible characters, which, when sharply dried, become blue.

Cobaltous Oxide, CoO, is obtained as a brown powder on heating cobaltous hydroxide away from contact with air.

Cobaltous Hydroxide, $Co(OH)_2$, is obtained as a rose-red precipitate on the addition of alkalies to hot cobaltous solutions. In cold solutions a blue basic salt is precipitated. Cobalt hydroxide yields a red-colored solution with ammonia water which absorbs oxygen from the air, becoming brown.

Cobaltous-cobaltic Oxide, Co_3O_4, is a compound corresponding to the magnetic oxide of iron, and is obtained when either of the other oxides of cobalt or the nitrate is heated in the air. It forms a black powder, which liberates chlorine when boiled with hydrochloric acid, yielding $CoCl_2$. This oxide is employed in decorating porcelain and preparing various salts of cobalt.

Cobaltic Oxide, Co_2O_3, corresponding to ferric oxide, is obtained as a dark-brown powder by gently igniting the nitrate; at higher temperatures it is converted into the Co_3O_4 and finally into CoO. Cobaltic oxide, when treated with hydrochloric or sulphuric acid, does not yield cobaltic salts; cobaltous compounds are produced with evolution of chlorine or oxygen. Cobalt oxide, when dissolved in diluted sulphuric acid and an alkali sulphate added, yields **cobalt alums.**

Cobaltic Hydroxide, $Co(OH)_3$, is obtained as a brownish-black precipitate if an alkaline hypochlorite or an alkali hydroxide with bromine or other suitable oxidizing agent is added to a cobaltous solution.

$$2CoCl_2 + 6NaOH + Cl_2 = 2Co(OH)_3 + 6NaCl.$$

This is dissolved by sulphuric acid with liberation of oxygen, and by warm hydrochloric acid with liberation of chlorine; cold dilute hydrochloric acid, however, dissolves it with scarcely any evolution of gas, forming Co_2Cl_6, which decomposes on heating, however, into cobaltous chloride and chlorine.

Cobaltous Sulphate, $CoSO_4.7H_2O$, forms dark-red, monoclinic prisms. It is isomorphous with $FeSO_4.7H_2O$, also forms double salts (*alums*) with alkali sulphates, as $K_2SO_4.CoSO_4.6H_2O$.

Cobaltous Nitrate, $Co(NO_3)_2.6H_2O$, forms red, deliquescent prisms.

Cobalt Double Salts.—Potassium-Cobaltic Nitrite, $Co(NO_2)_3.3KNO_2.1\frac{1}{2}H_2O$, is obtained as insoluble yellow crystals when potassium nitrite and acetic acid are added to a cobaltous salt. The Sodium Cobaltic Nitrite, T.S. (U.S.P.), is the corresponding soluble sodium salt, which is employed as a test for potassium. The quantitative separation of cobalt from nickel is based on the insolubility of the potassim-cobaltic nitrite in the presence of a large excess of potassium ions.

Potassium Cobalticyanide, $K_3Co(CN)_6$.—When the insoluble cobaltous cyanide, $Co(CN)_2$, is dissolved in a molecular quantity of potassium cyanide, a soluble potassium cobaltocyanide, $K_4Co(CN)_6$, is formed; this oxidizes in the air to the double cobalticyanide.

Cobalt Silicates.—When glass of any variety is fused with a cobalt salt a dark-blue color is obtained. This colored glass, when reduced to a powder, is used as a pigment under the name of ***smalt***. The application of ores of cobalt for this purpose appears to date from the sixteenth century. Commercial smalt, made from sand, potassium carbonate, and roasted cobalt ores, contains usually from 6 to 16 per cent. of cobalt.

Two other pigments are also obtained from cobalt oxide: ***Thenard's blue*** (or cobalt ultramarine), by igniting it with alumina, and ***Rinmann's green***, by igniting it with zinc oxide.

CHAPTER X

THE PLATINUM GROUP

Members of this group occur in the metallic state only, usually alloyed or associated together in placer deposits, sometimes accompanied by gold. The largest deposits are in the Ural Mountains of Russia; smaller quantities occur in California, Oregon, Borneo, Brazil, and Australia. According to their specific gravities, these metals may be divided into two groups, the *heavy* metals Os (22.48), Ir (22.38), Pt (21.45), and *light* metals, Ru (12.36), Rh (12.1), and Pd (11.9). These metals possess many properties in common.

PLATINUM

Symbol, Pt. *Atomic Weight,* 195.2. *Valence,* II and IV.

Occurrence.—Platinum (*platina,* the Spanish diminutive for silver), like gold, occurs widely distributed in nature, but nowhere is it found accumulated in quantity. It is generally found in the form of the so-called platinum ores, which are alloys of platinum with the other metals of this group, and in which gold, silver, copper, and iron frequently exist. It is, however, usually the chief constituent. These ores are found almost entirely in alluvial soil, and in the sand of rivers, usually in small, steel-gray flattened or angular grains. Platinum bearing sands containing but 3 grams per ton are worked.

Commercial gold and silver often contain small quantities of platinum.

Metallurgy.—The method employed embraces a series of chemical operations which consist in treating the metals with hydrochloric acid to dissolve any base metals, then under pressure with dilute aqua regia, which dissolves the platinum, palladium, and a portion of the rhodium, and leaves undissolved a mixture of osmium, iridium, ruthenium, and rhodium, known as *osmiridium.* The solution, after neutralizing with Na_2CO_3, is treated with $Hg(CN)_2$, which precipitates the palladium as cyanide. From the filtrate the platinum is precipitated as a double chloride of platinum and ammonium [$2NH_4Cl.PtCl_4$] by the addition of ammonium chloride. This, when ignited, leaves the metal in a finely divided state known as *spongy platinum.* The latter is compressed into a cake by powerful pressure, and is then welded at a white heat into a homogeneous mass. Deville's method, however, has almost entirely superseded that just mentioned. In this the platinum ore is melted with an equal weight of galena and half its weight of metallic lead. The platinum is thus taken up by the lead while the osmiridium remains unattacked. The platinum-lead alloy is then melted and exposed to a current of air, by which the lead is oxidized, the oxide flowing off as slag and the platinum being left as a porous mass. This is placed in a furnace made of lime, and melted by means of a powerful oxy-hydrogen blow-pipe flame of about 2100°. The complete separation of the metals of this group is difficult owing to their similarities and the influence of the presence of one metal over the other. For example, while platinum dissolves in aqua regia and iridium does not, yet on treating an alloy of the two with this acid, part of the iridium passes into solution, hence the methods of separation in use are far more complex than those outlined.

Platinum is a remarkable metal because of the following distinctive properties: (a) high specific gravity of 21.45; (b) high melting-point of 1755°; resistance to the action of concentrated acids; resistance to air at all temperatures; its low coefficient of expansion, which enables sealing into glass without loosening or cracking; when in a finely divided state it serves as a catalytic agent.

Properties.—In the compact state platinum is of silver white color. It possesses a decided metallic luster, great malleability, susceptibility of polish, and solidity. Next to gold and silver it is the most ductile of metals, having been drawn into wire of $^1/_{30000}$ inch in diameter. Its malleability is considerably lessened by contamination with other metals, and is particularly noticeable in commercial platinum which contains iridium. Platinum belongs to the most difficultly fusible metals, requiring the heat of the oxyhydrogen flame to melt it. Its melting point is 1755° and specific gravity 21.45. Like iron, it can be welded at a white-heat. It crystallizes in cubes and octahedra. At no temperature does it combine with oxygen. Like copper and silver, the melted metal possesses the property of absorbing oxygen, which, as the metal is allowed to cool, is given off, causing the phenomenon of " spitting."

Compact platinum does not absorb oxygen, but this condenses gas on its surface and is partly changed to ozone. This occurs even at 50°.

The strongly oxidizing action of the metal in such a condition may be conveniently illustrated by heating a small piece of platinum foil in the flame of a Bunsen burner, and then quickly extinguishing the flame, allowing the gas to escape. The foil glows, and if placed near the burner it becomes hot enough to inflame the gas. That this property is due to surface action seems to be proved by the fact that the more finely divided forms of the metal, *platinum-black* and *spongy platinum,* possess the same properties to still higher degrees.

Platinum absorbs hydrogen at a red heat and holds it at ordinary temperatures, but at a red heat *in vacuo* the gas is given off. When platinum is employed as the negative pole in the electrolysis of water it takes up hydrogen, which it will again give up by the employment of the hydrogen-laden metal as positive pole.

When a solution of platinic chloride is boiled with a reducing agent, as Rochelle Salt or a mixture of 3 volumes of glycerin with 2 volumes of a solution of KOH (sp. gr. 1.08), it is obtained in an extremely finely divided condition, known as *platinum-black.*

In the form of platinum-black the metal is capable of condensing 800 times its volume of oxygen. It thus becomes an energetic oxidizing agent; alcohol thrown upon it is at once ignited. Hydrogen when passed over it causes ignition. This property of platinum is known as *occlusion.* This same finely divided platinum possesses the remarkable property of inducing chemical combination between oxygen and sulphur dioxide, which is made use of in the *contact* process for the manufacture of sulphuric acid. It is a black, hard powder, which, by great pressure and rubbing, may be made to assume a white color. Repeated heating reduces its power to condense oxygen.

By forming an electric arc between platinum points under water, the metal is liberated in so fine a state that it passes into colloidal solution with a deep black color. This solution has a strong catalytic action and brings about many reactions, constituting what has been termed an " inorganic ferment."

Under no circumstances does platinum decompose water. Hydrochloric, hydrofluoric, nitric, and pure sulphuric acids singly do not attack platinum.

Nitro-hydrochloric acid easily and completely dissolves it. Vessels of platinum are readily attacked at high temperature by compounds containing phosphorus, arsenic, lead, caustic alkalies, alkali sulphides, and cyanides; solutions containing any of the halogens attack the metal when cold.

When alloyed with silver it is dissolved by nitric acid.

Platinum-ware should never be heated in the inner cone of a Bunsen-burner flame, as it is likely to injure the texture of the metal. Platinum vessels are usually cleaned by rubbing with moist, rounded sea-sand, or by fusing in them a quantity of acid potassium sulphate until white fumes of sulphur trioxide are evolved.

When iridium is present in platinum it makes the alloy less fusible, more rigid, harder, denser, and less readily attacked chemically than pure platinum. An alloy of 8 parts of platinum and 2 parts of iridium is only very slightly dissolved by nitro-hydrochloric acid. An alloy containing 10 per cent. of iridium is used in preparing the international standards meter and kilogram.

An alloy of palladium 20 p. and gold 80 p., called Palau, is useful as a substitute for platinum laboratory ware. Its specific gravity is 17.22 (at 18.4° C.) and melting point 1370°. Palau compares favorably with platinum in all respects.

Another substitute for platinum is an alloy of about equal parts of rhodium and gold known as Rhotanium. Two grades are offered, known as " A " which fuses at 1250° and " B " fusing at 1425°.

Two classes of compounds are known, the *platinous*, which are slightly basic with Pt as a dyad, and *platinic*, which are acid and Pt as a tetrad.

PLATINUM AND THE HALOGENS

Platinous Chloride, $PtCl_2$, is obtained by heating chlorplatinic acid above 230°; at a much higher temperature further decomposition takes place, leaving finally Pt.

It is a gray-green powder, insoluble in water and nitric acid, but soluble in hot hydrochloric acid. Platinous chloride is used for absorbing ethylene, C_2H_4.

Platinic Chloride, $PtCl_4$.—This chief salt of platinum is obtained by dissolving platinum in aqua regia, evaporating on a water-bath to a syrup, adding hydrochloric acid, and again evaporating to expel the excess of nitric acid. On standing, brownish-red deliquescent crystals of *Chloroplatinic Acid*. $H_2PtCl_6.6H_2O$ ($PtCl_4.2HCl.6Aq$), separate. This compound is known as *platinum chloride*, which is employed as a reagent in the quantitative separation of K, Na, NH_4, Cs, and Rb. These alkali metals form double platinic-chlorides as $2KCl.PtCl_4$. The alkaloids form similar insoluble double salts. If chloroplatinic acid be heated in dry HCl, the anhydrous, non-deliquescent $PtCl_4$ is obtained.

Platinous Bromide, $PtBr_2$, results as a brown-gray, insoluble mass when bromoplatinic acid is heated to 200°.

Platinic Bromide, $PtBr_4$, is not known except in combination with hydrobromic acid as bromoplatinic acid. The latter is produced by dissolving platinum in a mixture of nitric and hydrobromic acids; it crystallizes in deliquescent, dark-red prisms.

Platinous Iodide, PtI_2, is a black powder obtained by warming platinous chloride with potassium iodide.

Platinic Iodide, PtI_4.—By heating an excess of chloroplatinic acid with potassium iodide a black powder, insoluble in water and soluble in potassium iodide, is obtained.

Platinous Cyanides.—Cyanides of platinum have not been prepared pure, but the double *platinocyanides* are well known. The potassium platinocyanide is prepared by dissolving platinous chloride in a solution of potassium cyanide: $PtCl_2 + 4KCN = K_2Pt(CN)_4 + 2KCl$. Also by boiling spongy platinum with a solution of potassium cyanide; $Pt + 4KCN + 2H_2O = K_2Pt(CN)_4 + 2KOH + H_2$. This salt forms yellow prisms, blue by reflected light. The *barium platinocyanide,* $BaPt(CN)_4.4H_2O$, becomes luminous when exposed to Röntgen rays. All of the alkali platinocyanides are beautifully colored and possess strong dichroism.

PLATINUM AND OXYGEN

Platinous Oxide, PtO, and *Platinic Oxide,* PtO_2, are obtained as black powders by careful heating of the respective hydroxides.

Platinous Hydroxide, $Pt(OH)_2$, forms a black powder which possesses the characters of a weak base. It is obtained by digesting platinous chloride with potassium hydroxide.

Platinic Hydroxide, $Pt(OH)_4$, is obtained as a white, flocculent precipitate by boiling chloroplatinic acid with an excess of sodium hydroxide, and then acidifying the liquid with acetic acid.

Platinous Sulphide, PtS, and *Platinic Sulphide,* PtS_2, are precipitated from the corresponding chlorides when the latter, in aqueous solution, are treated with hydrogen sulphide. They are black-brown powders.

RHODIUM

Symbol, Rh. *Atomic Weight,* 102.9. *Valence,* II and IV.

Wollaston discovered this element in an American platinum ore in 1804, and on account of the rose-red color of its chloride gave to it the name rhodium (ῥόδον = a rose). Apart from its occurrence in platinum ores, rhodium occurs alloyed with gold. In the compact state it is a gray-white, malleable metal, which is more difficultly fusible than platinum, but more easily than iridium. Its specific gravity is 12.1 and melts at 1907°. It oxidizes superficially, becoming blue when strongly heated in the air or in contact with alkalies. Rhodium is insoluble in all acids with the exception of nitro-hydrochloric. Its alloys are, however, more easily dissolved. At a red heat chlorine produces with the finely divided metal red, insoluble rhodium chloride, $RhCl_3$, which forms double salts with the alkali chlorides; also its sulphate forms alums with alkali sulphates.

Rhodium gives oxides of the following compositions: RhO_3, Rh_2O_3, and RhO_2.

An alloy of Rh (10 per cent.) with platinum serving as one wire and platinum as the other, welded together at one extremity, serve as an extremely sensitive thermo-electric pyrometer.

An alloy of rhodium and gold is known as Rhotanium; see under Platinum.

RUTHENIUM

Symbol, Ru. *Atomic Weight,* 101.7. *Valence,* II and IV.

Ruthenium was first observed in 1828, by Osann, in the residues from the working of the Russian platinum ores.

The name ruthenium was applied to the new element because of the Russian origin of the ores.

It also occurs as sulphide in *laurite,* which is found along with platinum ores in Borneo and Oregon.

Ruthenium is a gray-white, brittle metal, which fuses at about 1900° and has a specific gravity of 12.3.

It is insoluble in acids excepting aqua regia, which dissolves the metal very slowly, forming the chloride $RuCl_3$.

Besides oxides of the same constitution as those yielded by rhodium, ruthenium also forms RuO_2 and RuO_4. By fusing the finely divided metal with potassium hydroxide and potassium nitrate, potassium rutheniate, K_2RuO_4, is obtained. It dissolves in water with a dark orange color; the solution blackens the skin.

PALLADIUM

Symbol, Pd. *Atomic Weight*, 106.7. *Valence*, II and IV.

In 1803 palladium was discovered by Wollaston in native platinum. He named it after the then recently discovered planet Pallas. It is alloyed with platinum in almost all of its ores.

In its appearance, luster, hardness, and malleability this metal is very similar to platinum. It is the most fusible of the platinum metals (1549° C.). Heated in air it becomes superficially oxidized, but at a higher temperature regains its luster. It has a specific gravity of 11.9.

Hot, conc. mineral acids and alkalies attack the finely divided metal. This element has an affinity for hydrogen that has characterized it above all others. If palladium foil be made the cathode in the electrolysis of water, the metal will take up 960 times its volume of hydrogen without change in appearance. The metal is said to *occlude* the gas. The ignited palladium foil will absorb 370 times its volume of hydrogen at 50°. This charged palladium is a strong reducing agent. Palladium generally occurs in commerce in foil.

Of the chlorine compounds of the metal only palladious chloride, $PdCl_2$, is known in the isolated state, although palladic chloride, $PdCl_4$, may result when the metal is dissolved in nitro-hydrochloric acid. When this solution is evaporated chlorine is given off, and brown-red prisms, having the composition $PdCl_2.2H_2O$, are obtained. The aqueous solution of the latter salt serves for the quantitative separation of iodine (as insoluble PdI_2) from bromine and chlorine. With the alkali chlorides comparatively insoluble, double chlorides are formed, *viz.*, K_2PdCl_4 or $2NH_4Cl.PdCl_4$.

IRIDIUM

Symbol, Ir. *Atomic Weight*, 193.1. *Valence*, II and IV.

Iridium was discovered along with osmium in 1804, by Smithson Tennant, in the *osmiridium* left in the working of platinum ores. On account of the manifold colors which the solution of its chloride showed, he designated it by its present name, from Iris, the rainbow. Besides the above source it is sometimes found alloyed with platinum alone. It is harder and less fusible than platinum, melting at 2290° C., and has a specific gravity of 22.38. It behaves somewhat like palladium when heated in air or oxygen. In the pure compact state it is insoluble in all acids. Only in the alloyed state is it soluble in nitrohydrochloric acid forming iridium dichloride, $IrCl_2$, and tetrachloride, $IrCl_4$.

The salts of iridium correspond to the oxides IO and I_2O_3. They are all recognized as compounds having weak properties both as acids and bases. Platinum is alloyed with iridium (10 per cent.) to increase its resistance to chemicals, rigidity and hardness; also for making the international standard weights and rules. It is used to tip gold pens.

OSMIUM

Symbol, Os. *Atomic Weight*, 190.9. *Valence*, II and IV.

Osmium was discovered in 1804, by Smithson Tennant, along with iridium, in the *osmiridium* or insoluble residue left upon treatment of the platinum ores with nitro-hydrochloric acid.

The name is from the Greek word οσμή, meaning odor.

The metal, when finely powdered, emits a peculiar, pungent, iodine-like odor, in consequence of the formation of osmic anhydride, OsO_4. Osmium is the heaviest metal known, having the specific gravity of 22.48. It is hard, bluish-white, and volatile at the temperature of melting iridium. Its melting point is about 2500° C. The metal combines with chlorine to give *osmium dichloride*, $OsCl_2$, and *tetrachloride*, $OsCl_4$.

The following oxides are known: OsO, Os_2O_3, OsO_2, and OsO_4, which is the most important.

Fuming nitric acid and nitro-hydrochloric acid convert osmium into osmic anhydride, OsO_4, which is also produced by heating the metal in air. Osmic anhydride, commercially known as *Osmic Acid*, forms colorless, glistening needles, which volatilize without decomposition. The vapors emitted by this substance are irritating to the eyes and suffocating. It is soluble in water, giving a colorless, neutral solution which has a caustic taste and the peculiar iodine-like odor of the anhydride.

Osmic anhydride (tetroxide) is an oxidizing agent. It is used as a stain in histological work. Osmic acid, H_2OsO_4, is not known in the free state.

Osmium tetroxide (OsO_4) serves as a very active contact oxidizer. For example, chlorates in neutral aqueous solution, through the addition of a very small quantity of osmium oxide, immediately liberate their oxygen. Alcohol is oxidized to aldehyde and acetic acid, anthracene to anthraquinone, in fact most difficultly oxidizable bodies may be quickly oxidized by means of a chlorate solution activated with osmium oxide. It was used as a contact substance in the Haber synthesis of ammonia.

PART IV.

ORGANIC CHEMISTRY.

CHAPTER I

INTRODUCTORY

1. Distinction between Organic and Inorganic Compounds.—It becomes necessary at the beginning of this section of chemistry to give a reason for the separation of carbon compounds from those of the other elements. Such a reason has in the past been found in the use of the terms *organic* as applied to the chemistry of the carbon compounds, and *inorganic* as applied to the chemistry of the other elements.

The same chemical forces undoubtedly act in both the organic and the inorganic worlds. The separation of the carbon compounds from those of the other elements, which is still maintained in most chemical text-books, is, therefore, at present mainly a matter of convenience. Owing to the peculiar tendency of the carbon atoms to aggregate together in groups and the facility with which the saturating hydrogen of "hydrocarbons," as the combinations of these two elements are called, is replaced, the number of carbon compounds capable of formation is an immense one. Besides the many thousands of these carbon compounds naturally occurring, the number artificially formed has grown enormously in recent years. It becomes eminently desirable, therefore, to classify them and study them apart from the compounds of the other elements.

2. Composition and Analysis of Organic Compounds. — Many organic compounds contain carbon and hydrogen only, and are known as "hydrocarbons." The other elements found at times as constituents of organic compounds are oxygen and nitrogen, and less frequently sulphur and phosphorus. The halogens and other elements are often introduced by substitution into the formulas of organic bodies.

The analysis of the carbon compounds may be either *qualitative* or *quantitative,* and both of these methods may be applied with reference to the *ultimate* (or *elementary*) and the *proximate* composition of the substance analyzed.

(*a*) *Qualitatively,* carbon is shown in many cases by the charring which takes place when the substance is heated on a strip of platinum foil. In case the material is volatile without decomposition, it is mixed with easily reducible substances, such as copper oxide or chromate of lead, placed in a tube sealed at one end, and heated, when the carbon is oxidized to carbon dioxide. The escaping gas may be conducted through lime-water, and the presence of carbon will be indicated by the turbidity produced in this.

The same mixture of the suspected organic compound with oxide of copper or chromate of lead when heated will give rise to the formation of water if hydrogen is present. This will condense in the cooler part of the tube or may be received in a weighed tube containing calcium chloride.

Organic nitrogenous substances heated in a tube closed at one end with soda-lime (a mixture of caustic soda with lime) will give off the nitrogen as ammonia, recognizable by the use of red litmus paper. Some nitrogenous compounds do not respond to this test. A test applicable, however, to all organic nitrogenous compounds is to heat the substance in a small dry test-tube with a fragment of metallic sodium and to test the metallic cyanide formed by dissolving the melted mass in water, filtering, heating with a few drops of ferrous sulphate and caustic soda solutions, and then adding ferric chloride. On the addition of hydrochloric acid, a precipitate of Prussian blue is obtained if nitrogen were originally present.

The halogens cannot always be detected by the direct addition of silver nitrate solution, as these may not be present as ions in solutions of the compounds. If the substance, however, be ignited with quicklime, the calcium halide so formed can be tested for with silver nitrate. Or the substance may be mixed with pure copper oxide and ignited on a loop of platinum wire. A blue color changing to green appearing in the flame will indicate chlorine, and a green color iodine. Still another method consists in heating the substance with fuming nitric acid and silver nitrate in a sealed tube, when the haloid silver salt is produced.

Sulphur can be detected by ignition with sodium, forming sodium sulphide, which is dissolved in water and tested for with sodium nitroprusside, yielding a purple coloration. Or the substance may be oxidized either, in case it be a solid, with a mixture of potassium hydroxide and nitre or, in case it be a liquid, with fuming nitric acid. The sulphur is thus converted into sulphuric acid, which is then tested for with barium chloride.

Phosphorus is also capable of oxidation into phosphoric acid by the same means, and this can be then tested for as usual with sodium molybdate. Ignition with powdered magnesium will cause the formation of a phosphide which on moistening with water will evolve phosphoretted hydrogen.

All other elements, after complete oxidation of the organic compound as above, may be tested for by the methods of inorganic chemistry.

(*b*) *Quantitatively,* carbon and hydrogen are always determined together by what is termed an organic combustion. In this case a weighed quantity of the substance is heated in a tube of difficultly fusible glass along with an easily reducible substance like oxide of copper or chromate of lead. The carbon is oxidized to carbon dioxide and the hydrogen to water, both of which are to be collected in weighed absorption vessels. The increase in weight of these allows of a determination of the amount of carbon and hydrogen respectively present in the substance burned. Either a tube sealed at one end may be used, in which case the sealed end is drawn out to a fine point so that at the end of the heating it may be broken and a current of purified air or oxygen passed through, or a tube open at both ends is taken. In the latter case the combustion is carried out from beginning to end in a current of oxygen freed from moisture and carbon dioxide gas by passage through suitable absorption bottles. The water produced by the oxidation of the hydrogen of the organic substance is caught in a weighed tube containing fused and granulated chloride of calcium, and the carbon dioxide produced by the oxidation of the carbon of the organic substance is caught in a weighed bulb apparatus containing strong caustic potash solution. The apparatus of Geissler shown in Fig. 134 is now generally used. One-ninth of the increase of weight of the chloride of calcium tube represents the weight of the hydrogen, while three-elevenths of the increase of weight of the potash bulbs represents the weight of the carbon.

If the organic compound is nitrogenous, a spiral of metallic copper or silver must be placed in the front end of the combustion tube and kept at a low red heat in order to prevent the oxides of nitrogen from going over in the absorption apparatus and vitiating the results. Organic compounds containing sulphur must be burned with chromate of lead, which will oxidize the sulphur and hold it as sulphate of lead. Halogens present in an organic compound are held as silver haloid salts by the use of the silver spiral before alluded to.

The nitrogen of an organic compound is either determined absolutely after liberation as gas and its volume measured, or it is converted into ammonia by combustion with soda-lime as in the Will-Varrentrap method, or by heating with strong sulphuric acid and potassium permanganate as in the Kjeldahl method. In the determination of nitrogen by volume use a tube open at both ends; one is connected with a graduated nitrometer containing a 30 per cent. solution of potassium hydroxide solution, while the other is connected with an apparatus for the generation and dry-

FIG. 134.

Geissler's potash bulbs.

ing of carbonic acid gas by means of which all air is removed from the apparatus before beginning the combustion and afterwards for removing all traces of nitrogen remaining. The substance is burned with copper oxide, a copper spiral being used of course in the front end of the tube to decompose oxides of nitrogen. In the soda-lime process the substance is burned in a tube closed at one end, somewhat shorter than the ordinary combustion tube, and the ammonia produced is absorbed in pure strong hydrochloric acid. We may then either determine the ammonia here caught as ammonium chloride by the use of platinic chloride, or, if a measured amount of hydrochloric acid of known strength was taken, may titrate back with normal alkali solution and so determine the ammonia indirectly. In the Kjeldahl process the substance is heated with concentrated sulphuric acid for some time to a temperature near the boiling point of the latter, the addition of small portions of powdered potassium permanganate near the end of the action sufficing to complete the ammonia formation. The mixture is then diluted with water, supersaturated with caustic soda, and the ammonia distilled off and determined volumetrically.

Oxygen is always determined by difference, as no reliable general method for its determination exists.

3. **Physical Properties of Organic Compounds.**—The physical properties are just as important points for observation in the case of organic compounds as with inorganic substances, only, instead of crystalline form, hardness, lustre, color, etc., the important properties for consideration in this connection are fusing point, boiling point, vapor-density, and in some cases optical properties.

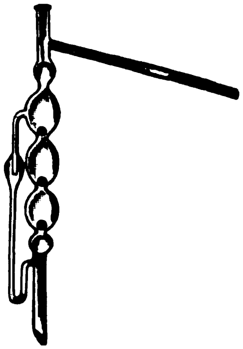
(*a*) *Fusing Point.*—Most organic solids, when sufficiently pure, fuse either with or without decomposition at a constant temperature. To determine the fusing point a small quantity of the substance carefully dried and pulverized is placed in a capillary tube sealed at one end, and this is attached by a rubber band or a piece of platinum wire to a thermometer in such a way that the capillary tube with the substance is immediately adjacent to the bulb of the thermometer. A round-bottomed flask with a long neck is then taken, and in this is placed concentrated sulphuric acid or colorless cottonseed oil so that the bulb of the flask is three-quarters full. The thermometer with capillary tube attached is held in position by passing it through a perforated cork fitted in the neck of the flask, and dips into the liquid far enough to allow the bulb and substance in the capillary to be covered. A small side tube fitted in the perforated cork allows the air to escape when the flask is heated. The heat is applied gradually, and the moment the substance in the capillary is in clear fusion the temperature is read off. (For more detailed directions and method of correction of thermometer reading, see U. S. Phar. IX revision, p. 596.

(*b*) *Boiling Point and Fractional Distillation.*—Most organic liquids boil without decomposition at a fixed temperature, which is called their boiling point. Even in the case of such liquids as cannot be distilled without decomposition under ordinary atmospheric pressure, it is often possible by distilling them under reduced pressure or *in vacuo* to get them to vaporize at a constant temperature. A boiling point, constant for the same atmospheric pressure, is taken as one of the most reliable indications of purity and identity of organic liquids.

To determine the boiling point the liquid is placed in what is termed a distillation bulb. This consists of a bulb with tall, narrow neck into the side of which at some height above the liquid is fused a delivery tube bending downward at an oblique angle. The neck of the distillation bulb is closed by a tight-fitting cork perforated for a slender thermometer. The latter must extend so far into the neck that the mercury bulb comes just below the lateral exit for the vapors, but never dips into the liquid. If in making a boiling-point determination any part of the mercury column extends above the neck of the distillation bulb where it is surrounded by vapor, a correction must be made depending upon the length of the column not surrounded by vapor. Of course, the boiling point is always dependent upon the atmospheric pressure, as indicated by the barometer (see page), and therefore the pressure must be noted in connection with each boiling-point determination. (For special details of manipulation of this determination, see U. S. Phar. IX, page 598.)

A mixture of organic liquids of different boiling points can often be separated into its components by what is termed fractional distillation, especially when the boiling points of the individual components are moderately removed from each other. In this case fractions of the distillate are caught separately at fixed intervals, say, every five or ten degrees, and these are then distilled by themselves and the portions coming over at approximately the same temperature added together. By repeating the operation several times the distillates show a tendency to accumulate at a few fixed temperatures corresponding to the boiling points of the components of the original mixture.

Fig. 135



The process of fractional distillation is much facilitated by the use of distillation bulbs with special arrangements for condensation in the vertical neck attached to the bulb or flask, such as the apparatus of Wurtz, Linnemann, and Hempel. (Fig. 135.) These accomplish a fractional condensation of the vapors corresponding to that effected in the column apparatus of the rectifier or tar distiller.

(*c*) *Determination of Molecular Weight.*—This determination has considerable importance in the study of organic compounds, as, for reasons to be explained later, ultimate organic analysis does not generally enable us definitely to determine molecular weight and molecular formulas. The molecular weights of bodies may be determined:

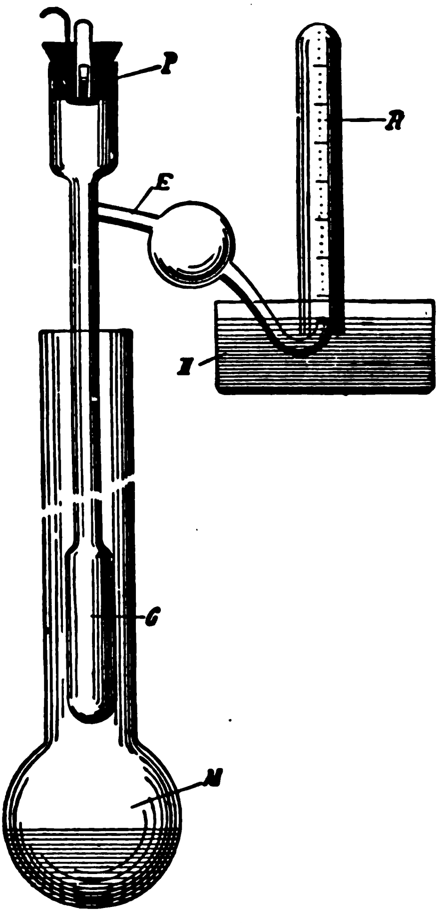
1. Measuring the vapor-density.
2. Raoult's method of measuring the lowering of the freezing point of a solution.
3. Beckmann's method of measuring the elevation of the boiling point of a solution.

1. For determination of *vapor-density* we can ascertain the weight of a definite volume of the vapor, which is then compared with the weight of the same volume of air under similar conditions of temperature and pressure, or the volume occupied by the vapor obtained from a fixed weight of the substance, or thirdly, the volume of another substance like mercury or air displaced by the vapor from a definite weight of the compound under investigation.

To the first class of determinations belongs the Dumas vapor-density method and to the second class the Hofman method, but both of these have been abandoned for the simpler method of Victor Meyer which illustrates the third class of determinations.

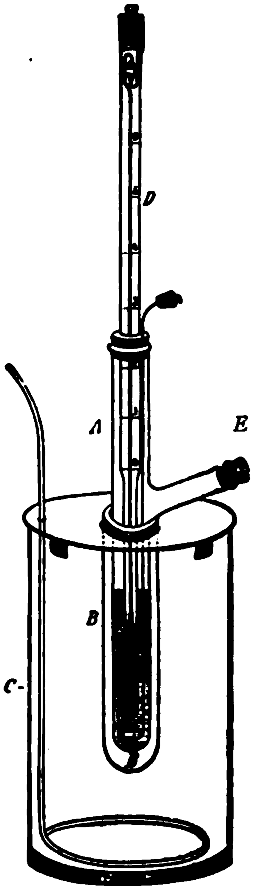
The apparatus for this is shown in Fig. 136. The vessel in which the substance is to be vaporized is shown at G. This is closed by a cork, perforated and fitted with a glass tube in which the little vessel with substance is placed as shown at P. The liquid in the mantle at M is first brought to boiling, and when air ceases to issue through the delivery tube at E, the eudiometer tube R is placed in position over the end of the delivery tube as shown in the illustration. The little tube containing the substance is then caused to fall by bending the wire support to one side. The vapor of the organic compound displaces an amount of air corresponding to its volume at the temperature of the experiment. Not more than 0.1 gram of the substance is needed for this method. From the results of this determination the vapor-density is calculated by the use of the following formula: $D = \frac{S\ 760(1.003665t)}{V.(B-w)0.001293}$, in which D stands for density, S for weight of sub-

Fig. 136



Victor Meyer's vapor-density apparatus.

Fig. 137



Beckmann's apparatus.

stance, t for temperature, V for volume of air displaced, B for barometric reading, and w for tension of the vapor of water at the temperature of the observation. Inasmuch as air is 14.435 times heavier than hydrogen, the value D must be multiplied by 14.435 to obtain vapor-density based on hydrogen, and by 28.87 to get the molecular weight of the substance used.

2. It has been long known that the vapor pressure of a liquid is diminished when a non-volatile substance is dissolved in it and that this diminution is proportional to the quantity of dissolved substance.

Accordingly the following rule has been established: "Equimolecular quantities of different substances, dissolved in equal volumes of the same solvent (benzene, glacial acetic acid, etc.), lower the vapor pressure to the same extent." The formula used is $M = c\frac{p}{t}$, where M is the molecular weight, c the constant for the liquid used, p the percentage of the substance contained in the solvent, and t the depression of the freezing point in degrees Centigrade.

The constants for the solvents most commonly used are found to be:

Benzene	53	Diphenylamine	88
Glacial Acetic Acid	39	Naphthalene	69
Nitrobenzene	70	Urethane	52.4
Phenol	77	p-Toluidine	51
Water	19	Thymol	92

A comparison of these constants shows that they bear the same ratio to each other as the molecular weights of the substances used as solvents.

For the carrying out of this determination Beckmann's apparatus, shown in Fig. 137, is generally used. A glass tube, A, with a side projection, is filled with 15–20 grams of the solvent (weighed accurately, however) and closed with a cork in which are placed an accurate thermometer, capable of adjustment for use at different temperatures and divided into hundredths of a degree, and a stout platinum wire, serving as a stirring-rod. This tube is placed in a somewhat wider tube, B, which serves as an air-jacket. The whole is suspended in a wide battery-jar, C, which contains cold water or a freezing mixture, the temperature of which should be from 2° to 5° below the freezing point of the solvent.

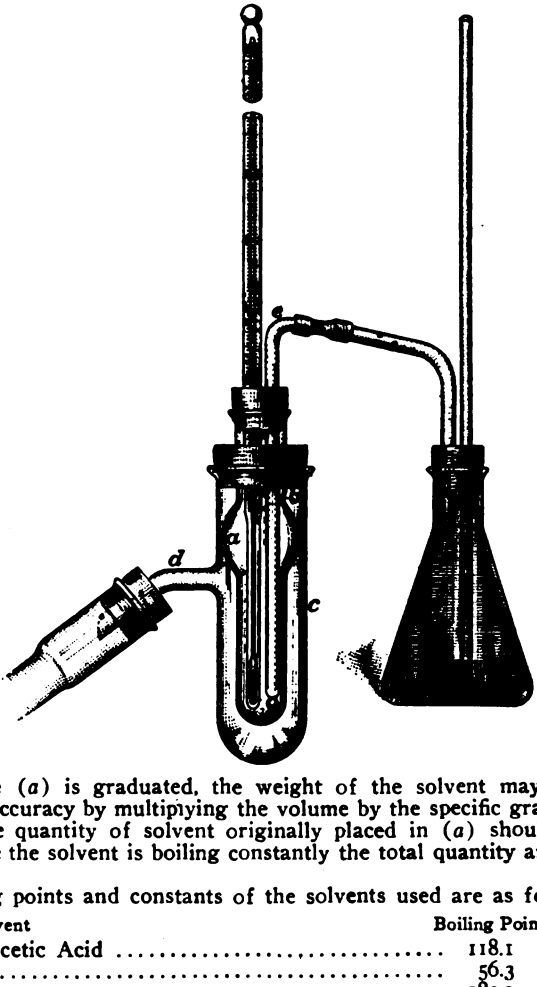
The congealing point of the solvent is first determined by cooling it several degrees below its freezing point; and then by agitation with the platinum rod (after adding platinum clippings) the formation of crystals is started. During this formation the temperature rises, and when the mercury becomes stationary, it indicates the exact freezing point of the solvent. After the mass has melted again, an accurately weighed amount of substance is introduced through E. When this has dissolved, the freezing point is redetermined as before.

3. Beckmann has also worked out a method by which the elevation in the boiling point of a liquid produced by dissolving any substance in it can be used for the determination of the molecular weight of the substance. The formula used is $M = c\frac{g}{G(t'-t)}$, where M is the molecular weight, c the constant indicating the molecular elevation of the boiling point for 100 grams of the solvent, g the weight of the substance, G the weight of the solvent, t the boiling point of the solvent, and t' the boiling point of the solution.

A simpler form of apparatus is that devised by Landsberger (Fig. 138). A suitable quantity of the solvent is placed in the tube (a), which is about 15 cm. in height and 3 cm. in diameter, and which has a small opening (b) for the escape of the vapor; this tube (a) is fitted by means of a cork into a larger one (c), which serves as an air-jacket, and the outlet (d) of which is connected with an ordinary Liebig's condenser. The inner tube (a) is closed with a cork through which pass a thermometer, graduated to 1/20°, and a tube (e), the end of which has been cut off in a slanting direction, or perforated with a number of holes. The solvent in the tube (a) is not heated directly, but only by the vapor of the same solvent, which is generated in the flask (f); in this way superheating is avoided.

The boiling point of the solvent alone is first determined by heating the solvent in the flask (f) and passing its vapor through the solvent in (a) until the thermometer shows a constant temperature; the solvent in (a) is then mixed with that in the flask (*f*), about the same quantity as originally used being poured back into the tube (*a*). A weighed quantity of the substance is now placed in (*a*) and vapor from (*f*) is again passed until the temperature is again constant. The difference between the two readings gives the elevation, *E*. The weight of the solvent in (*a*) at the time of the second reading has now to be found, and the molecular weight of the substance can then be calculated.

FIG. 138.



If the tube (*a*) is graduated, the weight of the solvent may be ascertained with sufficient accuracy by multiplying the volume by the specific gravity at the boiling-point. The quantity of solvent originally placed in (*a*) should be so chosen that by the time the solvent is boiling constantly the total quantity amounts to about 10 grams.

The boiling points and constants of the solvents used are as follows:

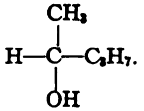
Solvent	Boiling Point	C°
Glacial Acetic Acid	118.1	25.3
Acetone	56.3	16.7
Aniline	183.0	32.2
Benzene	80.3	26.7
Carbon Disulphide	46.2	23.7
Chloroform	61.2	36.6
Ethyl Alcohol	78.3	11.5
Ethyl Ether	35.0	21.1
Methyl Alcohol	66.0	9.2
Phenol	183.0	30.4
Water	100.0	5.2

(*d*) *Optical Properties.*—Many organic compounds turn the plane of polarization of light. This may happen with the bodies in the solid state, as with camphor, $C_{10}H_{16}O$, or with others when solid as well as when in solution, as with strychnine sulphate; but most generally it is shown in liquids only, as with solutions of tartaric acid and the sugars and liquids like essential oils and many petroleums.

In many cases several optically active modifications of the same compound exist. Thus, a dextro-rotatory and a lævo-rotatory modification can be obtained, as in the case of tartaric acid. These will combine to form an inactive variety of the same compound. Conversely, the inactive variety can often be broken up into the two optically opposed varieties. This may be done in several ways. Inactive tartaric (racemic) acid may be transformed into the ordinary active variety by heating to 170° C., or the salts of the inactive acid will crystallize out as a mixture of the two opposing varieties. The addition of certain enzymes will also cause a change of an inactive variety into an active one.

The angle of rotation of the plane of polarized light in the case of an optically active substance is proportional to the thickness of the layer traversed. It is also dependent upon the wave-length of the light used for illumination in the instrument. Yellow monochromatic light from a sodium flame is generally used. It is also somewhat dependent upon temperature.

When the specific rotatory power of a substance is known, we can, in the case of a solution containing this substance as the only optically active ingredient, determine the percentage of material present from an observation of the angle of actual rotation. Thus, in the case of a sample of diabetic urine, we have observed an actual rotation of + 1.05°. Knowing the specific rotatory power of grape sugar to be 52.5° we make the calculation $p = \frac{100 + 1\ 5}{52\ 5 + \ \ 1} = 2.8$ per cent. grape sugar. In case the specific gravity of the solution is much over 1, that must also be used, multiplying it into the denominator. The practical use of the polariscope will be referred to again under *Sugars*.

An explanation of the optical activity of organic compounds has been offered in recent years by LeBel and Van t'Hoff. This is that optically active compounds contain one or more ***asymmetric*** carbon atoms—that is, carbon atoms each of the four affinities of which are joined to a different atom or group, as in the case of optically active amyl alcohol,  $H{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}{-}C_3H_7$. It has been found that all optically active substances contain such asymmetric carbon atom, but the converse is not invariably true.

4. Isomerism and Structural Formulas.—The results of an ultimate combustion analysis of an organic compound will give us nothing more than the ratio of the atoms composing it. Even with the molecular weight obtained by means of a vapor-density determination, we can give only what is called an *empirical* formula (that is, one which expresses the number of the several atoms present but with no information as to how they are joined together. We find, however, that there are numerous cases where several bodies may exist having the same percentage compositions, or even the same absolute number of the constituent atoms, and yet be quite different in physical properties. Thus CHO.H, formaldehyde, $C_2H_3O.OH$, acetic acid, and $CH_3.CHOH.COOH$, lactic acid, will have the same percentage composition although of different formulas. Again, pyrocatechin, resorcin, and hydroquinone all have the formula $C_6H_6O_2$ and yet are quite distinct in fusing points as well as in chemical reactions.

Bodies which have such points of agreement and yet are different are said to be *isomeric*.

We may distinguish four distinct cases of *isomerism*.

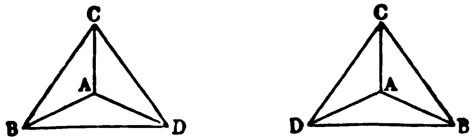
(*a*) *When* the isomeric bodies have the same percentage composition but a different molecular weight. Such bodies are said to be ***polymeric***. Thus, C_2H_4, ethylene; C_3H_6, propylene; C_4H_8, butylene; C_5H_{10}, amylene, are polymeric, the unit of increment being CH_2. CH_2O, formaldehyde; $C_2H_4O_2$, acetic acid; $C_3H_6O_3$, lactic acid; $C_6H_{12}O_6$, grape sugar, are also polymeric.

(*b*) When the isomeric bodies have the same molecular weight also, such bodies are said to be ***metameric***, as their difference is based upon a different arrangement of the atoms within the molecule. Thus, trimethylamine $H(CH_3)_3$ and propylamine $HH_2(C_3H_7)$ have equally the formula C_3H_9N; methyl ether $(CH_3)_2O$ and ethyl alcohol $C_2H_5.OH$ have equally the formula C_2H_6O.

(*c*) A third case of isomerism is what is termed ***physical isomerism***. This is believed to be due to a different geometrical position of the atoms in the molecule, as explained in the stereochemical theories, and may be briefly stated as follows:

If a carbon atom is combined with four different atoms or atomic groups no case of isomerism can arise on the ground of difference in chemical constitution, as in the class just mentioned. Yet different tetra substitution derivatives may exist in some cases. These are explained by noting the difference between a positive and a negative tetrahedron, as shown in Fig. 139.

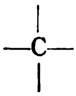
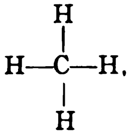
FIG. 139.

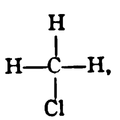


One of these figures is the reciprocal or reflection of the other. If we suppose the tetrad carbon atom to be in the centre of such a tetrahedron and the four saturating atoms or groups at the four angles, we will have in the two forms of tetrahedra illustrations of the two possible molecules. One of these may be optically dextro-rotatory and the other lævo-rotatory, as in the case of the two varieties of tartaric acid.

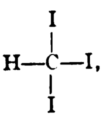
(*d*) We have yet the case of isomerism based upon change in the method of linking the hydrogen in the molecule. Such bodies are called *tautomeric*. Thus, the formula of hydrogen cyanide may be $N{\equiv}C{-}H$ or $C{\equiv}N{-}H$, and two series of derivatives readily changing into each other are formed, the cyanides and the isocyanides, according as one or the other molecular grouping exists.

Formulas which show the method of the linking of the constituent atoms are called ***rational*** or ***structural*** formulas. Their importance in organic chemistry, where differences in compounds may depend, as shown above, on the variations in the method of linking the elements, is obvious.

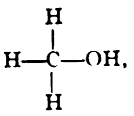
The tetrad character of the carbon element, to start with, is represented thus:  $\begin{array}{c} | \\ -C- \\ | \end{array}$ When these four bonds of the carbon are satisfied with hydrogen we have the fundamental hydrocarbon  $\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$, methane. The hydrogen atoms are readily replaceable by monad atoms and groups, and the substitution compounds so formed will be represented thus:



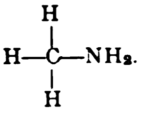
$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ Cl \end{array}$,



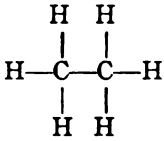
$\begin{array}{c} I \\ | \\ H-C-I \\ | \\ I \end{array}$,

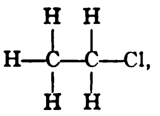


$\begin{array}{c} H \\ | \\ H-C-OH \\ | \\ H \end{array}$,

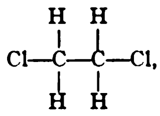


$\begin{array}{c} H \\ | \\ H-C-NH_2 \\ | \\ H \end{array}$.

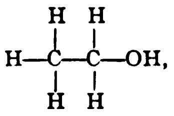
Several carbon atoms may be joined together by the aid of one or more bonds furnished by each of the carbon atoms. Thus, we have the hydrocarbon  $\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-H \\ |\ \ \ | \\ H\ \ H \end{array}$, ethane. In this case and in all its substitution derivatives the use of the structural formula becomes of great assistance in showing the nature and relationship of the molecule. We have among these derivatives



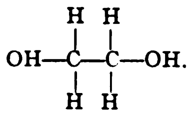
$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-Cl \\ |\ \ \ | \\ H\ \ H \end{array}$,



$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ Cl-C-C-Cl \\ |\ \ \ | \\ H\ \ H \end{array}$,

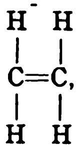
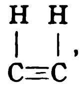


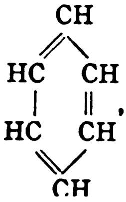
$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ H-C-C-OH \\ |\ \ \ | \\ H\ \ H \end{array}$,



$\begin{array}{c} H\ \ H \\ |\ \ \ | \\ OH-C-C-OH \\ |\ \ \ | \\ H\ \ H \end{array}$.

A more condensed form of rational formula is sometimes employed, as $CH_3.CH_2Cl$, $CH_2Cl.CH_2Cl$, $CH_3.CH_2OH$, $CH_2OH.CH_2OH$, in which the saturation of each individual carbon atom is shown without the aid of the graphic formulas showing the bonds.

In  $\begin{array}{c} H\ \ H \\ |\ \ \ | \\ C=C \\ |\ \ \ | \\ H\ \ H \end{array}$, ethylene, we have indicated a double linking of the carbon atoms, and in  $\begin{array}{c} H\ \ H \\ |\ \ \ | \\ C\equiv C \end{array}$, acetylene, a treble linking. The hydrogen atoms of these compounds are of course replaceable by monad atoms or groups, as in the case of hydrocarbons with the single linking.

Still more important becomes the structural formula in the case of the aromatic bodies such as benzene and other cyclic compounds. Here the fundamental hydrocarbon benzene is represented,  , that is, six carbon atoms alternately singly and doubly united, so that each carbon atom sacrifices three bonds in the linking of the molecule and has one free for combination with hydrogen or its equivalent replacing group.

Such a method of linking is generally known as the "closed-chain" structure, in distinction from the "open-chain" structure before shown with ethane and similar hydrocarbons.

5. Radicles, Residues, and Atomic Groups.—The residue remaining after taking away one or more atoms from an organic compound is often called a *radicle*. The valence of this radicle or residue depends upon the number of hydrogen atoms which must be added to make a saturated compound of it.

The relative importance of these radicles in the study of organic compounds is so great that at one time organic chemistry was defined as the "chemistry of compound radicles."

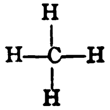
Thus, by the withdrawal of one hydrogen atom from the saturated hydrocarbon methane, CH_4, we obtain the monad radicle methyl, CH_3; by the withdrawal of two hydrogen atoms we get the dyad radicle methylene, CH_2; by the withdrawal of three hydrogen atoms we get the triad radicle methenyl, CH. Similarly, from ethane, C_2H_6, we get the monad radicle ethyl, C_2H_5, and from propane, C_3H_8, we get the monad radicle propyl, C_3H_7. These radicles are then very conveniently written as units in the rational formulas of organic compounds, as CH_3.Cl and CH_3.OH, known as methyl chloride and methyl alcohol respectively, or C_2H_5.Br and $(C_2H_5)_2O$, known as ethyl bromide and ethyl ether respectively.

Many of the inorganic groups or radicles are made use of here in the rational formulas of organic compounds, as $(OH)^{1}$ hydroxyl, $(NO_2)^{1}$ the nitro-group, $(NO)^{1}$ the nitroso-group, $(NH_2)^{1}$ the amido-group, $(NH)^{11}$ the imido-group, $(N)^{111}$ the nitril-group, $(—N=N—)^{11}$ the azo-group, and $(HSO_3)^{1}$ the sulphonic group.

Of the organic radicles, besides methyl, ethyl, propyl, etc., already mentioned, we have the aldehyde group $(CO.H)^{1}$, the carboxyl group $(COOH)^{1}$, the ketone group $(CO)^{11}$, and the cyanogen group $(CN)^{1}$.

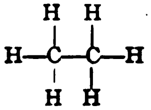
6. Homologous Series.—We have already shown the graphic formulas of methane and ethane, CH_4 and C_2H_6. By continuing the linking of the carbon atoms in the manner there shown we obtain propane, C_3H_8, butane, C_4H_{12}, pentane, C_5H_{12}, and a considerable series of hydrocarbons. It will be noticed that the successive members of his series differ by the constant increment CH_2. Such a series of compounds is called an ***homologous*** series. Not only may we have an homologous series of hydrocarbons but the homology may extend to the various classes of their derivatives. Thus, we have the homologous series of chlorides, $CH_3.Cl$, C_2H_5Cl, C_3H_7Cl, C_4H_9Cl, $C_5H_{11}Cl$, and the homologous series of alcohols, CH_3OH, C_2H_5OH, C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$.

The explanation of this constant increment CH_2 is had when we write the structural formulas of such a series as just given. Thus, the hydrocarbons before enumerated are:



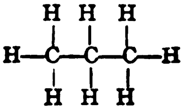
$$\begin{array}{c}H\\|\\H-C-H\\|\\H\end{array}$$

Methane.



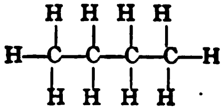
$$\begin{array}{c}H\ \ H\\|\ \ \ |\\H-C-C-H\\|\ \ \ |\\H\ \ H\end{array}$$

Ethane.



$$\begin{array}{c}H\ \ H\ \ H\\|\ \ \ |\ \ \ |\\H-C-C-C-H\\|\ \ \ |\ \ \ |\\H\ \ H\ \ H\end{array}$$

Propane.



$$\begin{array}{c}H\ \ H\ \ H\ \ H\\|\ \ \ |\ \ \ |\ \ \ |\\H-C-C-C-C-H\\|\ \ \ |\ \ \ |\ \ \ |\\H\ \ H\ \ H\ \ H\end{array}$$

Butane.

It will be seen here that in ethane each of the carbon atoms sacrifices one bond to hold together the molecule; that in propane, while each of the end carbon atoms sacrifices one bond, the middle carbon atom must sacrifice two bonds, leaving only two free to attach hydrogen; and in all subsequent members of the series the increase consists simply in inserting addition middle groups CH_2. If we compare such a series to a chain made up of connected links, we will see that, no matter how much we lengthen the chain, it can have only two end links. The lengthening is in effect but the insertion of more middle links. But in our hydrocarbon chain the middle links are the groups CH_2.

7. Outline of the Classification of Organic Compounds. — In studying the nature, composition, and relationship of organic compounds we soon find that the great majority of them can be arranged in either one or the other of two great classes—viz., the methane derivatives, sometimes called the ***aliphatic*** or fatty bodies, characterized by open atomic chain structure, and the *cyclic* or aromatic compounds (see p. 518) characterized by a closed chain of carbon atoms. These latter are again frequently divided into the *isocyclic* compounds in which the closed chains contain carbon atoms only (see page 518), and the *heterocyclic* compounds in which the closed chains contain one or more polyvalent atoms other than carbon (see p. 519). There are, it is true, some compounds which seem to show a transitional character from the one to the other of these groups and some which are not sufficiently understood to allow of their strict classification in this way.

If we take this first division of the subject, the methane derivatives, we have as the groups of compounds to be considered,—

1. **Hydrocarbons.**—Besides the saturated series already referred to and known specially as the paraffin series, we have unsaturated series of hydrocarbons, such as the olefine and the acetylene series. These are hydrocarbons stable enough to exist temporarily in the free state, but tending to take up either two or four atoms of halogens or monad groups and pass into saturated compounds. All of these hydrocarbons, however, both saturated and unsaturated, are open-chain hydrocarbons.

2. **Halogen Derivatives of the Hydrocarbons.**—If obtained from the saturated hydrocarbons they are substitution derivatives exclusively; if formed from unsaturated hydrocarbons they may be addition compounds as well.

3. **Nitro-Derivatives.**—These contain the monad group NO_2, replacing H of the hydrocarbon. They do not form so readily with the methane series of hydrocarbons as with benzene and its homologues.

4. **Alcohols.**—These are hydroxides of the hydrocarbon radicles and play the part of weak bases. They may be monatomic, diatomic, etc., according as one, two, or more hydrogen atoms are replaced by the corresponding number of OH groups.

5. **Ethers.**—The oxides of the hydrocarbon radicles, corresponding to the metallic oxides of inorganic chemistry, are termed simple ethers. Two different hydrocarbon radicles may be united by one oxygen atom and so constitute a " mixed ether."

6. **Thio-Ethers and Sulphonic Compounds.**—The first of these classes includes the sulphides of hydrocarbon radicles, the second contains the sulphonic group HSO_3.

7. **Aldehydes and Ketones.**—These classes represent the direct oxidation products of the alcohols. If the alcohol contain the group CH_2.OH, that is, belongs to the class of primary alcohols, by oxidation it will yield an aldehyde; if the alcohol, on the other hand, contain the group CH.OH, that is, belongs to the class of secondary alcohols, by oxidation it will yield a ketone. In the first case, the group CH_2.OH is changed by oxidation into CO.H, the characteristic aldehyde group; in the second

case, the group CH.OH is changed by oxidation into CO, the characteristic ketone group.

8. **Acids.**—When the oxidation of the alcohols or basic hydroxides is carried to completion, in the case of primary alcohols (those containing the $CH_2.OH$ group) the aldehyde is changed into the corresponding acid, the characteristic group of which is COOH. Acids are monobasic, dibasic, etc., according to the number of such groups they contain.

9. **Esters.**—These are salts containing an organic radicle as base, which is combined with either an inorganic or an organic acid.

10. **Amines and Amides.**—Both these classes are ammonia derivatives. If the hydrogen atoms of the ammonia molecule are replaced by a basic radicle we have an amine, if by an acid radicle an amide.

11. **Carbohydrates.**—These important compounds, known also as the "sugar and starch group," occupy the position of either aldehydes or ketones of hexatomic alcohols, and are treated as a separate group because of convenience and their common origin in the vegetable kingdom.

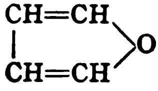
12. **Derivatives of Carbonyl.**—In these compounds the fundamental group is $(CO)^{11}$, which acts as an acid-forming radicle.

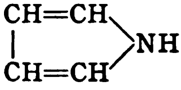
13. **Derivatives of Cyanogen.**—In these compounds the fundamental group is $(CN)^{1}$, which acts in general like the halogen elements.

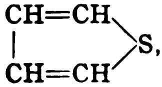
Intermediate between the open-chain hydrocarbons with their derivatives just enumerated and the closed-chain hydrocarbons of the benzene series containing six carbon atoms in the nucleus (true aromatic compounds) are several groups.

1. Polymethylenes and derivatives, including trimethylene, tetramethylene, and pentamethylene, which are all isocyclic compounds.

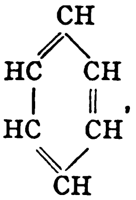
2. Heterocyclic compounds including:

(a) **Furfuran and its Derivatives.**—Furfuran, the starting-point of these compounds, has the structural formula  and shows a closed chain with four carbon atoms.

(b) **Pyrrol and its Derivatives.**—Pyrrol, the underlying compound in this case, has the structural formula , and also shows a closed chain with four carbon atoms.

(c) **Thiophen and its Derivatives.**—Thiophen, which is found as an accompaniment of benzene in coal-tar, has the structural formula , showing a closed chain with four carbon atoms.

The aromatic compounds, which, as said, form the second great class of organic substances, are derived from what are termed closed-chain series of hydrocarbons. In the isocyclic compounds of the aromatic series, six atoms of carbon seem to join together in the closed-chain structure and this molecule holds together through many reactions. We may also distinguish between aromatic compounds containing one nucleus and those containing more than one nucleus. Under the former class we have,—

1. **Hydrocarbons.**—These may be saturated, unsaturated, or addition hydrocarbons. They all contain the benzene nucleus, , however, as the central feature of the molecule, and its hydrogen atoms may be replaced by hydrocarbon radicles, as $C_6H_5.CH_3$.

2. **Halogen Derivatives.**—The halogen derivatives of the benzene hydrocarbons may be of two kinds, either with the halogen replacing hydrogen of the nucleus, as $C_6H_4Cl.CH_3$, or hydrogen of the side-group, as $C_6H_5.CH_2Cl$. These two compounds are, it is seen, isomeric.

3. **Sulphonic Derivatives.**—These compounds contain the HSO_3 group replacing hydrogen. They are more readily formed in the aromatic series than in the methane series and are correspondingly more important.

4. **Nitro-Derivatives.**—Here again the aromatic hydrocarbons are much more readily acted upon than the paraffin series. The action of strong nitric acid easily converts the hydrocarbons and many of their derivatives into the corresponding nitro-derivatives by replacing hydrogen by the group NO_2.

5. **Amido-Derivatives.**—By the action of reducing agents the nitro-derivatives are changed into the corresponding amido-derivatives, the NO_2 group being changed into the NH_2 group. These amido-derivatives, again, give rise to new compounds by the replacement of the hydrogen atoms of the NH_2 group by basic or acid radicals.

6. **Diazo- and Azo-Compounds. Hydrazines.** — Both the diazo- and the azo-compounds contain the dyad group $—N{=}N—$. In the former this group is combined on the one side only with a hydrocarbon radicle, and in the latter on both sides with hydrocarbon radicles. The aromatic hydrazines are substitution derivatives of hydrazine, $NH_2—NH_2$.

7. **Phenols and their Derivatives. Quinones.** — The hydroxyl derivatives obtained by replacing by OH the hydrogen in the benzene

nucleus of aromatic hydrocarbons are termed phenols. They act like weak acids. We may have monatomic, diatomic, and other phenols according to the number of OH groups so introduced.

The quinones are compounds in which two hydrogen atoms of the benzene nucleus are replaced by a dyad group (O_2).

8. **Aromatic Alcohols, Aldehydes, and Ketones.** — The aromatic alcohols are isomeric with the phenols, but contain the OH in the side-group, so that they contain the group CH_2OH, and hence are primary alcohols. The aromatic aldehydes are the products of oxidation of these alcohols.

The aromatic ketones, like the ketones of the methane series, contain the dyad group $(CO)^{II}$ linking together two hydrocarbon radicles, of which at least one contains the benzene nucleus.

9. **Phenol Alcohols and Phenol Aldehydes.** — When both hydrogen of the benzene nucleus and hydrogen of the side-group are replaced by OH groups, we have a phenol alcohol, and this by oxidation of the side-group yields a phenol aldehyde.

10. **Aromatic Acids and Phenol Acids.**—The product of the full oxidation of the aromatic alcohol is the aromatic acid. It contains the benzene nucleus joined with one or more COOH groups. If the benzene nucleus contain an OH group directly attached in addition, we have the phenol acid.

Under the head of aromatic compounds containing more than one nucleus we have several distinct cases to note.

1. **Compounds with Several Uncondensed Nuclei.**—We have here included the diphenyl group, the diphenylmethane and triphenylmethane groups, and the indigo group.

2. **Compounds with Two Condensed Nuclei.** — This includes naphthalene and its derivatives.

3. **Compounds with Three Condensed Nuclei.** — This includes anthracene, phenanthrene, and their derivatives.

11. **Heterocyclic Compounds Containing Nitrogen in the Nucleus,** including pyridine, quinoline, and acridine. The first of these corresponds to benzene, the second to naphthalene, and the third to anthracene, with one CH group of the nucleus replaced by nitrogen.

The pharmaceutically and medicinally important classes of *alkaloids* and *ptomaines* follow next. While these compounds have not as yet been sufficiently studied to enable us to classify them in all respects, they appear to be in large part complex derivatives of the bases pyridine and quinoline just referred to.

The classes of *terpenes* and *camphors* are also important as present in the many naturally occurring *essential oils*. With these are also to be considered their products of oxidation, the *resins*. Of these several groups are noted, such as oleo-resins, gum-resins, balsams, and hard resins.

The important class of *glucosides* are also considered as supplementary to the regularly classified compounds because of the variety of their composition, as shown by the decomposition products. With them are also noted a number of technically important *dye woods* and other vegetable principles.

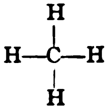
Lastly, the *protein substances* are to be considered, under which head the nature, classification, and reactions of albuminoids will be discussed.

CHAPTER II.

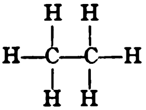
OPEN-CHAIN OR ALIPHATIC HYDROCARBONS.

I. The Saturated Hydrocarbons, or Paraffin Series.

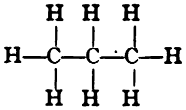
1. Composition, Nomenclature, and Molecular Constitution.—We have shown that, while the single atom of tetrad carbon can take up four atoms of hydrogen to form CH_4, two atoms of carbon, when linked together in the same molecule, can take up but six atoms of hydrogen, and three carbon atoms eight atoms of hydrogen. This is shown in the graphic formulas



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$



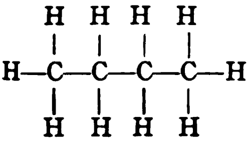
$$\begin{array}{cccc} & H & H & \\ & | & | & \\ H- & C- & C & -H \\ & | & | & \\ & H & H & \end{array}$$



$$\begin{array}{ccccc} & H & H & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array}$$

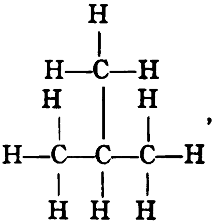
We have stated under the heading of "Homologous Series" that the difference between any two members of such a series is uniformly CH_2. We are, therefore, able to give a general formula for the entire series, by means of which the formula of any individual hydrocarbon in the series can be deduced. This general formula is C_nH_{2n+2}; that is, for a given number of carbon atoms there will be needed for saturation twice as many hydrogen atoms plus two. More than that number, it is seen from the graphic formulas, cannot be attached.

The first three hydrocarbons of this series, CH_4, C_2H_6, C_3H_8, can only be written structurally as represented above. The next one, however, C_4H_{10}, may be written in either one of two ways,—



$$\begin{array}{cccccc} & H & H & H & H & \\ & | & | & | & | & \\ H- & C- & C- & C- & C & -H \\ & | & | & | & | & \\ & H & H & H & H & \end{array}$$

or



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ & H- & C & -H & \\ & H & | & H & \\ & | & | & | & \\ H- & C- & C- & C & -H \\ & | & | & | & \\ & H & H & H & \end{array}$$

, or more compactly

$$CH_3.CH_2.CH_2.CH_3. \text{ and } \left.\begin{matrix}CH_3\\CH_3\\CH_3\\H\end{matrix}\right\} C.$$

In fact, these different graphic formulas represent two distinct compounds, one boiling at +1° C. and the other at —17° C., and known respectively as normal butane and iso-butane, which are isomeric with each other. In the case of C_5H_{12}, three isomeric compounds are possible and have been prepared, and with C_6H_{14} five isomers are possible and are known.

The hydrocarbons of this series have been prepared as far as $C_{35}H_{72}$. They are named by taking the names first applied to the radicals in the case of the first four members of the series, and after that the Greek numerals, and applying the uniform termination *ane*. A table of the hydrocarbons of the paraffin series, with melting and boiling points, is attached.

SATURATED HYDROCARBONS—C_nH_{2n+2}.

Formula.	Name.	Melting Point.	Boiling Point.	
CH_4.	Methane	—186°	—164°	
C_2H_6.	Ethane	. . .	—93°	
C_3H_8.	Propane	. . .	—45°	
C_4H_{10}.	Normal Butane	. . .	+1°	
"	Iso-Butane	. . .	—17°	
C_5H_{12}.	Normal Pentane	. . .	+37°	
"	Iso-Pentane	. . .	+30°	
"	Tertiary Pentane	—20°	+9°	
C_6H_{14}.	Hexane	. . .	69°	
C_7H_{16}.	Heptane	. . .	98°	
C_8H_{18}.	Octane	. . .	124°	
C_9H_{20}.	Nonane	—51°	150°	
$C_{10}H_{22}$.	Decane	—32°	173°	
$C_{11}H_{24}$.	Undecane	—26°	195°	
$C_{12}H_{26}$.	Dodecane	—12°	214°	
$C_{13}H_{28}$.	Tridecane	—6°	234°	
$C_{14}H_{30}$.	Tetradecane	+5°	253°	
$C_{15}H_{32}$.	Pentadecane	10°	270°	
$C_{16}H_{34}$.	Hexadecane	18°	287°	
$C_{17}H_{36}$.	Heptadecane	22°	303°	
$C_{18}H_{38}$.	Octadecane	28°	317°	
$C_{19}H_{40}$.	Nonadecane	32°	330°	
$C_{20}H_{42}$.	Eicosane	37°	205°	Under a pressure of 15 mm.
$C_{21}H_{44}$.	Heneicosane	40°	215°	
$C_{22}H_{46}$.	Docosane	44°	224°	
$C_{23}H_{48}$.	Tricosane	48°	234°	
$C_{24}H_{50}$.	Tetracosane	51°	243°	
$C_{27}H_{56}$.	Heptacosane	60°	270°	
$C_{31}H_{64}$.	Hentriacontane	68°	302°	
$C_{32}H_{66}$.	Dotriacontane	70°	310°	
$C_{35}H_{72}$.	Pentatriacontane	75°	331°	

2. Occurrence, Preparation, and Description of the More Important.—The hydrocarbons of the paraffin series occur abundantly, ready formed in nature, in various crude petroleums. The lower members of the series, which are gaseous at ordinary temperatures, also occur as natural gas, which escapes from the earth in many localities; the middle members of the series make up the bulk of the petroleums, and hold dissolved, when first taken from the earth, both the gases and the higher members of the series, which are solids. These latter may occur by themselves also as ozokerite, or natural paraffine.

These hydrocarbons are also formed in the dry distillation of many naturally-occurring substances, such as bituminous coal, shales, wood, and from fatty oils when distilled under strong pressure.

The first of the series, *methane*, is also found abundantly in nature as a product of decomposition, and owes its common name, "marsh gas," to such occurrence. Mixed with small quantities of carbon dioxide and nitrogen, it is formed whenever vegetable matter decomposes in the presence of water, as in the bottom of marshes and springs. Its formation here is due to the slow decomposition of the woody fibre under the special conditions of moisture, and probably the presence of micro-organisms, as it is known that cellulose may undergo a fermentative decomposition in their presence, with carbon dioxide and methane as sole products, according to the reaction: $C_6H_{10}O_5 + H_2O = 3CO_2 + 3CH_4$.

Methane also forms by the slow decomposition and change of bituminous coal, and hence is present in abundance in the galleries of coal-mines which are not properly ventilated. When mixed with air it constitutes the dangerous and explosive mixture known as "fire-damp." Under the name of "light carburetted hydrogen" it is known also in the distillation products of these coals. Thus, coal gas, as manufactured for illuminating purposes, contains from 30 to 40 per cent. of methane; "water gas," made by the action of steam on incandescent carbon, contains from 6 to 12 per cent.; while natural gas, now used in large quantities for fuel purposes, contains from 90 to 95 per cent. of methane.

Methane may be artificially formed by a variety of methods:

Sabatier and Senderens have found that when carbon mon-oxide and hydrogen are passed over reduced nickel at 200°–250° C., methane is formed: $CO + 3H_2 = CH_4 + H_2O$.

Or a mixture of carbon disulphide vapor and hydrogen sulphide passed over ignited copper will react: $CS_2 + 2H_2S + 8Cu = CH_4 + 4Cu_2S$. It is generally formed (although somewhat contaminated with ethylene and hydrogen) by the heating of anhydrous sodium acetate and soda-lime, according to the reaction $CH_3COONa + HONa = CH_4 + CO\left\{\begin{matrix}ONa\\ONa\end{matrix}\right.$, methane and sodium carbonate being in theory the sole products. Chemically pure methane is obtained by the reduction of methyl iodide, CH_3I, in alcoholic solution with copper-coated zinc (Gladstone and Tribe copper-zinc couple).

Methane is a colorless and odorless gas, condensable to a liquid under a pressure of 180 atmospheres at —11° C. It boils at —164° and solidifies at —186°. It burns with a pale, faintly luminous flame, and forms an explosive mixture with air.

Ethane is found in crude petroleum and in natural gas, and may be formed artificially by the action of zinc or sodium upon methyl iodide, as follows:

$$\begin{matrix}CH_3\\CH_3\end{matrix}\boxed{\begin{matrix}I & + & Na\\I & + & Na\end{matrix}} = 2NaI + \begin{matrix}CH_3\\|\\CH_3\end{matrix}.$$

It is a colorless and odorless gas, which can be liquefied at +4° by a pressure of 46 atmospheres. It burns with a pale flame.

Propane, normal *butane, pentane,* and *hexane,* all occur in crude petroleum, the latter two especially being present in gasoline and similar light fractions. Normal *heptane,* in addition to being present in petroleum, occurs in the oil from the *Pinus sabiniana,* or nut-pine, of California, and under the special name of " abietene " is used as a cleansing and solvent benzine.

The hydrocarbons from $C_{16}H_{34}$ on are solid at ordinary temperatures and make up the bulk of the products known as *petrolatum.* A mixture of these hydrocarbons of still higher fusing point constitutes the commercial product known as *paraffin.*

The name paraffin (from *parum affinis*), first applied to the solid products as obtained from bituminous coals, has been applied to the whole series of hydrocarbons to indicate the stable character of these compounds. They are incapable of combining with halogens or taking up any additional hydrogen, are not affected by any of the strong acids in the cold, and only slightly when heated, and are not easily oxidized by chromic acid or potassium permanganate.

3. **Pharmaceutically Important Products.**—The first of these is **Benzinum Purificatum,** U.S.P., and is stated to be " a purified distillate from American petroleum consisting of hydrocarbons, chiefly of the marsh-gas series." It is a transparent, colorless liquid, of neutral reaction, evaporating without residue and leaving no odor, of sp. gr. 0.638 to 0.660 at 25°, and distilling completely between 40° and 50° C. It is used as a solvent for fats, resins, rubber, and some of the alkaloids.

Petrolatum Liquidum, U.S.P., is stated to be " a mixture of liquid hydrocarbons obtained from petroleum."

Petrolatum, U.S.P., is stated to be " a purified mixture of semi-solid hydrocarbons obtained from petroleum." It is manufactured on a large scale under the trade names of vaseline, cosmoline, etc., by the filtration of oil residuums through heated bone-black or fuller's earth.

Petrolatum Album, U.S.P., is " Petrolatum wholly or nearly decolorized."

The liquid petrolatum is a colorless or more or less yellowish, oily, transparent liquid, without odor or taste. It has a sp. gr. of 0.828 to 0.925 at 25° C.; petrolatum, on the other hand, is " an unctuous mass of about the consistence of an ointment, varying in color from yellowish to light amber, having not more than a slight fluorescence, even after being melted, transparent in thin layers, completely amorphous, without odor or taste but giving off when heated a faint petroleum-like odor." The melting point of petrolatum is from 38° to 54° C., and it shows a sp. gr. of 0.820 to 0.865 at 60° C. It should not leave on incineration more than 0.05 per cent. of ash. Both these varieties are insoluble in water, scarcely soluble in cold or hot alcohol, or in cold absolute alcohol, but soluble in boiling absolute alcohol, and readily soluble in ether, chloroform, carbon disulphide, oil of turpentine, benzine, benzene, and fixed or volatile oils.

Paraffinum, U.S.P., is the solid commercial paraffin or paraffin wax, as it is often called. This is a white, waxy, inodorous, tasteless substance, of sp. gr. 0.890 to 0.905 at 25° C., melting (according to its source, whether from petrolatum, coal, or ozokerite) between 50° and 57° C.

4. **Technically Important Products.**—The most important industry based upon the utilization of the hydrocarbons of this series is the refining of petroleum, which, as before stated, is a naturally occurring hydrocarbon mixture. In the United States the earliest known deposits of petroleum were those of Western Pennsylvania. These oil-fields extend into New York State and into Western Virginia and Ohio. In the latter State (as well as in the province of Ontario, Canada) is also produced a petroleum of somewhat different character, viz., a sulphur-containing oil, which presents greater difficulties in refining. Petroleum is also found in a number of the Western States, but notably in Texas, Oklahoma and California, in which latter State it is of a heavier kind and contains hydrocarbons of another series known as polymethylenes, leaving an asphaltic residue. The most important foreign production is that of Baku, on the Caspian Sea, where enormous quantities of petroleum are obtained. Chemically it differs, however, from the Pennsylvania oil in containing a distinct series of hydrocarbons, the so-called "naphthenes" (see Aromatic Hydrocarbons).

The refining of petroleum consists first in submitting it to a fractional distillation, the products of which are benzine, naphtha, burning oils, and residuum. The latter is then distilled at a higher temperature in separate stills, and yields paraffin oils and a coke or petroleum pitch. All the fractions require a treatment with sulphuric acid, followed by washing and treatment with alkali to remove impurities and products of destructive distillation, which impair their color and burning qualities. The paraffin oils are then chilled by artificial means and paraffin scale separated out from the heavy oils, which then are known as lubricating oils. The paraffin scale when purified by melting, pressing, and filtration yields the white paraffin wax.

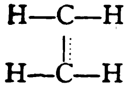
The most important test to be applied to a burning oil is the "fire test," which determines the temperature to which it may be heated without liberating vapors which, mixing with air, may produce an explosive mixture. The lowest legal test in any of the States is 110° F., and in many it is placed at 150° F.

II. THE UNSATURATED HYDROCARBONS OF THE OLEFINE SERIES.

Associated with the paraffin series or saturated hydrocarbons in petroleum, and capable of being formed in most cases of destructive distillation, is a series of hydrocarbons each member of which contains two hydrogen atoms less than the corresponding member of the saturated series. They possess the general formula C_nH_{2n}.

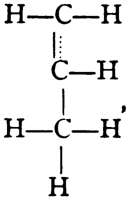
The first member of the series, CH_2, is apparently incapable of existing in the free state, although derivatives of it are known. The second hydrocarbon, C_2H_4, known as ethylene, the third, C_3H_6, known as propylene, and the succeeding ones as high as $C_{30}H_{60}$, are, however, obtainable.

The explanation generally accepted by chemists for their molecular structure is that in them two carbon atoms are temporarily doubly linked, but that, as this double linking is unstable, they act as unsaturated compounds, and readily unite with halogens and atomic groups to form saturated compounds. Thus we have for ethylene:



$$\begin{array}{c} H-C-H \\ \| \\ H-C-H \end{array}$$

and for propylene



$$\begin{array}{c} H-C-H \\ \| \\ C-H \\ | \\ H-C-H \\ | \\ H \end{array}$$

, or, written more compactly, $CH_2 = CH_2$ and $CH_2 = CH - CH_3$. Their most characteristic reaction is the direct combination with two atoms of the halogens to form *addition compounds,* while the saturated hydrocarbons of the paraffin series can only form *substitution compounds.* Thus, $C_2H_4 + Cl_2 = C_2H_4Cl_2$. They have been named by adding the termination *ene* to the name of the monad radical derived from the corresponding saturated hydrocarbon.

In their physical properties they resemble the methane homologues closely, the first three being gases, C_5H_{10} a volatile liquid, and the higher members being solids like the paraffins.

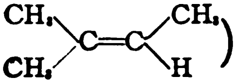
Most of the olefines are easily soluble in alcohol and ether but insoluble in water. Besides their ability to take up halogens to form addition compounds, they are characterized by a tendency to polymerize, especially in the presence of sulphuric acid or zinc chloride, and by the readiness with which they are oxidized by chromic acid or potassium permanganate.

It is stated that all compounds with doubly-linked carbon atoms give the ozone reaction, that is when dissolved in a suitable solvent they fix quantitatively and in the cold the ozone contained in a current of ozonized air passed through the solution; in this respect they differ from compounds with either a triple linking or a benzene double linking.

They are formed together with the paraffins by the destructive distillation of many substances, such as fats, waxes, lignite, and coal: illuminating gas consequently contains the olefines, and upon them in fact mainly depends its illuminating value.

Ethylene, C_2H_4, is present to the extent of from 5 to 6 per cent. in illuminating gas made from coal, but it is usually prepared by the action of an excess of strong sulphuric acid upon alcohol, the reaction being simply a dehydration of the alcohol: $C_2H_6O - H_2O = C_2H_4$.

It is a colorless gas, which may be liquefied at 0° C. by a pressure of 44 atmospheres. It is very slightly soluble in water and alcohol and burns with a luminous flame. It unites directly with an equal volume of chlorine to form ethylene dichloride, which condenses to oily drops, whence the name often given of "olefiant" (or oil-forming) gas. It combines with two atoms of hydrogen in the presence of spongy platinum or reduced nickel to form ethane, C_2H_6.

Propylene and the several isomeric *butylenes* have been prepared. Of the *amylenes*, one (trimethyl-ethylene,  $\left(\begin{array}{l} CH_3 \\ CH_3 \end{array}\right> C=C \left< \begin{array}{l} CH_3 \\ H \end{array}\right)$ has been introduced into medicine as an anæsthetic under the name of "pental." It is formed from tertiary amyl alcohol (amylene hydrate) by the action of dehydrating agents. It is a colorless, mobile, very volatile, and inflammable liquid, boiling at 37°–38° C. It is insoluble in water, but miscible in all proportions in chloroform, ether, and 90 per cent. alcohol.

Isomeric with the olefines are certain closed-chain hydrocarbons, such as *trimethylene*, C_3H_6, and *hexamethylene*, C_6H_{12}. These will be referred to later under Polymethylenes (see p. 612).

III. THE UNSATURATED HYDROCARBONS OF THE C_nH_{2n-2} SERIES.

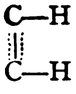
Hydrocarbons, containing two hydrogen atoms less than the corresponding members of the olefine series and four less than the members of the paraffin series, are known. They may belong either to the *allenes*, containing two double linkings, or the *acetylenes* containing one treble linking.

Allenes.—The first of these, *allene*, $CH_2 = C = CH_2$, is a colorless gas made only artificially.

The second, *erythrene*, $CH_2 = CH - CH = CH_2$, is a gas found in illuminating gas, and when heated with formic acid gives erytheritol.

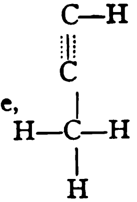
Isoprene, C_5H_8, is the methyl derivative of the preceding hydrocarbon and has the structural formula, $CH_2 = C(CH_3) - CH = CH_2$. It is obtained by distilling rubber and by several synthetic methods. It can be condensed by the action of concentrated HCl, by heat, by the action of sodium and other reagents forming artificial rubber. An isomer *piperylene*, C_5H_8, *diallyl*, C_6H_{10}, and *conylene*, C_8H_{14}, are also known.

Acetylenes.—To explain the unsaturated character of these hydrocarbons, we assume the following structural formula for acetylene,



$$\begin{array}{c} C-H \\ \vert\vert\vert \\ C-H \end{array}$$

or $CH\equiv CH$ and for the second member, allylene,



$$\begin{array}{c} C-H \\ \vert\vert\vert \\ C \\ \vert \\ H-C-H \\ \vert \\ H \end{array}$$

or $CH\equiv C-CH_3$.

The first five members of this series are

Acetylene, C_2H_2,
Allylene, C_3H_4,
Crotonylene or Butine, C_4H_6,
Valerylene or Pentine, C_5H_8,
Hexine, C_6H_{10}.

They are produced in the destructive distillation of many organic compounds, such as wood and bituminous coal. Acetylene, the first member of the series, is produced in a variety of additional ways. Thus, when methane, ethane, ethylene, alcohol, ether, and aldehyde are led through tubes heated to redness, acetylene is produced with separation of hydrogen and other products. The incomplete combustion of many carbon compounds also causes the formation of acetylene, as in the case of defective gas-burners and in the use of gas-stoves. The simplest reaction for its production is the passage of the electric spark between carbon points in an atmosphere of hydrogen. Acetylene, however, is most abundantly formed by the decomposition of metallic carbides in the presence of water according to the reaction: $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. Since the development of the electric furnace by Moissan and others the manufacture of carbides, such as calcium carbide, CaC_2, has assumed great importance because of the convenience with which they may be made to yield acetylene (see Calcium Carbide, p. 382).

Acetylene is a colorless gas with a peculiar penetrating odor, recognizable in cases of defective combustion with gas-burners. It burns from an ordinary burner with a rich, luminous, but sooty flame; from specially constructed burners with very narrow openings it can be made, on the other hand, to burn with a very pure, intense, whitish light. It forms explosive compounds with potassium, sodium, silver, and copper, in which one or both hydrogen atoms are replaced by metal. It is capable of uniting with hydrogen when a mixture of the two is passed over heated platinum black, four atoms being taken up and ethane being formed. It dissolves in large amount of acetone and is given off from this solution, contained in suitable receptacles, for use in oxy-acetylene welding and heating, steel of considerable thickness being readily cut through by the flame.

IV. UNSATURATED HYDROCARBONS OF THE SERIES C_nH_{2n-4}. AND C_nH_{2n-6}.

In the distillation products of cannel coal, as well as in bone oil (Dippel's oil), are contained hydrocarbons of the series C_nH_{2n-4}. These are unsaturated, and take up six atoms of bromine by addition to form saturated compounds. They precipitate ammoniacal silver and copper solutions like acetylene.

Two hydrocarbons of this character have been described, ***valylene***, C_5H_6, and *diallylene*, C_6H_8.

The terpenes, $C_{10}H_{16}$, which would answer to the general formula C_nH_{2n-4}, do not belong here, as they seem to contain an aromatic nucleus.

The only well-defined representative of the series C_nH_{2n-6} is *dipropargyl*, C_6H_6. This compound, isomeric with the aromatic hydrocarbon benzene, is an unsaturated open-chain hydrocarbon, as is shown by the readiness with which it adds on bromine and precipitates ammoniacal silver and copper salts.

CHAPTER III.

DERIVATIVES OF THE OPEN-CHAIN HYDROCARBONS.

I. HALOGEN DERIVATIVES.

1. Substitution Derivatives of the Paraffin Series.—Chlorine and bromine are capable of acting directly upon the hydrocarbons, replacing hydrogen. This action is facilitated by the presence of sunlight or substances which act as the "carriers" of the chlorine and bromine, such as iodine, ferric chloride, or antimony chloride. Iodine does not act directly upon the hydrocarbons, so that the iodides are generally obtained by the action of HI upon the several alcohols (see under Alcohols).

TABULAR VIEW OF THE HALOID DERIVATIVES OF THE PARAFFINS.

Mono-Derivatives:	Boiling Point.
Monochlor methane, or Methyl chloride, CH_3Cl	—22° C.
Methyl bromide, CH_3Br	+4°
Methyl iodide, CH_3I	44°
Monochlor-ethane, or Ethyl chloride, C_2H_5Cl	12°
Ethyl bromide, C_2H_5Br	39°
Ethyl iodide, C_2H_5I	72°
Propyl iodide, Isopropyl iodide, C_3H_7I	102°
Four isomeric varieties of Butyl iodide, C_4H_9I.	
Iso-amyl chloride, $C_5H_{11}Cl$	101°
Hexyl chloride, $C_6H_{13}Cl$	126°
Di-Derivatives:	
Dichlor-methane, or Methylene chloride, CH_2Cl_2	42°
Methylene bromide, CH_2Br_2	97°
Methylene iodide, CH_2I_2	180°
Ethylene chloride, $C_2H_4Cl_2$	84°
Ethylidene chloride,	57°
Tri-Derivatives:	
Trichlor-methane, or Chloroform, $CHCl_3$	61°
Bromoform, $CHBr_3$	151°
	Melting Point.
Iodoform, CHI_3	119°
Higher Substitution Products:	
Tetrachlor-methane, or Carbon tetrachloride, CCl_4	77°
Perchlor-ethane, C_2Cl_6	185°

Besides the direct substituting action of chlorine and bromine upon the hydrocarbons, we can use the action of the haloid acids, HCl, HBr, and HI, upon the corresponding alcohol, as shown in the reaction $C_2H_5.OH + HBr = C_2H_5Br + H_2O$, or the direct addition of these haloid acids to the olefine hydrocarbons according to the reaction $C_2H_4 + HCl = C_2H_5Cl$.

The halogen substitution products of these hydrocarbons are almost if not quite insoluble in water, but miscible to any extent with alcohol and ether. The lower ones in the series possess in general a sweet ethereal odor and produce insensibility and unconsciousness when inhaled.

Methyl Chloride, CH_3Cl, is prepared by heating methyl alcohol with a mixture of salt and sulphuric acid, or direct with dry hydrochloric acid gas in the presence of fused zinc chloride. It forms a colorless gas with ethereal odor, burning with green-edged flame. Under a pressure of 5 atmospheres it is liquefied, and this liquefied gas is now largely used as a means of artificial refrigeration and for local anæsthetic effect in surgery. A saturated solution of methyl chloride in chloroform constitutes the "compound liquid" used as an anæsthetic by Richardson. Methyl chloride is also made as a technical product by distilling the "vinasse" of the beet-sugar factories and heating the trimethylamine hydrochlorate obtained to 360° with hydrochloric acid. As so obtained it is used in the aniline dye color industry.

Methyl Iodide, CH_3I, is prepared from methyl alcohol, phosphorus, and iodine. It forms a colorless liquid, boiling at 44°, and is used in the manufacture of organic dye colors.

Ethyl Chloride, C_2H_5Cl, **Æthylis Chloridum,** U.S.P., is prepared in the same manner as methyl chloride. It is a colorless mobile liquid, boiling at 12°, only slightly soluble in water, but easily soluble in alcohol, which latter solution is sometimes known as solution of "chloric ether." Used by spraying as a local anæsthetic.

Ethyl Bromide, C_2H_5Br, is best prepared by the action of a mixture of sulphuric acid and alcohol upon potassium bromide followed by distillation. It forms a colorless mobile liquid, of sweet chloroform-like odor and burning taste, boiling at 38°–39°. It is insoluble in water, but miscible with alcohol, ether, chloroform, fatty and ethereal oils. As it is decomposed gradually by the influence of the air and light, it must be preserved in dark bottles. It has been repeatedly recommended and tried as an anæsthetic, but has not found general acceptance, perhaps because of its tendency to decompose, with production of free bromine and hydrogen bromide.

Methylene Chloride, CH_2Cl_2, can be prepared by the action of chlorine upon methane or methyl chloride, or by the action of nascent hydrogen upon chloroform. It forms a colorless liquid with chloroform-like odor, boiling at 42°. It has been found to possess properties very similar to chloroform, producing an anæsthetic effect slightly more transient in character. This pure methylene chloride must not be confounded with a preparation brought out under the same name in England, which has been shown to be a mixture of 1 volume methyl alcohol and 4 volumes of chloroform.

Ethylene Chloride, $C_2H_4Cl_2$, is one of two isomeric compounds. It possesses the structural formula $CH_2Cl.CH_2Cl$, while its isomer, ethylidene chloride, has the formula $CH_3.CHCl_2$. Ethylene chloride is sometimes known as the "oil of the Dutch chemists," or simply as "Dutch liquid," because the reaction whereby it was formed by the direct union of ethylene and chlorine gases was first discovered in Amsterdam. It is a colorless liquid, of chloroform-like odor and sweet taste, and has been used as a substitute for chloroform both for external applications and for inhalations.

Ethylidene Chloride, $C_2H_4Cl_2$, is obtained as a by-product in the manufacture of chloral, or can be prepared by the action of phosphoric chloride upon paraldehyde. It is a colorless liquid, smelling like chloroform and of a sweet taste. It has been proposed by Liebreich as a substitute for chloroform in cases of anæsthesia.

Trichlor-methane, $CHCl_3$, or **Chloroformum,** U.S.P., was discovered independently by Liebig and Soubeiran in 1831. Besides the preparation from methane by the action of chlorine, which is purely a theoretical process, we have three practical methods for its preparation.

(*a*) From alcohol by the action of chlorinated lime. This reaction most probably takes place in several stages. The chlorinated lime first oxidizes the alcohol to aldehyde according to the reaction:

$$C_2H_6O + CaOCl_2 = CaCl_2 + C_2H_4O + H_2O.$$

The aldehyde is then changed by the chlorinated lime into trichloraldehyde:

$$2C_2H_4O + 6(CaOCl_2) = 3CaCl_2 + 3Ca(OH)_2 + 2C_2HCl_3O.$$

The chloral thus formed is then decomposed by the alkaline calcium hydroxide:

$$2C_2HCl_3O + Ca(OH)_2 = Ca(CHO_2)_2 + 2CHCl_3$$

the end products being chloroform and calcium formate.

(*b*) From acetone by the action of chlorinated lime. This reaction, already pointed out by Liebig in 1832, has been taken up in recent years, and is now largely used in the manufacture of chloroform. It is as follows:

$$2C_3H_6O + 6CaOCl_2 = 2CHCl_3 + 2Ca(OH)_2 + Ca(C_2H_3O_2)_2 + CaCl_2.$$

(*c*) It has been made in recent years from carbon tetrachloride by reduction with nascent hydrogen generated by the action of water upon finely divided metals, such as Fe and Zn. It can also be made from chloral by the action of caustic alkalies, the reaction being analogous to that given under the first process.

Chloroform is a heavy, colorless, mobile, and diffusible liquid, of ethereal odor and burning, sweet taste. Specific gravity 1.49 at 15°. It boils at 60° to 61°. Chloroform is an excellent solvent for phosphorus, iodine, alkaloids, resins, caoutchouc, fats, fatty oils, etc. When exposed to the light it is liable to decomposition with liberation of hydrochloric acid and free chlorine, and hence must be kept in dark bottles. Its preserving qualities are improved by the addition of a small quantity of alcohol.

The most delicate chemical test for chloroform is the production of phenylcarbylamine, a compound of sickening odor when it is heated with alcoholic potash and aniline. One part of chloroform in 5000 to 6000 parts of solution can be detected in this way.

The most important medicinal use of chloroform is as an anæsthetic.

Tribromo-methane, $CHBr_3$, or **Bromoformum**, U.S.P., can be prepared from bromal by an analogous reaction to that used for preparing chloroform from chloral. It is a colorless liquid boiling at 148° C. and solidifying at 6° C. It smells like chloroform, and is somewhat used in medicine as an anæsthetic.

Tri-iodo-methane, CHI_3, or **Iodoformum**, U.S.P., has been made most generally by the action of iodine in the presence of an alkali or alkaline carbonate upon alcohol, the main reaction being expressed as follows:

$$C_2H_5OH + 4I_2 + 3K_2CO_3 = CHI_3 + KCHO_2 + 5KI + 2H_2O + 3CO_2$$

It is also made now by the action of iodine in the presence of an alkali upon acetone, the reaction being a very delicate one, serving to indicate traces of acetone, and known as the "iodoform test."

Much iodoform is now made electrolytically by electrolyzing an alkaline iodide in the presence of alcohol and an alkali, the essential reaction in the case being:

$$C_2H_5OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

Iodoform is in small, lemon-yellow, lustrous crystals of the hexagonal system, with a peculiar, very penetrating and persistent odor, resembling saffron. The crystals melt at 119° C. They are very slightly soluble in water, soluble in alcohol, ether, chloroform, benzine, and fixed and volatile oils. It has a strong anæsthetic and antiseptic action, and is much used in surgery.

Tetrachlor-methane, or carbon tetrachloride, CCl_4, is produced by the action of chlorine upon chloroform, or more generally the action of sulphur chloride upon carbon disulphide according to the reaction: $CS_2 + 2S_2Cl_2 = CCl_4 + 6S$. The sulphur so set free is again changed into S_2Cl_2 by the action of chlorine gas. It is a liquid boiling at 76.5° C.; used very extensively as a solvent in place of petroleum naphtha and carbon disulphide, being uninflammable.

Perchlor-ethane, C_2Cl_6, forms rhombic tablets of camphor-like odor. Fuse and boil at 185°.

2. **Halogen Derivatives of the Olefine Series.**—These may be either substitution derivatives, in which one or more H atoms of the unsaturated hydrocarbons are replaced by halogen, the double linking carbon atoms characteristic of the olefines remaining unchanged, or they may be addition compounds, in which case two atoms of halogen add on. In the compounds so formed the unstable double linking is broken up, and the products are in all respects identical with the dihalogen substitution derivatives of the paraffins. Thus, from ethylene, C_2H_4, we may obtain

C_2H_3Cl, monochlor-ethylene (vinyl chloride), and $C_2H_2Cl_2$, dichlor-ethylene, or we may get by addition $C_2H_4Cl_2$, ethylene chloride, already described under the preceding class. From propylene, C_3H_6, we may obtain C_3H_5Cl, monochlor-propylene (allyl chloride), representing the substitution derivatives, or $C_3H_6Cl_2$, propylene chloride, representing the addition compounds.

3. **Halogen Derivatives of the Acetylene Series.**—Here also both classes of compounds are possible,—substitution derivatives, in which the unstable treble linking still remains, and addition compounds, which pass into the class of olefine derivatives.

II. ALCOHOLS, OR HYDROXIDES OF THE HYDROCARBON RADICLES.

Alcohols are formed by the replacement of one or more hydrogen atoms of a hydrocarbon by the corresponding number of OH (hydroxyl) groups.

Alcohols with 1 hydroxyl group are termed *monatomic,* or monohydric alcohols; with 2 hydroxyl groups are termed *diatomic,* or *dihydric,* alcohols; with 3 hydroxyl groups are termed *triatomic,* or trihydric.

The highest of these classes as yet discovered in nature are the heptatomic alcohols, although higher ones have been obtained artificially. Two cases of isomerisms may arise among the alcohols: (*a*) when they are derived from isomeric hydrocarbons; thus, from butane, $CH_3.CH_2.CH_2.CH_3$, we obtain normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$, and from isobutane, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_3$, we obtain isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2\text{-}OH$; (*b*) according to the position taken by the replacing hydroxyl group; thus, while only one monatomic alcohol can be formed from methane, CH_4, and only one from ethane, $CH_3.CH_3$, from propane, $CH_3.CH_2.CH_3$, we can obtain normal propyl alcohol, $CH_3.CH_2.CH_2OH$, and isopropyl alcohol, $CH_3.CH.OH.CH_3$. Normal butane yields two isomeric alcohols, $CH_3.CH_2.CH_2.CH_2OH$ and $CH_3.CH_2.CH.OH.CH_3$, and isobutane yields two also, $\begin{matrix}CH_3\\CH_3\end{matrix}>CH—CH_2OH$ and $\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)—CH_3$.

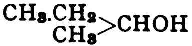
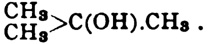
In looking at the formulas of these isomeric butyl alcohols it will be seen that we have three different types of monatomic alcohols: an alcohol containing the group $CH_2.OH$, known as a *primary* alcohol; an alcohol containing the group CH.OH, known as a *secondary* alcohol; an alcohol containing the group C(OH), known as a *tertiary* alcohol. We will find that these are important distinctions, as very different products are obtainable from the alcohols according as they belong to one or the other of these classes.

Secondary and tertiary alcohols are also known as *carbinols,* being considered as derivatives of methyl alcohol or carbinol, in which H atoms are replaced and the replacing groups are named.

Thus, $\begin{matrix}CH_3\\CH_3\end{matrix}>C(OH)—CH_3$ is called trimethyl-carbinol.

1. **Monatomic Alcohols from Saturated Hydrocarbons.** General formula, $C_nH_{2n+1}.OH$.

TABLE.

Name and Formula:	Boiling Point.
Methyl alcohol, $CH_3.OH$	66° C
Ethyl alcohol, $CH_3.CH_2OH$	78°
Normal propyl alcohol, $CH_3.CH_2.CH_2OH$	97°
Isopropyl alcohol, $CH_3.CHOH.CH_3$	83°
Normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2OH$	117°
Isobutyl alcohol,  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}>CH.CH_2OH$	108°
Methyl-ethyl carbinol,  $\genfrac{}{}{0pt}{}{CH_3.CH_2}{CH_3}>CHOH$	99°
Trimethyl carbinol,  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}>C(OH).CH_3$	83°
Normal amyl alcohol, $C_4H_9.CH_2OH$	137°
Fermentation amyl alcohol.  $\genfrac{}{}{0pt}{}{CH_3}{CH_3}>CH.CH_2.CH_2OH$	131°
Hexyl alcohol, $C_6H_{13}.OH$	157°
Heptyl alcohol, $C_7H_{15}.OH$	175°
Octyl alcohol, $C_8H_{17}.OH$	191°
Nonyl alcohol, $C_9H_{19}.OH$	213°
	Melting Point.
Decyl alcohol, $C_{10}H_{21}.OH$	7°
Dodecyl alcohol, $C_{12}H_{25}.OH$	24°
Tetradecyl alcohol, $C_{14}H_{29}.OH$	38°
Hexyadecyl (cetyl) alcohol, $C_{16}H_{33}.OH$	49°
Octadecyl alcohol, $C_{18}H_{37}.OH$	59°
Ceryl alcohol, $C_{27}H_{55}OH$	79°
Myricyl alcohol, $C_{30}H_{61}.OH$	85°

The lower members of the series are mobile liquids soluble in water, the middle members are oily liquids only slightly soluble in water, and the higher ones are solid crystalline bodies. The lowest members possess an alcoholic odor, those over C_5 an odor of fusel oil, and both have a burning taste, while the highest members are odorless and tasteless solids.

Among the general methods for the formation of alcohols may be mentioned:

(*a*) The action of moist silver oxide upon the halogen derivatives of the paraffins, as $C_2H_5I + AgOH = C_2H_5.OH + AgI$.

(*b*) The decomposition of the esters by boiling with caustic alkalies. This decomposition is frequently spoken of as the "saponification" of the esters, because of the well-known illustration of the decomposition of the fats:

$$\underset{\text{Methyl Salicylate.}}{CH_3.OC_7H_5O_2} + KOH = CH_3.OH + \underset{\text{Potassium Salicylate.}}{C_7H_5O_2.OK.}$$

(*c*) The treatment of primary amines with nitrous acid:

$$C_2H_5.NH_2 + NO.OH = C_2H_5.OH + N_2 + H_2O.$$

(*d*) The fermentation of many of the carbohydrates (as grape sugar) with yeast will produce the lower alcohols. (See Fermentation.)

Among the special methods for the formation of alcohols may be mentioned:

(*a*) The reduction of monobasic acids and aldehydes with nascent hydrogen to form primary alcohols.

(*b*) The reduction of ketones with nascent hydrogen to form secondary alcohols.

The alcohols, it must be remembered, are hydroxides of radicles which have in general a basic character. They are, therefore, weak bases. Thus, the hydrogen of the hydroxyl group is replaceable by acid radicles, forming ethereal salts or "esters." At the same time, this hydrogen is also replaceable by strong metals like Na and K, forming "alcoholates." The action of haloid acids will also replace the OH group by halogen, water forming at the same time. Thus, $C_2H_5.OH + HBr = C_2H_5Br + H_2O$. Oxidizing agents readily act upon them, changing primary alcohols to aldehydes and monobasic acids, and secondary alcohols to ketones, while tertiary alcohols are split up into compounds with a lesser number of carbon atoms.

Methyl Alcohol, $CH_3.OH$, derives its name from μέθυ, wine, and ὕλη, wood, which idea is also conveyed in its popular name of "wood-spirit." It occurs as salicylic ester in oils of sweet birch and wintergreen, and is produced in the destructive distillation of wood and the "vinasse" of the beet-sugar refineries.

To prepare it in quantity, the crude pyroligneous acid of the wood distilleries is neutralized with lime, and the volatile portions then distilled off. After repeated rectification, the methyl alcohol is finally freed from acetone and accompanying impurities by treating with fragments of fused $CaCl_2$ which, combined with the methyl alcohol to form a compound $CaCl_2(CH_4O)_4$, which is stable at 100° C., when acetone and impurities are distilled off and then the compound decomposed by addition of water.

Methyl alcohol forms a colorless liquid, boiling at 66°, and with a sp. gr. 0.8. It burns with a non-luminous flame, and mixes with water in all proportions. It is a solvent for fatty oils, camphors, resins, and fats. It has an intoxicating effect, and in concentrated form is poisonous. It is used very extensively in varnish-making as a solvent and for denaturing grain alcohol for industrial uses.

Ethyl Alcohol, $C_2H_5.OH$ (Alcohol, U.S.P.).—This, the most important of the monatomic alcohols, occurs only sparingly in nature, being found as butyric ether in some plants, as the Umbellifera, and in the animal kingdom, as in diabetic urine. It may be formed in several ways:

From ethane by conversion into C_2H_5Cl, and saponification of this latter (see preceding page) by moist silver oxide.

From ethylene and concentrated sulphuric acid and decomposition of the resulting ethyl-sulphuric acid by water:

$$C_2H_4 + SO_2(OH)_2 = C_2H_5.HSO_4.$$
$$C_2H_5.HSO_4 + H_2O = C_2H_5OH + H_2SO_4.$$

It is formed, however, almost invariably by the "alcoholic fermentation" of sugar. (See Fermentation.) The reaction whereby the sugar yields alcohol and carbon dioxide, $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, is not a complete one, as some 5 per cent. of the sugar breaks up into other products, such as glycerin and succinic acid. A number of the homologues of ethyl alcohol are also formed, and are known collectively as "fusel oil."

While alcohol may be purified by repeated distillation, it is not possible to free it from water by this means. On a large scale in the several forms of rectifying columns it is possible to bring the alcohol to 98–99 per cent., but on the small scale to not over 95 per cent. The remaining portion of water must be taken out by chemical dehydrating agents, like heated carbonate of potash, anhydrous sulphate of copper, or standing, followed by a distillation over quicklime. The alcohol thus obtained is the **Alcohol Dehydratum,** U.S.P.

The presence of water in alcohol may be shown by admixture with benzene. This will mix to a clear liquid with alcohol containing not more than 3 per cent. of water. If the percentage begins to exceed this, the mixture becomes turbid. Anhydrous copper sulphate will also indicate the presence of water by changing from white to blue in color. Absolute alcohol boils at 78.5° C., becomes viscid at —100° C., and solidifies at —130°. Its specific gravity is 0.7937 at 15° C. It is very hygroscopic. Alcohol is a solvent for many organic compounds, such as fats, resins, and oils.

A very delicate test for alcohol (although not characteristic of alcohol only) is the iodoform test. The liquid to be tested is warmed with a small quantity of iodine dissolved in iodide of potassium solution, and sodium hydrate is added until the mixture is faintly yellow. In the presence of alcohol the characteristic smell of iodoform is obtained, and gradually the fine yellow crystals separate.

Benzoyl chloride, C_6H_5COCl, is also a delicate test for alcohol, with which it forms ethyl benzoate (benzoic ether), the smell of which is readily recognized. The commonest impurities of alcohol are aldehyde, which readily forms by oxidation, and fusel oil, which accompanies it in the products of fermentation. The former is detected by shaking up with a small quantity of potassium hydroxide solution, whereby a brown aldehyde resin is formed; the latter is detected by evaporation of the suspected alcohol on the hand or from a piece of blotting-paper.

Besides alcohol (containing 94.9 per cent. by volume of ethyl alcohol) and alcohol absolutum, the United States Pharmacopœia recognizes **Alcohol Dilutum,** the latter containing from 48.5 to 49.5 per cent. by volume of absolute ethyl alcohol.

Alcohol has a dehydrating action upon vegetable and animal tissues. It coagulates albumin and prevents the decay of the tissue. Taken in small amount it has a slight stimulant effect; in larger doses it lowers the temperature and acts as an intoxicant, while in excessive amounts it is poisonous, and when injected into the veins it causes death. A portion of the alcohol taken into the system is burned to carbon dioxide and water; the remainder passes off through the lungs and the urine unchanged.

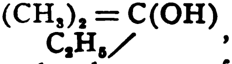
For an account of alcoholic beverages, see Fermentation Industries.

Propyl Alcohols, C_3H_7OH.—The normal propyl alcohol, $CH_3.CH_2.CH_2OH$, is contained in fusel oil, from which it may be obtained by fractionation. It may also be obtained by the action of sodium amalgam upon propion-aldehyde, or by the action of certain fissure ferments upon glycerol.

It is a liquid of spirituous odor, resembling that of methyl alcohol, boiling at 97.4°, and readily miscible with water, but can be separated out again by addition of calcium chloride. Isopropyl, or secondary propyl alcohol, $CH_3.CH(OH)CH_3$, may be obtained from isopropyl iodide (the product of the action of HI upon glycerol), or by the action of sodium amalgam upon acetone. Colorless liquid, boiling at 82.8°.

Butyl Alcohols, $C_4H_9.OH$.—The normal butyl alcohol, $CH_3.CH_2.CH_2.CH_2.OH$, is present in fusel oil, being formed especially in the wine-yeast fermentation and in the fermentation of maize or potato starch by Fernbach's process, when 65 per cent. of the fusel oil obtained is butyl alcohol. It boils at 117°, and has a peculiar odor, inciting to coughing when inhaled. It is not so readily soluble in water, and may readily be separated out on addition of calcium chloride. Isobutyl alcohol, $\begin{matrix}CH_3\\CH_3\end{matrix}> CH.CH_2OH$, known frequently as fermentation butyl alcohol, is the most important of the butyl alcohols. It is contained in fusel oil, especially in potato fusel oil, and obtained in the beer-yeast fermentation. Colorless liquid, boiling at 108°, with a fusel smell, resembling that of wild jasmine.

Tertiary butyl alcohol, or trimethyl carbinol, $(CH_3)_3{\equiv}C(OH)$, is contained in small quantity in fusel oil. Spirituous smell resembling that of camphor. The remaining butyl alcohol, known as secondary butyl alcohol (see table), is only obtained synthetically.

Amyl Alcohols, $C_5H_{11}.OH$.—Of the eight possible isomeric alcohols, only four require mention. Normal primary amyl alcohol is contained in small quantity in fusel oil, and can be prepared by the reduction of normal valeric aldehyde. Its boiling point is 137°. Isobutyl carbinol, $(CH_3)_2 = CH.CH_2.CH_2OH$, forms the chief constituent of fermentation amyl alcohol obtained from potato fusel oil. It also is found in Roman chamomile oil in combination with angelic and tiglic acids. It boils at 131°, and has a strong, irritating odor. It is intoxicating even in dilute solutions, and is the cause of the peculiar toxic after-effects of intoxication by brandy and other ardent spirits. It is optically inactive. Methyl-propyl carbinol, or active amyl alcohol, is also contained in fermentation amyl alcohol. It turns the plane of polarization to the left. Boiling point, 112.5°. Tertiary amyl alcohol, or dimethyl-ethyl carbinol,  $\begin{matrix}(CH_3)_2 = C(OH)\\ C_2H_5/\end{matrix}$, has been introduced to medicine in recent years under the name of "amylene-hydrate," and recommended as an hypnotic. It is made from amylene, C_5H_{10} (see p. 527), by shaking this up with sulphuric acid, whereby amyl-sulphuric acid, $SO_2\left\{\begin{matrix}OH\\O(C_5H_{11})\end{matrix}\right.$, is formed. This, on distillation with aqueous alkalies, is decomposed into amylene hydrate and alkaline sulphate. The amylene hydrate is a colorless, oily liquid, of penetrating odor, which recalls camphor, peppermint, and paraldehyde. It boils at 102.5°, and has a specific gravity of 0.812 at 12°. It is soluble in 8 parts of water, and miscible in all proportions with alcohol, ether, chloroform, benzine, glycerin, and fatty oils. It is sensitive to light and very hygroscopic. As an hypnotic, it is said to occupy a position intermediate between chloral hydrate and paraldehyde.

Hexyl Alcohols, $C_6H_{13}.OH$.—The normal primary hexyl alcohol is contained as a butyric ester in the seeds of *Heracleum giganteum*. A primary hexyl alcohol is also obtained from wine fusel oil, and a secondary alcohol from mannite through the intermediate formation of secondary hexyl iodide.

Heptyl Alcohols, $C_7H_{15}.OH$.—The normal primary heptyl alcohol is obtained by the reduction of œnanthol, a normal aldehyde which forms on the distillation of castor oil.

Octyl Alcohol, $C_8H_{17}.OH$.—The normal primary octyl alcohol is found as an acetic ester in the several varieties of *heracleum*.

The normal primary alcohols, $C_{10}H_{21}.OH$, $C_{12}H_{25}.OH$, $C_{14}H_{29}.OH$, $C_{16}H_{33}.OH$, and $C_{18}H_{37}.OH$, were prepared artificially by Krafft, in 1881, by reducing the corresponding acids with zinc-dust and acetic acid. They are solids, like paraffin in appearance.

Cetyl Alcohol, $C_{16}H_{33}.OH$, formerly known as *ethal*, is found in combination with palmitic acid as the chief constituent of spermaceti (**Cetaceum**, U.S.P.). The alcohol crystallizes in small leaflets, fusing at 49° and boiling at 189.5°.

Octadecyl Alcohol, $C_{18}H_{37}.OH$, is also found in the form of esters in spermaceti.

Ceryl Alcohol, $C_{27}H_{55}.OH$, is found as cerotic ester in Chinese wax, and as palmitic ester in the ripe capsules of the poppy. The ceryl esters are also present in carnauba wax and in beeswax. The alcohol fuses at 76°–79°.

Myricyl Alcohol, $C_{30}H_{61}.OH$, is present as palmitic ester in beeswax and in carnauba wax, from which latter it is most conveniently extracted by saponification with alcoholic potash. The alcohol melts at 85° C.

2. Monatomic Alcohols from Unsaturated Hydrocarbons, $C_nH_{2n-1}.OH$.—These alcohols are derivatives of the olefine hydrocarbons, and, like them, contain the unstable double linking of two carbon atoms. They, therefore, like them, can take up two atoms of hydrogen or halogen element or one molecule of a haloid acid, forming thereby saturated alcohols, which may contain one or two replacing halogen atoms in the radical which is combined with the hydroxyl.

Vinyl Alcohol, $CH_2 = CH.OH$, corresponding to ethylene, $CH_2 = CH_2$, has been found as an impurity in ordinary ether, but has not been isolated, as the isomeric acetaldehyde, $CH_3.CHO$, results in endeavoring to prepare it.

Allyl Alcohol, $CH_2 = CH—CH_2OH$, corresponding to propylene, C_3H_6, is found in crude wood-spirit, and may be readily obtained by distilling glycerol with oxalic acid, the reaction being $C_3H_8O_3 - H_2O - O = C_3H_6O$, showing that the oxalic acid acts as a reducing and dehydrating agent. It is a mobile, colorless liquid, of penetrating, unpleasant odor, boiling at 96.6°, and miscible with water.

3. **Other Monatomic Alcohols from Unsaturated Hydrocarbons.**—The alcohols, $C_nH_{2n-3}OH$, are derivatives of acetylene and its homologues, and, like them, contain the unstable treble linking of two carbon atoms.

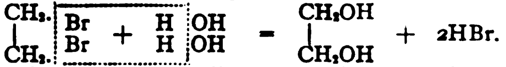
Propargyl Alcohol, $CH \equiv C - CH_2OH$, corresponding to allylene, C_3H_4, is obtained from monobromallyl alcohol by splitting off HBr, effected by the action of concentrated aqueous potash. It is a mobile, pleasant-smelling liquid, lighter than water, boiling at 114°.

Geraniol, $C_{10}H_{17}.OH$ (see also p. 701) is an unsaturated aliphatic alcohol containing two double linkings.

Cholesterol, $C_{27}H_{46}O$, is also an unsaturated alcohol with two double linkings which occurs in combination with various fatty acids in lanolin (**Adeps Lanæ,** U.S.P., and **Adeps Lanæ Hydrosus,** U.S.P.), the purified fat of sheep's wool.

4. **Diatomic Alcohols or Glycols.** General formula, $C_nH_{2n}(OH)_2$.—If two hydrogen atoms of a hydrocarbon of the paraffin series be replaced by two OH groups, we obtain a diatomic alcohol or glycol (from γλυχύς, sweet). Thus, from ethane, C_2H_6, we obtain ethylene glycol, $C_2H_4(OH)_2$. The two OH groups do not, however, attach to the same carbon atoms, so that, while theoretically both ethylidene glycol, $CH_3.CH(OH)_2$, and ethylene glycol, $CH_2OH—CH_2OH$, are possible, only the latter can be obtained. For this reason also, the first of the series of glycols, methylene glycol, $CH_2(OH)_2$, cannot be obtained in the free state, although ethers corresponding to it are known. (See Methylal, p. 551.)

Glycols are formed most readily by forming first the dibromides of the hydrocarbons and then replacing the bromine atoms by hydroxyl groups. This can be effected by boiling the dibromides with water to which potassium carbonate or lead hydroxide has been added to take up the hydrogen bromide liberated, the reaction being:



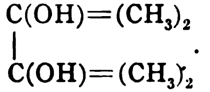
$$\begin{array}{l} CH_2. \\ | \\ CH_2. \end{array}\boxed{\begin{array}{lcl} Br & + & H \\ Br & & H \end{array}}\begin{array}{l} OH \\ OH \end{array} = \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2HBr.$$

They are also formed by the direct combination of the olefine hydrocarbons with hydrogen peroxide, or by oxidation of the olefines by potassium permanganate: $C_2H_4 + H_2O + O = C_2H_4(OH)_2$.

The glycols are mostly syrupy, sweet-tasting liquids of relatively high boiling point. They are readily soluble in water and alcohol, insoluble in ether. The double tertiary glycols, known specially as "pinacones," are, however, solid crystalline compounds.

Ethylene Glycol, $CH_2OH.CH_2OH$, is prepared from ethylene bromide, $C_2H_4Br_2$, and water in the presence of potassium carbonate. It is formed also along with trimethylamine on boiling an aqueous solution of cholin, a decomposition product of lecithin and protagon (see p. 581): $C_5H_{15}NO_2 = (CH_3)_3N + C_2H_4(OH)_2$. It is a sweetish, syrupy liquid, boiling at 197°.

Propylene Glycols, $C_3H_6(OH)_2$.—Two isomeric forms are known, α-propylene glycol, $CH_3.CH(OH).CH_2OH$, and β-propylene glycol, CH_2-$OH.CH_2.CH_2OH$. The former of these can be prepared from propylene bromide, but is most easily obtained by distilling glycerin with caustic soda. It boils at 188°, and is converted by fissure ferments into a dextro- and a lævo-rotatory modification; the β-propylene glycol is also known as trimethylene glycol, and may be prepared from trimethylene bromide, or produced in the fissure fermentation of glycerin. It boils at 216°.

Hexylene Glycols, $C_6H_{12}(OH)_2$.—The most interesting compound of this formula is the so-called "pinacone," or tetramethyl-ethylene, glycol, 

$$\begin{array}{l} C(OH)=(CH_3)_2 \\ | \\ C(OH)=(CH_3)_2 \end{array}$$

. It is most readily formed when acetone is reduced by metallic sodium in the presence of potassium carbonate. It forms a white, crystalline mass, with camphor-like odor, melting at 42° and boiling at 171°–172°. By oxidation it is reconverted into acetone.

Other glycols of high molecular weight are found in the natural waxes. Thus, from carnauba wax has been obtained a glycol of the formula $C_{25}H_{50}(OH)_2$, melting at 103.5°, and the white wax obtained from the cochineal insect under the name of *coccerin* on saponification yields *cocceryl alcohol*, $C_{30}H_{60}(OH)_2$.

5. **Triatomic Alcohols, or Glycerols.**—General formula, $C_nH_{2n-1}(OH)_3$.—When three atoms of hydrogen in a hydrocarbon of the paraffin series are replaced by OH groups, we have a triatomic alcohol, or *glycerol*. Such alcohols act like triacid bases, and can combine with one, two, or three molecules of a monobasic acid.

The glycerols are colorless, syrupy liquids, readily soluble in water, and of high boiling point.

The first of the series, that derivable from methane, is unknown. Its formula, $CH(OH)_3$, would be too unstable to allow of its isolation, as a molecule of water would undoubtedly split off from the three OH groups here indicated as attached to the same carbon atom. Its ethyl ester, $CH(OC_2H_5)_3$, is, however, known under the name of orthoformic ether (see p. 546).

The second glycerol of the series corresponding to ethane is also unknown. Its formula, $C_2H_3(OH)_3$, also indicates that to one of the carbon atoms two OH groups would be attached, which gives us an unstable molecule. Its ethyl ether, $C_2H_3(OC_2H_5)_3$, is, however, known under the name of ortho-acetic ether.

Propenyl Glycerol, $C_3H_5(OH)_3$ (**Glycerinum**, U.S.P.), is the triatomic alcohol corresponding to propane, and has the structural formula, CH_2-$OH—CHOH—CH_2OH$. It occurs abundantly in nature in combination with the so-called fatty acids as esters of these latter, making up the bulk of the vegetable and animal fats and oils (see p. 575).

It is also produced in the alcoholic fermentation of sugar, and hence is found in most alcoholic beverages. It is also present in the urine as glycerin-phosphoric acid, a decomposition product of lecithin and protagon. It may be formed artificially by the action of water at 170° upon trichlorhydrin (trichlorpropane), $C_3H_5Cl_3$.

Practically, it is always obtained by the decomposition of the fats in connection with the manufacture of soaps and stearic acid. This decomposition may be effected by the aid of water in the form of super-heated steam, by alkalies and metallic oxides, or by heating with sulphuric acid. For a fuller account of these methods, see section on Fat Industries.

Anhydrous glycerol is a thick, colorless liquid, of specific gravity 1.27, while the U.S.P., *glycerinum* (95 per cent.) has a sp. gr. 1.249 at 25°. It solidifies at low temperatures to monoclinic crystals, which fuse at 20° C. It boils at 290°, but in its ordinary impure state cannot be distilled at ordinary pressures without decomposition. It is very hygroscopic, and mixes with water and alcohol in all proportions. It is insoluble in ether, chloroform, carbon disulphide, benzine, benzene, and fixed or volatile oils. It is an excellent solvent for a great range of substances, such as bromine and iodine, alkaline chlorides, fixed alkalies, some of the alkaline earths, as lime, and a number of neutral salts. It also is said to have antiseptic properties.

Both glycerol and its naturally occurring compounds, the fats, decompose when heated, with the production of acrid penetrating vapors of acrolein and similar products.

Butenyl Glycerol, $C_4H_7(OH)_3$, *Amyl Glycerols,* $C_5H_9(OH)_3$, and *Hexyl Glycerols,* $C_6H_{11}(OH_3)$, have all been obtained.

6. Tetratomic Alcohols. General formula, $C_nH_{2n-2}(OH)_4$.—If four hydrogen atoms of a saturated hydrocarbon be replaced by four OH groups, we obtain a tetratomic alcohol, which corresponds to a tetracid base. While the four OH groups characteristic of these alcohols seem to require at least four carbon atoms in the molecule, and hence no stable tetratomic alcohols can be expected from methane, ethane, or propane, yet ethers from these lower hypothetical alcohols have been obtained. Thus, ortho-carbonic ether, $C(OC_2H_5)_4$, a liquid of ethereal odor, boiling at 159°, corresponds to an alcohol, $C(OH)_4$.

Erythrol (or Phycite), $C_4H_6(OH)_4$, occurs free in *Protococcus vulgaris,* and combined with orsellic acid as an ester (erythrin) in many lichens and algæ. It forms large quadratic crystals, easily soluble in water, difficultly soluble in alcohol, and insoluble in ether. They fuse at 112° and boil at 330°.

Penta-erythrol, $C_5H_8(OH)_4$, has also been made artificially.

7. Pentatomic Alcohols. General formula, $C_nH_{2n-3}(OH)_5$.—Pentatomic alcohols have not been found in nature, and until very recently had not been obtained artificially. They have been obtained, however, in several cases by the reduction of certain *pentoses* (see Carbohydrates).

Arabinol, $CH_2OH—(CH.OH)_3—CH_2OH$, has been prepared by the reduction of arabinose, $C_5H_{10}O_5$, with the aid of sodium amalgam. It fuses at 102°, and has a lævo-rotatory power in aqueous solution on the addition of borax.

Xylinol, $C_5H_{12}O_5$, has been prepared by a similar method from xylose, $C_5H_{10}O_5$. It has not as yet been obtained crystalline, and is optically inactive.

Rhamnitol, $C_6H_{14}O_5$, prepared from rhamnose, $C_6H_{12}O_5$, is a homologue of the foregoing. It fuses at 121°, and is right-rotatory in aqueous solution even without the addition of borax.

8. **Hexatomic Alcohols.** General formula, $C_nH_{2n-4}(OH)_6$.—Several alcohols of the formula $C_6H_{14}O_6$ have been found in nature, and have excited interest because of their close relation to one of the groups of carbohydrates or sugars. The nature of their relation and a method for the synthetic formation of them from these sugars have both been indicated in connection with the classic work of Emil Fischer on the Carbohydrates.

Mannitol, $CH_2OH—(CHOH)_4—CH_2OH$, is found in many plants, as in the larch, in celery, in the leaves of *Syringa vulgaris*, in sugar-cane, in *Agaricus integer* (of the dry substance of which it forms 20 per cent.), in rye-bread, and notably in the manna ash (*Fraxinus ornus*), the dried juice of which constitutes **Manna,** U.S.P.

Mannitol crystallizes from water in thick rhombic prisms, or from alcohol in silky needles, melts at 165°–166°, is only moderately soluble in water, scarcely soluble in cold alcohol, and insoluble in ether. Its aqueous solution turns the plane of polarization very slightly to the left, but in the presence of borax and other salts it is strongly dextro-rotatory.

It has been obtained artificially by Fischer from both mannose and fructose (lævulose) by reduction with sodium amalgam in neutral or weakly acid solution; when produced from fructose, sorbitol, an isomeric alcohol, always accompanies it. Mannitol also is formed from some of the sugars in the processes of fermentation, as in the lactic acid fermentation, and in especially large amount in the mucous fermentation of cane sugar.

Fischer has shown that there are three mannitols obtainable: the ordinary mannitol is the dextro-rotatory variety, and is always obtained in the reduction of *a*-mannose; a lævo-rotatory mannitol is obtained by the reduction of *l*-mannose; and an inactive mannitol is obtained from the inactive mannose. The three varieties, besides differing in their optical characters, differ slightly in their fusing points and their crystalline forms.

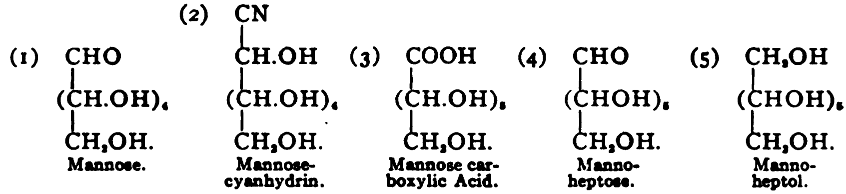
Sorbitol, $C_6H_8(OH)_6$, is found in the berries of the mountain ash and in the fruit of the plum, cherry, apple, pear, etc. It crystallizes out of water in small, colorless needles, which contain water of crystallization. The anhydrous substance fuses at 110°–111°. It is slightly lævo-rotatory in simple aqueous solution, but in the presence of borax is dextro-rotatory. It has been prepared synthetically from dextrose, and represents the dextro variety of sorbitol only, the lævo-sorbitol having been also prepared.

Dulcitol (Melampyrite), $C_6H_8(OH)_6$, is found in certain plants like the *Melampyrum nemorosum*, but more particularly in the manna from

Madagascar, and has been made synthetically by the reduction of lactose and gelactose. It crystallizes in monoclinic prisms, fuses at 188.5°, and is still more difficultly soluble in water than mannite. Dulcitol is optically inactive and not capable of being resolved into active modifications.

Rhamno-hexitol, $C_7H_{10}(OH)_6$, a homologue of the preceding, has been prepared from rhamno-hexose, $C_7H_{14}O_6$. It crystallizes from hot alcohol in small, colorless prisms, melting at 173°, and is dextro-rotatory.

9. Heptatomic to Nonatomic Alcohols.—Starting with the group of sugars (hexoses) corresponding to the hexatomic alcohols, Emil Fischer has built up synthetically several alcohols of higher classes. Thus, the addition of hydrogen cyanide to a hexose will give what is termed a nitrile; this when saponified yields an acid with seven carbon atoms, which can be reduced by sodium amalgam in successive steps to a sugar and a heptatomic alcohol. We may illustrate this in the case of mannose:



$$
\begin{array}{ccccc}
 & (2)\ \begin{array}{l} CN \\ | \\ CH.OH \\ | \\ (CH.OH)_4 \\ | \\ CH_2OH. \end{array} & & & \\
(1)\ \begin{array}{l} CHO \\ | \\ (CH.OH)_4 \\ | \\ CH_2OH. \end{array} & & (3)\ \begin{array}{l} COOH \\ | \\ (CH.OH)_5 \\ | \\ CH_2OH. \end{array} & (4)\ \begin{array}{l} CHO \\ | \\ (CHOH)_5 \\ | \\ CH_2OH. \end{array} & (5)\ \begin{array}{l} CH_2OH \\ | \\ (CHOH)_5 \\ | \\ CH_2OH. \end{array}
\end{array}
$$

Mannose. Mannose-cyanhydrin. Mannose carboxylic Acid. Mannoheptose. Mannoheptol.

In this way an artificial, *δ-mannoheptol,* $C_7H_{16}O_7$, was prepared by Fischer, and later its identity with the naturally occurring *Perseitol* was established.

Perseitol is found abundantly in the fruits and leaves of *Laurus persea.* It crystallizes from water in microscopical needles, melting at 188°. Its aqueous solution alone is inactive but on the addition of borax becomes strongly dextro-rotatory.

By analogous synthetical reactions to those given above, there has been obtained from mannoheptose an octatomic alcohol, *δ-mannoctol,* $C_8H_{10}(OH)_8$. By the same method, starting from δ-glucose, there have been obtained the following synthetic alcohols: *α-glucoheptol,* $C_7H_{16}O_7$, fusing at 127°–128°; *α-gluco-octol,* $C_8H_{18}O_8$, fusing at 141°; and *α-glucononol,* $C_9H_{20}O_9$, fusing at 194°.

III. Ethers or Oxides of the Hydrocarbon Radicles.

The ethers may also be considered as the anhydrides of the alcohols. Thus, $2C_2H_5.OH = (C_2H_5)_2O + H_2O$. It may be, however, that two different alcohols can thus be united by the loss of one molecule of water. The resulting ether will then contain two different hydrocarbon radicles. united by oxygen. Such a compound would be a mixed oxide. We distinguish, therefore, between the two classes, and have ***simple ethers*** or oxides of a single radicle, and ***mixed ethers*** or oxides of mixed radicles. In both these cases, however, the radicles are obtained directly from the hydrocarbons by the loss of one or more hydrogen atoms, and are the same as unite with hydroxyl to form the alcohols. These alcohols, it will be remembered, were spoken of as basic hydroxides, so the oxides will be basic oxides. Compounds where a basic or alcohol radicle is united by oxygen to an acid radicle used to be known as *compound ethers,* but, as they are really ethereal salts, they have been given the name of *esters,* to mark the distinction and to separate them clearly from the basic oxides or ethers.

We may distinguish between the ethers of the monatomic alcohols and those of higher alcohols.

1. **Ethers of the Monatomic Alcohols.**—These may be formed in several ways. By heating the alcohols with sulphuric acid the ethers can readily be obtained. The reaction goes on in two stages, however, as illustrated in the case of ethyl ether:

(*a*) $C_2H_5.OH + SO_2(OH)_2 = SO_2(OH).OC_2H_5 + H_2O.$

(*b*) $SO_2(OH)OC_2H_5 + C_2H_5.OH = C_2H_5.OC_2H_5 + SO_2(OH)_2.$

In the first reaction a compound known as ethyl-sulphuric acid (see p. 570) is formed, which then reacts with a second molecule of alcohol to form ethyl oxide or ether, and sulphuric acid is regenerated. Another general method for ether formation is to treat the halogen derivatives of the hydrocarbons with a sodium alcoholate or with alcoholic potash: $C_2H_5I + C_2H_5.ONa = C_2H_5.OC_2H_5 + NaI.$

By the direct union of acetylene and hydrogen, ethylene can be formed and ethylene unites with sulphuric acid to form ethyl sulphuric acid which decomposes with water to form ether.

Senderens has also changed alcohol vapor quantitatively into ether by passing it over aluminum oxide heated to 260° C.

The ethers are very stable. Ammonia, alkalies, dilute acids, and metallic sodium have no action upon them. They can be changed back into the corresponding alcohols by superheating with water in the presence of some acid, such as sulphuric.

Methyl Ether, $(CH_3)_2O$, is prepared from methyl alcohol and sulphuric acid. At ordinary temperatures it is a gas, but can be changed by pressure or cold into a mobile liquid. Boils at —21° C., and burns with bluish flame.

Ethyl Ether, $(C_2H_5)_2O$ (**Æther,** U.S.P.), also known popularly as "sulphuric ether," because prepared by the aid of sulphuric acid. It is prepared by the reactions given above. As in these reactions the sulphuric acid is re-formed after serving to convert the alcohol into ether, it would seem as if the process might be kept up continuously. In fact, it is possible with small amounts of sulphuric acid to convert large quantities of alcohol into ether. The method is sometimes called the "continuous etherification process," but a limit is reached in the power of the sulphuric acid because side reactions interfere. Some sulphuric acid is reduced to sulphurous acid, and the slight impurities in the alcohol become carbonized. The temperature of the reaction must be kept as near 140° C. as possible, as at a higher temperature the acid acts dehydrating upon the alcohol, and at a lower temperature alcohol distils over unchanged. The product is washed with milk of lime to remove the sulphurous acid, then rectified, and the water and alcohol removed by chloride of calcium. The official ether is composed of about 96 per cent. by weight of absolute ether and about 4 per cent. of alcohol containing a little water.

To obtain absolute anhydrous ether, it must be treated with metallic sodium and again distilled.

Common ether is a transparent, mobile liquid, having a characteristic ethereal odor, and a burning, sweetish taste. Its specific gravity is 0.725 to 0.728 at 15° C., or 0.716 to 0.717 at 25° C. It boils at about 35.5 (the absolute ether boils at 34.97°) and melts at —117.4°. It is somewhat soluble in water (1 part in 10 parts water at 15° C.) and miscible in all proportions with alcohol, chloroform, benzine, benzene, fixed and volatile oils. Its vapor is very inflammable and forms an explosive mixture with air. Ether is a solvent for fats, resins, and many alkaloids; for bromine, iodine, phosphorus, and in the manufacture of collodion and artificial silk. It is used in medicine largely as an anæsthetic.

In the manufacture of ether, as carried out on a large scale, two side products are obtained that may be mentioned. "Light oil of wine" is obtained as a liquid, boiling between 150° and 300°; it is a mixture of ethers, ketones, and hydrocarbons. "Heavy oil of wine," which boils above 300°, is a mixture of esters of sulphuric acid and olefine hydrocarbons.

Hoffmann's Anodyne is a mixture of ether, alcohol, and ethereal oil.

Methyl-ethyl Ether, $\left.\begin{matrix}CH_3\\ C_2H_5\end{matrix}\right\} O$, is an example of the mixed ethers. It is made conveniently by the action of ethyl iodide upon sodium methylate:

$$C_2H_5I + NaOCH_3 = NaI + \left.\begin{matrix}CH_3\\ C_2H_5\end{matrix}\right\} O.$$

Methyl-ethyl ether is a colorless liquid of peculiar odor, which boils at 11° C. and is very inflammable. Compressed in liquid form in cylinders, it comes occasionally into use as an anæsthetic, being recommended by Richardson as a substitute for chloroform.

Allyl Ether, $(C_3H_5)_2O$, is the oxide of the unsaturated radicle allyl and corresponds to allyl alcohol, $C_3H_5.OH$. It boils at 82°.

2. Ethers of the Diatomic Alcohols.—We may have several classes of compounds here, either the compounds of the dyad radicle and monad radicles like methyl and ethyl linked by oxygen, or the simple oxides of the dyad alcohol radicles. Thus, we have from $C_2H_4(OH)_2$, ethylene glycol, $C_2H_4\left\{\begin{matrix}OH\\ OC_2H_5\end{matrix}\right.$ and $C_2H_4(OC_2H_5)_2$, or C_2H_4O, which is simply ethylene oxide.

Ethylene Oxide, $\begin{matrix}CH_2\\ CH_2\end{matrix}\!\!>O$, may be obtained by decomposing the halogen derivatives of the glycols by aqueous alkalies. It is isomeric with acetaldehyde (see p. 549), but does not reduce ammoniacal silver solution as does aldehyde. It is a strong base, and precipitates the hydroxides of magnesium, aluminum, copper, and iron from the salts.

3. **Ethers of the Triatomic and Tetratomic Alcohols.**—While methenyl glycerol, $CH(OH)_3$, is unknown in the free state, as stated before (see p. 540), its ethyl ether is known. The so-called *orthoformic ether*, $CH(OC_2H_5)_3$, is this compound. Boiling point, 145°–146°. From propenyl glycerol or common glycerol, $C_3H_5(OH)_3$, we have similarly three ethers: $C_3H_5(OH)_2OC_2H_5$, $C_3H_5(OH)(OC_2H_5)_2$, and $C_3H_5(OC_2H_5)_3$. The first of the tetratomic alcohols, $C(OH)_4$, was also stated to be unknown in the free state, but its ethyl ether is known under the name of *ortho-carbonic ether*, $C(OC_2H_5)_4$. It is an aromatic-smelling compound, boiling at 158°-159°.

IV. SULPHO-ALCOHOLS, SULPHO-ETHERS, AND SULPHONIC COMPOUNDS.

The sulpho-alcohols have long been known under the name of *mercaptans* (from *mercurio aptum*, because of the readiness with which they combine with mercuric oxide), and contain the radical SH in combination with the hydrocarbon radical, instead of OH as in alcohols. They are formed by the action of potassium sulphydrate upon the iodides of the paraffine hydrocarbons. Thus, $C_2H_5I + KSH = C_2H_5SH + KI$.

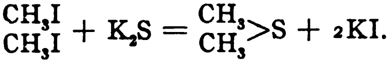
The combinations of the mercaptans with metallic oxides are known as *mercaptides*. They also combine with aldehydes and ketones, producing in the former case *mercaptals*, and in the latter *mercaptols*. The mercaptans when oxidized yield the *sulphonic acids*, compounds containing the group HSO_3 in combination with the hydrocarbon radical. Thus, $C_2H_5SH + O_3 = C_2H_5.HSO_3$. On the other hand, the oxidation of the mercaptols yields the class of *sulphonals*.

The mercaptans are liquids of most unpleasant and piercing odor, resembling that of leeks. They are nearly insoluble in water, and the lower members are very volatile. They are inflammable.

Methyl Mercaptan, CH_3SH, is a liquid of unpleasant odor, boiling at 6° C. It is formed by the action of anaërobic micro-organisms upon albumin, and is, therefore, found among human intestinal gases.

Ethyl Mercaptan, $C_2H_5.SH$, is a liquid which boils at 36.2°, and is of extremely unpleasant odor. It is now made on a large scale as furnishing the starting-point for the manufacture of sulphonal and trional.

The thio-ethers, or sulphur ethers, are made by distillation of the iodides of the hydrocarbon radicals with potassium sulphide:



$$\begin{matrix} CH_3I \\ CH_3I \end{matrix} + K_2S = \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>S + 2KI.$$

They are colorless liquids, of unpleasant odor, which are soluble in alcohol but not in water. By their oxidation they yield first *sulphoxides* and then *sulphones:* $(CH_3)_2S$; $(CH_3)_2SO$; $(CH_3)_2SO_2$.

The most important of the thio-ethers is:

Allyl Sulphide, $(C_3H_5)_2S$, known as "garlic oil," is obtained from the leaves of the garlic (*Allium sativum*) and the seeds of many of the Cruciferæ. It probably does not exist originally as such, but results as a decomposition product from more complicated materials. It boils at 140°. It can also be formed artificially from allyl iodide and potassium sulphide.

The sulphides of propyl, butyl, and amyl have recently been identified by Mabery as present in the crude petroleum of Lima, Ohio, and in Canadian petroleums.

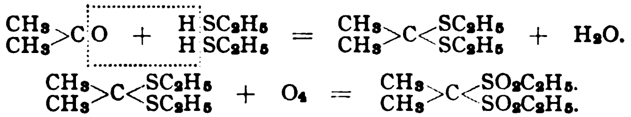
The sulphonic acids and salts contain the sulphonic group, HSO_3, combining directly, with the valence one, with the hydrocarbon radicals. They may be formed by boiling iodides of the hydrocarbon radicals with alkaline sulphites, $C_2H_5I + K_2SO_3 = C_2H_5KSO_3 + KI$, or by the oxidation of mercaptans, sulphides, and sulphocyanates with nitric acid, as before noted.

Methyl-sulphonic Acid, $CH_3.SO_3H$, has been prepared as a syrupy liquid.

Ethyl-sulphonic Acid, $C_2H_5.SO_3H$, forms a deliquescent crystalline solid. A derivative of this, amido-ethyl-sulphonic acid, is known as *taurin*, and is present in the gall, in combination with cholic acid, as taurocholic acid.

Reference was made, under mercaptans, to the fact of their combining with ketones to form mercaptols. This reaction is a fundamental one in the preparation of the important product known as *sulphonal*.

Sulphonal (**Sulphonmethanum**, U.S.P.) (Diethyl-sulphone-dimethyl-methane), $\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$. This compound is prepared from ethyl mercaptan in two reactions. First, 2 molecules of the mercaptan unite with 1 molecule of acetone, with the elimination of water, to form the corresponding mercaptol. This is then oxidized by an acidified potassium permanganate solution. The reactions are:



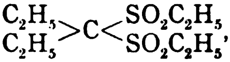
$$\begin{matrix}CH_3\\CH_3\end{matrix}>C\,O + \begin{matrix}H\,SC_2H_5\\H\,SC_2H_5\end{matrix} = \begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} + H_2O.$$

$$\begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix} + O_4 = \begin{matrix}CH_3\\CH_3\end{matrix}>C<\begin{matrix}SO_2C_2H_5.\\SO_2C_2H_5.\end{matrix}$$

Sulphonal forms colorless, odorless, and tasteless crystals, melting at 125°–126°, and boiling, with slight decomposition only, at 300°. More soluble in hot than in cold water; soluble in boiling alcohol. The solutions have a neutral reaction. If a small quantity of sulphonal be heated in a small test-tube with powdered charcoal, the characteristic odor of mercaptan is obtained. It is used very successfully as an hypnotic and soporific.

Trional (**Sulphonethylmethanum**, U.S.P.) (Diethyl-sulphone-methylethyl-methane), $\begin{matrix}CH_3\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$. If, instead of acetone (dimethylketone), we take methyl-ethyl-ketone for the reaction with mercaptan, we obtain the product known as trional, which forms colorless, lustrous, and odorless crystals, melting at 76°, soluble in hot water, easily soluble in alcohol and ether. Its therapeutic action is similar to that of sulphonal, but it is said to act more rapidly and in smaller doses.

Tetronal (Diethyl-sulphone-diethyl-methane),



$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>C<\begin{matrix}SO_2C_2H_5\\SO_2C_2H_5\end{matrix}$, is made by using diethyl-ketone (propione) instead of acetone for the reaction with mercaptan. It forms colorless, lustrous scales, which melt at 85°, easily soluble in boiling water and in alcohol, and moderately soluble in ether. It is very similar in its action to trional.

V. Aldehydes and Ketones.

In speaking of these compounds under the head of Classification of Organic Compounds (see p. 516), they were referred to as products of oxidation of the alcohols. They are alike in this common derivation, but differ because of a fundamental difference in the alcohols from which they may be derived. Thus, if a primary alcohol containing the group —CH_2OH is oxidized, it first loses two hydrogen atoms, and we have the group —CO.H, characteristic of aldehydes; if, on the other hand, a secondary alcohol containing the group $\overset{|}{\underset{|}{C}}H.OH$ is oxidized, it loses two hydrogen atoms, and we have the group $\overset{|}{\underset{|}{C}}O$, characteristic of ketones. Conversely, by the action of sodium amalgam upon aldehydes we get primary alcohols, while the action of the same reagent upon ketones gives us secondary alcohols. Another important difference between the two classes is, that aldehydes readily and in some cases spontaneously pass to a fuller stage of oxidation, viz., acids, in which the —CO.H group is changed to a —CO.OH group, while the ketones represent the final products of oxidation of the secondary alcohols.

They have some reactions in common and some which are distinctive of each class. Both aldehydes and ketones combine with alkaline bisulphites to form crystalline compounds, which, therefore, serve for their extraction and purification when admixed with other organic compounds. Both combine with hydrocyanic acid to form addition compounds known as *nitriles*, which, when saponified, yield acids by the change of the CN group to COOH. Both react with mercaptans (see p. 546). Both unite with hydroxylamine, $NH_2.OH$, to form *oximes*, known respectively as *aldoximes* and *ketoximes;* and both unite with hydrazines (see Phenylhydrazine, p. 637) to form a class of compounds called *hydrazones.*

The most important of the reactions which are characteristic of aldehydes alone are the reducing action upon ammoniacal silver solutions, whereby a silver mirror is obtained, and the formation of crystalline addition compounds with ammonia.

1. **Aldehydes of Saturated Alcohols.** General formula, $C_nH_{2n}O$.

Formaldehyde, HCO.H.—A mixture of gaseous methyl alcohol and air is led over gently-heated copper oxide, yielding a solution of formaldehyde in methyl alcohol. It is a gas of pungent odor, condensible to a liquid boiling at —21°, which reduces ammoniacal silver solution in the cold. It polymerizes very readily to form paraformaldehyde (**Paraformaldehydum,** U.S.P.), $C_3H_6O_3$, a white crystalline mass liberating formaldehyde when in aqueous solution, or under other conditions to produce a substance known as " formose," from which Emil Fischer has isolated *a-acrose,* a sugar of the formula $C_6H_{12}O_6$.

Under the name of solution of formaldehyde (**Liquor Formaldehydi,** U.S.P.) an aqueous solution containing not less than 37 per cent. by weight of absolute formaldehyde is official. It is undoubtedly an antiseptic of great power, and as such has been used in surgical practice as well as for the preservation of foods and drinks, although open to objection and prohibited by pure-food legislation.

Acetaldehyde, CH_3.COH.—This compound, obtained from common, or ethyl, alcohol, was first called aldehyde from *alcohol dehydrogenatum,* to indicate that its formula differed from that of alcohol in having lost two hydrogen atoms. It is found in both crude wood-spirit and grain-spirit, from the latter of which it can be obtained in the first running of the rectifying stills. It is most generally obtained, however, by the oxidation of ethyl alcohol with the aid of sulphuric acid and potassium dichromate or manganese dioxide. Ammonia gas is passed into an ethereal solution of this crude distillate, and the crystalline aldehyde-ammonia separated out. This compound is distilled with dilute sulphuric acid, when pure aldehyde can be collected. It is a colorless, mobile liquid, boiling at 21°, of a sharp and suffocating odor. In contact with a little hydrochloric or sulphuric acid or zinc chloride it quickly polymerizes and yields

Paraldehyde, $(C_2H_4O)_3$ (**Paraldehydum,** U.S.P.).—This is a colorless, transparent liquid, with a strong, characteristic, but not unpleasant odor, and a burning and cooling taste. It melts at 10.5° C., and boils at 123°–125°. It is soluble in 8 parts of water at 25° C., and miscible in all proportions with alcohol, ether, and fixed or volatile oils.

Another polymeric form of aldehyde is *Metaldehyde,* $(C_2H_4O)_x$, which is produced from aldehyde at low temperatures, and is crystalline, subliming at 112°–115°. When heated to 120° under pressure it changes back to aldehyde.

By the action of chlorine upon alcohol chlorine substitution derivatives of aldehyde are formed, one, two, or three hydrogen atoms being replaced by chlorine. The most important of these derivatives is *Trichloraldehyde* (or chloral), CCl_3.COH. This is an oily liquid, boiling at 98° C., of sharp, characteristic odor, which combines with sodium bisulphite, ammonia, and hydrogen cyanide like aldehyde, and like it reduces an ammoniacal silver solution. It crystallizes with one molecule of water to form

Chloral Hydrate (**Chloralum Hydratum,** U.S.P.) $CCl_3.COH + H_2O$. —The facts that chloral and water combine with development of heat, and that certain reactions given with chloral are not obtained with chloral hydrate, make it clear that this solid is not a mere hydrate, but a true chemical compound. It forms monoclinic crystals, fusing at 58° and boiling at 97°. It is freely soluble in water, alcohol, or ether; also in chloroform, benzine, benzene, carbon disulphide, and fixed and volatile oils.

Chloral is manufactured on a large scale by saturating ethyl alcohol with chlorine, first in the cold and afterward with the aid of heat. After cooling there separates out a crystalline mass known as ***chloral-alcoholate,*** $CCl_3.CH{>}\genfrac{}{}{0pt}{}{OH}{OC_2H_5}$. This is then heated with strong sulphuric acid, and when hydrochloric acid gas no longer escapes the chloral is distilled off. It is again rectified and mixed with the water necessary for the formation of the chloral hydrate. The action of chlorine upon alcohol is said to be aided by the presence of substances known as "chlorine carriers," like iodine. Ferric chloride also has been proposed, in which case it is said that the chloral-alcoholate is not formed as an intermediate product.

One of the most important reactions of chloral is its decomposition by alkalies and the resulting production of chloroform, according to the reaction: $CCl_3.COH + NaOH = CHCl_3 + HCOONa$, whereby chloroform and sodium formate result. The purest chloroform is now made by this method from crystallized chloral hydrate. Chloral hydrate is an important hypnotic and sedative.

Among the compounds of chloral that deserve mention because of their proposed use in medicine are:

Chloral Cyanhydrate, $CCl_3.COH.HCN$, which forms white, crystalline masses, smelling like chloral hydrate, and melting at 61°. This compound has been recommended for use instead of bitter-almond water, as 6.46 grams of it will contain uniformly 1 gram of anhydrous prussic acid.

Chloralformamide, $CCl_3CH(OH)NH.COH$, is a compound of chloral and formamide (see p. 581). It forms white, lustrous crystals, melting at 114°–115°; slowly soluble in cold water, decomposed by hot water, readily soluble in alcohol. Used as a soporific, being decomposed in the blood into chloral and ammonium formate.

Chloralose, $C_8H_{11}Cl_3O_6$, is the name given to a compound obtained by heating chloral and glucose, according to the reaction:

$$CCl_3.CO.H + C_6H_{12}O_6 = C_8H_{11}Cl_3O_6 + H_2O.$$

It forms fine, colorless needles, melting at 184°–185°; difficultly soluble in cold water, more easily in warm water, easily soluble in alcohol. It is recommended as an hypnotic.

Chloral also combines with antipyrin in two proportions, the monochloral-antipyrine (or *hypnal*) and the bichloral-antipyrine.

Neither bromal, $CBr_3.COH$, nor iodal, $CI_3.COH$, has found any use in medicine.

Butyraldehyde, $CH_3.CH_2.CH_2.COH$, results from the oxidation of butyl alcohol. It is also obtained by the oxidation of albuminoids by chromic acid. Its chlorine derivative:

Butyl Chloral, $C_4H_5Cl_3O$, also forms a hydrate which has been used in medicine as a substitute for chloral hydrate.

Œnanthaldehyde (Œnanthol), $C_7H_{14}O$, is an aldehyde obtained in quantity by the distillation of castor oil under reduced pressure, as the ricinoleic acid of the oil splits up, according to the reaction:

$$C\text{-}H_{34}O_3 = C_7H_{14}O + C_{11}H_{20}O_2.$$

Œnanthol is a strongly refracting liquid of penetrating aromatic odor. Used in the manufacture of higher fruit ethers (see p. 571).

2. **Aldehydes of Unsaturated Alcohols,** $C_nH_{2n-2}O$—These correspond to the unsaturated alcohols derived from the olefine hydrocarbons. They are, of course, unsaturated bodies also.

Acrolein, $CH_2 = CH.COH$, is the aldehyde corresponding to allyl alcohol, $C_3H_5.OH$. It is produced whenever glycerin is decomposed with loss of water; hence, in the superheating or distillation of the fats, as shown in the reaction $C_3H_5(OH)_3 - 2H_2O = C_3H_4O$. Liquid of sharp, irritating odor, causing tears, boiling at 52.4°.

Croton Aldehyde, C_4H_6O.—The next aldehyde in this series is found in the first runnings of raw spirits. Sharp-smelling liquid, boiling at 104°–105°. Reduces silver oxide, and is thereby oxidized to crotonic acid.

3. **Acetals.**—The acetals result from the union of alcohol with aldehydes with the elimination of water, or from the oxidation of the alcohols when they are producing along with the aldehydes.

Methylal, $HCH<\genfrac{}{}{0pt}{}{OCH_3}{OCH_3}$, is obtained by oxidizing methyl alcohol with sulphuric acid and manganese dioxide, fractioning the product, and collecting the fraction boiling between 40° and 50°. Mobile, colorless liquid, of penetrating, aromatic odor, boiling at 42°. Used in medicine as an hypnotic.

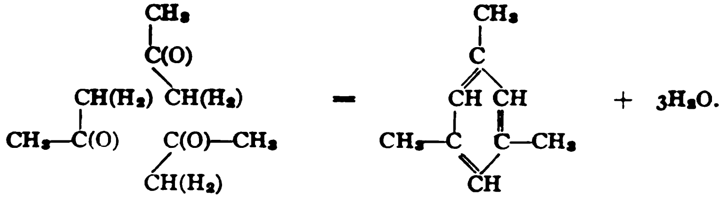
Acetal, $CH_3.CH<\genfrac{}{}{0pt}{}{OC_2H_5}{OC_2H_5}$, is found in the raw grain spirit when filtered through charcoal. Colorless liquid of agreeable taste, boiling at 104°, slightly soluble in water, very soluble in alcohol and ether.

4. **Oximes.**—By the reaction of hydroxylamine upon aldehydes are formed either monoximes or dioximes. A derivation of the latter class is *dimethyl-glyoxime*, used as a sensitive reagent for nickel salts.

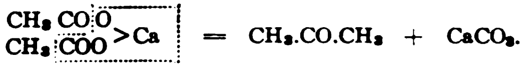
5. **Ketones.**—The ketones are most readily distinguished from the aldehydes by their behavior to oxidizing agents. They are not affected by weak oxidizing agents; hence ammoniacal silver solution is not reduced by them as it is by aldehydes. Chromic acid and energetic oxidizing agents act upon them, but the ketone molecule is broken up thereby, and they yield acids with a smaller number of carbon atoms. Thus,

acetone, $CH_3—CO—CH_3$, when oxidized yields acetic acid, CH_3COOH, CO_2, and H_2O.

The ketones show, like the aldehydes, a tendency to condense or polymerize. With acetone this condensation (by heating in the presence of concentrated sulphuric acid) gives rise to mesitylene, an aromatic hydrocarbon:



Dimethyl-ketone or *Acetone* (**Acetonum,** U.S.P.), $CH_3—CO—CH_3$, is found in small amount in normal human urine, in the blood, and in secretions; the amount is notably increased in cases of diseases like diabetes mellitus. It is contained in crude wood-spirit, and is a product of the distillation of sugar, gums, cellulose, etc. Technically it is obtained by the dry distillation of calcium acetate, according to the reaction:



$$\begin{matrix}CH_3\,CO\,O\\CH_3\,COO\end{matrix}>Ca = CH_3.CO.CH_3 + CaCO_3.$$

Is a liquid of ethereal, refreshing odor, boiling at 56.5° C. Soluble in water, alcohol, and ether. Sodium amalgam reduces it to isopropyl alcohol. A trace of acetone may be detected by the addition of a solution of iodine in potassium iodide along with an alkali, when iodoform is obtained, the odor and color of which are distinctive. Acetone is used largely as a solvent for resins and varnishes; in recent years in the manufacture of chloroform (see page 531), in large amount in the manufacture of smokeless powder and as a denaturant for spirit.

Methyl-ethyl Ketone, $CH_3.CO.C_2H_5$, is also contained in crude wood-spirit.

Methyl-nonyl Ketone, $CH_3.CO.C_9H_{19}$, is the chief constituent of oil of rue, from *Ruta graveolens.* Oil of pleasant odor, boiling at 224°. Yields on oxidation acetic and nonylic (pelargonic) acids, the latter of which is used in the manufacture of fruit ethers.

VI. ACIDS AND DERIVATIVES OF ACIDS.

In speaking of the distinction between aldehydes and ketones (see p. 548), mention was made of the fact that aldehydes as the product of the oxidation of primary alcohols did not represent the final result of oxidation, but that the COH group of the aldehyde readily changed to a COOH group by a more complete oxidation. We may illustrate this by the example of ethyl alcohol: $CH_3.CH_2OH$, ethyl alcohol; $CH_3.COH$, acetaldehyde; CH_3COOH, acetic acid.

The group which is taken as characteristic of the acid is —CO.OH, known as "carboxyl," and the presence of one such group gives us a monobasic organic acid. If the alcohol contain two groups—CH_2OH, as in diatomic alcohols, the complete product of oxidation will contain two groups—COOH, and we shall have a dibasic acid.

The organic acids, like the alcohols, are hydroxides,—that is, contain the OH group combined with a radicle,—but they are acid hydroxides instead of basic hydroxides. Therefore the radicle which is present combined with the —OH is spoken of as an acid radicle, while the alcohol radicle was a basic radicle. We shall see that the acid radicle always bears a very simple relation to the alcohol or basic radicle from which it has been derived. What the difference is may be seen by comparing the formulas given above. Ethyl alcohol, CH_3CH_2OH, contains the radicle *ethyl*, C_2H_5, combined with OH, while acetic acid, $CH_3.CO.OH$, contains the radicle *acetyl*, CH_3CO, combined with OH. The acid radicle we find to be formed from the alcohol radicle by the exchange of two H atoms for an O atom.

1. **Saturated Monobasic Acids** (*Fatty Acid Series*), $C_nH_{2n}O_2$.—These are formed from the primary monatomic alcohols of the paraffin series by oxidation. They may also be formed from the cyanides of the hydrocarbon radicles next lower in the series by saponification, as in the reaction:

$$CH_3.CN + 2H_2O = CH_3.COOH + NH_3;$$

that is, methyl cyanide will yield acetic acid and ammonia. By this means we may pass up the series from one hydrocarbon or alcohol radicle to the acid corresponding to the next higher hydrocarbon.

The higher members of this series of acids occur abundantly in nature in the natural fats and oils combined with glycerin, and in the waxes with monatomic alcohols as base, to form esters or salts.

Formic Acid, HCO.OH, was first obtained from the bodies of ants (*Formica rufa*), whence the name. It also occurs in the bristles of the stinging nettle, the fruit of the soap-tree, and in tamarinds and fir-cones; also in perspiration, urine, and the juice of flesh. It is made artificially by a variety of reactions, some of which are direct syntheses from inorganic materials. Thus, the action of moist carbon monoxide upon dry sodium hydroxide (or, better, granular soda-lime) at temperatures of 160°-200°, will give us a rapid and abundant production of sodium formate: $CO + NaOH = HCO.ONa$.

It may also be obtained by the oxidation of methyl alcohol; by the reaction of water upon hydrogen cyanide in the presence of acids or alkalies, according to the reaction $HCN + 2H_2O = HCOOH + NH_3$; by the decomposition of chloroform and chloral by alkalies: or, finally, by the heating of oxalic acid in the presence of glycerin. This method has been largely employed, as the glycerin is regenerated and so can convert large quantities of oxalic acid into formic acid. The reactions are:

$$C_3H_5(OH)_3 + \begin{array}{c}COHO\\ |\\ COOH\end{array} = C_3H_5(OH)_2OCHO + CO_2 + H_2O.$$

$$C_3H_5(OH)_2OCHO + H_2O = HCOOH + C_3H_5(OH)_3.$$

Formic acid is a colorless liquid with penetrating odor. The liquid produces a painful inflammation if dropped upon the skin, but acts as a powerful antiseptic solution. Formic acid in solution may be recognized by the reducing power it exerts upon silver and mercury salt solutions. Thus, metallic silver is separated out on heating formic acid with silver nitrate solution, while white calomel is separated out on adding formic

TABLE OF THE SATURATED MONOBASIC ACIDS (FATTY ACIDS).

Name.	Formula.	Melting Point.	Boiling Point.
Formic	$H.COOH$	9°C.	99°
Acetic	$CH_3.COOH$	17°	118°
Propionic	$CH_3.CH_2.COOH$	—36°	141°
Butyric, Normal	$CH_3.(CH_2)_2.COOH$	0°	163°
Butyric, Iso	$(CH_3)_2{=}CH.COOH$	—79°	154°
Valeric, Normal	$CH_3.(CH_2)_3.COOH$	—58°	186°
Valeric, Iso	$(CH_3)_2{=}CH.CH_2.COOH$	—51°	175°
Methyl-ethyl-acetic	$\begin{matrix}CH_3\\C_2H_5\end{matrix}{>}CH.COOH$	Liquid.	177°
Trimethyl-acetic	$(CH_3)_3{\equiv}C{-}COOH$	35°	164°
Caproic	$C_6H_{12}O_2$	—2°	205°
Œnanthic	$C_7H_{14}O_2$	—10°	224°
Caprylic	$C_8H_{16}O_2$	16°	236°
Pelargonic	$C_9H_{18}O_2$	12°	254°
Capric	$C_{10}H_{20}O_2$	31°	269°
Undecylic	$C_{11}H_{22}O_2$	28°	*213°
Lauric	$C_{12}H_{24}O_2$	44°	*226°
Tridecylic	$C_{13}H_{26}O_2$	40°	*236°
Myristic	$C_{14}H_{28}O_2$	54°	*248°
Pentadecylic	$C_{15}H_{30}O_2$	51°	*257°
Palmitic	$C_{16}H_{32}O_2$	62°	*269°
Margaric	$C_{17}H_{34}O_2$	60°	*277°
Stearic	$C_{18}H_{36}O_2$	69°	*287°
Nondecylic	$C_{19}H_{38}O_2$	66°	*298°
Arachidic	$C_{20}H_{40}O_2$	77°	. .
Behenic	$C_{22}H_{44}O_2$	76°	. .
Lignoceric	$C_{24}H_{48}O_2$	80°	.
Cerotic	$C_{27}H_{54}O_2$	78°	. .
Melissic	$C_{30}H_{60}O_2$	90°	. .

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*Boiling points under a pressure of 100 mm.

acid to corrosive sublimate solution. Formic acid unites with inorganic bases to form salts called *formates*, all of which are easily soluble except the lead and mercurous salts. The formates containing organic bases will be spoken of under "Esters."

Acetic Acid, $CH_3.COOH$, was known to the ancients in the form of wine vinegar, and in a purer and more concentrated form to the alchemists. It is found partly free and partly combined with potassium and calcium in various plant juices, and in the perspiration, milk, urine, muscles, and excrementa of animals. It results from the fermentative decomposition of albuminoids and glue, and the dry distillation of wood, starch, and sugar. A complete synthesis of it has been accomplished by the oxidation of acetylene, which (see p. 527) can be built up from carbon and hydrogen. Thus, $CH\equiv CH + H_2O + O = CH_3COOH$.

The two great sources of acetic acid, however, are the acetic fermentation of alcoholic liquids (see Fermentation), and the dry distillation of wood. As made from this latter source it is known as "pyroligneous" acid, and is quite impure from the presence of creosote and other empyreumatic products found in wood-tar. It is purified by neutralizing with milk of lime, whereby the "brown acetate of lime" is obtained. This is purified by roasting off the tarry impurities, decomposed with hydrochloric acid, and the acetic acid distilled off. It may be further purified by the recrystallization of the sodium salt.

Acetic acid when pure is a strongly acid liquid of pungent odor, burning the skin, and solidifying in the cold to crystalline plates, melting at 15°, and boiling at 118°; sp. gr. at 15° 1.055. This is known as glacial acetic acid (**Acidum Aceticum Glaciale,** U.S.P.). Two other strengths of acid are also official, one containing about 36 per cent. by weight of absolute acetic acid (**Acidum Aceticum,** U.S.P.), and a still more dilute acid containing 6 per cent. by weight of absolute acetic acid (**Acidum Aceticum Dilutum,** U.S.P.).

The glacial acetic acid has a strong solvent power for many organic substances, and hence is frequently used as a solvent from which to crystallize out organic preparations. Acetic acid may be detected by first neutralizing with ammonia and then adding ferric chloride, when a blood-red color of ferric acetate is obtained, which color is destroyed by heating with hydrochloric or sulphuric acids, or by heating with alcohol and sulphuric acid, when the characteristic odor of acetic ether is obtained.

The salts of acetic acid are known as *acetates*. All the neutral salts are soluble in water, but insoluble basic acetates of several of the heavy metals are obtained. The official metallic acetates are:

Potassii Acetas, U.S.P., $KC_2H_3O_2$.—A white, deliquescent salt, odorless, and of a saline taste, readily soluble in water and alcohol.

Sodii Acetas, U.S.P., $NaC_2H_3O_2 + 3H_2O$.—Colorless, monoclinic prisms, odorless, and of saline taste, efflorescing in dry air. Soluble in water, less readily soluble in alcohol.

Plumbi Acetas, U.S.P., $Pb(C_2H_3O_2)_2 + 3H_2O$.—Forms colorless, shining transparent, monoclinic prisms, with faintly acetous odor, and a sweetish, astringent, and metallic taste. Efflorescent, and absorbing carbon dioxide in air, easily soluble in water, and moderately soluble in alcohol.

Zinci Acetas, U.S.P., $Zn(C_2H_3O_2)_2 + 2H_2O$.—Soft, white, monoclinic plates, of pearly lustre, faintly acetous odor, and astringent, metallic taste. Gradually effloresces in the air. Easily soluble in water, moderately soluble in alcohol.

Besides these crystalline salts, we have several acetates official in solution, as **Liquor Ammonii Acetatis,** U.S.P.; **Liquor Ferri et Ammonii Acetatis,** U.S.P., and **Liquor Plumbi Subacetatis,** U.S.P.

The most important acetates, in addition to those just mentioned, are ferrous acetate, $Fe(C_2H_3O_2)_3$, largely used, under the name of "iron liquor," as a mordant in dyeing; aluminum acetate, $Al(C_2H_3O_2)_3$, used for the same purpose, under the name of "red liquor;" neutral and basic acetates of copper, $Cu(C_2H_3O_2)_2$ and $Cu(C_2H_3O_2)_2 + CuO$, used, under the name of "verdigris," in paint colors; and a double acetate and arsenite of copper, known as "Paris green."

Propionic Acid, $C_3H_5O.OH$, is so named because it is the first of this series which can be separated from its aqueous solution in an oily layer by the addition of calcium chloride and similar salts, hence πρὼτυς, the first, πιον, fat. It is contained in human urine and in perspiration, in the fruit of *Gingko biloba* and other plants, and in crude wood vinegar. It can be formed by the oxidation of propyl alcohol, by the saponification of ethyl cyanide, and by the action of ferments upon glycerol and upon malate and lactate of calcium.

It is a liquid of peculiar odor, boiling at 141° C.

Butyric Acids, $C_4H_7O.OH$.—The two butyl alcohols (see page 537), both being primary alcohols, may yield on oxidation corresponding acids. The normal butyric acid, $CH_3.CH_2.CH._2COOH$, is found, combined with glycerin, in freshly-made butter, and in the free state in rancid butter. The free acid is also found in perspiration, in the contents of the intestines, and in the fæces. It is also produced readily by fermentation, either from sugar by the butyric fermentation or from albuminoids, like fibrin and casein, or from glycerol by fissure ferments.

Liquid of sharp, rancid odor, boiling at 163°, soluble in water, but separating on addition of calcium chloride.

The isobutyric acid, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CH.COOH$, is found in many plants, as in *Ceratonia siliqua,* in the root of *Arnica montana,* and as ester in Roman chamomile oil and croton oil. Liquid smelling like the normal butyric acid, but more sparingly soluble in water, and boiling at 154°.

Valeric Acids, $C_5H_9O.OH$.—The normal valeric acid is found in crude wood vinegar, and may be obtained by the oxidation of the normal amyl alcohol. Liquid smelling like butyric acid, boiling at 184°–185°, and optically inactive.

Isovaleric acid, $\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}{>}CH.CH_2COOH$, is found abundantly in dolphin oil and in the root of *Valeriana officinalis.* It is also found in human excrement, and is a product of the decomposition of albuminoids, hence its occurrence in old cheese. It may be obtained most readily by the oxidation of the amyl alcohol of fermentation by the aid of sulphuric acid and potassium bichromate. Liquid of strong, unpleasant odor of valerian, boiling at 175°. Several of the metallic valerates are of importance in medicine. These are:

Ammonii Valeras, U.S.P., $NH_4C_5H_9O_2$.—Colorless, crystalline plates with the odor of valerian, of a sharp, sweetish taste. and deliquescent in moist air. Soluble in water, alcohol, and ether.

Zinci Valeras, U.S.P., $Zn(C_5H_9O_2)_2 + 2H_2O$.—White, pearly scales, having the odor of valerianic acid, and a sweetish, astringent, and metallic taste. Not very soluble in water; more soluble in alcohol.

The other varieties of valeric acid are only of theoretical interest as yet.

Caproic Acid, $C_6H_{11}O.OH$.—The normal caproic acid is found in cocoanut oil and Limburg cheese, and is produced in the butyric fermentation of sugar and the oxidation of albuminoids, and as glycerin ester in butter made from goat's milk. Like valeric acid, it has a very persistent and unpleasant odor of perspiration and rancid butter.

Caprylic Acid, $C_8H_{15}O.OH$, is found, with caproic and capric acids, in the butter from goat's milk (whence the names), and in butter, cheese, and wine fusel oil.

Pelargonic Acid, $C_9H_{17}O.OH$, is found among the volatile constituents of the plant *Pelargonium roseum.*

Lauric Acid, $C_{12}H_{24}O_2$, is contained as glyceride in the oil from *Laurus nobilis,* as well as in cocoanut oil, pichurim beans, dika bread, and in spermaceti.

Myristic Acid, $C_{14}H_{28}O_2$, is contained in nutmeg butter and in oil of iris. Small quantities have also been found in butter and in spermaceti.

Palmitic Acid, $C_{16}H_{31}O.OH$, is found abundantly in combination with glycerin as an ester "palmitin" (see p. 573). The acid is best extracted from Japan wax or from palm oil. It may also be formed by fusing oleic acid or cetyl alcohol with solid potassium hydroxide. White scales melting at 60°.

Margaric Acid, $C_{17}H_{33}O.OH$, was formerly supposed to be present in the natural fats, but the supposed acid was found to be a mixture of palmitic and stearic acid. Margaric acid has, however, been made synthetically from cetyl cyanide, $C_{16}H_{33}.CN$.

Stearic Acid, $C_{18}H_{35}O.OH$ (**Acidum Stearicum,** U.S.P.), as commercially obtainable, forms a hard, white, somewhat glossy solid, odorless and tasteless, and permanent in the air. Insoluble in water, moderately soluble in cold alcohol, readily soluble in boiling alcohol and ether. Stearic acid melts at 69.2° C.

Zinci Stearas, U.S.P., is a fine white bulky powder, insoluble in water, alcohol or ether.

Arachidic Acid, $C_{20}H_{39}O.OH$, is present in earth-nut oil (from *Arachis hypogœa*). It is also contained in cacao oil.

Lignoceric Acid, $C_{24}H_{47}O.OH$, is found in the free state in the paraffin of beechwood tar, and as glyceride in earth-nut oil.

Cerotic Acid, $C_{27}H_{53}O.OH$, is found in the free state as the chief constituent of beeswax, also as the ceryl ester in Chinese wax, and in wool suint. It is also obtained by the oxidation of paraffine with chromic acid or dilute nitric acid.

Melissic Acid, $C_{30}H_{59}O.OH$, is obtained from myricyl alcohol by fusion with potassium hydroxide or soda-lime. It is also found free in beeswax.

2. Unsaturated Monobasic Acids (*Oleic Acid Series*), $C_nH_{2n-2}O_2$.—These acids are the derivatives of the olefine hydrocarbons and the unsaturated monatomic alcohols of the formula $C_nH_{2n}O$. Being unsaturated, they can combine directly with two atoms of halogen, and in some cases two atoms of hydrogen or one molecule of haloid acid. Upon this reaction is based the method of the quantitative analysis of fatty oils by determining the "iodine figure" or the "bromine figure," showing the percentage of unsaturated acids present. The acids of this series may be formed by the oxidation of the corresponding alcohols or aldehydes, by saponifying the cyanides of the unsaturated alcohols, thus forming the acid next higher in the series, and lastly, by heating the monohalogen substitution products of the saturated fatty acids with alcoholic potash.

The lowest members of the series are only obtained synthetically; the higher ones, on the other hand, are found as glycerides in animal and vegetable fats.

Acrylic Acid, $C_3H_4O_2$.—By the oxidation of either allyl alcohol or acroleïn. Generally obtained from β-iodopropionic acid, which is distilled with oxide of lead. Unpleasant acrid and penetrating smelling liquid. Crystallizes when cooled. Boiling point 140°; easily soluble in water.

Crotonic Acid, $C_4H_6O_2$.—Three isomeric varieties are known, of which the first and the second occur in crude pyroligneous acid, while the third is found in Roman chamomile oil.

Angelic Acid and *Tiglic Acid*, $C_5H_8O_2$.—The former of these isomeric acids is found in angelica root as well as in Roman chamomile oil, where it is present as an ester; the latter, also, in the Roman chamomile oil as amyl ester.

Hypogæic Acid and *Physetolic Acid*, $C_{16}H_{30}O_2$.—The former of these isomeric acids is found in the fruit of the earth-nut (*Arachis hypogæa*) as glyceride, and forms crystals, melting at 33°; the latter is found in sperm oil (from the head of *Physeter macrocephalus*), and melts at 30°. The first acid yields, on distillation, sebacic acid, while the second does not yield this product; the first is changed by nitrous acid into an isomeric modification; the second is not affected by nitrous acid.

Oleic Acid, $C_{18}H_{34}O_2$ (**Acidum Oleicum**, U.S.P.), is found abundantly in nature as glyceride in all the fat oils, both vegetable and animal. A colorless oil, forming white needles when chilled. Melting point 14°. The oil has a sp. gr. of about 0.900 at 15° C. It is insoluble in water, soluble in alcohol, chloroform, benzene, benzine, oil of turpentine, and fixed and volatile oils. It cannot be vaporized without decomposition. A small quantity of nitrous acid changes it into the isomeric *Elaidic acid*, which is white and crystalline, fusing at 45°.

Oleic acid can also be changed into the solid stearic acid by Sabatier's reaction with hydrogen in the presence of finely divided nickel.

Döglinic Acid, $C_{19}H_{36}O_2$, found as glyceride in the oil of *Balæna rostrata* (dögling whale). Oil solidifying at low temperatures.

Erucic Acid, $C_{22}H_{42}O_2$, is found in black and white mustard seed oil. It forms needles melting at 33°–34°. With a small quantity of nitrous acid, is changed into the isomeric *brassidic acid*.

3. **Unsaturated Monobasic Acids** (*Propiolic Acid Series*), $C_nO_{2n-4}O_2$. —The acids of this series correspond to the acetylene hydrocarbons, and are capable of adding on four atoms of halogens like iodine. They may be formed by the direct addition of carbon dioxide to the sodium compounds of the acetylene hydrocarbons, as:

$$\underset{\text{Acetylene-sodium.}}{CH\equiv CNa} \quad + \quad CO_2 \quad = \quad \underset{\text{Propiolate of Sodium.}}{CH\equiv C.COONa.}$$

Propiolic Acid, $C_3H_2O_2$.—In physical characters very similar to propionic acid. Forms silky needles melting at 6°, and boils at 144°. Easily soluble in water and alcohol.

Tetrolic Acid, $C_4H_4O_2$, and *Sorbic Acid*, $C_6H_8O_2$, follow in this series.

4. **Unsaturated Monobasic Acids** (Diolefine Series, $C_nH_{2n-4}O_2$).

Linoleic Acid, $C_{18}H_{32}O_2$, is found as glyceride in linseed oil (from the seeds of *Linum usitatissimum*). A yellow oil, rapidly resinifying in the air. This acid is important as the basis of "drying oils."

Supplement to the Unsaturated Acids:

Ricinoleic Acid, $C_{18}H_{34}O_3$, the characteristic acid of castor oil, is very similar to oleic acid, but contains one alcoholic OH group. It is oily and solidifies at —6° to —10°. It does not absorb oxygen from the air, and hence does not resinify.

5. **Derivatives of the preceding Monobasic Acids.**—(*a*) *Halogen Compounds of the Acid Radicles.* Just as we have the chlorides, bromides, etc., of the basic or alcohol radicles, so we can have chlorides, etc., of the acid radicles. The best example of this class is *Acetyl chloride*, $C_2H_3O.Cl$. This is a colorless mobile liquid boiling at 55° C., which is decomposed on contact with water and is of great value as a reagent because of its ready reaction with alcohols and amines to form acetyl derivatives.

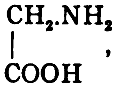
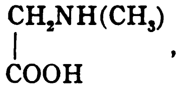
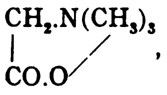
(*b*) *Acid Anhydrides.* Of great importance in synthetic reactions also are the oxides of the acid radicles, or acid anhydrides. *Acetic Anhydride* $(C_2H_3O)_2O$ is a mobile liquid of penetrating odor, boiling at 137° C., used extensively in acetylating.

(*c*) *Substituted Fatty Acids.*—The hydrogen atoms of the radicles in these acid hydroxides are replaceable by halogen atoms, by the nitro group (NO_2), the amido group (NH_2), the cyanogen group (CN), etc. These substituted acids do not lose their character as acid hydroxides, but may form corresponding salts and esters. A few of the most important of these derivatives will be noted.

Chloracetic Acids.—Monochloracetic, Dichloracetic, and Trichloracetic acids are all known, the formulas being $CH_2Cl.COOH$, $CHCl_2.COOH$, and $CCl_3.COOH$. *Trichloracetic acid* (**Acidum Trichloraceticum** U.S.P.) is readily formed by the oxidation with nitric acid of the corresponding aldehyde, chloral. It forms white deliquescent crystals with slight characteristic odor and is very soluble in water, alcohol and ether. It decomposes easily, the aqueous solution even on boiling, into chloroform and carbon dioxide. It is a powerful caustic, and has been used in medicine for this purpose. It precipitates albumin solutions quantitatively, does not affect albumin peptones, but precipitates gelatin peptones and gelatin solutions. It is adapted for the quantitative determination of albumin.

The nitro-fatty acids are of no special importance. With tin and hydrochloric acid they yield the corresponding amido-fatty acids. The amido-fatty acids are more important, because they are among the commonest of the decomposition products of the albuminoids.

Amido-formic Acid, NH_2COOH. (See Carbamic Acid, under Carbonyl Compounds.)

Amido-acetic Acid, $CH_2(NH_2).COOH$.—This important substance, known also as "glycocoll," is readily obtained by boiling glue or silk with alkalies or acids, by the decomposition of hippuric acid (see p. 652) with hydrochloric acid, or by heating monochloracetic acid with ammonia. It forms large, colorless, rhombic prisms, easily soluble in water, insoluble in absolute alcohol and ether; melts with decomposition at 232° to 236.° As an amido-acid it unites in itself both the properties of a base and an acid. It forms a hydrochloride on the one hand, and a well-crystallized copper salt on the other. Substitution derivatives from glycocoll are also obtained by the replacement of the hydrogen of the amido group. Thus, from glycocoll,  $\begin{array}{l}CH_2.NH_2\\ |\\ COOH\end{array}$, we obtain methyl-glycocoll, or *sarcosine*,  $\begin{array}{l}CH_2NH(CH_3)\\ |\\ COOH\end{array}$, which is a decomposition product of creatine and caffeine (see p. 607), and trimethyl-glycocoll, or *betaine*,  $\begin{array}{l}CH_2.N(CH_3)_3\\ |\quad\quad /\\ CO.O\end{array}$, which is contained in beet-root and cotton-seed, and is related to choline.

Amido-propionic Acid, $CH_3.CH(NH_2).COOH$, is also known as "alanine." It can be obtained by the action of dilute acids upon silk or the action of hydrocyanic acid upon aldehyde-ammonia. Hard needles of sweetish taste.

Amido-butyric Acid, $NH_2.(CH_2)_3.COOH$.—One of the amido-butyric acids is piperidinic acid, which results from oxidation of piperyl-urethan.

Amido-valeric Acid, $NH_2(CH_2)_4.COOH$.—One of the amido-valeric acids has been obtained in the decomposition of fibrin and flesh, and of conine and piperidine derivatives, and has also been found in the pancreas of the ox.

Amido-caproic Acid, $C_5H_{10}(NH_2)COOH$.—This important substance is known also as "leucine," and is found widely spread in both animal and vegetable material. It is found in old cheese, in the animal organism, in the gastric salivary gland, and along with tyrosine is a constant product of the digestion of albumin in the small intestine and of the decay of albuminous substances; it is also found in the shoots of the vetch and the gourd. Most conveniently made by boiling clippings of horn with dilute sulphuric acid. .Forms scales soluble in water, difficultly soluble in cold, more readily soluble in hot alcohol. Leucine is dextrorotatory, but is made inactive by heating with baryta water.

5. **Acids derived from Diatomic Alcohols.**—The diatomic alcohols or glycols have, it will be recalled, two alcoholic hydroxyl groups and act like diacid bases. If these two hydroxyl groups are both attached so as to furnish primary alcohol groups $CH_2.OH$, we may obtain by oxidation two groups, COOH, characteristic of organic acids. At the same time one alcoholic group may be oxidized, while the other remains unchanged. Thus, we obtain from diatomic alcohols two series of acids: one a series of diatomic but monobasic compounds which are half alcohol and half acid; and a second series of diatomic and dibasic compounds which are purely acid in character.

TABLE OF THE ACIDS DERIVED FROM DIATOMIC ALCOHOLS.

Diatomic Alcohol. General Formula, $C_nH_{2n+2}O_2$.	Monobasic Alcohol-Acid. Formula, $C_nH_{2n}O_3$.	Dibasic Acids. Formula, $C_nH_{2n-2}O_4$.
Ethylene glycol, $\begin{array}{l}CH_2OH\\ \vert\\ CH_2OH.\end{array}$	Glycollic acid, $\begin{array}{l}CH_2OH\\ \vert\\ COOH.\end{array}$	Oxalic acid, $\begin{array}{l}COOH\\ \vert\\ CO.OH.\end{array}$
Propylene glycol, $\begin{array}{l}CH_2OH\\ \vert\\ CH_2\\ \vert\\ CH_2OH.\end{array}$	Lactic acid, $\begin{array}{l}C_2H_4.OH\\ \vert\\ COOH.\end{array}$	Malonic acid, $\begin{array}{l}COOH\\ \vert\\ CH_2\\ \vert\\ COOH.\end{array}$
Butylene glycol, $\begin{array}{l}CH_2OH\\ \vert\\ C_2H_4\\ \vert\\ CH_2OH.\end{array}$	Oxybutyric acid, $\begin{array}{l}C_3H_6OH\\ \vert\\ COOH.\end{array}$	Succinic acid, $\begin{array}{l}COOH\\ \vert\\ C_2H_4\\ \vert\\ COOH.\end{array}$
Amylene glycol, $\begin{array}{l}CH_2OH\\ \vert\\ C_3H_6\\ \vert\\ CH_2OH.\end{array}$	Oxyvaleric acid, $\begin{array}{l}C_4H_8.OH\\ \vert\\ COOH.\end{array}$	Pyrotartaric acid, $\begin{array}{l}COOH\\ \vert\\ C_3H_6\\ \vert\\ COOH.\end{array}$

The alcohol acids are obtained by the regulated oxidation of the glycols, or by the action of moist silver oxide or water alone upon the monochlor derivatives of the fatty acids. Thus, glycollic acid is derived from monochloracetic acid: $CH_2Cl.COOH + H_2O = CH_2(OH).COOH + HCl$.

Glycollic Acid, $CH_2OH.COOH$, is found in unripe grapes and in the leaves of the wild vine. Forms colorless needles, melting at 78°–79°. Easily soluble in water, alcohol, and ether.

Lactic Acid, $C_2H_4.OH.COOH$.—Two isomeric acids are indicated by theory: Ethylidene-lactic acid, $CH_3.CH(OH).COOH$, and ethylene-lactic acid, $CH_2OH.CH_2.COOH$. Of the first of these, however, there are two physical isomers, the optically inactive ethylidene-lactic acid (lactic acid of fermentation) and the active ethylidene-lactic acid (sarco-lactic acid.)

Fermentation lactic acid (**Acidum Lacticum,** U.S.P.) occurs in opium, sauerkraut, the gastric juice and the gray matter of the brain. It is produced by the lactic fermentation of sugar (see p. 598), and hence contained in such products as sour milk, koumiss, kefir, etc. The official lactic acid contains 75 per cent. of absolute lactic acid, and is a colorless, syrupy liquid, odorless, of acid taste, and sp. gr. about 1.206 at 25° C. It is hygroscopic, and freely miscible with water, alcohol, or ether; insoluble in chloroform, benzine, or carbon disulphide. Lactic acid when heated in dry air gives rise to characteristic anhydrides. Thus, $2C_3H_6O_3 - H_2O = C_6H_{10}O_5$, *Lactic Anhydride,* and this at a higher temperature again loses a molecule of water, yielding *Lactide,* $C_6H_8O_4$, a stable compound crystallizing in colorless tablets, melting at 125°, and boiling undecomposed at 255°.

Calcii Lactas, U.S.P., forms white granular masses, odorless, soluble in 20 parts of water and almost insoluble in alcohol.

Sarco-lactic (or Para-lactic) acid is found in the muscles (hence also in extract of beef), in the blood, and in the urine after strong muscular exertion. It is the dextro-rotatory modification, and can be produced together with the lævo-rotatory modification by splitting up the inactive or ordinary lactic acid. This is accomplished by the fractional crystallization of the strychnine salt.

Ethylene-lactic (or Hydracrylic) acid forms a syrupy mass. It differs from ordinary lactic acid in yielding carbonic and oxalic acids on oxidation instead of acetic acid, and in not yielding an anhydride on heating. but breaking up into water and acrylic acid, whence the name hydracrylic.

Oxybutyric Acid, $C_3H_6OH.COOH$.—An optically active (lævo-rotatory) modification of this acid is found in the urine and the blood of diabetic patients.

The dibasic acids result when the diatomic alcohols are oxidized with nitric acid or by the saponification of the cyanogen derivative of the fatty acids.

Oxalic Acid, $COOH.COOH$, occurs in many plants, as in wood-sorrel (*Oxalis acetosella*), in the form of KHC_2O_4, in the varieties of Rumex, as $Na_2C_2O_4$ in varieties of *Salicornia,* and as CaC_2O_4 in rhubarb, beets, etc. It may be formed by the oxidation of sugar, starch, etc., with nitric acid, by fusing cellulose (sawdust) with potassium and sodium hydroxides or more recently by heating potassium formate, to which a little potassium oxalate has been added, with a slight excess of alkali. It crystallizes with $2H_2O$, is soluble in water, more difficultly soluble in alcohol, almost insoluble in ether. Decomposes on strong heating, or in the presence of dehydrating agents like sulphuric acid, according to the reaction:

$$COOH\text{—}COOH = CO_2 + CO + H_2O.$$

When heated with glycerol, formic acid is produced.

Forms monoclinic prisms, which effloresce in dry air. Is used extensively in calico printing as a mordant, as a solvent for iron stains, and in the analytical laboratory as a reagent for lime. But a single metallic oxalate is now official:

Cerii Oxalas, U.S.P., " consists chiefly of a mixture of cerium, didymium, and lanthanum oxalates, with other rare earths of this group." It forms a white, granular powder, without odor or taste, permanent in air. Insoluble in water, alcohol, ether, or solutions of potassium or sodium hydroxide, soluble in diluted sulphuric or hydrochloric acids.

The calcium salt is insoluble, and at times occurs in urinary concretions; the double potassio-ferrous oxalate has a powerful reducing action on silver and platinum salts, and is used in photography as a developing solution.

Malonic Acid, $COOH.CH_2.COOH$, occurs in beet-root, and may be produced from malic acid by oxidation with chromic acid, whence the name. It forms large plates readily soluble in water, alcohol, and ether, melting at 133°–134°.

Succinic Acid, $COOH.C_2H_4.COOH$, is found in amber, in various resins and lignite, in the poppy, in unripe grapes, and in urine and blood. It may be obtained by the oxidation of the higher fatty acids, the fats, and waxes with nitric acid, from gums and sugars by fusing with caustic potash, and as a side-product in the alcoholic fermentation of sugar. It is usually obtained by distilling amber or by the fermentation of a solution of tartrate of ammonia. It crystallizes in prisms or tablets, fuses at 182°, and boils at 235°, yielding, however, the anhydride. It is soluble in water and ether, more difficultly in alcohol. The most important salt is the basic ferric succinate, which is insoluble, and by means of which iron is sometimes separated qualitatively from other metals.

Pyrotartaric Acid, $COOH.C_3H_6.COOH$.—Of the several isomeric forms, the most important are glutaric acid, the normal pyrotartaric acid, which is found in suint of sheep's wool and in the juice of the beet-root, and methyl-succinic acid.

Of the higher acids of this series may be mentioned *Adipic Acid,* $(CH_2)_4.(COOH)_2$, obtained by the oxidation of the fats by nitric acid; *Suberic Acid,* $C_8H_{14}O_4$, obtained by the action of nitric acid upon cork tissue; *Sebacic Acid,* $C_{10}H_{18}O_4$, obtained by the dry distillation of spermaceti and fats containing oleic acid; and *Rocellic Acid,* $C_{17}H_{32}O_4$, found in the lichen *Rocella fuciformis.*

From unsaturated alcohols containing two $CH_2.OH$ groups may also be prepared acids which will, of course, show the unsaturated character. They bear to the acids just described the same relation that the oleic acid series does to the fatty acid series. They have the general formula $C_nH_{2n-4}O_4$. The most important are:

Fumaric and *Maleic Acids,* $C_2H_2(COOH)_2$.—The first of these isomeric acids is found in *Fumaria officinalis,* in mushrooms, and in Iceland moss. It is formed from malic acid by the loss of water, and from albuminoids by the action of aqua regia. Under the influence of nascent hydrogen, it takes up two H atoms and yields succinic acid. When heated strongly for a time it changes into the isomeric maleic acid. This acid may also be obtained by the distillation of malic acid. It is more soluble in water than fumaric acid.

6. Acids derived from Triatomic and Higher Alcohols.—No matter what number of OH groups contained in the alcohols, whether three, as in the glycerols, or four, five, or six, the presence of a group, CH_2OH, gives rise to the acid character in the products of oxidation, and the basicity of the acid depends upon the number of the $CH_2.OH$ groups so changed to COOH.

Glyceric Acid, $CH_2OH.CHOH.COOH$, results from the careful oxidation of glycerol with nitric acid, and is obtained also in the spontaneous decomposition of nitroglycerin. Syrup, soluble in water and alcohol.

Tartronic Acid, COOH.CHOH.COOH, results from oxidation of glycerol with potassium permanganate. Prismatic crystals easily soluble in water and alcohol, difficultly soluble in ether. Melting point 185°.

Malic Acid, $COOH.CH_2.CHOH.COOH$, known also as oxysuccinic acid, is very widely distributed in the vegetable kingdom, being found in unripe apples, quinces, grapes, barberries, etc. It may be formed also from succinic acid, on the one hand, by replacing an H atom by OH, or from tartaric acid, on the other hand, by reduction with HI.

It forms hygroscopic needles, easily soluble in water and alcohol, only slightly soluble in ether. Melting point 100°. Heated to 120°–130° it yields fumaric acid, and at 175°–180° maleic acid is formed.

The amides and amines of malic acid will be considered farther on.

Tricarballylic Acid, $C_3H_5.(COOH)_3$, occurs in unripe beets, and is prepared synthetically from glycerol through the intervention of the bromine and cyanogen compounds of the glyceryl radicle, C_3H_5. Its relations to citric and aconitic acids are seen from the table, and it can be formed from both by simple reactions. It forms prisms, melting at 166°, soluble in water.

Aconitic Acid, $C_3H_3(COOH)_3$, is an unsaturated acid. It is found in nature in *Aconitum napellus, Achillea millefolium,* in the sugar-cane, and the beet-root. It is also readily prepared by quick heating of citric acid, when a molecule of H_2O separates. It forms crystals, melting at 186°. Easily soluble in water.

Erythric Acid, $C_3H_4(OH)COOH$, is formed by the oxidation of erythrol with nitric acid or platinum black.

TABLE OF ACIDS DERIVED FROM HIGHER ALCOHOLS.

Alcohols.	Monobasic Acids.	Dibasic Acids.	Tribasic Acids.
Triatomic:			
CH_2OH. | Glycerol, $CHOH$. | CH_2OH.	CH_2OH. | Glyceric, $CHOH$. | $COOH$.	$COOH$ | Tartronic, $CHOH$ | $COOH$ Malic, $CH_2.CHOH(COOH)_2$.	Tricarballyic, $C_3H_5.(COOH)_3$. Aconitic, $C_3H_3(COOH)_3$.
Tetratomic: Erythrol, $C_4H_6(OH)_4$.	Erythritic, $C_3H_4(OH)_3COOH$.	Tartaric, $C_2H_2(OH)_2(COOH)_2$.	Citric, $C_3H_4(OH)(COOH)_3$.
Pentatomic: Arabol, Xylitol, } $C_5H_7(OH)_5$.	Arabonic, Xylonic, } $C_4H_5(OH)_4$-$COOH$.	Trioxyglutaric, Aposorbic, } $(CHOH)_3$-$(COOH)_2$.	Oxycitric, $C_3H_3(OH)_2(COOH)_3$
Rhamnitol, $C_6H_9(OH)_5$.	Rhamnonic, $C_5H_7(OH)_4COOH$. Saccharinic, $C_5H_7(OH)_4COOH$.		
Hexatomic:			
Mannitol, $C_6H_8(OH)_6$.	Mannitic, Gluconic, Gulonic, } $C_5H_6(OH)_5.COOH$.	Saccharic, { $C_4H_4(OH)_4$-$(COOH)_2$.	
Dulcitol, $C_6H_8(OH)_6$.	Galactonic, Talonic, } $C_5H_6(OH_5)$-$(COOH)_2$.	Mucic, $C_4H_4(OH)_4(COOH)_2$.	

Both monobasic and dibasic heptonic, octonic, and monnonic acids have also been obtained in connection with the synthetic work of Emil Fischer upon the sugars. They are as yet of theoretical interest only.

Tartaric Acid, COOH.CHOH.CHOH.COOH (**Acidum Tartaricum,** U.S.P.), is sometimes known also as dioxy-succinic or oxy-malic acid, in order to indicate its relation to these well-known acids. Tartaric acid exists in four *physically isomeric* modifications: dextro-tartaric, lævo-tartaric, racemic or inactive tartaric, and meso-tartaric. The first of these is the naturally occurring variety. It occurs partly free and partly as potassium or lime-salt in the juice of the grape and other fruits. The acid potassium tartrate which is found in the grape juice becomes insoluble as fermentation proceeds, and the liquid becomes alcoholic, and separates as "argols" in the wine-casks. This is purified by conversion into the lime-salt from which the acid is liberated with H_2SO_4. The pure acid forms colorless, monoclinic prisms or white powder, with an acid taste, and permanent in the air. It is soluble in water and alcohol, difficultly soluble in ether, nearly insoluble in chloroform, benzene, or benzine. Melting point 135°. It reduces an ammoniacal silver solution upon warming. When strongly heated carbonizes and gives off a characteristic "caramel" odor. The most important tartrates are:

Neutral Potassium Tartrate, $K_2C_4H_4O_6 + \frac{1}{2}H_2O$, which forms monoclinic prisms easily soluble in water.

Acid Potassium Tartrate, $KHC_4H_4O_6$, or **Potassii Bitartras,** U.S.P., —This compound, known as "cream of tartar," forms small rhombic crystals, odorless, and having a pleasant acidulous taste, sparingly soluble in cold water and in alcohol. This is the most important technical salt of tartaric acid and is manufactured on a large scale for use in baking powders as well as in medicine.

Potassii et Sodii Tartras, U.S.P., $KNaC_4H_4O_6 + 4H_2O$.—This compound, known also as Rochelle or Seignette salt, forms large colorless, rhombic prisms, odorless, and with a cool, saline taste. The crystals effloresce slightly in dry air. Soluble in water, almost insoluble in alcohol.

Antimonii et Potassii Tartras, U.S.P., $2K(SbO)C_4H_4O_6 + H_2O$.—This compound, known also as "tartar emetic," forms colorless, transparent crystals, becoming opaque and white on exposure to the air. Soluble in water, but insoluble in alcohol. It is poisonous and acts as an emetic, and is used as a mordant in dyeing.

Ferri et Ammonii Tartras, U.S.P., and **Ferri et Potassii Tartras,** U.S.P., are uncrystallizable double salts, which are obtained as syrupy solutions and dried in films, which are then broken up, and constitute what are called "scale preparations."

The *Lævo-tartaric Acid* is like the dextro-tartaric in its chemical properties, but is the opposite in its behavior toward polarized light. When equal quantities of both acids are mixed together in aqueous solution, the solution becomes warm, and we obtain

Racemic Acid, $C_4H_6O_6 + H_2O$.—Racemic acid is found sometimes in grape juice, and in the mother liquor from the crystallization of tartar. Its crystals are rhombic, efflorescent, and less soluble than those of dextro-tartaric acid. It is optically inactive. Its salts are called racemates. When the sodium-ammonium salt is crystallized from solution, the crystals obtained show hemihedral faces (*i.e.*, only one-half the faces of the normal figure are developed). Pasteur first observed that these crystals differed, part being dextro-hemihedral, and part being lævo-hemihedral, and that the lævo-hemihedral crystals were dextro-rotatory in solution, and *vice versa*. If, then, the two kinds of crystals are separated from each other mechanically, and the free acid liberated from each, it is found that we have no racemic acid remaining; but in the one case have dextro-tartaric, and in the other case lævo-tartaric acid.

If to a solution of ammonium racemate be added the ferment *Penicillium glaucum*, the dextro-tartaric acid is decomposed faster than the lævo-tartaric, and the latter may thus be obtained.

Meso-tartaric Acid is also an inactive variety, but is not decomposable like racemic acid into active modifications. It is produced along with racemic acid in different reactions. Forms efflorescent plates, fusing at 146°.

Citric Acid, $C_3H_4(OH)(COOH)_3$ (**Acidum Citricum**, U.S.P.).—This important acid occurs in the free state in lemons, oranges, etc., and, mixed with malic acid, in gooseberries, currants, and mulberries, and, as calcium salt, in wood, potatoes, beet-root, etc. Is prepared generally from lemon juice, which contains 6 to 7 per cent. of the acid. The acid is separated in the form of the difficultly soluble lime-salt; this is decomposed by sulphuric acid, and the acid solution concentrated in vacuo to the point of crystallization. A new source of citric acid manufacture has been recently announced, which may prove to be more economical than the extraction from lemon juice. Dr. Carl Wehmer has discovered that sugar solutions exposed to the action of certain mould fungi (*Citromyces pfefferianus* and *C. glaber*), the spores of which are present in the atmosphere, become transformed into citric acid. It is claimed that 11 kilograms of sugar treated in this way have yielded 6 kilograms of crystallized citric acid. The acid crystallizes with one molecule of water in colorless, rhombic prisms, which are odorless, and have an agreeable acid taste; effloresce in warm air, and deliquesce when exposed to moist air. Is soluble in water and alcohol, slightly soluble in ether. When heated to 135° it loses all of its water of crystallization, melts at 153°, and breaks up at a higher temperature into aconitic acid and water, and then into itaconic acid and CO_2.

The official metallic citrates are:

Potassii Citras, U.S.P., $K_3C_6H_5O_7 + H_2O$.—Forms colorless crystals or white granular powder, odorless, and with a cooling, saline taste.

Sodii Citras, U.S.P., $2Na_3C_6H_5O_7 + 11H_2O$. Forms a white granular powder, odorless, and having a cooling, saline taste. It slowly effloresces on exposure to dry air.

Lithii Citras, U.S.P., $Li_3C_6H_5O_7$.—Forms a white powder, odorless, with a cooling, faintly alkaline taste, deliquescent on exposure to air.

Bismuthi Citras, U.S.P., $BiC_6H_5O_7$.—Forms a white amorphous or faintly crystalline powder, odorless, tasteless, and permanent in air.

Besides these crystalline salts, we have as evaporated syrups or "scale preparations:" **Bismuthi et Ammonii Citras,** U.S.P., **Ferri Citras,** U.S.P., and **Ferri et Ammonii Citras,** U.S.P. The magnesium citrate is also official in **Liquor Magnesii Citratis,** U.S.P.

The monobasic pentatomic acids, *arabonic*, *xylonic*, *rhamnonic*, and *saccharinic* acids, are obtained by the oxidation of the corresponding pentose sugars. They possess only a theoretical interest.

Oxycitric Acid, $C_3H_3(OH)_2(COOH)_3$, is found in beet and turnip juice, and has been prepared artificially from aconitic acid.

The monobasic and dibasic hexatomic acids are obtainable both from the hexatomic alcohols mannitol and dulcitol and from the sugars related to them. The dibasic acids especially are produced from a variety of sources among the class of carbohydrates.

Saccharic Acid, $(CHOH)_4(COOH)_2$, is produced by the oxidation of cane-sugar, dextrose, mannitol, or starch by nitric acid. Brittle, very hygroscopic mass, easily soluble in water. The ammonium salt of saccharic acid is decomposed at 160° into pyrrol, ammonia, and carbon dioxide: $C_6H_8(NH_4)_2O_8 = C_4H_5N + 2CO_2 + NH_3 + 4H_2O$.

Mucic Acid, $(CHOH)_4.(COOH)_2$, is obtained by the oxidation of milk-sugar, gums, and mucilages by nitric acid. White crystals, fusing at 213°, difficultly soluble in water. The ammonium salt decomposes like the corresponding salt of saccharic acid into pyrrol, carbon dioxide, and ammonia.

7. **Aldehydic and Ketonic Acids.**—Mention was made under the oxidation products of diatomic alcohols of alcohol acids. It is obvious that another intermediate class may be aldehyde acids, and where secondary alcohol groups exist, combined in the same molecule with primary alcoholic groups, we may obtain ketonic acids, or acids in which we have both the ketone group, CO, and the carboxyl group, COOH.

Glyoxalic Acid, CHO.COOH, is an aldehyde acid found in unripe fruits, such as grapes, gooseberries, etc. It crystallizes in prisms, easily soluble in water.

Glycuronic Acid, $COH.(CHOH)_4.COOH$, is an aldehydic acid obtained by the reduction of saccharic acid. It also possesses interest as being found in the urine as a decomposition product after taking internally such substances as camphor, phenol, phenetol, α- and β-naphthol.

Pyroracemic Acid, $CH_3.CO.COOH$ (aceto-formic acid), is a ketone acid resulting from the dry distillation of tartaric, racemic, and glyceric acids. It is a colorless liquid, soluble in water, alcohol, and ether, boiling with slight decomposition at 165°–170°, and smelling of acetic acid and extract of beef.

Aceto-Acetic Acid, $CH_3.CO.CH_2COOH$, is a strongly acid liquid miscible with water, and breaking up upon warming into acetone and carbon dioxide. Its ethyl ester is obtained in the form of its sodium compound by the action of sodium upon ethyl acetate, and from the ester the free acid is obtained by saponification.

Levulinic Acid, $CH_3.CO.CH_2.CH_2COOH$ (aceto-propionic acid), results from the action of acids upon cane-sugar, lævulose, cellulose, gum, starch, and other carbohydrates. A condensation product of levulinic acid with phenyl-hydrazine is known in medicine under the name of "antithermin."

VII. ESTERS, OR ETHEREAL SALTS.

These are bodies formed by the replacement of the hydrogen of an acid, whether inorganic or organic, by an alcohol radical as base. They are, as stated, ethereal salts, and may include acid, neutral, and basic salts, or esters, as more generally termed.

1. **Esters of Inorganic Acids.**—The esters of the haloid acids have already been described as the halogen derivatives of the hydrocarbons.

The esters of nitrous acid are obtained by passing nitrous fumes into the alcohols, or by the action of copper and nitric acid upon the same. They are liquids of aromatic odor, and very low boiling points, and are easily saponifiable. Nascent hydrogen reconverts them into alcohol, ammonia being formed at the same time.

Methyl Nitrite, CH_3ONO, is gaseous at ordinary temperatures.

Ethyl Nitrite, $C_2H_5O.NO$, is a mobile liquid of penetrating ethereal odor and peculiar stinging taste. Boils at 18°, and burns with a bright white flame. Its alcoholic solution is the **Spiritus Ætheris Nitrosi,** U.S.P., known also as "sweet spirit of nitre." This is stated by the U.S. Pharmacopœia to be "an alcoholic solution of ethyl nitrite yielding, when freshly prepared, not less than 4 per cent. of ethyl nitrite." The official spirit is 22 times the weight of ethyl nitrite contained. It is now made by the action of sulphuric acid upon a mixture of sodium nitrite and alcohol.

Amyl Nitrite, $C_5H_{11}O.NO$ (**Amyl Nitris,** U.S.P.), is a liquid containing about 80 per cent. of amyl (chiefly iso-amyl) nitrite. Forms a clear, yellow or pale yellow liquid, of peculiar, ethereal, fruity odor, and pungent, aromatic taste. Almost insoluble in water, soluble in alcohol and ether. Sp. gr. 0.865–0.875 at 25° C. Boils at 96° to 99° C., yielding an orange-colored vapor. It is used in medicine, producing expansion of the blood-vessels and relaxation of the contractile muscles.

Isomeric with the nitrites of the alcoholic radicals are the nitro-derivatives of the hydrocarbons, which are formed by the action of metallic nitrites upon the halogen derivatives of the hydrocarbons. Thus, nitroethane, $C_2H_5.NO_2$, is isomeric with ethyl nitrite, $C_2H_5O.NO$.

The esters of nitric acid are obtained by the action of nitric acid upon the alcohols. However, as nitric acid tends to have an oxidizing action upon the alcohols, whereby nitrous acid is formed and in consequence the nitrous esters, urea is added, which decomposes the nitrous acid as formed and nitric esters are the sole product.

Methyl Nitrate, $CH_3.NO_3$, is a colorless liquid, boiling at 66°. Its vapor heated above the boiling point decomposes with explosive violence.

Ethyl Nitrate, $C_2H_5.NO_3$, is a mobile liquid of agreeable odor and sweet taste, but with bitter after-taste. It burns with a white flame. Boiling point 86°. Its vapor is also explosive when heated.

Glycollic Dinitrate, $C_2H_4(NO_3)_2$, is prepared by acting on glycol with sulphuric and nitric acids. It is a yellowish liquid, insoluble in water, which is saponified by alkalies, and explodes on being heated.

Glyceryl Trinitrate, $C_3H_5(NO_3)_3$.—This important compound, commonly known as " nitroglycerin," is formed by the action of a cold mixture of concentrated nitric acid and sulphuric acids upon glycerol. It is a colorless or slightly yellowish oil, insoluble in water, soluble in alcohol and ether. It has a sweet, burning, aromatic taste, and is poisonous. It crystallizes at —20° in needles. It burns without explosion when in a thin film, but when quickly heated or struck explodes with terrible violence. When mixed with infusorial earth in the proportion of 3 parts to 1, it forms dynamite, which is not affected so readily by simple percussion, but is exploded by fulminate of mercury with great force. Nitroglycerin is saponified by alkalies and by sulphide of ammonium.

A one-per-cent. alcoholic solution of nitroglycerin constitutes the **Spiritus Glycerylis Nitratis,** U.S.P.

Nitro-erythrite, $C_4H_6(NO_3)_4$, and *Nitro-mannite,* $C_6H_8(NO_3)_6$, are similar esters of nitric acid, and are like nitroglycerin in explosive character, although less violent.

The esters of sulphuric acid are formed by the action of sulphuric acid upon the alcohols. As sulphuric acid is dibasic, two series of esters are possible, just as acid and neutral sulphates of inorganic bases are formed.

Acid Ethyl Sulphate (or Ethyl-sulphuric Acid), $C_2H_5HSO_4$, is obtained on mixing equal parts of absolute alcohol and concentrated sulphuric acid. The free acid is a syrup easily soluble in water. Under the old name of " sulpho-vinic acid," it has long been known as the intermediate product in the " continuous ether process " (see p. 544). Its salts, formerly called " sulphovinates," crystallize well. They are, of course, double sulphates of ethyl and metallic base.

Neutral Ethyl Sulphate, $(C_2H_5)_2SO_4$, is a colorless, oily liquid, insoluble in water, of a pleasant peppermint odor. It boils at 208°. The corresponding esters of sulphurous acid are known, but are prepared with more difficulty, as the isomeric sulphonic acid derivatives (see p. 547) tend to form by the reaction with metallic sulphites.

Calcii Glycerophosphas, U.S.P., $C_3H_5(OH)_2Po_4Ca$, is a fine white powder somewhat hygroscopic.

Sodii Glycerophosphas, U.S.P., $C_3H_5(OH)_2Po_4Na_2$, white monoclinic scales or white powder with a saline taste. Soluble in water, nearly insoluble in alcohol.

The esters of silicic and carbonic acids are also known. The last of these will be referred to later. (See Carbonyl Derivatives.)

2. Esters of Organic Acids.—These form in some cases by the direct action of the acids upon the alcohols, but more generally it is necessary to provide for taking up the water which forms in the reaction. This is done by the addition of sulphuric acid as dehydrating agent to the mixture of alcohol and organic acid, or still more readily by passing dry HCl gas into a mixture of the alcohol and acid. This probably acts by first forming an acid chloride with the radicle of the organic acid, and this then reacts with the alcohol.

The esters of the lower members of the fatty acid series are for the most part colorless, neutral liquids, which volatilize without decomposition. As a rule they are insoluble in water, but soluble in alcohol and ether. The esters of the higher acids are solids, and play an important part in nature as the natural fats and waxes.

The esters are, without exception, saponifiable; that is, under the influence of water or alkalies and acids they break up into the free alcohol and acid, or alkaline salt of the acid, in case alkalies are used for the saponification.

Ethyl Formate, $HCO.OC_2H_5$.—Boils at 55°. Is employed in the manufacture of artificial rum or arrack, as well as in peach essence and other fruit essences.

Ethyl Acetate, $C_2H_3O.OC_2H_5$.—Present to the extent of about 90 per cent. in **Æther Aceticus, U.S.P.** Boils at 77.5°; is a transparent, colorless liquid of fragrant and refreshing odor and a peculiar acetous and burning taste; is moderately soluble in water, easily soluble in all proportions in alcohol, ether, fixed and volatile oils. It is inflammable, burning with a yellowish flame and acetous odor. Besides being used internally in medicine, it is largely used in admixture in fruit essences and as a solvent.

Amyl Acetate, $C_2H_3O.OC_5H_{11}$.—Boiling point 138°. This ester has a characteristic fragrant odor of pears, and hence is the basis of the artificial pear essence. It is also used largely as an ingredient in the manufacture of pyroxylin varnishes, owing to its solvent power.

Octyl Acetate, $C_2H_3O.OC_8H_{17}$.—Boiling point 210°. Forms the chief constituent of the oil from the fruit of *Heracleum spondylium.*

Ethyl Butyrate, $C_4H_7O.OC_2H_5$.—Boiling point 120.9°; possesses the characteristic odor of pineapples, and hence is used in that fruit essence.

Iso-amyl Butyrate, $C_4H_7O.OC_5H_{11}$.—Boiling point 178.6°. Is also used in the manufacture of banana essence.

Ethyl Iso-valerate, $C_5H_9O.OC_2H_5$.—Boiling point 134.3°. Is a constituent of melon and peach oils.

Iso-amyl Iso-valerate, $C_5H_9O.OC_5H_{11}$.—Boiling point 196°. Is the chief constituent of apple essence.

Iso-amyl Caprinate, $C_{10}H_{19}O.OC_5H_{11}$.—Boiling point 275°, with partial decomposition. This is the chief constituent of wine fusel oil, and under the misapplied name of "œnanthic ether," gives the bouquet to wine.

Cetyl Palmitate, $C_{16}H_{31}O.OC_{16}H_{33}$.—Fusing point 53.5°. This ester forms the chief constituent of spermaceti (**Cetaceum, U.S.P.**), a peculiar, fatty solid obtained from the head of the sperm whale (*Physeter macrocephalus*). This solid ester is held dissolved in the sperm oil during the life of the animal, and after death, with the disappearance of the animal heat, it crystallizes out. It forms a white, somewhat translucent, slightly unctuous mass, of a scaly, crystalline fracture and pearly lustre; odorless, and with a bland, mild taste. Sp. gr. .938 to .944 at 25° C. It is insoluble in water, and nearly so in cold alcohol; soluble in boiling alcohol, also in ether, chloroform, carbon disulphide, fixed and volatile oils.

Ceryl Palmitate, $C_{16}H_{31}O.OC_{27}H_{55}$.—Fusing point 79°. Is the chief constituent of opium wax.

Myricyl Palmitate, $C_{16}H_{31}O.OC_{30}H_{61}$.—Fusing point 72°. Is the part of beeswax insoluble in alcohol, the soluble part consisting largely of cerotic acid (see p. 558). Beeswax (**Cera Flava,** U.S.P.) is an animal product, being the material of the cell walls of the combs of the *Apis mellifica,* or honey bee. It is a yellowish to brownish-yellow solid, having an agreeable, honey-like odor, and a faint, balsamic taste. Sp. gr. 0.951 to 0.960 at 25°; melting point 62°–64°. It is insoluble in water, sparingly soluble in cold alcohol, but almost completely soluble in boiling alcohol. It is completely soluble in ether, chloroform, and fixed and volatile oils.

Beeswax is bleached white to adapt it for use in candle-making and other purposes. This is accomplished either by the action of light and air (air-bleached wax), or by the use of oxidizing agents, such as potassium dichromate, potassium permanganate, and hydrogen dioxide (chemically-bleached wax). The product is a yellowish-white solid (**Cera Alba,** U.S.P.), which is slightly more crystalline than the yellow wax, and contains rather more free acid.

Ceryl Cerotate, $C_{27}H_{53}O.OC_{27}H_{55}$.—Fusing point 82°. Forms the chief ingredient of Chinese insect wax. It is also found in opium wax.

Myricyl Cerotate, $C_{27}H_{53}O.OC_{30}H_{61}$, is found in carnauba wax.

Probably the most important of the esters of organic acids, however, are the compounds of the triatomic alcohol glycerol. The esters of this alcohol with the members of the fatty acid series make up the bulk of the vegetable and animal fats and fatty oils. While glycerol as a triacid base can form esters containing one, two, or three molecules of fatty acid, we find that the naturally occurring compounds are exclusively neutral esters,—that is, contain three molecules of a monobasic acid in combination with the base. The mono-acid and di-acid compounds can be formed artificially, however, in many cases.

The most important of the glycerol esters are:

Monoformin, $C_3H_5(OH)_2OCHO$, and *Diformin,* $C_3H_5(OH)(OCHO)_2$, have been obtained artificially; the former by heating glycerol with oxalic acid to 190°, and the latter as a side-product in the manufacture of formic acid by the action of oxalic acid on glycerol at 140°.

Monoacetin, $C_3H_5(OH)_2OC_2H_3O$, and *Diacetin,* $C_3H_5(OH)(OC_2H_3O)_2$, are both obtained by the prolonged action of glacial acetic acid upon glycerol under pressure. They are liquids of high boiling point. *Triacetin,* $C_3H_5(OC_2H_3O)_3$, is found naturally in certain fats, as in the oils from the seeds of *Euonymus europæus.* Is also made artificially by the action of glacial acetic acid upon glycerol in the presence of anhydrous sodium acetate.

Tributyrin, $C_3H_5(OC_4H_7O)_3$, can be made from glycerol and normal butyric acid. Is found naturally in milk fat, and hence in butter, to which it gives an agreeable taste and odor. Mass of buttery consistence, boiling at 285°. Decomposes spontaneously in presence of air and moisture into butyric acid and glycerol.

Tri-isovalerin, $C_3H_5(OC_5H_9O)_3$, is found in dolphin oil.

Tricapronin, $C_3H_5(OC_6H_{11}O)_3$.—The glyceride of isobutylacetic acid, $C_6H_{12}O_2$, is found in cow's butter, goat's milk, and in cocoanut oil.

Tricaprylin, $C_3H_5(OC_8H_{15}O)_3$.—The glyceride of the normal caprylic acid is also found in cow's butter, goat's milk, and in cocoanut oil.

Tricaprin, $C_3H_5(OC_{10}H_{19}O)_3$.—The glyceride of this acid is found in goat's milk and in cocoanut oil.

Trilaurin, $C_3H_5(OC_{12}H_{23}O)_3$, forms crystalline needles, melting at 45°. This glyceride forms the chief constituent of cocoanut oil, and is found also in palm-nut oil and bayberry oil.

Trimyristin, $C_3H_5(OC_{14}H_{27}O)_3$, forms crystalline plates, melting at 55°. Is found in nutmeg butter, in palm-nut oil, cocoanut oil, goose fat, and cow's butter.

Tripalmitin, $C_3H_5(OC_{16}H_{31}O)_3$, forms indistinct crystals, fusing at 62°. Insoluble in water and alcohol, easily soluble in ether. This glyceride is one of the most abundant of the constituents of the natural fats, being found in most liquid fats and oils. Obtained from palm oil or butter, from Chinese vegetable wax by first pressing out and then treating repeatedly with hot alcohol, whereby free palmitic or oleic acids go into solution. The residue is then crystallized out of ether.

Tristearin, $C_3H_5(OC_{18}H_{35}O)_3$, occurs in most of the solid fats and in a large number of the liquid fats associated with palmitin and olein. It is difficult to obtain the tristearin perfectly free from tripalmitin, even after repeated crystallizations, but it has been claimed that it can be obtained perfectly free from the seeds of *Brindonia indica*. Fuses at first at 55°, but after repeated melting shows a permanent melting point of 71.5°.

Triarachin, $C_3H_5(C_{20}H_{39}O)_3$.—This glyceride is found in earth-nut oil as well as in cocoanut oil, and the fat from the seeds of *Nephelium lappaceum*.

Tribenin, $C_3H_5(OC_{22}H_{43}O)_3$.—A glyceride found with olein in oil of ben from *Moringa oleifera*.

Trihypogæïn, $C_3H_5(OC_{16}H_{29}O)_3$.—This glyceride occurs along with triarachin and triolein in earth-nut oil.

Triolein, $C_3H_5(OC_{18}H_{33}O)_3$, occurs abundantly in nature in the non-drying fatty oils, as olive and almond oils. May be obtained approximately pure by agitating olive or almond oil with a cold concentrated aqueous solution of caustic soda, which saponifies the palmitin and leaves the most of the olein unchanged. Is liquid at ordinary temperatures, but solidifies below 0°, and can be distilled in a vacuum. Only slightly soluble in alcohol, easily soluble in ether. By treatment with nitrous acid it is converted into solid white elaïdin, a polymeric compound.

Tridoeglin, $C_3H_5(OC_{19}H_{35}O)_3$.—The glyceride of doeglic acid forms the chief constituent of the oil of the doegling, or bottle-nose whale.

Trierucin, $C_3H_5(OC_{22}H_{41}O)_3$.—This glyceride occurs in the oil of the white and the black mustard-seed, in rape oil and grape-seed oil. Nitrous acid converts it into the isomeric *tribrassidin*.

Trilinolein, $C_3H_5(OC_{18}H_{31}O)_3$.—This glyceride is the characteristic constituent of the drying oils, such as linseed oil, poppy-seed oil, sunflower oil, and hempseed oil. It does not yield a solid product with nitrous acid, but is characterized by the readiness with which it absorbs oxygen and thickens with the formation of resinous products.

Triricinolein, $C_3H_5(OC_{18}H_{33}O_2)_3$.—This glyceride is the peculiar constituent of castor oil. It forms a solid polymeric product known as ricinelaidin when treated with nitrous acid.

The vegetable fats seem to be found in all parts of the plant, but especially in the seeds and fruit, although at times in the root and the leaves also; in the animal, fats are present in all the tissues and organs, and in all fluids except the normal urine. The fats with the carbohydrates and the albuminoids form the three great classes of food materials needed for the animal organism. The great bulk of the natural fats contain four glycerol esters, trilaurin, tripalmitin, tristearin, and triolein. Of these the first three are solid at ordinary temperatures, while the fourth is liquid. The consistency of a fat, therefore, is mainly determined by the proportion of these several ingredients, the solid fats containing larger amounts of palmitin and stearin, and the fatty oils being especially rich in olein.

All the fats are lighter than water; they cannot be distilled under ordinary pressure without decomposition, acroleïn (see p. 551) being a chief product of the decomposition. While most of them in a pure and fresh condition are colorless and neutral in reaction, by prolonged exposure to the air they undergo change, become yellowish, develop a strong, unpleasant odor and an acid reaction. They become "rancid," that is, the ester decomposes spontaneously, and the free fatty acid is recognizable. Some of the fatty oils, moreover, on exposure to the air absorb oxygen, developing so much heat thereby as to inflame wool and cotton tissues soaked with the oil. Such oils are known as "drying oils." They become thick and finally dry to translucent resinous masses, which makes them of value for painting and varnish-making. These drying oils owe their character mainly to the fact that they are glycerides of linoleic acid (see p. 559) instead of oleic acid.

A classification of the fats, the fatty oils, and the waxes, which is based partly upon physical properties and partly upon chemical differences, is that of A. H. Allen, which is here given:

(*a*) *Olive Oil Group.*—Vegetable oleins. Vegetable non-drying oils. Lighter than groups *b*, *c*, and *d*. Yield solid elaidins with nitrous acid. Includes olive, almond, earth-nut, and ben oils.

(*b*) *Rape Oil Group.*—Non-drying oils from the *cruciferæ*. Yield pasty elaidins and have higher iodine and saponification equivalents than group *a*. Includes rape-seed, colza, and mustard oils.

(*c*) *Cotton-seed Oil Group.*—Intermediate between drying and non-drying oils. Undergo more or less drying on exposure. Yield little or no elaidin. Includes cotton-seed, sesame, sunflower, hazel-nut, beech-nut and soya bean oil.

(*d*) *Linseed Oil Group.*—Vegetable drying oils. Yield no elaidin. Of less viscosity than the non-drying oils. Includes linseed, hemp-seed, poppy-seed, walnut, and Chinese wood oils.

(*e*) *Castor Oil Group.*—Medicinal oils. Very viscous and of high density. Includes castor and croton oils.

(*f*) *Palm Oil Group.*—Solid vegetable fats. Do not contain notable quantities of the lower fatty acids. Includes palm oil, cacao butter, nutmeg butter, and shea butter.

(*g*) *Cocoanut Oil Group.*—Solid vegetable fats, in part waxlike. Several contain notable proportions of the glycerides of lower fatty acids. Includes cocoanut oil, palm-nut oil, laurel oil, Japan wax, and myrtle wax.

(*h*) *Lard Oil Group.*—Animal oleins. Do not dry notably on exposure, and give solid elaidins with nitrous acid. Includes neat's-foot oil, bone oil, lard oil, and tallow oil.

(*i*) *Tallow Group.*—Solid animal fats, predominantly glycerides of palmitic and stearic acids, although butter contains lower glycerides. Includes tallow, lard, bone fat, wool fat, butter fat, oleomargarine, and manufactured stearin.

(*j*) *Whale Oil Group.*—Marine animal oils. Characterized by offensive odor and reddish-brown color when treated with caustic soda. Includes whale, porpoise, seal, menhaden, cod-liver, and shark-liver oils.

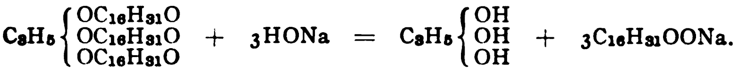
(*k*) *Sperm Oil Group.*—Liquid waxes. Are not glycerides, but esters of monatomic alcohols. Yield solid elaidins. Includes sperm oil, bottlenose or doegling oil, and dolphin oil.

(*l*) *Spermaceti Group.*—Waxes proper. Are compound ethers or esters of higher monatomic alcohols, with higher fatty acids in the free state. Includes spermaceti, beeswax, Chinese wax, and carnauba wax.

The composition of the natural fats as essentially compounds of the fatty acids with glycerol was first definitely ascertained by Chevreul in 1823, and with this knowledge was also indicated the means of decomposing them. Chevreul first used alkalies for that purpose, and that method is still applied if the alkaline salts of the fatty acids (soaps) are desired. For the purpose of obtaining the fatty acids as such, or the glycerol other methods have been adopted.

We may summarize the several methods employed for this decomposition under three headings, although practically there are additional methods of decomposition in use which involve a combination of several of these general reactions.

1st. The decomposition of the fats by the action of alkalies. This original method of Chevreul is only employed when the manufacture of a soap is the end desired. We may illustrate it by the example of the reaction between palmitin and an alkali such as would take place in the manufacture of a palm-oil soap.



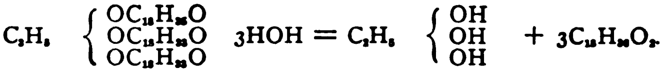
$$\underset{\text{Tripalmitin.}}{C_3H_5\left\{\begin{matrix}OC_{16}H_{31}O\\OC_{16}H_{31}O\\OC_{16}H_{31}O\end{matrix}\right.} + 3HONa = \underset{\text{Glycerol.}}{C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.} + \underset{\text{Sodium Palmitate.}}{3C_{16}H_{31}OONa.}$$

2d. The decomposition of the fats by the action of metallic oxides in the presence of water. Chevreul's use of alkalies was replaced already in 1831 by that of lime, suggested by De Milly, and the use of lime and water under pressure constitutes the "autoclave" process of to-day. This will be referred to and illustrated later in a short section on the "Industries of the Fats." Pharmacists make use of a reaction of this kind in the manufacture of lead plaster (**Emplastrum Plumbi,** U.S.P.), in which the olein of olive oil is decomposed by litharge in the presence of water:

$$2C_3H_5\left\{\begin{matrix}OC_{18}H_{33}O\\OC_{18}H_{33}O\\OC_{18}H_{33}O\end{matrix}\right. + 3PbO + 3HOH = 2C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. + 3Pb(OC_{18}H_{33}O)_2$$

Triolein. Glycerol. Lead Cleate.

3d. The decomposition of the fats by the action of steam or water under pressure. The discovery of the possibility of effecting the "saponification" of the fats by water alone, made in 1854 by Tilghman, has since been utilized very extensively under various forms of procedure. The reaction may be illustrated by the decomposition of stearin:



$$C_3H_5\left\{\begin{matrix}OC_{18}H_{35}O\\OC_{18}H_{35}O\\OC_{18}H_{35}O\end{matrix}\right. 3HOH = C_3H_5\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right. + 3C_{18}H_{36}O_2.$$

Stearin. Glycerol. Stearic Acid.

The decomposition by sulphuric acid with after-distillation of the fatty acids is nothing more than a saponification by water in the presence of the acid, although with certain classes of fats it has advantages in increasing the yield of solid fat acids.

The decomposition of fats by enzymes has also been made a working method quite recently. The enzyme contained in the castor oil bean has been found best adapted for this. An emulsion of fat, water, 10 per cent. of ground castor oil bean, and a small amount of free acid are used, when the decomposition proceeds rapidly.

Twitchell's reagent (a benzene-sulphonic compound of oleic acid) is also used to split up fatty oils and greases and has come into large use.

INDUSTRIES OF THE FATS

The great importance of many of the vegetable and animals fats as raw materials of large industries justifies us in noticing these industries in outline, and giving a short account of the practical side of them.

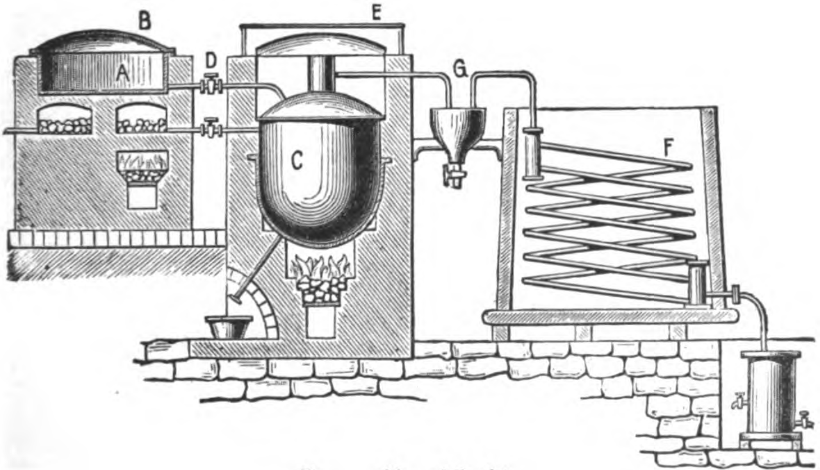
1. **Soap-making.**—Soaps are most generally made by the direct saponification of the fat with alkali, although where the fatty acids have been obtained in the free state and then worked as described later for the extraction of the solid acids for candle-making, the oleic acid, or "red oil," remaining over is utilized for soap-making. Soaps are made chiefly from tallow, cotton-seed oil, cocoanut oil, palm oil, and olive oil. We may divide the soaps first into the *hard soaps,* in which the base is soda or a mixture of soda and potash, and *soft soaps,* in which the base is potash. In the manufacture of this latter class the drying oils are preferably used, as in the official **Sapo Mollis,** U.S.P.

True hard soaps are manufactured by boiling the fats in open vessels, with the aid of steam heat, with alkaline lyes of gradually increasing strength, until products of definite character are obtained. The "soap-copper" is an iron kettle, or series of kettles, set in masonry and equipped with pipes for both open and closed steam, and provided with an outlet for the discharge of the waste lyes when required. Strong lyes are not used at first or saponification will not take place. A soda-lye of about 11° B., equal to one-fourth that needed for complete saponification, is first run in with the melted fat. When this mixture becomes homogeneous, lye of 20° to 25° B., equal in amount to that taken before, is cautiously added, and boiling is kept up until a sample taken out has a firm consistence between the fingers. It is then salted with a brine of 24° B., and the contents of the copper allowed to stand for several hours at rest. Two layers will then have formed, an upper layer of soap-paste containing water, and a lower one, of "spent-lye," containing the salt and the glycerol in solution. After removing this spent-lye from below, the rest of the caustic soda for saponification is run in and the soap boiled up again.

If a "rosin soap" is desired the rosin is added at this stage, otherwise a "curd soap" is the product. The boiling is now continued until the frothing subsides and the mixture boils clear. The contents of the copper are then boiled with open steam, and a small quantity of lye of 12° B. is run in until the soap separates in flakes and feels hard when cold. Boiling is usually continued for several hours to insure complete saponification, and it is then allowed to separate and harden. If it is transferred to the cooling-frames before this hardening and separation is completed, a mottled soap may be obtained. A solution of ferrous sulphate added at this point produces a peculiar greenish mottled appearance, becoming red on exposure to the air, characteristic of Marseilles and Castile soaps. In smooth or "cut soaps" water or thin lye is added to the contents of the copper before the soap separates finally to form the curd, and is taken up, giving a smooth yet firm surface to the soap instead of the hard granular appearance of the true curd soap.

In the "cold process" soaps, exact weights of well-refined fats and the necessary caustic soda are used and added together at once. After short standing, they are agitated in a revolving copper provided with paddles, at a temperature of not over 120° F. The materials rapidly coalesce, although the reaction is only finished after some days' standing in the cooling-frames. It is obvious that in this case all the glycerol of the fats originally taken remains distributed throughout the soap. Filling and padding materials can also be added in this case, and will be held in the soap. A small quantity of cocoanut oil added to the tallow or other fat facilitates the working of this cold process.

FIG. 140.



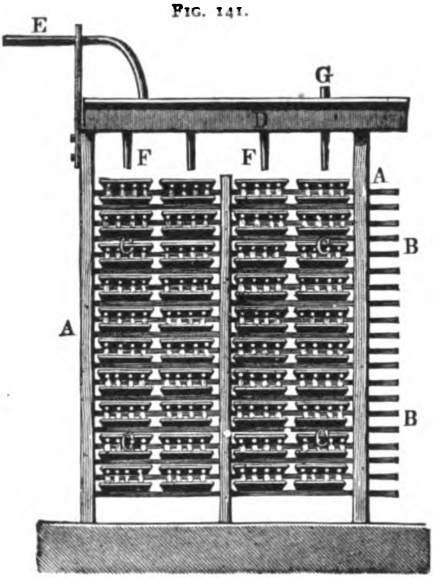
Decomposition of the fats.

When "red oil" or oleic acid from the stearic acid candle manufacture is used, it may be saponified either with alkali or with alkaline carbonate, although the former is preferred. The oleic acid may also be changed first into the isomeric elaidic acid by the action of nitrous acid, and a very fine soap is then obtained resembling a tallow soap.

Compact soaps may contain from 10 to 25 per cent. of water, smooth or cut soaps may contain from 25 to 45 per cent., and filled soaps from 45 to 72 per cent. of water, besides the glycerol and impurities.

2. Stearic Acid Candle Manufacture.—Where the solid fatty acids are desired for the manufacture of candles, the fats are saponified either by the "autoclave process" of Milly, in which lime and hot water, under a pressure of 8 to 10 atmospheres, are made to decompose the fats, or they are decomposed with superheated steam, either with or without the addition of sulphuric acid. In the former process the lime forms a lime soap, which is afterwards decomposed by sulphuric acid, and the free fat acids are thoroughly washed by the aid of steam. The amount of lime taken is not sufficient to completely neutralize the fatty acids, as the steam decomposes the lime soap first formed and allows the base to attack fresh quantities of the fat. In the second process, that of superheated steam, the products are obtained quite pure and free from all foreign matters. As carried out in the Wilson and Gwynne form of apparatus, it is shown in Fig. 140. The fat is first heated in A by waste heat from the superheater below, and then flows into the retort C, which must be kept at from 290° to 315° C., and for this purpose is covered in. The superheated steam at 315° C. comes into the retort by the side tube; after some 24 to 36 hours the contents of the retort are distilled off, the fatty acids condensing first, and the watery glycerol passing on to the farther condensing vessel. In this way a very pure commercial glycerol is obtained as well as pure fatty acids. If the temperature much exceed 315° C., acrolein forms from the decomposition of the glycerol. For the extraction of the hard stearic acid the washed fatty acids are now melted and run into troughs or dishes of tin, as shown in Fig. 141. These are placed in a room at a temperature of 20° to 30° C. and kept for two or three days, to allow the palmitic and stearic acids to crystallize, when the contents are emptied into canvas or woolen bags and pressed in an hydraulic press. The liquid oleic acid runs off, and the cakes of crude stearic acid obtained are melted and again put to crystallize at a somewhat higher temperature than before. A thorough pressing will now leave the stearic acid sufficiently firm for candle-making. A little wax or paraffin is usually added to take away the very crystalline structure, which unfits stearic acid somewhat for candle-making.

Fig. 141.



Granulation of stearic acid.

3. **Oleomargarine or Artificial Butter.**—When very pure fats are taken and care is exercised in the melting and rendering, it is possible to separate solid stearin by a chilling process similar to that just described for stearic acid, and obtain as a liquid product the mixture of olein and palmitin known popularly as "oleomargarine oil." This so-called "oleo oil" is then churned with about 10 per cent. of its weight of milk, with the addition of a little butter color, and the product is salted and brought into the market as oleomargarine butter. In making what is called "butterine," neutral lard is added to the oleo oil and milk before churning, and then finished as before. At times a small quantity of sesame oil or cottonseed oil is added to soften the texture of the product.

4. **Manufacture of Glycerol and Nitroglycerin.**—Glycerol is obtained in connection with the saponification of fats by the autoclave process with lime or the saponification with superheated steam. The glycerol from the lime process is obtained in a very dilute state at first, and must be concentrated. This is done by the aid of steam, at first with free access of air, and later in vacuo. The product, brought to a specific gravity of 1.22, has a brown color and is known as "raw glycerin." It is then filtered through bone-black in closed and jacketed filters, and distilled with the aid of steam. The glycerol which distils over from the saponification in the apparatus of Wilson and Gwynne, before described, is more concentrated and freer from impurities. It still requires, however, the concentration and after-distillation with steam heat.

Nitroglycerin is a technical product of great commercial importance, because of its large use in mining and blasting operations. It is manufactured on a large scale, but every stage of the process must be watched with the greatest care because of the extreme danger connected with its explosions. The nitrating mixture consists of 5 parts of concentrated sulphuric acid and 3 parts of nitric acid of 1.48 sp. gr. The glycerol must be relatively pure and of sp. gr. about 1.26. The acid mixture having been placed in a wooden tank lined with lead, and cooled by coils of leaden pipe through which ice water is circulating, to 14° to 16° C., the glycerol is run in through a small pipe, or, better, in a fine spray through a metal sieve. The liquid must be kept continuously mixed during the nitration, and the temperature not allowed to rise above about 18°. If the temperature rise suddenly or continue rising, the contents of the tank must be allowed to run at once into a larger receptacle containing cold water. The nitration of 730 pounds of glycerol takes from ½ to 2½ hours. When it is completed the product is run into a vessel containing water at 21°. As the nitroglycerin separates, it is then washed first with pure water, then with water containing some soda solution, and finally with strong soda solution. The yield of nitroglycerin is greater in winter than in summer, varying from 950 to 1200 pounds of nitroglycerin from 630 pounds of glycerol. The several operations of nitration, separation, and washing are all carried out in detached buildings, and, as far as possible, compressed air is used for effecting the mixing and washing.

5. **The Utilization of the Drying Oils in Paints and Varnishes.**—In the classification of the oils (see p. 574) the distinction was made between drying and non-drying oils. This distinction is based upon differences in chemical composition. The drying oils, like linseed oil, contain large amounts of the glyceride of linoleic acid, which differs from oleic acid chiefly in its power of absorbing oxygen and becoming resinous. This tendency is notably accelerated by boiling the oils with certain mineral compounds like litharge, manganese dioxide, and the acetates and borates of lead, manganese, and zinc. These are known therefore as "dryers" because of the drying quality they impart to the oils. This is of great importance in the manufacture of paints and varnishes. In a paint we have the finely divided color thoroughly rubbed up and incorporated with boiled linseed oil, and this is then thinned out with oil of turpentine. In varnishes we have solutions of hard resins in oil, also thinned out, if necessary, with oil of turpentine. The resins so used are amber, copal, damar, animé, etc.

Printers' ink is also a thoroughly boiled linseed oil varnish with which is incorporated the lamp-black or other color and a small quantity of soap. Oilcloth and linoleum are also products into which boiled linseed oil enters.

VIII. AMINES AND AMIDES.

The introduction of an alcohol or basic radical into the ammonia molecule, replacing one or more hydrogen atoms, gives us an *amine*, and just as ammonia can combine with a haloid acid to form an ammonium salt, so the amine or derived ammonia can unite with the chloride, bromide, or iodide of an alcohol radical to form a derived ammonium salt in which, for instance, the four hydrogen atoms of NH_4Cl may be replaced by alcohol radicals.

We may have *primary*, *secondary*, or *tertiary* amines, according as one, two, or three atoms of hydrogen in NH_3 are replaced. We may also have monamines, diamines, or triamines, according as one, two, or three molecules of ammonia are represented. Thus:

$NH_2.CH_3$, methylamine, is a primary amine.
$NH.(CH_3)_2$, dimethylamine, is a secondary amine.
$N(CH_3)_3$, trimethylamine, is a tertiary amine.
$(NH_2)_2.C_2H_4$, ethylenediamine, is a diamine.
$N(C_2H_5)_4OH$, tetraethyl ammonium hydroxide, is a quaternary base.
$N(CH_3)_4I$, tetramethyl ammonium iodide, is a quaternary salt.

The amines containing the lower alcohol radicals bear a close resemblance to ammonia, being strongly basic, having an ammoniacal odor, forming white clouds with hydrochloric acid, forming salts with haloid acids, which salts unite to form crystalline double salts with gold and platinic chlorides. The ammonium bases are solid, very hygroscopic, and exceedingly like potash in properties.

The amines are formed by acting directly upon ammonia with the halogen compound of the alcohol radical, only in this case the primary amine first formed again reacts with the haloid compound producing the secondary amine, and so on, so that the result of the reaction is usually a mixture of primary, secondary, tertiary, and even quarternary bases. The nitro-paraffins, like $CH_3.NO_2$, are also reducible with nascent hydrogen to amines. This reaction has less importance here, however, than under the aromatic nitro-derivatives like nitrobenzene.

1. **Monamines.**—*Methylamine*, CH_3NH_2, is found naturally occurring in *Mercurialis annua* and *M. perennis*, in herring brine, in the distillation products of wood, bones, and beet-root molasses, and in the products of the decomposition of morphine, codeine, kreatin, sarcosin, and glycocoll. It is most easily prepared from acetamide, caustic soda, and bromine. Colorless gas, smelling like ammonia, and at the same time with a fish-like odor; burns with a yellowish flame. Forms a crystalline hydrochloride and sulphate.

Dimethylamine, $(CH_3)_2NH$, occurs also in herring brine and is formed in the decomposition of fish. Found also in Peruvian guano and in pyroligneous acid. It results, moreover, from the decomposition of glue and yeast. Liquid boiling at 8°–9° C.

Trimethylamine, $(CH_3)_3N$, is found quite widely distributed,—in the leaves of *Chenopodium vulvaria*, in *Arnica montana*, in *Cratægus oxyacantha*, and abundantly in herring brine. Formed also in the decomposition of lecithin, protagon, neurin, and betaïn (hence in beet sugar molasses distillation), also from alkaloids like narcotine and codeine by the action of alkalies. Liquid, with a strong odor of decomposing fish, boiling at 9° C.

The isomerism of trimethylamine, $(CH_3)_3N$, and propylamine, C_3H_7-NH_2, has led to the erroneous use of the latter name at times. Thus, the so-called "propylamine hydrochlorate," used at one time in medicine as a remedy for rheumatic ailments, was a salt of trimethylamine.

Tetramethyl Ammonium Iodide, $N(CH_3)_4I$, is obtained readily by the direct action of CH_3I upon ammonia. It crystallizes in white needles or prisms, and has a bitter taste.

Tetramethyl Ammonium Hydroxide, $N(CH_3)_4OH$, forms fine hygroscopic needles.

Ethylamine, $C_2H_5.NH_2$, colorless liquid, boiling at 19°, with a strong ammoniacal smell and biting taste. It differs from ammonia in dissolving $Al(OH)_3$, but does not dissolve $Fe(OH)_3$.

Diethylamine, $(C_2H_5)_2NH$, boils at 56°. *Triethylamine*, $(C_2H_5)_3N$, is an oily, strongly alkaline liquid, boiling at 90°. It is found in the decomposition of fish tissue.

Trimethyl-vinyl Ammonium Hydroxide (Neurin), $N(CH_3)_3C_2H_3.OH$.—This base, containing the unsaturated radical vinyl, results when lecithin and protagon, which are found in nerve and brain tissue, are boiled with baryta. Very soluble in water, and of alkaline reaction. Extremely poisonous.

Trimethyl-oxyethyl Ammonium Hydroxide (Choline or Bilineurin), $N(CH_3)_3(C_2H_4OH).OH$, is found in the bile (χολή, bile), brain, yolk of egg, etc., being combined with glycerin-phosphoric acid as *lecithin*. It is also present in herring brine, hops, beer, and in many fungi. Choline is a strong base, difficultly crystallizable, and deliquescent. It is not poisonous.

2. **Diamines.**—*Ethylene-diamine*, $C_2H_4(NH_2)_2$, is a colorless liquid, boiling at 123°, easily soluble in water, not miscible with benzene and ether. It smells faintly ammoniacal, and has a caustic taste.

Diethylene-diamine, $(C_2H_4)_2(NH)_2$.—This base, known also as "Piperazin," is formed by the heating of the ethylene-diamine hydrochloride. Rhombic tablets, fusing at 104° and boiling at 145°. Used considerably in medicine because of its solvent action on uric acid and gouty concretions.

Trimethylene-diamine, $C_3H_6(NH_2)_2$.—Oily liquid, boiling at 136°.

Tetramethylene-diamine, $C_4H_8(NH_2)_2$.—This base, known also as "Putrescin," results from the decomposition of flesh, hence contained in the cadaver. The free base smells like spermatic fluid, boils at 156°–157°, and is poisonous. It is also found in the urine and fæces in cystinuria.

Pentamethylene-diamine, $C_5H_{10}(NH_2)_2$.—This base is known as "Cadaverine." It is formed in the decomposition of flesh and fish, and, as the name indicates, is found in the cadaver. The free base boils at 178°–179°, and smells like spermatic fluid. Is poisonous. The chlorhydrate when heated breaks up into piperidine, $C_5H_{11}N$, and ammonium chloride.

Hexamethylene-tetramine, $(CH_2)_6N_4$ (**Hexamethylenamina**, U.S.P.).--A condensation product obtained by the action of ammonia upon formaldehyde. It forms colorless, lustrous, odorless crystals having when in aqueous solution an alkaline reaction. It is soluble in water, less readily in alcohol and difficultly soluble in ether. It has been used in medicine under the names of "urotropin" and "formin" as well as under its proper chemical name.

The amides and imides are derivatives of ammonia, in which one or more hydrogen atoms are replaced by acid radicals. They are easily distinguished from the amines by their ready saponification. They decompose on heating with acids or alkalies, or even with water, into their components, acid and ammonia. They may be formed by the action of ammonia upon the chlorides of the acid radicals, by the dry distillation of the ammonia salts of the fatty acids, and other methods.

Formamide, $HCO.NH_2$, is obtained by heating ammonium formate to 230°. Liquid boiling at 195° with partial decomposition into NH_3

and CO. Its compound with chloral has already been noted (see Chloralamide, p. 526). It dissolves mercuric oxide, forming, with elimination of water, a compound "mercury-formamidate," $\begin{matrix}HCO.NH\\HCO.NH\end{matrix}>Hg$, which is used somewhat in medicine. The compound is stable in the presence of albuminoids, but is decomposed by dilute acids or alkalies, with separation of fine gray metallic mercury.

Acetamide, $C_2H_3O.NH_2$.—Obtained by heating ammonium acetate to 230°. Forms crystals easily soluble in water and alcohol, fusing at 82°, and boiling at 222°. Has a characteristic odor, recalling mice. *Diacetamide*, $(C_2H_3O)_2NH$, forms a white mass, fusing at 78° and boiling at 223°. *Triacetamide*, $(C_2H_3O)_3N$.—White needles, melting at 79°; neutral reaction.

The amido acids have been noted in part as derivatives under the several fatty acids (see p. 560). Some additional compounds of this class remain to be noted.

Amido-succinic Acid (Aspartic Acid), $COOH.CH_2.CH(NH_2).COOH$, is readily obtained by boiling asparagin with acids or alkalies. Formed also in the decomposition of albuminoids, horn, and glue, with acids or alkalies. It forms small rhombic tablets easily soluble in hot water. Nitrous acid changes it into malic acid.

Amido-succinamide (Asparagin), $COOH.CH_2.CH(NH_2).CONH_2$, occurs very widely distributed in the vegetable kingdom, as in sugar-beets, potatoes, in the shoots of many vegetables, in sweet almonds and asparagus, whence the name. Forms lustrous rhombic crystals, easily soluble in hot water, insoluble in alcohol and ether. Is a monobasic acid, which combines with bases, acids, and salts. It forms a crystalline blue copper salt, which is nearly insoluble in water.

Amido-pyrotartaric Acid (Glutamic Acid), $COOH.C_3H_5(NH_2).COOH$, occurs along with aspartic acid in all the decompositions of albuminoids, etc. Forms rhombic crystals, melting at 202°, soluble in water, difficultly soluble in alcohol.

Amido-pyrotartaramide (Glutamine), $COOH.C_3H_5(NH_2).CONH_2$, accompanies asparagin in many plants, and is best obtained from the fresh juice of the sugar-beet.

Appendix to Amines and Amides.—Analogous to the organic ammonia derivatives are the corresponding compounds derived from *phosphine*, PH_3, from *arsine*, AsH_3, and *stibine*, SbH_3. Ethyl phosphine and triethyl-phosphine are both liquids of powerful and disagreeable odor, which readily ignite, and burn in the air like the spontaneously inflammable phosphine. Tetraethyl-phosphonium iodide is also known. The organic arsenic compounds are primary, secondary, and tertiary arsines. Of these the best known are the secondary compounds. When an acetate like $KC_2H_3O_2$ is distilled with arsenous oxide, As_2O_3, there is produced a compound, $\begin{matrix}As(CH_3)_2\\|\\As(CH_3)_2\end{matrix}$, known as *cacodyl* (from κακώδης, stinking), together with the oxide of the same, $\begin{matrix}(CH_3)_2As\\(CH_3)_2As\end{matrix}>O$, known as cacodyl oxide. The corresponding acid is $H(CH_3)_2AsO_2$ and of this the sodium salt is used medicinally. **Sodii Cacodylas**, U.S.P., $Na(CH_3)_2AsO_2$, forms a white, odorless, deliquescent powder.

The antimony, boron, and silicon compounds have also been obtained, the last named derived from SiH_4, resembling the methane derivatives.

Organo-metallic compounds, such as zinc-methyl, $Zn(CH_3)_2$, and zinc-ethyl, $Zn(C_2H_5)_2$; mercury-methyl, $Hg(CH_3)_2$, and mercury-ethyl, $Hg(C_2H_5)_2$; aluminum-methyl, $Al(CH_3)_3$; lead-methyl, $Pb(CH_3)_2$, and lead-ethyl, $Pb(C_2H_5)_2$; and tin-tetramethyl, $Sn(CH_3)_4$, and tin-tetraethyl, $Sn(C_2H_5)_4$, have all been prepared.

IX. CARBOHYDRATES.

We find very widely distributed in the vegetable kingdom a class of compounds which are of the greatest importance as food-products in the support of animal life, and play an important part in the nutrition of the living organism. These compounds have been termed "carbohydrates," because they contain along with carbon the elements hydrogen and oxygen in the ratio of 2 to 1, or as they exist in water. They also bear a simple relation to the hexatomic alcohols mannitol and dulcitol (see p. 542), the formulas of which were $C_6H_{14}O_6$. As the formula of one group of carbohydrates is $C_6H_{12}O_6$, and several of them can be formed by the careful oxidation of these hexatomic alcohols, it was supposed they contained an aldehyde or ketone group, and in fact they are now recognized as aldehyde or ketone alcohols. A second group of the carbohydrates, with the formula $C_{12}H_{22}O_{11}$, seems to be simply anhydrides of the first group of aldehyde or ketone alcohols; and the third group, with the formula $(C_6H_{10}O_5)_n$, are still more complex anhydrides. The process of "hydrolysis" is capable of causing these anhydrides to take up water and yield compounds of the other group. Despite the large number of these carbohydrates occurring in nature, until very recently it had not been found possible to form any of them by synthetic means. A beginning has now been made in this work, however, by the German chemist Emil Fischer, and, while the more important of the carbohydrates still remain incapable of artificial formation, the way is clearly indicated. The number of artificial compounds formed makes it necessary to broaden the classification hitherto adopted, and, instead of the old grouping of *Glucoses*, $C_6H_{12}O_6$, *Sucroses*, $C_{12}H_{22}O_{11}$, and *Amyloses*, $(C_6H_{10}O_5)_n$, we now classify them as follows:

1. Monosaccharides.

Trioses.—Glycerose, $C_3H_6O_3$ (prepared from glycerol by oxidation).

Tetroses.—Erythrose, $C_4H_8O_4$ (prepared from erythrol by oxidation).

Pentoses.—Arabinose, $C_5H_{10}O_5$ (prepared by the action of dilute sulphuric acid upon lævo-rotatory gum arabic); xylose, $C_5H_{10}O_5$ (prepared by boiling beech-wood and jute with dilute acids); ribose, $C_5H_{10}O_5$ (prepared from arabinose by heating with pyridine); rhamnose or isodulcitol, $C_5H_9(CH_3)O_5$, a methyl-pentose (prepared by the decomposition of glucosides like quercitrin); fucose, $C_5H_9(CH_3)O_5$ (obtained from sea-weeds by hydrolysis).

Hexoses are divided into two groups,—the *aldoses*, in which the aldehydic character is shown, and the *ketoses*, in which the ketone character is indicated by their reactions. To the aldose group belong mannose, $C_6H_{12}O_6$ (obtained by the careful oxidation of mannitol); glucose, $C_6H_{12}O_6$ (of which the dextro-rotatory variety is the naturally occurring dextrose); gulose, $C_6H_{12}O_6$ (obtained as yet only artificially); galactose, $C_6H_{12}O_6$ (obtained by the inversion of milk sugar); talose, $C_6H_{12}O_6$ (obtained as yet only artificially); rhamno-hexose, $C_6H_{11}(CH_3)O_6$ (obtained artificially from rhamnose). To the ketose group belong fructose (or levulose), $C_6H_{12}O_6$ (obtained along with dextrose in the inversion of cane-sugar); acrose, $C_6H_{12}O_6$ (obtained as yet only artificially); sorbinose, $C_6H_{12}O_6$ (obtained from mountain-ash berries).

Heptoses.—Manno-heptose, $C_7H_{14}O_7$ (obtained artificially from mannose); gluco-heptose, $C_7H_{12}O_7$ (obtained artificially from glucose).

Octoses.—Manno-octose, $C_8H_{16}O_8$ (obtained artificially from mannose); gluco-octose, $C_8H_{16}O_8$ (prepared from the corresponding glucose).

Nonoses.—Manno-nonose, $C_9H_{18}O_9$ (prepared from the corresponding mannose); gluco-nonose, $C_9H_{18}O_9$ (prepared from the corresponding glucose).

2. Disaccharides and Trisaccharides.

Tribioses and *Tetrabioses* are as yet unknown.

Pentabioses.—Arabinon, $C_{10}H_{18}O_9$ (has been prepared by the moderated action of dilute sulphuric acid upon arabic acid).

Hexabioses.—Sucrose (cane sugar), $C_{12}H_{22}O_{11}$; lactose (milk sugar), $C_{12}H_{22}O_{11} + H_2O$; maltose, $C_{12}H_{22}O_{11}$; isomaltose, $C_{12}H_{22}O_{11}$; trehalose (mycose), $C_{12}H_{22}O_{11}$; melabiose (eucalyn), $C_{12}H_{22}O_{11}$; turanose, $C_{12}H_{22}O_{11}$ (obtained by the partial hydrolysis of melezitose).

Hexatrioses.—Meletriose (raffinose), $C_{18}H_{32}O_{16}$; melezitose, $C_{18}H_{32}O_{16}$.

3. Polysaccharides.

(*a*) *Crystallizable Polysaccharides.*—Gentianose (from *Gentiana lutea*); lactosin (from *Silena vulgaris*); and stachyose (from *stachys tuperifera*).

(*b*) *Uncrystallizable Polysaccharides.*—These include three subgroups of related compounds:

Starches, lichenin (from Iceland moss), inulin (from *Inula helenium*), triticin, and glycogen (or animal starch).

Dextrine (or artificial gum), natural gums (including gum arabic, wood-gum, bassorin, etc.), and pectin substances.

Cellulose, lignin, and tunicin (or animal cellulose).

The monosaccharides as a class are neutral, taste sweet, and are colorless and odorless. They are all easily soluble in water, difficultly soluble in absolute alcohol, and insoluble in ether. They are easily oxidizable, and therefore all reduce alkaline solutions of metallic salts. The solution usually taken for this reaction is an alkaline solution of copper tartrate known as "Fehling's solution." This reaction takes place quantitatively, and hence Fehling's solution serves as a means of estimating sugars.

According to the U. S. Pharmacopœia, it is prepared thus: "Dissolve 34.66 gm. of carefully selected, small crystals of pure cupric sulphate, showing no trace of efflorescence or adhering moisture, in a sufficient quantity of water to make the solution measure, at 25° C. (77° F.), exactly 500 c.c. Keep this solution in small, well-stoppered bottles. Dissolve 173 gm. of crystallized potassium and sodium tartrate, and 50 gm. of sodium hydroxide in a sufficient quantity of water to make the solution measure, at 25° C. (77° F.), exactly 500 c.c. Keep the solution in small, rubber-stoppered bottles. For use, mix exactly equal volumes of the two solutions at the time required. One cubic centimeter of the mixed solution is the equivalent of:

Cupric sulphate, crystallized, $CuSO_4 + 5H_2O$	0.03466
Cupric tartrate, $CuC_4H_4O_6 + 3H_2O$	0.03688
Dextrose, anhydrous, $C_6H_{12}O_6$	0.00500
Cane sugar (inverted)	0.00475
Milk sugar, anhydrous, $C_{12}H_{22}O_{11}$	0.00678"

Very characteristic for the monosaccharides is the reaction with phenyl-hydrazine, $C_6H_5.NH.NH_2$. When this reagent in dilute acetic acid solution is heated with these compounds, they form difficultly soluble and crystalline ***osazones***, by means of which they can be separated and identified.

The monosaccharides are not equally subject to the decompositions in the presence of micro-organisms known as "fermentations." The trioses, hexoses, and nonoses appear to be readily fermentable, while the pentoses, heptoses, and octoses are not decomposed.

The trioses, tetroses, and pentoses are not of sufficient importance to require more than the mention already given in the classification. The hexoses, however, include not only a number of important, naturally occurring sugars, but compounds obtained in the hydrolysis of the di-, tri-, and polysaccharides.

Mannose, $C_6H_{12}O_6$, is obtained by the careful oxidation of mannitol and by the hydrolysis by means of dilute sulphuric acid of many natural carbohydrates, such as salep mucilage and hemicellulose from vegetable ivory-nuts, palm-nuts, etc. Hard, friable powder, easily soluble in water, and fermentable with yeast.

Dextrose, $C_6H_{12}O_6$.—This is the most widely distributed of the hexose class. It occurs, under the common name of "grape sugar," along with levulose (fruit sugar) in most sweet fruits and juices. Grape juice contains 10 to 30 per cent., figs 12 per cent., sweet cherries 9 to 10 per cent., apples and pears 7 to 10 per cent., plums and apricots 2 to 5 per cent. Small amounts of this sugar are found in the blood as well as in most of the organs and tissues of the body. In the disease known as "diabetes mellitus" the urine contains larger amounts (as high as 8 to 10 per cent.). It is most readily prepared by the hydrolysis (inversion) of the carbohydrates of the higher classes, like cane sugar, which yields a mixture of equal molecules of dextrose and levulose, and starch, which yields products like dextrin and maltose, which gradually pass into dextrose. The commercial glucose (or starch sugar) (**Glucosum**, U.S.P.) is, however, never perfectly converted, and contains, besides dextrine and maltose, unfermentable sugars as alterative products.

Dextrose crystallizes out of alcohol or from concentrated aqueous solution at 30°–35° in anhydrous needles or hard crusts, which fuse at 146°. At ordinary temperatures it crystallizes out of aqueous solution with 1 molecule of water in warty masses. It is distinctly inferior in sweetness of taste to cane sugar.

Galactose, $C_6H_{12}O_6$, is produced along with dextrose by the hydrolysis of milk sugar as well as from many other carbohydrates, such as gums. Is also obtained as a decomposition product of the cerebrin of the brain. Crystallizes in small crystals, fusing at 168°, and is fermentable.

Levulose, $C_6H_{12}O_6$, known also as fruit sugar, is found along with dextrose, and at times with cane sugar, also in ripe fruits, also found in honey. By boiling cane sugar with dilute acids equal molecules of dextrose and levulose are produced. It is also formed by the decomposition of inulin with dilute acids. Forms a syrup or needles, which unite to rounded aggregates, and fuse at 95°. Tastes sweet, and is lævo-rotatory. Is fermentable by yeast, but more slowly than glucose. It forms a difficultly soluble compound with calcium oxide, $C_6H_9(CaOH)_3O_6$, by means of which it can be separated from the more soluble dextrose compound when the two are present together, as an invert sugar.

Levulose has also been introduced into medicine under the name of "diabetin," and is made from invert sugar, as indicated above.

Acrose, $C_6H_{12}O_6$ (so named because prepared from acroleïn), is an artificial sugar first made by Emil Fischer, and is interesting as having yielded by various synthetical reactions three other artificial sugars,—mannose, glucose, and fructose.

The heptoses, octoses, and nonoses have as yet only a theoretical interest.

The disaccharides are a most important class, and include several of the best known of the sugars. Under the group hexabioses we have sucrose, or cane sugar, lactose, or milk sugar, and maltose, or malt sugar, as the most important. All these sugars are capable of inversion or hydrolysis in the presence of dilute acids as well as certain ferments, and then yield products belonging to the class of monosaccharides. Thus, sucrose, on inversion, yields a mixture of dextrose and levulose; milk sugar yields dextrose and galactose; and maltose yields dextrose alone. Milk sugar and cane sugar are not fermentable with yeast until after inversion; maltose is at times fermentable. Cane sugar has no effect upon Fehling's solution, while milk sugar and maltose have a reducing effect.

Sucrose (or Cane Sugar), $C_{12}H_{22}O_{11}$ (Saccharum, U.S.P.), is very widely distributed in nature, especially in the sugar-cane (*Saccharum officinarum*), which contains from 16 to 20 per cent.; in the sugar-beet, which contains from 12 to 18 per cent.; in the sorghum-cane, which contains from 7 to 10 per cent.; in the sugar-maple, the juice of which contains from 3 to 4 per cent.; in Indian corn, and in many fruits. The extraction and commercial manufacture is practically limited to the two sources first named, the sugar-cane and the sugar-beet. An outline of the process of manufacture will be appended to this section.

Pure sucrose crystallizes in anhydrous, monoclinic crystals, melting at 160°. Easily soluble in water, difficultly soluble in alcohol, insoluble in ether, chloroform, or carbon disulphide. Is dextro-rotatory, its specific rotatory power being $+66.5°$ for rays $[a]_D$.

The optical analysis of sugar solutions is effected by the aid of the polariscope (see p. 111), an instrument in which the ray of polarized light is made to pass through a definite length (usually 100 or 200 mm.) of a solution made up by dissolving a definite weight of the sugar (26.048 gm. in most instruments) in 100 mils of pure water, and filtering if necessary. The plane of the ray is rotated thereby through a certain angle, and on rotating the analyzing prism of the polariscope through a corresponding angle in the opposite direction the effect is just compensated for. The circular scale on the tube rotated is graduated in percentage numbers, so that the percentage strength of the sample in pure sugar can be read off at once.

Cane sugar does not reduce Fehling's solution, nor is it directly fermentable with yeast, as is dextrose. Prolonged contact with the yeast, however, brings about an inversion through the action of the soluble ferment *invertin* present in the yeast, and then the products of the inversion, dextrose and levulose, at once ferment. Cane sugar unites with lime and strontia to form insoluble saccharates, such as $C_{12}H_{22}O_{11} + 3CaO$ and $C_{12}H_{22}O_{11} + 2SrO$. Concentrated sulphuric acid dehydrates and chars the sugar, producing a coke. Prolonged action of dilute hydrochloric acid converts sugar into levulinic acid (see p. 569).

Lactose, or Milk Sugar, $C_{12}H_{22}O_{11} + H_2O$ (**Saccharum Lactis,** U.S.P.).—This variety of sugar occurs in the milk of the mammalia to the extent of from 3 to 6 per cent., and is usually obtained from the "whey" or thin liquid which remains when the casein has been coagulated by rennet. It crystallizes in hard, white crystals with 1 molecule H_2O. It is less sweet than cane sugar, and less soluble in water; insoluble in alcohol, ether, and chloroform. It is dextro-rotatory, $[a]_D = 52.5°$. It differs from cane sugar in having a direct reducing power on Fehling's solution.

Maltose, $C_{12}H_{22}O_{11}$, results from the action of the diastase of malt upon starch during the germination of cereals (as in malting of grain), and also as an intermediate product on boiling starch with dilute sulphuric acid. It forms fine, white needles, crystallizes with 1 molecule of H_2O, and is easily soluble in water. It is strongly dextro-rotatory, $[a]_D = +137°$. It reduces Fehling's solution, the reducing power being about two-thirds that of dextrose, is easily decomposed by alkalies, is fermented with yeast, and yields on hydrolysis with dilute acids only dextrose. Neither maltose nor lactose reduces Barfoed's reagent (an acetic acid solution of copper acetate), and in this way may be distinguished from dextrose. It has been found that maltose can be produced by the action of an enzyme *maltase* on a concentrated solution of dextrose, this being the only synthesis of a diose from a monose so far known. The same enzyme maltase may also work to split up maltose into dextrose, so that it is a reversible reaction.

Isomaltose, $C_{12}H_{22}O_{11}$, is formed synthetically from dextrose by the prolonged action of strong hydrochloric acid at 10°–15°, and is contained in commercial starch sugar because of such retrograde action. It is also a product of the action of diastase upon starch, and is present in malt; as it undergoes fermentation only slowly, it is usually present unchanged in fermented malt liquors, such as beer, amounting to 25–30 per cent. of the beer extract, at times. It is intensely sweet, and changes at 65° into yellowish-brown products of roasting, which are also sweet and give character to the roasted malt.

The most important trisaccharide is

Melitriose or Raffinose, $C_{18}H_{32}O_{16} + 5H_2O$.—This sugar is found in the sugar-beet, and hence obtained in the working of the molasses from the same; also in the Eucalyptus manna, in cotton-seed cake, etc. Is less soluble in water than cane sugar, and almost devoid of sweet taste. Strongly dextro-rotatory, $[a]_D = 103.9°$. It does not reduce Fehling's solution. Readily fermentable with yeast. When inverted, yields first fructose and melibiose and the latter is then decomposed into galactose and dextrose.

The crystallizable polysaccharides mentioned are as yet of slight importance. The uncrystallizable polysaccharides, on the other hand, include compounds of the greatest importance in the growth of vegetable life, and as the basis of food preparations used for human sustenance.

Starch, $(C_6H_{10}O_5)_n$ **(Amylum, U.S.P.)**, is very widely distributed, being contained in all assimilable plants, in which it constitutes a reserve material. As such it is contained especially in the roots, tubers, seeds, fruit, and in the medullary rays of the trees during the winter. During the movement of the sap of the plant it is changed into sugar. Starch is extracted practically from potatoes (containing 21 per cent.), from maize, or Indian corn (containing 50 per cent.), from wheat (containing 64 per cent.), and from rice (containing 77 per cent). Specially rich in starch also are the tropical plants, such as arrow-root, sago, and manihot.

Starch consists of a white, velvety, somewhat hygroscopic powder, recognized under the microscope as made up of granules of round or slightly elongated shape which show a concentric structure. The interior substance of the granule, or the true starch material, is called "granulose," and is readily dissolved under the action of diastatic ferments, while the exterior shell is a cellulose material called "farinose," and is not acted upon by ferments.

The most complete classification of the starches is that of Muter, as amplified by Blyth, by which they are divided into five groups, on the basis of their physical and microscopical differences, as follows:

(*a*) *The potato group* includes such oval or ovate starches as give a play of colors when examined by polarized light and a selenite plate, and have the hilum and concentric rings clearly visible. It includes *tous-les-mois*, or canna arrow-root, potato starch, maranta, or St. Vincent arrow-root, Natal arrow-root, and curcuma arrow-root.

(*b*) *The leguminous starches* comprise such round or oval starches as give little or no color with polarized light, have concentric rings all but invisible, though becoming apparent in many cases on treating the starch with chromic acid, while the hilum is well marked and cracked or stellate. It includes the starches of the bean, pea, and lentil.

(*c*) *The wheat group* comprises those round or oval starches having both hilum and concentric rings invisible in the majority of granules. It includes the starches of wheat, barley, rye, chestnut, and acorn, and a variety of starches from medicinal plants, such as jalap, rhubarb, senega, etc.

(*d*) *The sago group* comprises those starches of which all the granules are truncated at one end. It includes sago, tapioca, and arum, together with the starch from belladonna, colchicum, scammony, podophyllum, canella, aconite, cassia, and cinnamon.

(*e*) *The rice group.* In this group all the starches are angular or polygonal in form. It includes the starches of oats, rice, buckwheat, maize, dari, pepper, as well as ipecacuanha.

In addition to the differences in form and marking mentioned above, the starch-granules differ in size according to their different sources, so that under the microscope they can be distinguished by the measurement of the average diameter of the granule. This ranges, according to Karmarsch, from .01 to .185 millimeter, or from .0004 to .0079 inch.

Starch is insoluble in cold water, alcohol, and ether; on warming with water it begins to swell up at 55° C., and at 70° to 80° the granules burst and it becomes a uniform, translucent mass known as "starch paste," which is not, however, a solution, as the water can be frozen out of it. Boiled with water for a long time it goes into solution, one part dissolving in fifty parts of water. The prolonged action of glycerol at 190° also causes the change into *soluble starch.* The action of heat upon starch is to change it gradually into dextrine, which is soluble in cold water. Both the starch-granules and the starch paste are colored intensely blue by iodine. The compound formed is a weak addition compound, and the blue color disappears on heating, but returns again on cooling. This starch reaction serves to indicate the existence of the starch molecule in any vegetable extract, and the gradual breaking down of this molecule under the influence of hydrolysis can also be checked off by noting the iodine reaction. Thus, under the influence of dilute acids dextrine and dextrose are produced, the latter eventually as sole product. Many ferments, like saliva, the pancreatic ferment, and especially the diastase of malt, produce in the starch a somewhat similar change, and yield maltose, $C_{12}H_{23}O_{11}$, and a number of intermediate products between this and starch. These changes and the distinguishing tests by which they may be recognized may be stated as follows:

Starch		gives a blue iodine reaction.
Soluble starch (amylo-dextrine)		gives a blue iodine reaction.
Dextrines	Erythro-dextrine	gives a violet and red iodine reaction.
	Achroo-dextrine	gives no iodine reaction.
	Malto-dextrine	gives no iodine reaction.
Maltose		reduces Fehling's solution but not Barfoed's reagent.
Dextrose		reduces Fehling's solution and also Barfoed's reagent.*

A mixture of strong nitric acid and sulphuric acids in cold acts upon starch, producing nitro starch, which is analogous to nitrocellulose, and may be obtained in the same degrees of nitration.

Lichenin is prepared from lichens as a gelatinous mass (Iceland moss), soluble in water, and precipitable in flocks on addition of alcohol.

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* Sadtler's Industrial Organic Chemistry, 4th Ed., p. 187.

Inulin $(C_6H_{10}O_5)_2$, is obtained from the roots of *Inula helenium*, from the *Dahlia*, *Helianthus*, and other sources. Forms a white powder made up of microscopical spherules. Easily soluble in water and in copper oxide-ammonia (Schweizer's reagent). Does not reduce Fehling's solution, but does reduce ammoniacal silver solution.

Glycogen, $(C_6H_{10}O_5)_n$.—Known also as animal starch. Is found most abundantly in the livers of mammalia and in notable quantities in the tissues of the embyro. White, amorphous powder, soluble in water to an opalescent dextro-rotatory liquid, which is colored red with iodine. After the death of the animal the glycogen changes to dextrose very rapidly, and the same change takes place when it is boiled with dilute acids, while ferments change it into maltose.

Dextrine, $(C_6H_{10}O_5)_2$.—This substance can be formed from starch by the action of dilute acids, of diastase, or by heat alone. In the latter case the reaction is merely one of molecular rearrangement, and may be approximately expressed by the reaction $2(C_6H_{10}O_5)_3 = 3(C_6H_{10}O_5)_2$. In the other cases it is probable that hydrolysis gives rise to several successive changes, and different dextrines are considered as being formed successively, such as *erythro-dextrine*, *achroo-dextrine*, and *malto-dextrine*. Technically, dextrine is obtained by the heating of starch after moistening with dilute acids. Dextrine is a white or yellowish-brown powder, readily soluble in water, from which solution it may be precipitated on addition of alcohol. Gives a red color with iodine. Is dextrorotatory. It does not reduce Fehling's solution nor Barfoed's reagent. It is not directly fermentable, but in the presence of diastase it goes over into fermentable products. Dextrine is used as a substitute for the natural gums in calico-printing and manufacture of textile goods, for a stiffening material, and for glazing paper and card-board, and enters into many food products.

The natural gums are a class of vegetable products which occur at times as amorphous, translucent, or transparent exudations, as in the case of gum arabic, or are extracted by dilute alkalies from the plants, and then are thrown out of solution on addition of hydrochloric acid and alcohol, as in the case of the wood-gums. These gums are soluble in water, forming thick, sticky solutions, which can be filtered, however. They do not reduce Fehling's solution, but by heating with dilute acids yield monosaccharides like arabinose, xylose, dextrose, and galactose.

Somewhat similar products, but only partially soluble in water, are the vegetable mucilages. These do not dissolve, but swell up with water to form liquids which cannot be filtered.

Gum Arabic (Arabin or Calcium Arabate).—This substance (**Acacia**, U.S.P.) is an exudation from the acacia and mimosa species of Africa and the Orient. It contains about 3 per cent. of ash, and on adding hydrochloric acid to the aqueous solution and precipitating with alcohol, a colorless, amorphous substance is obtained. This is arabic acid. **On** hydrolysis it yields galactose, arabinose, and a pentabiose named **arabi-**

non. The so-called "metapectic acid," from the pulp of the sugar-beet, is considered to be identical with arabic acid.

Related to the acacia gums are *wood-gum*, from the wood of foliage trees, yielding xylose on hydrolysis; *cherry-gum*, the gum of cherry- and almond-trees, yielding *l*-arabinose on hydrolysis; *peach-gum*, from the peach-tree, yielding arabinose and galactose on hydrolysis; *barley-gum*, obtained in the nitrogen-free extractive material of cereals, yielding galactose and xylose.

Bassorin is the mucilaginous constituent of gum bassorin and gum tragacanth (**Tragacantha,** U.S.P.).

Carragheen is the mucilaginous constituent of Irish moss (**Chondrus,** U.S.P.). Is not precipitated from its solutions on addition of alcohol; yields galactose on hydrolysis with dilute sulphuric acid. The pectine substances which are found in certain fruits like apples and pears, and in fleshy roots like the beet and the carrot, are also closely related to the carbohydrates. Their concentrated solutions gelatinize on cooling.

Cellulose is the name given to the material of which the growing plant-cell is composed; as the membrane becomes older incrustations of mineral salts occur, and the cellulose also undergoes partial change into lignin, a closely related substance.

Cellulose is insoluble in the ordinary solvents, and therefore to prepare it in a state of purity the plant-fibres like cotton and flax are treated successively with water, alcohol, ether, dilute alkalies, dilute hydrochloric and hydrofluoric acids. The residual fibre is then chemically pure cellulose. We have an example of this in Swedish filter paper, which has been prepared in this way for quantitative analytical use. The cotton fibre is also conveniently purified, and then furnishes a very pure cellulose (**Gossypium Purificatum,** U.S.P.). Pure cellulose is amorphous, and, as stated, insoluble in ordinary solvents. It is soluble, however, in an ammoniacal solution of cupric hydroxide (Schweizer's reagent), and is thrown out of this solution on addition of acids and salts. After washing with alcohol it forms a white, amorphous powder. Boiling with dilute acids converts it into dextrine and dextrose, while concentrated sulphuric acid converts it into *amyloid*, an amorphous, translucent mass.

In the manufacture of parchment-paper advantage is taken of this amyloid formation. Unsized paper is passed rapidly through strong sulphuric acid, which causes a superficial change of the cellulose into amyloid; the paper is then washed with water to free it from the adhering acid and hung up to dry. The paper is thus made much stronger and less pervious to liquids, as the pores are filled with the colloidal cellulose.

A mixture of nitric and sulphuric acids has a "nitrating effect," and gives rise to a series of nitric esters or so-called "nitrocelluloses." Taking the formula of cellulose as $C_{12}H_{20}O_{10}$, we have a series beginning with a dinitrate, $C_{12}H_{18}O_8(NO_3)_2$, and running to the hexanitrate, $C_{12}H_{14}O_4(NO_3)_6$. Of these the highest (the hexanitrate) constitutes the true explosive *gun-cotton* and is insoluble in alcohol, ether, or a mixture of the two.

A mixture of the tetranitrate and the trinitrate, on the other hand, constitutes **Pyroxylinum,** U.S.P., and is soluble in a mixture of alcohol and ether, the solution forming **Collodion, U.S.P.** In the preparation of this latter the Pharmacopœia prescribes the dissolving of 40 grams of pyroxylin in a litre of the solvent, made up of 3 parts of ether and 1 part of alcohol. From this solution on evaporation of the solvent the pyroxylin is left as a transparent, flexible film.

Celluloid will be noted under the "Industries of the Carbohydrates," following this section.

Cellulose xanthate (obtained by the action of carbon disulphide upon alkali treated cellulose), and cellulose acetate are both manufactured as the basis of artificial silk fibre.

Lignin is the alteration substance which in most kinds of wood incrusts the true cellulose. It is not affected by dilute acids and alkalies, but is readily oxidized and dissolved by chlorate of potash and nitric acid. It shows two very characteristic color reactions: it is colored intensely yellow with aniline sulphate, and bright red with a solution of phloroglucin in strong hydrochloric acid. These tests serve to identify bleached wood-fibre in paper in which it may be present.

Tunicin (Animal Cellulose) is a closely related material found in the tissues of some animals (*Ascidia*). It is amorphous, and insoluble in ordinary solvents, but soluble in copper oxide-ammonia solution. It yields glucose on hydrolysis.

INDUSTRIES OF THE SUGARS, STARCH AND CELLULOSE.

1. The Manufacture of Raw and Refined Sugars.—The two sources for the industrial manufacture of sugars have already been stated to be the sugar-cane and the sugar-beet. The former is grown chiefly in the tropics, West Indies, Java, Brazil, Central America, and Louisiana. The juice is extracted by crushing in roll-mills, or by the process of diffusion, the cane having been cut obliquely in chips. It is at once treated with milk of lime in order to neutralize the organic acids present, which otherwise would start fermentation and rapidly "invert" the cane sugar. This is called "defecating," and causes the rising of a scum of lime-salts, which is skimmed off. The juice properly defecated is then to be evaporated. This is almost universally effected in vacuum-pans, several of which may be connected, forming a "double effect" or "triple effect" pan. By this means the juice is rapidly concentrated at a relatively low temperature, and so the darkening of the product is prevented as well as the formation of molasses. Sulphurous acid or sulphites are also used at times to bleach the juice. The product of this evaporation then allowed to crystallize gives us the raw sugar and a molasses or syrup. This latter is made to yield a second grade of sugar. In the extraction of sugar from the sugar-beet, the process of diffusion is almost universally applied, the beets being sliced and then being placed in large vessels called diffusion-cells. These are arranged in batteries of eight, ten, or a dozen, and warm water is passed through them, taking up successively more and more of the sugar until the solution is quite strong while the beets are becoming more and more exhausted. This solution is then treated with an excess of lime, and the excess removed by what is termed carbonatation with carbon dioxide gas. The insoluble carbonate of lime is then removed by the aid of a filter-press, and the juice obtained clear. The liming and treatment with carbon dioxide may be repeated, and then the juice is concentrated to the crystallizing point in the vacuum-pan. The refining of raw sugars, whether from the sugar-cane or the sugar-beet, is essentially the same. The raw sugars are "melted," that is, dissolved in hot water, and then the solution is defecated with the aid of blood albumin, filtered through bag-filters (or filter-presses in the case of beet sugar), and then through bone-black, from which it comes practically colorless. It is then evaporated in vacuum-pans to the crystallizing point or "strike," and allowed to cool and thoroughly crystallize. The magma of crystals and syrup is then put into a centrifugal and the syrup separated. The grocery sugars are ready for barreling as they come from the centrifugal, while the white crystal sugars are dried by a current of hot air before being finished.

2. **The Manufacture of Commercial Glucose.**—This is made exclusively from starch by the action of dilute acids, and in this country the starch used is that obtained from Indian corn. Sulphuric acid is generally employed, and the inversion of the starch is carried out in either open or closed "converters." The amount of oil of vitriol used is from one-half pound to one and a quarter pounds per hundred pounds of starch. The starch and water are taken of a gravity of from 18° to 21° B., and the pressure amounts to from forty-five to seventy-five pounds per square inch. In the manufacture of "glucose syrup," the conversion is not so complete, and the quantity of dextrine is larger than where the solid "grape sugar" is to be obtained as the product. Anhydrous crystallized dextrose can also be obtained as the end product of this inversion of starch by Dr. Behr's patent.

3. **The Manufacture of Starch.**—Starch is obtained commercially from Indian corn, from wheat, and from potatoes. As made from corn in this country, the corn is first steeped in water at a temperature not exceeding 140° F. for from three to ten days, the water being renewed frequently. The softened corn is then ground between burr-stones, while a stream of water is kept running continuously into the hopper. As it is ground, the thin paste is carried on to a series of rotating or shaking sieves. The magma so obtained is then run over inclined sieves of silk bolting-cloth, when the starch goes through as a milky liquid, and is run into settling vats. It is here treated with a weak alkaline solution, to dissolve and remove the gluten, oil, etc., and thoroughly washed by agitation and decantation. It is finally allowed to settle, and dried first in boxes with perforated bottom, and then upon plaster of Paris supports while dried with warm air. 56 ℔s. of corn in this way are made to yield 28 ℔s. of purified starch. In the manufacture of starch from wheat, the large amount of gluten makes it necessary to take measures to remove it. This is done in the "sour" process by fermentation, the acetic and other organic acids produced rapidly dissolving the gluten and liberating the starch-granules.

4. **The Manufacture of Paper from Cellulose.**—The materials utilized in paper-making, are all cellulose-containing substances, such as linen and cotton rags, esparto grass, straw, jute, manila, and wood-fibre. The first chemical treatment after the mechanical preparation of the material is ordinarily the boiling with caustic alkali. In the case of the rags, this has the effect of thorough cleansing; in the case of esparto, straw, etc., it combines with the resin and silica, liberating the cellulosic fibre; in the case of wood, however, the action is necessarily a more fundamental one, as the true cellulose is not only incrusted with mineral matter, but combined with lignin. In the preparation of chemical wood-pulp, there are two distinct processes, the "soda-pulp process" and the "sulphite process." In the former, the chipped wood is digested under several atmospheres' pressure with caustic alkali to effect its disintegration; in the latter, calcium or magnesium bisulphite is used, also under considerable pressure, to effect this disintegration. After a thorough washing of the disintegrated pulp, it may be bleached if intended for white paper. This is done with bleaching-powder solution, the excess of chlorine being removed with sodium thiosulphate, known therefore, as "antichlor." The bleached pulp is then mixed with the proper filling material and sizing, and is ready to go to the "fourdrinier" or paper machine.

5. **The Manufacture of Gun-cotton, Pyroxylin, and Celluloid.**—In the manufacture of the true gun-cotton, the maximum of nitration is sought, and the nitrating mixture is hence of the strongest nitric and sulphuric acids, in the proportion of 3 parts of the latter to 1 part of the former. This acid mixture is cooled first, and then the cotton is immersed and left for twenty-four hours to complete the nitration. It is then centrifugated, stirred up thoroughly with cold water, again centrifugated and washed systematically with warm water to which some soda has been added. The gun-cotton is usually preserved in the moist state, and dried only when needed for use. The explosive variety of gun-cotton may be used either as loose fibre or as compressed cartridge or paper sheets. When lighted, it burns quickly without smouldering or leaving any residue. When heated slowly it begins to decompose, and above 130° C. it explodes. It is insolu-

ble in water, alcohol, ether, chloroform, and acetic acid, in dilute acids and alkalies. It is somewhat soluble in acetone and wood-spirit.

In the manufacture of pyroxylin, or soluble gun-cotton, the nitric acid taken is less concentrated, and a somewhat higher temperature is used. Potassium or sodium nitrate is also used at times with the sulphuric acid as the nitrating mixture. 20 parts of pulverized potassium nitrate with 31 parts of sulphuric acid of 1.835 sp. gr. may be used. In this mixture the cotton may be left for 24 hours at a temperature of from 28° to 30° C. If relatively stronger nitrating mixtures are used, the time of immersion may be much reduced.

The pyroxylin obtained is washed with cold water until it shows no acid reaction and finally with boiling water.

In recent years an important class of metal varnishes or lacquers have been introduced in which pyroxylin is the basis. This is dissolved in either methyl alcohol, acetone, methyl and amyl acetates, or mixtures of these. Petroleum naphtha is also added to these solvents to facilitate the drying. These varnishes leave a perfectly transparent and flexible film of pyroxylin, which protects the metal to which it has been applied and will not crack or peel when properly used.

The conversion of pyroxylin into celluloid is accomplished by effecting a thorough incorporation with the former of a certain amount of camphor. It is possible to accomplish this by heat without the use of any solvent, for either the camphor or the pyroxylin, as the camphor at the temperature of its fusion becomes a sufficient solvent for the pyroxylin to effect complete physical admixture. The mixture of the two materials is made while the pyroxylin is still in a partially moist condition, and they are ground together with care in closed drums. The mixture is then put through heated rolls to melt the camphor and cause them to combine. If coloring matter is to be added, it is put in before this melting of the camphor, which distributes it uniformly. The camphor may also be used in solution in methyl or ethyl alcohol.

The product is the well-known celluloid, which may be transparent or opaque, colored uniformly, or mottled and striated in imitation of ivory, coral, amber, tortoise-shell, agate, and other substances. It cannot be caused to explode by heat, friction, or percussion. It is readily soluble in glacial acetic acid, and on diluting with water both camphor and pyroxylin are reprecipitated. It is rapidly soluble in warm, moderately concentrated nitric acid, and also with ease in a hot concentrated solution of caustic soda. Ether dissolves out the camphor from celluloid, and wood spirit behaves similarly. Ether-alcohol (3 to 1) dissolves both the nitro-cellulose and camphor, leaving the coloring and inert matters as a residue. The density of celluloid ranges from 1.310 to 1.393. When heated to 125° C. it becomes plastic, and can be moulded into any desired shape.

X. FERMENTATION AND FERMENTATION INDUSTRIES.

We include under the name of fermentations certain methods of decomposition of organic compounds which presuppose the presence of definite substances called "ferments," which do not, however, apparently take part in the chemical reactions but act after the manner of the inorganic catalytic agents. Their presence in relatively small amount suffices to bring about the decomposition of large quantities of the fermentable material.

The ferments which seem to determine the decomposition may be either soluble unorganized ferments or insoluble organized ferments, which are minute vegetable growths. The decompositions which are brought about by organized ferments differ quite notably in their results from those which can be induced by mere chemical reagents. Thus, the decomposition of sugar into alcohol and carbon dioxide, as it is brought about by the activity of the yeast-cell, cannot be brought about by purely chemical treatment. On the other hand, the action of the unorganized ferments is much more analogous to that induced by chemical reagents. Thus, the hydrolytic action of diastase on starch can also be perfectly imitated by treating with dilute acids. Buchner has, however, recently shown that the liquid expressed from fresh yeast cells after triturating them can produce all the changes attributed to the cells themselves, and that it owes its activity to an enzyme called *zymase* which is produced by the cells.

With regard to the chemical nature of the *enzymes*, or soluble ferments, we only know that they belong to the class of proteids. A recent analysis of diastase by Lintner may be taken as typical of the class: carbon 46.66 per cent.; hydrogen, 7.35 per cent.; nitrogen, 10.42 per cent.: sulphur, 1.12 per cent.; and oxygen, 34.45 per cent.

While soluble in water and glycerol they are insoluble in alcohol, and are precipitated from aqueous solution on addition of lead acetate. Their activity is destroyed by heating, that of diastase at 75° C., and all by boiling with water. Their activity is not destroyed by the presence of antiseptics, which arrest the action of the organized ferments. Thus, chloroform, thymol, and salicylic acid will all arrest the activity of the organized growth but not interfere with that of the soluble ferments. Sodium fluoride in 1-per-cent. solution is said to entirely check the growth of the organized ferment, but is without action on those which are soluble.

Foremost among the soluble ferments is *diastase*. This is the ferment formed from the albuminoids of the cereals during the process of germination. It is specially developed in the malting process as applied to barley. Its chief function is the saccharification of the starch of the grain, changing it into dextrine, maltose, and dextrose. The chemical reactions may be summarized as follows:

$$(C_6H_{10}O_5)_3 + H_2O = C_{12}H_{20}O_{10} + C_6H_{12}O_6.$$
$$(C_6H_{10}O_5)_3 + 2H_2O = C_{12}H_{22}O_{11} + C_6H_{12}O_6.$$
$$(C_6H_{10}O_5)_3 + 3H_2O = 3C_6H_{12}O_6.$$

The amount of starch that a given quantity of diastase can convert cannot be stated with absolute certainty, as it varies with the conditions of its preparation, the strength of the infusion, and other points. Its progress can, of course, be controlled by the iodine reaction, as stated under starch. Commercial extracts of malt are infusions of malted barley, which contains the products of the inversion of the starch. The solid extracts obtained by evaporation of these infusions in vacuo at low temperatures should be readily soluble, and should show that they still contain active diastatic ferment by being able to convert their own weight of starch within a short time. The saliva also contains a soluble ferment, which is sometimes called salivary diastase, because of its similarity to the vegetable diastase. The name *Ptyalin* is also given to this substance at times. Another ferment of similar character is the *amylopsin* of the pancreatic juice.

Invertin (or Invertase) is found in the yeast-plant, and is capable of inverting cane sugar according to the reaction $C_{12}H_{22}O_{11} + H_2O - 2C_6H_{12}O_6$. Its presence here explains why cane sugar will ferment in the presence of yeast after some considerable time, the invertase having meanwhile caused its change into invert sugar. The same ferment seems to be present in the intestinal juice, where its function is to make the cane sugar of foods assimilable by first converting it into invert sugar.

Emulsin (or Synaptase) is found in sweet and bitter almonds. Its function as a soluble ferment is to decompose glucosides. Thus, it decomposes the amygdalin of the bitter almond, salicin, helicin, phloridzin, and arbutin.

Myrosin is a similar ferment found in the black mustard seeds, which by its action on the myronate of potash in the seed liberates the mustard oil as one of the decomposition products.

Pepsin, contained in the gastric juice of animals, and *trypsin*, found in the pancreatic juice, both have what is termed a "proteolytic" power, or ability to digest or decompose proteid matter.

Pepsin, U.S.P., is described as a proteolytic ferment or enzyme obtained from the glandular layer of the fresh stomach of the hog, and capable of digesting not less than 3000 times its own weight of freshly coagulated and disintegrated egg albumin. It is obtained as a fine white or yellowish-white powder or in scales or grains, soluble in water or glycerol, but insoluble in alcohol. It can bear a dry heat of 110° without losing its activity, but heated with acidulated water to 100° it is deprived of all proteolytic power. The products which result from the action of pepsin and trypsin upon albuminoid material are called *peptones*. The pancreatic juice contains besides the trypsin another soluble ferment known as *steapsin*, which has the power of emulsifying and partially saponifying fats. The mixture of enzymes naturally existing in the pancreas of warm-blooded animals and usually obtained from the fresh pancreas of the hog is the **Pancreatinum**, U.S.P.

Corresponding to these peptonizing ferments of animal origin is a vegetable ferment, *papaïn*, obtained from the milky juice of *Carica papaya*. It is a white, amorphous powder, soluble in water and glycerol. It peptonizes proteids very readily, acting like trypsin. It is claimed for it, moreover, that it digests and removes the membrane of croup and diphtheria.

The ferment which is extracted from the mucous membrane of the stomach, and which has the power of coagulating the casein of milk, has been called *rennin* (or présure). The preparation called rennet is usually obtained from the stomach of the calf.

Urease is the name given to the enzyme which, equally with organized ferments, is capable of bringing about the ammoniacal fermentation. The reaction for the decomposition of urea is $CO(NH_2)_2 + 2H_2O = (NH_4)_2CO_3$.

A few additional enzymes have been specifically studied, such as *pectase*, characteristic of the pectic fermentation of fruits, etc.

The organized ferments or vegetable growths may be divided into three classes: first, mould growths; second, yeast-plants, or the different species and varieties of *Saccharomyces*; and third, bacteria, belonging to several different genera.

The mould growths at times are able to induce fermentations, but their action consists much more in secondary changes effected in the fermenting bodies or the products of fermentation. *Penicillium glaucum*, the most widely distributed mould growth, is capable of bringing about a number of chemical decompositions. It is said to furnish a soluble ferment capable of inverting cane sugar. *Aspergillus glaucus* possesses a diastatic ferment. For the preparation of the Japanese saké (or rice-wine) is used the *Aspergillus oryzæ*, which comes on the rice grains. The varieties of Mucor (*M. racemosus* and *M. mucedo*) develop some degree of fermentation in dextrose, invert sugar, and maltose. *Oidium lactis* is found in milk.

Much the best defined of all these changes, however, is the alcoholic fermentation as developed by the activity of the yeast-plant. As before stated, it is sugars of the formula $C_6H_{12}O_6$ that are directly acted upon. According to Pasteur, about 95 per cent. of the sugar is decomposed, according to the reaction $C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$, while the rest is decomposed according to secondary reactions, yielding a variety of products, of which glycerol and succinic acid are the most notable. This most important reaction is developed by the species of the genus *Saccharomyces*. The species *Saccharomyces cerevisiæ* is recognized as the special ferment of beer, while *Saccharomyces ellipsoideus* is the ferment of wine. Of the *S. cerevisiæ*, moreover, two well-characterized varieties can be distinguished. The first of these is most active at ordinary temperatures (16°–20° C.), and develops its full fermentative activity in the course of 3 to 4 days; the second develops its activity at a lower temperature (6°–8° C.), and the action is much slower. The first of these yeast-plants, placed in a sugary liquid, is brought by the liberated carbon dioxide to the surface, and hence is said to develop a surface fermentation, while the second remains at the bottom during its whole activity, and the action is called a bottom fermentation. Upon the use of these two varieties is based two distinct methods of beer brewing.

Within recent years much attention has been paid to pure cultures of the yeast-plant, and in this way much more regular and uniform fermentations have been produced with the result in a better product. This work was initiated largely by Hansen, of Copenhagen.

The special conditions of the alcoholic fermentation are: first, an aqueous sugar solution containing 1 part of sugar to from 4 to 10 parts of water. Second, the presence of a yeast ferment or the press-juice from the same. If this is not added in already developed and active condition, or if the fermentation is to be a spontaneous one,—that is, brought about by the spores present in the air,—the conditions for the growth of the yeast-spores must be present; the solution must contain protein material and phosphates of the alkalies and alkaline earths. Third, the temperature must range between the limits 5°–30° C., or, more narrowly 9°–25°. Above 30° the butyric fermentation tends to develop rather than the alcoholic, and other decompositions ensue.

Fernbach has also worked out a process whereby under the influence of certain cultures starch is directly fermented to fusel oil and acetone, 42 per cent. of the starch being so converted.

Ehrlich has recently shown that the fusel oil (see p. 537) in the ordinary fermentation is produced not from the sugar but from the products of decomposition of proteid matter such as the amido-acids and, moreover, not by the action of bacteria but under the influence of the vital activity of the yeast itself. The most important of the amido-acids in this connection are leucin (see p. 561) and isoleucin.

The number of changes brought about by organized ferments of the third class or bacteria is very great. Thus, *Bacillus subtilis, B. amylobacter,* and *B. termo* bring about a peptonization of albuminoids which, under the influence of these bacteria, decompose into leucin, tyrosin, and ammonia. The butyric acid ferment seems to be the starch converting *Bacillus amylobacter* (*Clostridium butyricum, Vibrio butyricus*), although butyric acid is not the only product developed by it.

The acetic fermentation is developed by at least three kinds of bacteria. *Bacterium aceti* was discovered by Pasteur, while Hansen has found two additional acetic ferments, *Mycoderma cerevisiæ* and *Mycoderma pasteurianum,* the latter being the most characteristic.

A series of bacteria which develop turbidity in beer as well as an unpleasant odor and taste are known collectively as "Sarcina." The most important of them, discovered by Lintner, is *Podiococcus cerevisiæ.*

The acetic fermentation is that which most readily develops from the alcoholic and follows it often as a spontaneous change. It requires, besides the presence of a dilute alcohol or alcohol containing liquid, the presence of nitrogenous compounds and salts, and is, above all, what is termed an *aërobic* fermentation,—that is, requires the presence of oxygen. The temperature most favorable for the development of the acetic ferment is between 18° and 35° C. The reaction is purely one of oxidation, $C_2H_6O + O_2 = C_2H_4O_2 + H_2O$, and can be brought about by chemical means, such as the action of platinum black on dilute alcohol, etc.

The lactic fermentation takes place without the necessity of oxygen, and hence is termed an *anaërobic* fermentation. It takes place in neutral or alkaline solutions, and is hindered by the presence of small amounts of acid. By it galactose, from the inversion of sugar of milk, is simply decomposed, according to the reaction $C_6H_{12}O_6 = 2C_3H_6O_3$. The most favorable temperature is from 35° to 40° C.

The butyric fermentation is like the lactic, and generally follows it. It is also *anaërobic*. The reaction for the production of butyric acid by this fermentation is $2C_3H_6O_3 = C_4H_8O_2 + 2CO_2 + 2H_2$. Other organic compounds, besides sugar, are capable of undergoing this fermentation.

Glycerol, under the influence of bacteria, is decomposed into normal butyl alcohol, normal butyric acid, ethyl alcohol, and caproic acid. As the conditions for the lactic and butyric fermentations, both as to temperature and absence of free oxygen, exist in the intestines, these fermentations take place there, the sugars, organic acids, soluble proteids, and mucus being the material acted upon. The products, as seen in the reactions above, are lactic and butyric acids and carbon dioxide and hydrogen gases. These gases distending the bowel produce the painful symptoms of colic, etc.

The effect of temperature upon the several ferments is shown in the graphic illustration Fig. 142, as well as the influence of temperature upon the decomposition of starch by diastase. On the right side of the figure the regularly-dotted line represents the yeast curve. As the temperature rises from 0° C. its activity increases until the maximum is reached at about 33° C., when it diminishes again, and at 50° or thereabouts it is killed. The activity of the acetic ferment is represented at the same time by the irregularly-dotted line, and that of the lactic ferment by the black line.

Fig. 142.

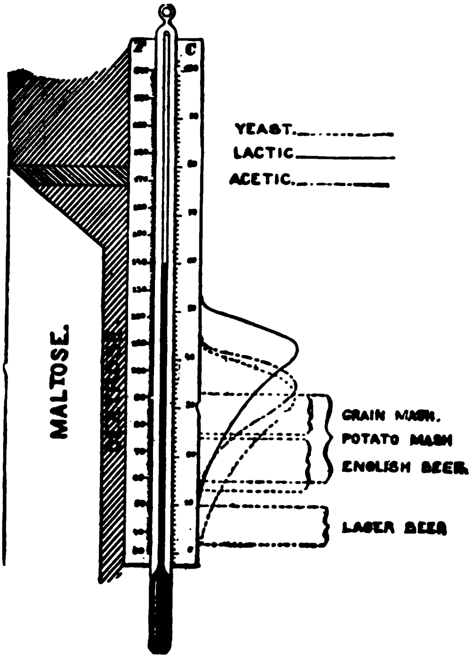


Diagram of temperatures.

FERMENTATION INDUSTRIES.

The most important industrial utilizations of the results of fermentation are those in which the alcoholic fermentation of sugar- and starch-containing materials enters.

1. The Malting and Brewing of Beer, Ale, etc.—Malt liquors, as they are termed, are the products of the fermentation of infusions of malted grain, flavored by the bitter extract from hops, and contain from 3 to 7 per cent. of alcohol, together with extractive matter made up of the peptones from the alteration of albuminoids and the carbohydrates from the alteration of the starch of the original grain. The malting process is carried out so as to allow the barley or other grain to germinate, whereby the character of the albuminoids is changed and the ferment diastase is developed, which then begins to act on the starch, the germination and change being stopped at a certain stage by heating in a kiln. Besides the diastase a second soluble ferment is formed during the malting process, the so-called "peptase," which in the mash process changes the proteids of the malt into peptones and para-peptones, which give nutritive value to beer. Wheat, corn, and rice are used at times as partial substitutes, but the bulk of the grain used is always barley. The finished malt is always yellow or amber-colored shading to brown. The crushed malt is then put through what is termed the mashing process, which is for the purpose of obtaining an infusion containing maltose and dextrine, as well as to allow the diastase to complete the hydrolysis of the starch, changing it into the products before described under the Carbohydrates. This infusion is then strained off and boiled while the hops are added. The "wort," as the liquid is now called, is then cooled, preparatory to the fermentation. This cooling is effected as rapidly as possible, so that the lactic fermentation and similar changes may not develop, and that the spores of foreign yeast ferments may not have access to the liquid. The thick magma of yeast-cells is then added in the proper amount and the fermentation started, which, as before stated, may be a surface fermentation or a bottom fermentation, according to the temperature and the character of the yeast used. The products differ according to the character of the malt used, whether light or dark, and the character of the fermentation, whether a rapid or a slow one.

2. The Manufacture of Wines.—While the name wine is often used to include products of the spontaneous alcoholic fermentation of any sweet fruit or berry, it is usually limited to the product of the fermentation of the grape, which alone is cultivated on an extensive scale throughout the civilized world for the manufacture of wine. The raw material here is the "must," or expressed juice of the grape, which may be fermented either alone or in contact with the "marc," as the pressed pulp and skins are called. The must contains: first, from 16 to 28 per cent. of fermentable sugar (a mixture of dextrose and levulose); non-nitrogenous extract (pectin substance and salts, chiefly of tartaric acid); albuminoids, and free acids (tartaric, malic, and succinic). The percentages of the sugar and the free acids are the most important elements in deciding the probable value of the wine obtainable from the must. The fermentation is a spontaneous one and a protracted one, as, after the full development of the alcoholic strength of the wine, it is left to ripen and develop by an after-fermentation the fruit essences or esters, which give the flavor and bouquet to the wine. In the case of red wines, the main fermentation is allowed to take place with the marc added to the must, so that as the alcohol is developed it may dissolve out the coloring matter of the skins as well as some of the tannin, which is of benefit in effecting a more rapid separation of the protein materials. During the secondary fermentation these deposit upon the inner walls of the storage casks *argols*, or impure acid potassium tartrate (German, weinstein), with some yeast and albuminoid matter. The first fermentation of the must lasts from 1 to 4 weeks, the secondary fermentation from 3 to 6 months, and then the wine is put into casks to ripen, which continues during from 2 to 8 years.

In the manufacture of champagnes and effervescing wines, after the secondary fermentation is nearly finished a mixture of alcohol and pure cane sugar is added, and the wine is bottled so that the supplementary fermentation may continue and develop alcohol and carbon dioxide again. The pressure which develops from this dissolved gas may rise to from 4 to 5 atmospheres.

The percentage of alcohol by weight in wines varies within wide limits, ranging from 5 per cent. in light Rhine wines to 18 per cent. in sherry and port wine.

3. The Manufacture of Distilled Liquors or Ardent Spirits.—In this industry the effort is made to push the fermentation to the fullest possible limit, so that the maximum quantity of alcohol may be produced, and then this product of fermentation is distilled, and it may be redistilled in order to get a distillate richer in alcohol than the fermentation product itself can be. The end product sought may be either an alcoholic beverage, which is the product of the distillation, or a raw spirit, which is then redistilled and strengthened until the "rectified spirit" is obtained, which is used as a basis of many lines of manufacture for the chemist and the pharmacist. The raw materials for this industry may be: first, alcoholic liquids themselves, products of fermentation, which are to be redistilled (such as wines used for manufacture of brandies); second, sugar-containing materials (such as cane-molasses used for manufacture of rum, and beet-molasses and sweet fruits used for fruit brandies); and third, starch-containing cereals and all materials capable of hydrolysis by diastase and fermentation (such as corn, rye, barley, rice, and potatoes). In case the last-named materials are used, the preparation of the wort is the first step. This is analogous to the method already described under malt liquors, except that the whole of the starch is to be converted if possible into maltose, which is directly fermentable, and the dextrine must be thoroughly changed into sugar. The fermentation of the distiller's wort is also somewhat different from that of the brewer, as the maximum percentage of alcohol is to be attained. The yeast is, therefore, a surface yeast, and a maximum temperature of 33° to 34° is attained.

In case molasses is to be fermented for rum, the fermentation is a spontaneous one, the nitrogenous matters present making the addition of yeast unnecessary.

The product of the first distillation of any of these thoroughly fermented mixtures, especially those obtained from grain mashes, is a "raw spirit," containing sharp, aldehydic constituents on the one hand, and higher alcohols (fusel oil) on the other hand, in addition to the ethyl alcohol. These are, as far as possible, to be eliminated or changed by the process of rectifying; and then by storage the supplementary changes of the higher alcohols into ethers are completed.

Rectified Spirit is the most concentrated alcohol obtainable by distillation. The U. S. Pharmacopœia, under **Alcohol**, U.S.P., calls for a spirit containing 92.3 per cent. by weight of real alcohol, and of sp. gr. 0.816 at 15° C.

Proof-Spirit has a sp. gr. of 0.9198 at 15.5° C. and according to Fownes contains 49.24 per cent. by weight of alcohol.

Brandy (formerly official) is, or should be, the direct product of the distillation of French wines. A great deal of it, however, is factitious, being mixtures of grain-spirit and water to which different coloring and aromatic substances have been added.

Whiskey (formerly official) is the spirit obtained from the fermented wort of corn, rye, and barley, either raw or malted.

Rum is a spirit obtained in the West Indies from the molasses of the sugar-cane by fermentation and distillation.

Gin is common grain-spirit distilled and aromatized with juniper berries.

4. **The Manufacture of Acetic Acid and Vinegars.**—The acetic ferment, as before stated, requires for its growth the presence of oxygen. When the germs coming from the air drop into a dilute alcoholic liquid which is suited for their growth they develop rapidly over the surface of the liquid and form a gelatinous skin, which thickens and falls to the bottom of the vessel because of its increasing weight. Another skin forms at once again, and this in turn is replaced by a third, and so on until the liquid is exhausted of assimilable material. This skin, called the "mother of vinegar," consists of a multitude of minute fissure ferments. The raw materials furnishing vinegar under the influence of the acetic fermentation are, first, wine; second, spirits; third, malt wort or beer; fourth fermented fruit juices other than wine; and fifth, sugar-beets. The wines used are those of inferior vintages and such as are unfit for drinking as wine. They should not exceed 10 per cent. in alcoholic strength. The spirits used for vinegar-making must be so diluted with water and vinegar already formed that the alcoholic strength ranges between 3 and 10 per cent. The malt wort used for malt vinegar is completely fermented and then passed through a filter of wood chips into the acetifier. Cider from apples and perry from pears are about the only fruit juices besides wine fermented for the production of vinegar. Sugar-beets are used somewhat in France for vinegar-making.

Three vinegar-making processes are in use with some special modifications. First, the Orleans process, in which a series of mother-casks, or "acetifiers" holding from fifty to one hundred gallons are used. These are partially filled with hot vinegar, and the wine is added in successive portions, and corresponding portions siphoned off into storage-vats at intervals. The wine vinegars obtained in this way have an agreeable aroma, that made from white wines being the most esteemed. The second process is the so-called "quick-vinegar process." It is used in Germany and this country for spirit vinegar, and in England for malt vinegar. The vinegar-former in this process is an upright cask. About a foot above the true bottom of the cask it has a perforated false bottom and the space between the false bottom and a wooden disk set in near the top is filed with beech-wood shavings. Just under the false bottom a series of holes is bored in the side of the cask extending all the way around. The shavings are first boiled in water and dried, then soured or soaked in warm vinegar for twenty-four hours before being put in the cask. Air circulates through the space filled with the beech shavings, entering through the holes below, and escaping through the glass tubes in the wooden disk above. The weak alcoholic liquid is then allowed to slowly trickle down through the shavings. The third process is Pasteur's process, using the vinegar fungus, or "mother of vinegar" directly, and causing it to propagate in a liquid containing suitable food (phosphates of potassium, magnesium, and lime).

Cider vinegar, as is well known, is the result of a spontaneous acetification. The different vinegars may contain from 3½ to 6 or even 8 per cent. of acetic acid. The other constituents vary with the different kinds of materials used in the vinegar formation.

Factitious vinegars are often made from pyroligneous acid flavored with acetic ether and colored with caramel color.

XI. Derivatives of Carbonic Acid.

Carbonic acid, $CO(OH)_2$, is not known in the free state, but is supposed to exist in aqueous solution in water charged with CO_2. Both this anhydride and the metallic salts of carbonic acid have already been discussed under Inorganic Chemistry, but a number of organic compounds may properly be considered as derivatives of it, and will be mentioned.

1. Sulphur Derivatives of Carbonic Acid.—From the anhydride carbon dioxide we have, by replacement with sulphur, two derivatives:

Carbon Oxysulphide, COS, is formed when a mixture of sulphur vapor and carbon monoxide is led through a red-hot tube, $CO + S = COS$; also by heating together urea and carbon disulphide, according to the reaction: $CO(NH_2)_2 + CS_2 = COS + NH_4CNS$.

Very inflammable gas, of peculiar odor, burning with blue flame.

Carbon Disulphide, CS_2 (**Carbonei Disulphidum,** U.S.P.), is formed by heating carbon in sulphur vapor. When pure, has but slight odor, and is a colorless, highly refractive liquid. After exposure to the light it takes a yellow color from liberation of sulphur, and develops an offensive odor. Boils at 47°, solidifies at —116°, and melts again at —110°. Easily soluble in alcohol, ether, chloroform, benzene, fixed and volatile oils; insoluble in water. Sp. gr. 1.268. Inflammable, burning with bluish flame. Is used for dissolving caoutchouc and for the extraction of fats and fatty oils from oil seeds and from bones and wool.

Three thio-carbonic acids are possible, $CS\left\{\begin{matrix}SH\\SH\end{matrix}\right.$, $CO\left\{\begin{matrix}SH\\SH\end{matrix}\right.$, and $CS\left\{\begin{matrix}SH\\OH\end{matrix}\right.$. Of these, it is only necessary to consider the last, derivatives of which possess some importance. The ethyl derivative of this acid is called

Xanthogenic Acid, $CS\left\{\begin{matrix}SH\\OC_2H_5\end{matrix}\right.$. The potassium salt of this acid is formed when carbon disulphide is added to alcoholic potash solution. This salt, $CS\left\{\begin{matrix}SK\\OC_2H_5\end{matrix}\right.$, is used extensively as an antidote for the *phylloxera* insect in the disease of grape-vines and in the manufacture of artificial indigo. The copper salt, known also as "cuprous xanthate," is a yellow, insoluble compound, the formation of which serves as a characteristic test for carbon disulphide.

2. **Esters of Carbonic Acid.**—Both the neutral ester, $CO(OC_2H_5)_2$, known as ethyl carbonate, and the acid ester, $CO\left\{\begin{matrix}OH\\OC_2H_5\end{matrix}\right.$, known as ethyl-carbonic acid, are known. The former is a neutral liquid of agreeable odor, lighter than water, and insoluble in the latter. Boils at 126°. The latter is the counterpart of ethyl-sulphuric (sulphovinic) acid, and is not known in the free state, but only in its salts.

3. **Chlorides of Carbonic Acid.**—From the anhydride carbon dioxide we have the derivative *carbon oxychloride*, $COCl_2$. It is obtained by direct combination of carbon monoxide and chlorine in sunlight, and also by the oxidation of chloroform by means of chromic acid. It is a colorless gas (known also as phosgene gas), condensing to a liquid below 8°, and of powerful, suffocating odor. It is employed in the preparation of salicylic acid from benzene.

Chloro-carbonic Acid, $COCl(OH)$, is the acid chloride of carbonic acid. Both the free acid and the metallic salts are unstable, and cannot be obtained. Its esters, however, can be prepared, as $COCl(OC_2H_5)$, which is obtained by the action of phosgene gas upon absolute alcohol.

4. **Amides of Carbonic Acid.**—From carbonic acid we may obtain two amides, both compounds of importance, $CO\left\{\begin{matrix}OH\\NH_2\end{matrix}\right.$, known as carbamic acid, and $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, carbamide, or urea.

Carbamic Acid, $CO(NH_2)OH$, is not known in the free state. The alkaline and alkaline earth-salts, however, are well known. The ammonium salt is recognized as present in the official **Ammonii Carbonas,** U.S.P. It results whenever dry carbon dioxide and ammonia gases are allowed to react on each other: $CO_2 + 2NH_3 = CO\left\{\begin{matrix}ONH_4\\NH_2\end{matrix}\right.$. When heated it loses a molecule of water and urea is formed. The esters of carbamic acid are sometimes called *Urethanes*.

Ethyl-urethane, $CO\left\{\begin{matrix}OC_2H_5\\NH_2\end{matrix}\right.$. (**Æthylis Carbamas,** U.S.P.).—This is the compound usually known under the simple name of "Urethane." It is formed by the action of an excess of alcohol upon urea nitrate in closed vessels at a temperature of 120°–130°, the products of the reaction being ammonium nitrate and ethyl urethane. It forms colorless, prismatic crystals, fusing at 47°–50°, which are odorless, and have a cooling, saline taste. Soluble in water, alcohol, and ether. Is used as a soporific.

Chloral-urethane (or Uraline), *Somnal* (a solution of chloral hydrate and urethane in alcohol), and *Phenyl-urethane* (or Euphorine) are other preparations of the urethane class.

Urea (or Carbamide), $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, is found in human urine, in that of other mammalia, birds, reptiles, and fishes. A grown man produces about 30 gms. daily. It is the final decomposition product from the oxidation of the nitrogenous compounds in the organism. It is also found in the blood, serous fluids, aqueous humor, milk, and perspiration. It was the product of the first organic synthesis made by Wöhler in 1828, who, on evaporation to dryness of an aqueous solution of ammonium cyanate, obtained urea by molecular rearrangement: $CNONH_4 = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$. It may also be formed from ammonium carbamate, from ammonia and phosgene gas, from cyanamide and water and from alkaline cyanides by the process of Buchner recently published. The reactions are $NaCN + \text{air} = NaCNO + 2H_2$ and $NaCNO + NH_3 + H_2O + CO_2 = NaHCO_3 + CO(NH_2)_2$. This latter process is now being developed on an industrial scale. It may be obtained from urine by adding nitric acid, separating the crystals of urea nitrate, and decomposing these with barium carbonate. Urea forms quadratic prisms, melting at 132°, easily soluble in water and alcohol, but not in ether or chloroform. Urea forms crystalline compounds with both bases and acids, as well as with salts.

Urea is recognized by several characteristic tests. The addition of mercuric nitrate to dilute solutions containing urea causes a white precipitate of a urea-mercuric nitrate compound; if urea crystals be touched with a drop of a concentrated aqueous solution of furfurol, and then a drop of strong hydrochloric acid, a violet color passing into purplish-violet is produced.

Urea may be determined quantitatively when in solution in several ways. First, by the aid of a standard solution of mercuric nitrate (1 c.c. of which corresponds to 0.01 gm. of urea). To a measured volume of the urea solution the mercuric nitrate solution is added until all the urea has been precipitated as the double salt ($2CN_2H_4O,Hg(NO_3)_2,3HgO$) and a slight excess of mercury is in the solution. This is recognized by addition of a drop of caustic soda, which gives a yellow precipitate when the mercury is in excess, but a white one as long as urea is present in the solution. This is known as Liebig's method. Second, to the urea solution (urine) is added sodium hypobromite, and the nitrogen evolved is collected in a suitable apparatus and measured. The reaction is: $CON_2H_4 + 3NaOBr = N_2 + Na_2CO_3 + NaBr + 2HBr + H_2O$. This is known as Hüfner's method.

Biuret, $C_2H_5N_3O_2$, results when urea is heated to 150°–170°, ammonia splitting off. Forms long needles, fusing at 190°. When it is dissolved in caustic soda and a little cupric sulphate is added, an onion-red to violet color is obtained, known as the "biuret reaction." This reaction is also given by peptones and by albuminoids after boiling with alkalies.

Thio-urea (Sulphurea), $CS\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, is formed from ammonium sulphocyanate by prolonged fusion, a molecular rearrangement taking place. $CNS.NH_{41} = CS(NH_2)_2$. Heavy rhombic prisms, melting at 172°.

Sucrol (or Dulcin), $CO\left\{\begin{matrix}NH_2\\NH.C_6H_4OC_2H_5\end{matrix}\right.$.—This is urea in which a hydrogen atom is replaced by the *p-phenetol* radicle (see Aromatic Compounds). This compound has been brought forward in medicine as a substitute for "saccharin," to be used for sweetening in foods for diabetic and similar cases. It is claimed to be free from influence upon the circulation, the respiration, the nerves, and the digestive organs. 0.025 gram of the sucrol is said to equal 5 grams of cane sugar in sweetening power.

The entrance of acid radicles in place of one or more hydrogen atoms of urea gives rise to the important classes of *Ureïdes.* When boiled with alkalies (saponified) they decompose into urea and the acid of which the radicle was present. We may distinguish the two classes, *Monureïdes* and *Diureïdes,* according as one or two molecules of urea are present in combination. Of the latter class are a number of compounds which exist ready formed in the vegetable or animal kingdom, such as xanthine, hypo-xanthine, theobromine, caffeine, allatoïn, and uric acid.

Hydantoïn (Glycolyl-urea), $C_3H_4N_2O_2$, belongs to the class of monureïdes. It is formed by the action of concentrated hydrogen iodide upon allantoïn. (See above.) Forms needles, fusing at 215°, easily soluble in hot water.

Hydantoïc Acid (Glycoluric Acid), $C_3H_6N_2O_3$, is formed by boiling hydantoïn with baryta water or heating urea with glycocoll to 120°–125°. Forms prisms readily soluble in hot water.

Methylhydantoïn, $C_4H_6N_2O_2$, is formed by fusing together urea and sarcosine (methyl-glycocoll), or by heating creatine with baryta water.

Barbituric Acid (Malonyl-urea), $C_4H_4N_2O_3$, is formed by heating malonic acid and urea in the presence of phosphorus oxychloride, which acts as a dehydrating agent. Forms prisms readily soluble in hot water. Boiled with alkalies it decomposes into urea and malonic acid.

Diethyl-barbituric acid (*veronal*) and sodium dimethyl-barbituric acid (*veronal sodium*) have been extensively used as soporifics.

Alloxan (Mesoxalyl-urea), $C_4H_2N_2O_4$, results from the oxidation of uric acid with nitric acid. On further oxidation yields parabanic oxide and carbon dioxide. Decomposes on boiling with alkalies into mesoxalic acid and urea. Alloxan colors the skin purplish-red and imparts to it an unpleasant odor. By reduction with the aid of H_2S it is changed into *Alloxantin,* $C_8H_4N_4O_7$. This attracts oxygen from the air and changes into *Murexide* (Ammonium Purpurate), $C_8H_4(NH_4)N_5O_6$.

Alloxantic Acid (Mesoxaluric Acid), $C_4H_4N_2O_5$, is formed from alloxan by boiling with baryta water. Decomposes on boiling into mesoxalic acid and urea.

Of the Diureïdes, or compounds formed from two molecules of urea, the most important is *Uric Acid,* $C_5H_4N_4O_3$. It is found in urine. The urine of a healthy man contains daily from 0.4 to 0.8 gm. of uric acid. It is, however, especially to be found in the excrements of birds and reptiles, which often consist largely of uric acid and alkaline urates. It is wanting in normal blood, but may be present here under pathological conditions. Gouty concretions and urinary calculi are composed in part of urates. It is usually extracted from the excrement of serpents or guano by the aid of caustic soda, and the free uric acid precipitated from the filtered solution on addition of hydrochloric acid. Insoluble in cold water; difficultly soluble in hot water; insoluble in alcohol and ether. It is soluble in hot solutions of sodium phosphate and acetate, in concentrated sulphuric acid, and in glycerin. A hot, aqueous solution of lithium carbonate also dissolves it abundantly.

Salts of Uric Acid.—Uric acid is a weak, dibasic acid, and forms difficultly soluble salts. ***Acid ammonium urate***, $C_5H_2(NH_4)N_4O_3$, is found frequently in calculi from the bladder and kidneys, in the urine of birds and amphibia, and in human urine as a sediment after fermentation begins. ***Acid sodium urate*** is a chief constituent of the excrement of serpents. It is also found as a sediment in urine, and is recognized by its brick-red color. ***Acid potassium urate*** is also found in urinary sediment. The most characteristic test for the recognition of uric acid is the ***murexide test***. The substance is evaporated with a little nitric acid, leaving a yellowish or reddish residue. After cooling, this is moistened with a little ammonia, when the purplish-red color of murexide (acid ammonium purpurate) is developed. A drop of potassium or sodium hydroxide changes this color to the blue color of the potassium or sodium purpurate.

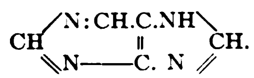
Carnine is supposed to be dimethyl-uric acid, $C_5H_2(CH_3)_2N_4O_3$. It is found to the amount of 1 per cent. in Liebig's extract of meat.

Fischer has shown that uric acid and a large number of related compounds are derivatives of a common substance called *purine*, $C_5H_4N_4$, which has been obtained from uric acid by the action of $POCl_3$ followed by treatment with nascent hydrogen.

Purine is a white crystalline substance melting at 216°–217° C. and easily soluble in water. It acts like a weak base. Uric acid is therefore a trioxypurine.

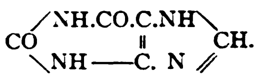
This important relationship of purine, xanthine and uric acid is best shown by the use of the graphic formulas:

Purine:



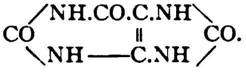
$$\mathrm{CH}\begin{array}{l}\diagup\mathrm{N{:}CH.C.NH}\diagdown\\ \qquad\qquad\ \|\\ \diagdown\!\!\diagdown\mathrm{N}\text{——}\mathrm{C.\ N}\diagup\!\!\diagup\end{array}\mathrm{CH.}$$

Xanthine:



$$\mathrm{CO}\begin{array}{l}\diagup\mathrm{NH.CO.C.NH}\diagdown\\ \qquad\qquad\quad \|\\ \diagdown\mathrm{NH}\text{——}\mathrm{C.\ N}\diagup\!\!\diagup\end{array}\mathrm{CH.}$$

Uric acid:



$$\mathrm{CO}\begin{array}{l}\diagup\mathrm{NH.CO.C.NH}\diagdown\\ \qquad\qquad\quad \|\\ \diagdown\mathrm{NH}\text{——}\mathrm{C.NH}\diagup\end{array}\mathrm{CO.}$$

Xanthine, $C_5H_4N_4O_2$ (Dioxypurine), is found in small amount in urine and in the organs of the animal body. Also in certain plants, as in tea, malted barley, mould growths, etc. It is formed from guanine by the action of nitrous acid. Its lead compound, $C_5H_2PbN_4O_2$, is changed by the action of methyl iodide into theobromine.

Guanine (Imidoxanthine), $C_5H_5N_5O$, is found in guano and in the muscles, pancreas, spleen, liver, lungs, and retina, and in the excrement of snails, scorpions, and cephalopods. It is also found in plants, in the young sprouts of grass, oats, etc. Forms a white, chalk-like powder, insoluble in water, soluble in ammonia.

Theophylline (**Theophyllina,** U.S.P.) is 1 : 3 Dimethylxanthine. It occurs in tea leaves and has recently been made on a large scale synthetically and introduced into medicine.

Theobromine (3 : 7 Dimethylxanthine), $C_5H_2(CH_3)_2N_4O_2$, is found in cacao beans (the fruit of *Theobroma cacao*) to the amount of 1.5 per cent. As before stated, it may also be made synthetically from xanthine. Colorless, microscopical crystals of bitter taste, subliming undecomposed at 290°–295°.

An official salt is **Theobrominæ sodio-salicylas,** U.S.P.

Caffeine (or Theine) is Trimethylxanthine, $C_5H(CH_3)_3N_4O_2$ (**Caffeina,** U.S.P.). It is found in almost all parts of the coffee-tree, the seeds containing 2 per cent. and the leaves 1¼ per cent.; in the leaves of the tea-plant; in the leaves and twigs of Paraguay tea (*maté*), and in kola nuts. Forms long needles of a silky lustre, subliming at 180° and fusing at 234°–235°. Is decomposed by chlorine into dimethyl-alloxan and methyl-urea. Difficultly soluble in cold water; easily soluble in hot water and in chloroform.

Other official preparations of caffeine are: *Caffeina citrata* and *Caffeinæ sodio-benzoas.*

Hypoxanthine or Sarcine (Oxypurine), $C_5H_4N_4O$, is found in small amount in normal urine. Also in different organs of the body and in plants, as in yeast-cells, lycopodium, germinating seeds, etc.

Adenin (Amidopurine), $C_5H_5N_5$, is found in the pancreas, in the spleen, and in tea-leaves. Formed also by boiling yeast with dilute sulphuric acid. The action of nitrous acid changes it into hypoxanthine.

5. **Amidines of Carbonic Acid.**—When the oxygen of the carbonyl group in urea is replaced by the imido group NH, we have $C(NH)<^{NH_2}_{NH_2}$. This compound is *Guanidine,* CH_5N_3. Readily deliquescing crystalline mass, absorbing carbon dioxide from the air.

By the replacement of hydrogen atoms in guanidine by acid radicles we obtain derivatives analogous to the ureïdes derived from urea.

Glycocyamine (Guanidine-acetic Acid), $C_3H_7N_3O_2$.—From the addition of cyanamide to glycocoll, or from guanidine carbonate and glycocoll.

Creatine (Methyl-glycocyamine), $C_4H_9N_3O_2$, is found in the muscular juice of many animals, even invertebrates, in the blood, and in serous fluids. It may be formed also by the addition of cyanamide to sarcosine (methyl-glycocoll). Is chiefly obtained from extract of meat.

Creatinine (Anhydride of Creatine), $C_4H_7N_3O$, is formed by boiling creatine with acids. Is found also in the urine. It combines with acids and salts. A characteristic compound is that formed with chloride of zinc, difficultly soluble in water, almost insoluble in alcohol.

XII. CYANOGEN AND ITS DERIVATIVES.

The cyanogen compounds contain the monad radicle $(CN)^1$. The free molecule of cyanogen, like the molecule of chlorine, must be double this atomic group.

Cyanogen, $\begin{array}{c}CN\\ |\\ CN\end{array}$ or $(CN)_2$, is found free in the gases of blast-furnaces, and is formed when the electric spark is passed between carbon points in an atmosphere of nitrogen. May be conveniently prepared by heating oxalate of ammonium: $C_2O_4(NH_4)_2 = (CN)_2 + 4H_2O$, or by heating mercuric cyanide.

Colorless gas, with peculiar penetrating odor resembling bitter almonds. Very poisonous. It burns with a peach-red color. Is soluble in water and alcohol. These solutions become dark on standing, with separation of a brown powder, known as azulmic acid, while oxalic acid, ammonia, formic and hydrocyanic acids, and urea are found in the liquid.

Paracyanogen $(CN)_x$, is a polymer of cyanogen, and is formed as a by-product when cyanogen is made from mercuric cyanide.

1. **Hydrogen Cyanide and other Cyanides.**—The union of the radicle CN with hydrogen gives us a compound, HCN, analogous to HCl or HBr in its general chemical relations.

Hydrogen Cyanide (Prussic Acid), HCN, is a decomposition product from many organic compounds, as amygdalin of bitter almonds, etc. May be prepared by the decomposition of metallic cyanides (whether simple or double salts) with mineral acids; usually prepared thus from potassium ferrocyanide (see next page): $K_4Fe(CN)_6 + 5H_2SO_4 = 6HCN + FeSO_4 + 4KHSO_4$.

Is a colorless liquid, solidifying at —15° and boiling at 26.5°. It is miscible with water, and burns with a violet flame. It is a deadly poison.

When absolutely pure it can be preserved, but in the presence of traces of water or ammonia it decomposes on standing, separating out brown flocks of azulmic acid. The addition of small quantities of mineral acids renders the aqueous solution more stable. Its dilute aqueous solution is official as **Acidum Hydrocyanicum Dilutum,** U.S.P., and contains about 2 per cent. by weight of absolute HCN.

Hydrocyanic acid is a weak monobasic acid, and forms numerous metallic cyanides. The most important are:

Potassium Cyanide is obtained commercially by fusion of anhydrous potassium ferrocyanide: $K_4Fe(CN)_6 = 4KCN + Fe + 2C + N_2$ by the Frank-Erlwein process of fusing two mols. calcium cyanide with alkali, or by heating potassium carbonate with carbon in a current of ammonia. Forms colorless deliquescent cubes, readily soluble in water, but only slightly so in alcohol. Acts as a reducing agent, taking oxygen and becoming cyanate. Is used for the reduction of metallic oxides, in photography to dissolve the haloid silver salts and silver stains, and in galvanoplastic work for electro-silvering and gilding.

Sodii Cyanidum, U.S.P., forms white opaque masses, odorless when dry, deliquescent in the air and developing the odor of HCN. Readily soluble in water. It is made mainly by the Castner process of treating a mixture of metallic sodium and carbon in a current of ammonia to produce sodium cyanamide, which at a higher temperature decomposes into sodium cyanide and carbon.

Silver Cyanide forms a white powder, odorless and tasteless, turning brown on exposure to light. *Mercuric Cyanide,* forms colorless prisms, soluble in water and alcohol. When heated in a glass tube the salt decrepitates and decomposes, giving off cyanogen gas and leaving metallic mercury.

The soluble metallic cyanides, like potassium cyanide, dissolve the insoluble cyanides, and then double cyanides are formed. There are two classes of these double cyanides, distinguished by their behavior on addition of dilute mineral acids. One class, like the double cyanides of potassium and silver, gold, zinc, nickel, etc., break up with separation of the insoluble cyanide and liberation of hydrogen cyanide; the other class do not liberate HCN, but a complex acid is formed in which the CN group is combined with hydrogen and the heavy metal. Thus, $K_4Fe(CN)_6$ is potassium ferrocyanide, and on addition of dilute acid liberates $H_4Fe(CN)_6$, called hydrogen ferrocyanide, and $K_3Fe(CN)_6$, which may be taken as the equivalent of the formula of potassium ferricyanide, on addition of dilute acid liberates $H_3Fe(CN)_6$, called hydrogen ferricyanide. Similar double cyanides with the metal remaining as an integral part of the free acid are formed with manganese and cobalt.

Potassium Ferrocyanide (Yellow Prussiate of Potash), $K_4Fe(CN)_6 + 3H_2O$ (**Potassii Ferrocyanidum**, U.S.P.), was made on a large scale by fusing animal scrap, like horns and hoofs of cattle, blood, leather, etc., with potashes, and adding metallic iron. The fused mass is lixiviated with water, filtered, and crystallized. The reactions which take place may be expressed thus:

$$4C + 2N + K_2CO_3 = 2KCN + 3CO$$
$$6KCN + FeS = K_4Fe(CN)_6 + K_2S.$$

Very much is now obtained from the ferric hydroxide used in the purification of illuminating gas. It forms yellow crystals of the tetagonal system, easily soluble in water, insoluble in alcohol. It is not poisonous. Oxidizing agents like chlorine convert it when in solution into ferricyanide of potassium. With ferric salts it yields an insoluble blue compound, ferric ferrocyanide, known as "Prussian blue," $Fe_4[Fe(CN)_6]_3$. Other insoluble ferrocyanides are those of copper, which is brown, and zinc, which is white. Yellow prussiate of potassium is used technically in the manufacture of Prussian blue, of potassium cyanide, and of hydrogen cyanide.

Potassium Ferricyanide (Red Prussiate of Potash), $K_6Fe_2(CN)_{12}$, is produced by oxidizing the ferrocyanide in solution. Forms red, rhombic crystals, readily soluble in water. The solution gradually decomposes in the light with the formation of the yellow prussiate. In the presence of free alkali it has an oxidizing action, and is changed thereby into the yellow prussiate. With ferrous salts forms a blue precipitate, ferrous ferricyanide (Turnbull's blue).

By the action of nitric acid upon ferrocyanides are formed nitroprussides.

Sodium Nitroprusside, $Na_2Fe(CN)_5(NO) + 2H_2O$, crystallizes in red prisms, readily soluble in water. Serves as a delicate test for soluble sulphides even in dilute solution, giving a fine but transient purplish color.

The cyanides in which an alcohol radical replaces the hydrogen of HCN form two series isomeric with each other, known as the *Nitriles* and the *Isonitriles*. This isomerism is explained by the assumption that in the nitriles the atoms in the CN group are linked in one way, $N \equiv C-$, and in the isonitriles they are linked in another way, $C \equiv N-$, the nitrogen being triad in the one class and pentad in the other. To the first class belong methyl cyanide or acetonitrile, $CH_3.CN$, ethyl cyanide or propionitrile, C_2H_5CN, etc. These form an homologous series, it is seen, with HCN, which might be called formonitrile. They are all poisonous liquids.

A nitro product of methyl cyanide is the very unstable *fulminic acid*, $CH_2(NO_2).CN$, the mercury salt of which is obtained when a solution of mercuric nitrate reacts with alcohol, and is known as *fulminate of mercury*. This is also explosive, and is used for percussion caps and for fuses to explode dynamite cartridges.

The Isocyanides or Isonitriles differ in many respects from the corresponding cyanides. They are liquids of extremely sickening odor, but are *not* poisonous like the cyanides. They are sometimes called *carbylamines*, as $CH_3.NC$, methyl isocyanide, or methyl carbylamine. The production of one of this class, phenyl carbylamine, when chloroform is heated with aniline and alcoholic potash, was given as a test under Chloroform (see p. 531).

2. Cyanic and Cyanuric Acids.—By the replacement of an H atom in HCN by the group OH we obtain CN.OH. This compound is not known in the free state, but only in its esters. The isomeric compound, CO.NH, however, is known as *Isocyanic Acid*, a very unstable, volatile liquid, which readily polymerizes, and yields Cyanuric Acid, $(CONH)_3$, and *Cyamelide*, $(CONH)_x$.

Potassium Isocyanate (commonly called Cyanate), CONK, is obtained by fusing potassium cyanide or yellow prussiate of potash with metallic lead or manganese peroxide. Forms white scales, easily soluble in water and alcohol.

Ammonium Isocyanate (commonly called Cyanate), $CON.NH_4$, is a white, crystalline mass, which changes on heating into the isomeric compound urea, $CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$. (See p. 604.)

3. Sulphocyanic and Isosulphocyanic Acids.—Corresponding to cyanic and isocyanic acids are the sulphur compounds $N \equiv C-SH$, sulphocyanic acid, and CS.NH, isosulphocyanic acid. The metallic salts are derivatives of the first of these.

Potassium Sulphocyanate, CNSK, is readily obtained by fusing ferrocyanide of potassium with sulphur and potash. Colorless, deliquescent prisms, soluble in water, with considerable lowering of temperature.

Ammonium Sulphocyanate, $CN.SNH_4$, is obtained by the action of carbon disulphide upon concentrated ammonia in alkaline solution. Colorless, deliquescent prisms, easily soluble in water. These sulphocyanates are used as reagents to distinguish ferric from ferrous solutions, giving with the former blood-red coloration, while remaining colorless with the latter.

Mercuric Sulphocyanate, $(CN.S)_2Hg$, is a white, insoluble powder. When heated, swells up enormously as it is decomposed. Used in toys known as "Pharaoh's serpents."

Of the esters two series are known, the Sulphocyanates and the Isosulphocyanates. To the first class belong *Ethyl Sulphocyanate*, $CN.SC_2H_5$, and *Allyl Sulphocyanate*, $CN.SC_3H_5$. This latter is the starting-point in the manufacture of artificial mustard oil. By the action of allyl iodide on an alcoholic solution of potassium sulphocyanate this sulphocyanate of allyl is made. It is then distilled, when, by molecular rearrangement, it becomes *Allyl Isosulphocyanate*, $CS.NC_3H_5$, or true mustard oil (**Oleum Sinapis Volatile,** U.S.P.). It is also obtained from the seeds of the black mustard by distillation with water. It forms a liquid slightly soluble in water, of irritating odor, inciting to tears and producing blisters upon the skin. Boils at 151°.

The esters of isosulphocyanic acid are often known collectively as "mustard oils." Thus, we have *methyl-mustard oil*, $CS.NCH_3$; *ethyl-mustard oil*, $CS.NC_2H_5$; *n-propyl-mustard oil*, $CS.NC_3H_7$.

4. **Amides of Cyanogen.**—The only important compound in this series is *Cyanamide*, $CN.NH_2$. May be formed by the action of ammonia upon cyanogen chloride in ethereal solution. Colorless, deliquescent crystals, easily soluble in water, alcohol, and ether. By the action of dilute acids it takes up the elements of water and becomes urea: $CN.NH_2 + H_2O = CO\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$, and in analogous manner it takes up H_2S and becomes sulphurea, $CS\left\{\begin{matrix}NH_2\\NH_2\end{matrix}\right.$. When heated with ammonia salts it yields salts of guanidine.

A metallic derivative of cyanamide known as *Calcium cyanamide*, $CaCN_2$, was found by Frank to be formed by the action of atmospheric nitrogen upon red hot calcium carbide, according to the reaction: $CaC_2 + N_2 = CaCN_2 + C$. This compound has assumed great commercial importance both for direct use as a fertilizer and because it liberates ammonia under the influence of steam at a high temperature according to the reaction:

$$CaCN_2 + 3H_2O = 2NH_3 + CaCO_3.$$

CHAPTER IV.

CLOSED-CHAIN GROUPS WITH LESS THAN SIX CARBON ATOMS.

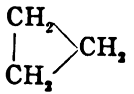
THE compounds thus far considered were all derivatives of methane and the similar hydrocarbons, which, whether saturated or unsaturated, had the one feature in common, that they were *open-chain* hydrocarbons; that is, aggregates of carbon atoms linked together in such a way that the end carbon atoms were distinguished from those occupying a middle position in the molecular grouping.

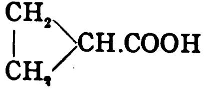
For benzene and the so-called "aromatic compounds," on the other hand, we must assume that the molecule contains six carbon atoms linked together in a closed chain, so that no one of the six is an end carbon atom. The presumptions in favor of this theory will be stated in the next chapter. We have, however, several classes of transition compounds from the open-chain compounds to the closed-chain compounds of the benzene series.

We have first, certain *isocyclic* (see p. 516) compounds containing less than six atoms of carbon in the closed chain or ring, and second, certain *heterocyclic* (see p. 516) compounds containing also a lesser number of carbon atoms.

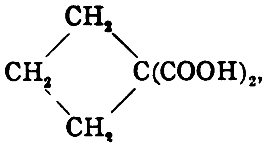
I. Isocyclic Compounds.

1. *Trimethylene* (Cyclopropane) *derivatives.*

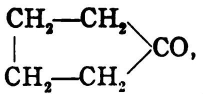
Trimethylene,  is obtained by the action of sodium upon trimethylene bromide, $CH_2Br.CH_2.CH_2Br$.

Trimethylene carboxylic acid,  is also known.

2. *Tetramethylene* (Cyclobutane) *derivatives.*

Tetramethylene itself is not known, but *tetramethylene-dicarboxylic acid,*  has been obtained.

3. *Pentamethylene* (Cyclopentane) *derivatives.*

Keto-pentamethylene,  is obtained by the dry distillation of the calcium salt of adipic acid. From this is then obtained—

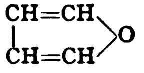
Pentamethylene, which is a colorless liquid boiling at 50° C.

4. *Hexamethylene* derivatives will be described later as obtained from the benzene hydrocarbons.

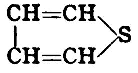
II. Heterocyclic Compounds.

We have to note here three compounds which show this transition character. These are *Furfurane* (or *Furane*), C_4H_4O, *Thiophene*, C_4H_4S, and *Pyrrol*, C_4H_4NH. Of these, the first is most nearly related to the methane derivatives, being formed in many cases in the decomposition of the sugars and carbohydrates, and the other two accompany benzene in the products of destructive distillation, and more nearly resemble the true aromatic compounds. The structural formulas given to the three compounds show a close similarity and relationship, and the fact that all three may be derived from the same compounds by three different reactions goes to establish this relationship.

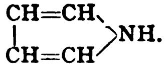
The formulas ascribed to them are:



Furfurane.



Thiophene.



Pyrrol.

All three are liquids, boiling at relatively low temperatures,—furfurane at 32°, thiophene at 84°, and pyrrol at 130°.

All three are insoluble, or only slightly soluble, in water, but easily soluble in alcohol and ether. They show analogous color reactions. All three give blue or violet coloring matters with isatin and sulphuric acid; the vapor of pyrrol colors a pine shaving that has been moistened with HCl carmine-red (whence the name, from πυρρός, fiery-red), while furfurol vapor colors it an emerald-green.

All three are derived from mucic acid by different reactions. Mucic acid destructively distilled yields first pyromucic acid (furfurane-carboxylic acid), $C_4H_3O(COOH)$, and this on further heating splits off CO_2, and yields furfurane; by the dry distillation of ammonium pyromucate is obtained pyrrol; and by the action of hydrogen sulphide upon pyromucic acid is formed thiophene.

Similarly all three are derived from acetonyl-acetone by different reactions, and both pyrrol and thiophene from succinic acid by the action of different reagents.

1. Furfurane and its Derivatives.—*Furfurane* (or *Furane*), C_4H_4O, is formed by the distillation of pine wood. Is a colorless, mobile liquid of chloroform-like odor, boiling at 32°. It is recognized by the emerald-green color which it imparts to a pine shaving which has been moistened with hydrochloric acid. Besides furfurane, methyl-furfurane appears to be present also in pine-wood tar.

Furfurol (Furfurane Aldehyde), $C_4H_3O.COH$, results from the oxidation of the sugars with manganese dioxide and sulphuric acid, as well as from the distillation of the pentoses, bran, sawdust, starch, gum arabic, etc., with sulphuric acid. It is contained in beer and in fusel oil, and hence in brandy. It is also a decomposition product of the albuminoids. It is a colorless oil boiling at 162° C., of agreeable odor, resembling that of bitter almonds, turning brown in the air. As an aldehyde it reduces ammoniacal silver solution.

Pyromucic Acid, $C_4H_3O.COOH$, is the acid corresponding, and is produced by the oxidation of furfurol as well as in the dry distillation of mucic acid. Needles or plates, melting at 134°, resembling benzoic acid in appearance.

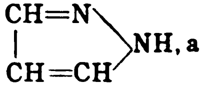
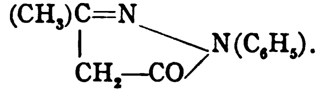
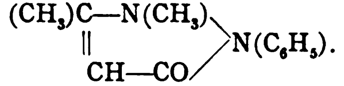
2. **Thiophene and its Derivatives.**—*Thiophene*, C_4H_4S, accompanies benzene, C_6H_6, in coal-tar, and is only separated from it with difficulty. Its homologues likewise accompany those of benzene, displaying nearly the same boiling points and many similar reactions. It is separated from the crude benzene of coal-tar by shaking out with successive quantities of concentrated sulphuric acid, in which it is soluble. Is a liquid of weak odor, boiling at 84°. The most delicate test for it is the blue color due to the formation of indophenin, obtained on shaking a solution containing it with sulphuric acid and isatin.

Two thiophene derivatives have been recommended for use in medicine: *Thiophene Di-iodide*, $C_4H_2I_2S$, and *Sodium Thiophene-sulphonate*, C_4H_3-$S.SO_3Na$.—The former, which is recommended as a substitute for iodoform, is in colorless, readily volatile crystals, melting at 40.5° C. The odor is aromatic but not unpleasant. It is insoluble in water, but easily soluble in ether, chloroform, and in hot alcohol. It contains 75.5 per cent. of iodine and 9.5 per cent. of sulphur. The second compound is a white, crystalline powder, recommended for use in salve in cases of prurigo.

3. **Pyrrol and its Derivatives.**—*Pyrrol*, C_4H_4NH, is obtained in the dry distillation of bones and in coal-tar. It is a liquid, boiling at 130°, and smelling like chloroform. Is insoluble in water and alkalies, soluble in alcohol, ether, and dilute acids.

Tetra-iodopyrrol or *Iodol* (**Iodolum**, U.S.P.), C_4I_4NH.—When iodine in alcoholic solution acts upon pyrrol, especially in the presence of an alkali, a substitution compound, to which the name of iodol has been given, separates out in a grayish-brown, crystalline powder, insoluble in water, soluble in alcohol. It is used as an odorless substitute for iodoform, and is especially characterized by its high percentage of iodine (88.97 per cent.).

Pyrazol, $C_3H_4N_2$. By the action of hydrazine, $NH_2.NH_2$, upon epichlorhydrin, $(C_3H_5)OCl$, is formed pyrazol, a crystalline solid melting at 70° C., which may be considered as pyrrol with one CH group replaced by N.

Antipyrin or *Phenyl-dimethyl-pyrazolon* (**Antipyrina**, U.S.P.), $C_{11}H_{12}$-N_2O.—By the action of phenyl-hydrazine, $C_6H_5.NH.NH_2$, upon aceto-acetic ether (see p. 568) water and a molecule of alcohol are split off, and a compound is obtained which is called phenyl-methyl-pyrazolon. This would be a derivative of the base pyrazol,  a compound differing from pyrrol only in the substitution of the nitrogen atom for the triad group CH. In the phenyl-methyl-pyrazolon we would have besides the substitution of the radicals phenyl and methyl the change of a CH group for the dyad group CO, making its structural formula  When this is methylated by the action of methyl iodide, there is formed the hydrogen iodide compound of the new base phenyl-dimethyl-pyrazolon, which possesses the structural formula 

The free base comes into commerce as a white, crystalline powder, melting at 113°, almost odorless, easily soluble in water, alcohol, chloroform, difficultly soluble in ether. As a base it forms addition salts with the acids like ammonia. It shows two characteristic color reactions: with ferric chloride it is colored deep red, which color is changed by sulphuric acid into bright yellow; with nitrous acid a green color, and in concentrated solutions a separation of green crystals of isonitroso-antipyrin, $C_{11}H_{11}N_3O_2$. Both these reactions are adapted for the recognition of antipyrin in urine.

***Pyramidon,* $C_{13}H_{17}N_3O$.—By reducing isonitroso-antipyrin and methyl**ating the product is obtained pyramidon as a colorless crystalline powder somewhat soluble in water. Is an antipyretic resembling antipyrin.

Antipyrin Salicylate (Salipyrin), $C_{11}H_{12}N_2O.C_7H_6O_3$, forms a colorless, crystalline powder, melting at 92°. Used as an antineuralgic remedy.

Iodo-pyrin (Iodo-antipyrin), $C_{11}H_{11}IN_2O$, forms lustrous, colorless, prismatic needles, difficultly soluble in cold water, more readily in hot water. Melts at 160°.

Naphtho-pyrin (β-naphtol-antipyrin) is a molecular combination of β-naphtol and antipyrin. Recently introduced into medicine.

Monochloral-antipyrin (Hypnal) and *Bichloral-antipyrin* have been mentioned under Chloral-hydrate (see p. 549).

Tolypyrin (Tolyl-dimethyl-pyrazolon), $C_{12}H_{14}N_2O$, is a homologue of antipyrin. Made by using instead of phenyl-hydrazine the homologous compound *p*-tolyl-hydrazine in the reaction with aceto-acetic ether. Colorless crystals, fusing at 136°–137°, soluble in water and alcohol, difficultly soluble in ether. Shows the same color reaction with ferric chloride and nitrous acid as antipyrin.

Tolypyrin Salicylate (Tolysal), $C_{12}H_{14}N_2O.C_7H_6O_2$, is formed by the direct union of the two components. Is in every way analogous to antipyrin salicylate.

CHAPTER V.

CLOSED-CHAIN OR AROMATIC COMPOUNDS.

I. ISOCYCLIC HYDROCARBONS AND DERIVATIVES.

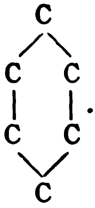
IN studying the methane derivatives we had several series of hydrocarbons, of which that containing the maximum hydrogen in any given case for the amount of carbon present was called the Paraffin series, and had assigned to it the general formula C_nH_{2n+2}. This series was also termed the saturated series of hydrocarbons, because no addition compounds could be formed. The explanation of this fact and the verification of the general formula just stated were both found in the structural formulas, showing an open-chain formation with single linking of adjacent carbon atoms. The other series of hydrocarbons, with the general formulas C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}, respectively, were all unsaturated hydrocarbons and ready to unite directly with halogen atoms and atomic groups to form addition compounds. The explanation of this fact was also given in the structural formulas, which showed an open-chain formation, but with double and treble linking between certain of the carbon atoms. This form of linking was seen to be unstable, and hence the tendency to pass into saturated compounds with an open-chain structure and single linking of the carbon atoms.

We meet, however, in the Benzene series of hydrocarbons, which are the products of the distillation of many complex substances, and which are found to be the fundamental substances of an immense number of compounds occurring in the vegetable kingdom, hydrocarbons of the general formula C_nH_{2n-6}, which are relatively stable and more like saturated than unsaturated hydrocarbons. While it is true that addition of halogen atoms may be effected within certain limits, these compounds do not tend to form as readily as substitution compounds, in which the hydrogen atoms of the original hydrocarbons are readily replaced by halogens and radicals like methyl and ethyl.

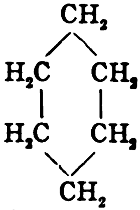
The fundamental hydrocarbon of this series is benzene, C_6H_6, and the homologues are formed by the replacement of one or more of these six hydrogen atoms by methyl and ethyl groups. The limit of this replacement is reached, of course, when six hydrogen atoms have been exchanged for other atoms or atomic groups. Both the hydrocarbons of this series and the substitution derivatives are more stable than the addition compounds before referred to. Moreover, all the derivatives of benzene can be converted either into benzene itself or into very nearly allied compounds by relatively simple reactions. Benzene is, then, in a peculiar degree both the starting-point and the basis of the compounds connected with it.

It is obvious, then, that benzene and its homologous hydrocarbons must be differently constituted structurally from the paraffin series or anv of the unsaturated series that are convertible into methane derivatives by addition. The benzene derivatives are not convertible into marsh-gas derivatives by addition of halogen or other atomic groups; benzene, C_6H_6, cannot be converted into hexane, C_6H_{14}, by any means, direct or indirect. As stated before, addition compounds can be formed. We can obtain $C_6H_6Cl_6$ and from this C_6H_{12}, but the addition of hydrogen stops there. It is strikingly evident, from this and many similar observations, that C_6H_6 is a peculiarly-constituted molecule, which resists change and remains substantially intact through all the substitutions that may be effected. We cannot transform it into a simpler molecule containing 5, 4, or 3 carbon atoms; when oxidized, which is only accomplished with difficulty, it goes into carbon dioxide and water.

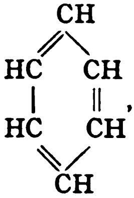
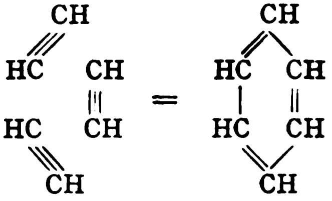
1. Theories as to the Structure of the Benzene Molecule.—The theory as to the constitution of the benzene molecule which has found general acceptance is that of Kekulé, first published in 1866. This not only explains known facts with regard to benzene and its thousands of derivatives, but has found confirmation in the discovery and preparation of the immense numbers of so-called "coal-tar" products which are chemically grouped and classified by its aid. According to this theory the six carbon atoms are linked together in such a way as to form a *closed chain*. We may arrange them in a continuous chain of which the two ends are connected together, but there is no reason here for making it a longitudinal chain. Therefore the six carbon atoms may be considered as placed at equal distances apart on the circumference of a circular ring, or in any other position that might be assumed by a closed chain of six units, but for convenience in writing the hexagon figure is usually chosen. The benzene molecule would then show as its framework



. Each of these carbon atoms has attached to it one atom of saturating hydrogen in the formula C_6H_6. If each carbon atom had two hydrogen atoms attached we would have



or C_6H_{12}, and it is obvious that the four bonds of tetrad carbon would be satisfied.

But C_6H_6 is the formula of the stable molecule and not C_6H_{12}. The latter readily gives up six atoms of hydrogen on oxidation. Kekulé, therefore, considers that each carbon atom in the benzene molecule is linked doubly with one other carbon. This would make an alternate single and double linking, as shown in the formula , and chemists have generally adopted this graphic expression for the benzene molecule. This formula agrees very well with the formation of benzene from acetylene, $H—C \equiv C—H$, three molecules of the latter uniting at a low red heat to form one molecule of benzene, or the formation of mesitylene (trimethyl-benzene)  from acetone (see p. 552) when the latter is distilled with concentrated sulphuric acid. It also explains the capability of benzene and its derivatives to form addition compounds up to a certain limit.

2. Formation of Benzene Homologues.—We have following benzene, C_6H_6, toluene, C_7H_8, xylene, C_8H_{10}, etc., as far as $C_{12}H_{18}$. A slight examination of these compounds, as, for example, with oxidizing agents, shows that there are two parts in them of very different stability, a *nucleus*, C_6H_5 or C_6H_4, not oxidizable, and one or two *side-groups*, CH_3, which have replaced hydrogen atoms of the original C_6H_6, and are easily oxidized to COOH groups. In other words, toluene is methyl-benzene, xylene is dimethyl-benzene, etc., and their formulas may be written $C_6H_5.CH_3$ and $C_6H_4(CH_3)_2$, etc., up to hexamethyl-benzene, $C_6(CH_3)_6$, when this series of homologues stops. It is true we can have ethyl-benzene and diethyl-benzene or methyl-propyl-benzene and similar derivatives, but these are not found in any great number in nature. Nor are their derivatives of the same importance as those of the methylated benzenes.

3. Differences between the Benzene Hydrocarbons and the Open-Chain Hydrocarbons.—(*a*) We notice first that the action of concentrated nitric acid is quite different. With the closed-chain hydrocarbons a hydrogen atom of the nucleus is readily replaced by the group NO_2, as $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, the product being called nitrobenzene. With paraffin hydrocarbons nitric acid has little or no action, even when heated for a time.

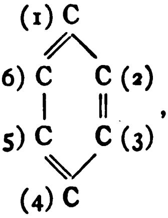
(*b*) With concentrated sulphuric acid the benzene hydrocarbons give rise to sulphonic acids, as $C_6H_6 + SO_3H.OH = C_6H_5(SO_3H) + H_2O$, the product being called benzene-sulphonic acid. Concentrated sulphuric acid has no action on the paraffin hydrocarbons, and with the olefines it forms addition compounds without displacement of hydrogen.

(*c*) As mentioned before, under the influence of oxidizing agents the homologues of benzene are easily oxidized, yielding the corresponding carboxylic acids. Thus, toluene, $C_6H_5—CH_3$, is oxidized by dilute nitric acid or by chromic acid to benzoic acid, $C_6H_5.COOH$. The open-chain hydrocarbons are only acted upon by oxidizing agents with great difficulty.

(*d*) The hydroxyl derivatives like $C_6H_5.OH$ are quite different from the simple OH derivatives of the paraffin or other open-chain hydrocarbons. The former have more of an acid character, while the latter are basic hydroxides. Thus, C_6H_5OH is phenol or carbolic acid, while $C_2H_5.OH$ is ethyl alcohol, which forms esters or salts with the acids.

4. Isomerism in the Closed-Chain Hydrocarbons.—In the hydrocarbons of the paraffin series it is possible to obtain isomeric mono-substitution derivatives, as, for example, normal propyl chloride, $CH_2Cl.CH_2.CH_3$, and isopropyl chloride, $CH_3.CHCl.CH_3$; in the case of benzene, isomeric mono derivatives *cannot* be obtained. The six hydrogen atoms of the benzene seem to possess an equal value. It is a closed-chain structure, and it matters not at what point in the ring thus formed the single substitution takes place. This fact has been proved experimentally. It is different when two atoms of hydrogen in the benzene molecule are replaced by other atoms or groups. These di-substitution derivatives may exist in three isomeric modifications. We may have three dichlor-benzenes, three dimethyl-benzenes, three dinitro-benzenes, etc. This also has been established experimentally, and the limit set at three.

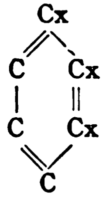
If we now look at the benzene molecule as figured in Kekulé's theory, we see the explanation of this fact. Taking the structural formula

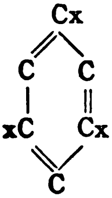


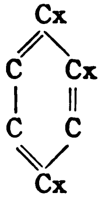
, and numbering the carbon atoms from the top going to the right, we have for the purpose of representation each one indicated. Now, if the replacement take place at (1) and (2), or (2) and (3), or (3) and (4), or (4) and (5), or (5) and (6), or (1) and (6), the resulting di-substitution compound is one and the same substance. While we figure this hexagon structure for convenience of explanation of the observed characters of benzene, we do not for one moment pretend that it has a fixed position in space with a north and a south corner, or with two eastern and two western carbon atoms. But in the cases just mentioned *the substitution has taken place in connection with adjacent or directly connected carbon atoms*. To distinguish them all such di-substitution compounds are called *ortho* compounds, as ortho-dichlor-benzene. If the replacement take place at the carbon atoms marked (1) and (3), or (2) and (4), or (3) and (5), or (4) and (6), or (5) and (1), or (6) and (2), the resulting di-substitution compound is one and the same substance. In these cases *the substitution has taken place in connection with carbon atoms separated by one intervening carbon atom.* Such compounds are called *meta* compounds, as meta-dimethylbenzene. If the replacement take place at the carbon atoms marked (1) and (4), or (2) and (5), or (3) and (6), the resulting di-substitution compound is one and the same substance. In these cases *the substitution has taken place in connection with carbon atoms separated by two intervening carbon atoms.* Such compounds are called *para* compounds as para-dinitro-benzene. Frequently these designations are indicated by the initials only, as *o*-oxybenzoic acid, *m*-xylene, and *p*-phenolsulphonic acid.

When three hydrogen atoms of the benzene molecule are replaced the case becomes more difficult. We may have three contingencies to consider here: (1) all three substituting atoms or groups are alike; then three isomers may exist; (2) of the substituting elements two are alike and the third is different; in this case six isomers may form; (3) if all three substituting elements are different, ten isomers may form.

When more than three substitutions take place, the number of isomers becomes very great.

In distinguishing between the different tri- and tetra-substitution derivatives, at times the designations *v* (standing for *vicinus*, neighboring), *s* (standing for symmetrical), and *a* (standing for asymmetrical) are used. Thus, 

would indicate a trisubstitution derivative which would be marked *v*, as *v*-trinitro-benzene, while the figures 

and 

would be designated by the *s* and *a* respectively, as *s*-trimethyl-benzene and *a*-trichlor-benzene.

These cases of isomerism, it will be noticed, are all concerned with the position in the nucleus assumed by the replacing atom or group. We may also have side-group isomerism, as normal propyl-benzene and isopropyl-benzene.

More important than this last, however, is the case where a substituent enters the benzene nucleus in one case and the side-group in another case, giving us the so-called "mixed isomerism." Thus, $C_6H_4Cl.CH_3$, monochlor-toluene, and $C_6H_5CH_2Cl$, benzyl chloride, or $C_6H_4(CH_3)_2$, xylene, and $C_6H_5.C_2H_5$, ethyl-benzene, are isomeric.

The determination of the nature of a di-substitution derivative of benzene, whether ortho, meta, or para, is to be accomplished by the treatment with reagents, whereby the nature of the side-group may be changed and the product studied as to its properties. Ortho derivatives through a series of such changes will remain ortho derivatives, and so with the meta and the para compounds. By such a series of transformations it becomes possible correctly to identify the nature of the original compound.

CHAPTER VI.

ISOCYCLIC COMPOUNDS CONTAINING ONE NUCLEUS.

In explaining the theories held as to the fundamental differences between the aromatic compounds and the open-chain hydrocarbons and their derivatives, we have touched only upon the structure of benzene, taking it as the type of closed-chain compounds, and, in fact, the starting-point from which they are derived. We will see, however, later, that two or more of these benzene nuclei may unite, either by simple linking without condensation, or by condensing together to form a compound nucleus, obviously related to the simpler benzene molecule, but built up by its doubling or trebling itself. Thus, diphenyl, diphenyl-methane, triphenyl-methane, and indigo all represent aromatic compounds with more than one benzene nucleus in which the parts are linked together without condensation of the nuclei. On the other hand, naphthalene, anthracene, phenanthrene, quinoline, and acridine all represent molecules formed by the condensation of benzene nuclei.

We shall first confine our attention to those aromatic compounds in which a single benzene nucleus appears as the basis of the molecule

I. HYDROCARBONS.

1. **Saturated Hydrocarbons.**—We have here to deal with benzene and its homologues. They occur to some extent in the free state in nature, being found in Galician and Hanoverian petroleum, and even in small amount in Pennsylvania petroleum. They are obtained, however, most abundantly as the product of the destructive distillation of bituminous coal, and hence are contained in coal-tar. This is a very complex mixture, and more than forty distinct compounds of the aromatic class have been identified in it. When roughly fractioned from the tar-stills it yields three main fractions: (1) The light oil, sp. gr. 0.9, boiling point up to 150°, which contains mainly benzene and its homologues, with some naphthalene; (2) middle oil, sp. gr. up to 1.01, boiling point 150° to 210°, which contains especially naphthalene, phenol and cresol and quinoline bases; and (3) heavy oil, sp. gr. up to 1.04, boiling point from 210° to 300°, containing besides naphthalene and the quinoline bases chiefly anthracene and phenanthrene.

From the first of these fractions, by careful fractionating with the aid of column stills, the benzene hydrocarbons may be obtained. Their separation, however, is not entirely possible by fractional distillation alone, but requires special treatment with reagents.

Benzene is also obtained extensively from both retort gas and coke-oven gas by washing these with oils which absorb the benzene, and from petroleum vapors by cracking processes involving heat and pressure.

Benzene derivatives can be formed from bodies of the methane series by a number of reactions, some of which may be noted.

Acetylene polymerizes at a low red heat, three molecules uniting to form one molecule of benzene. This has been illustrated graphically (see p. 618). Allylene, C_3H_4, in the same way polymerizes to form mesitylene or trimethyl-benzene, C_9H_{12}, when distilled with dilute sulphuric acid. Ketones condense to benzene hydrocarbons when distilled with concentrated sulphuric acid, as for example:

$$3CH_3.CO.C_2H_5 = C_6H_3(C_2H_5)_3 + 3H_2O.$$

Bromacetylene CBr : CH also may be converted into (symmetrical) tribrombenzene simply by leaving it exposed to direct sunlight according to the following reaction:

$$3C_2HBr = C_6H_3Br_3.$$

Hexyl iodide, $C_6H_{13}I$, can be converted into hexachlor-benzene, C_6Cl_6, by heating it with ICl_3, and into hexabrom-benzene, C_6Br_6, by heating the hexyl iodide with bromine at 260°.

Mellitic acid, $C_6(COOH)_6$, is produced by the oxidation of graphite or lignite by means of potassium permanganate.

These methods, however, may be said to be isolated reactions, and not used as general methods for their production. Among the general methods may be mentioned:

1. By treating a mixture of brominated hydrocarbon and methyl or ethyl iodide with sodium in etheral solution: $C_6H_5Br + CH_3I + Na_2 = C_6H_5.CH_3 + NaI + NaBr$.

2. By the action of methyl chloride upon benzene or its homologues in the presence of aluminum chloride: $C_6H_6 + 2CH_3Cl = C_6H_4(CH_3)_2 + 2HCl$.

3. The benzene hydrocarbons result from their respective carboxylic acids by distilling them with soda-lime: $C_6H_5.COOH = C_6H_6 + CO_2$.

4. From sulphonic acids by the separation of the SO_3H group: $C_6H_4(CH_3)SO_3H + H_2O = C_6H_5(CH_3) + H_2SO_4$.

5. By distillation of the phenols with zinc-dust.

The general characters of the benzene hydrocarbons that seem most important are:

1. They may all be distilled without decomposition. Most of them are colorless liquids of peculiar aromatic odor. Durene, penta- and hexamethyl-benzene are crystalline solids at ordinary temperatures.

2. As before stated, they readily form nitro and sulphonic derivatives.

3. Benzene oxidizes with some difficulty to oxalic, formic, and carbonic acids; the aromatic hydrocarbons with side-groups are readily oxidized to acids, as $C_6H_4(CH_3)_2 = C_6H_4(COOH)_2$.

4. By reduction with hydrogen iodide under pressure at high temperatures the benzene hydrocarbons add on hydrogen up to the limit of six atoms.

5. The halogens form with benzene in sunlight addition compounds like $C_6H_6Cl_6$. On the other hand, in diffused daylight they form substitution compounds like C_6H_5Cl.

BENZENE SERIES. SATURATED HYDROCARBONS. GENERAL FORMULA, C_nH_{2n-6}.

C_6H_6	C_6H_6, Benzene, boiling point, 80.4°.			
C_7H_8	$C_6H_5.CH_3$, Toluene, boiling point 111°.			
C_8H_{10}	$C_6H_4(CH_3)_2$, Xylenes: *o*- b. p. 142°, *m*- b. p. 139°, *p*- b. p. 137°.	$C_6H_5(C_2H_5)$, Ethyl-benzene, boiling point 134°.		
C_9H_{12}	$C_6H_3(CH_3)_3$, Trimethyl-benzenes: *s*- = Mesitylene, b. p. 163°. *a*- = Pseudo-cumene, b. p. 169°. *v*- = Hemellithene, b. p. 175°.	$C_6H_4(CH_3)(C_2H_5)$, Methyl-ethyl-benzenes, or Ethyl-toluenes: *o*- b. p. 160°, *m*- b p. 159°, *p*- b. p. 162°.	$C_6H_5(C_3H_7)$, Normal propyl-benzene, b. p. 157°. Isopropyl-benzene (cumene), b. p. 153°.	
$C_{10}H_{14}$	$C_6H_2(CH_3)_4$, Tetramethyl-benzenes: *s*- = Durene, m. p. 79°, b. p. 190°. *a*- = Isodurene, b. p. 195°. *v*- = Prehnitene, m. p. —4°, b. p. 204°.	$C_6H_3(CH_3)_2(C_2H_5)$, Dimethyl-ethyl-benzenes. Six isomers possible.	$C_6H_4(C_2H_5)_2$. Diethyl-benzenes (3). $C_6H_4(CH_3)(C_3H_7)$. Cymene, b. p. 176°. Six isomers possible.	$C_6H_5(C_4H_9)$, Butyl-benzenes. Four isomers possible.
$C_{11}H_{16}$	$C_6H(CH_3)_5$, Pentamethyl-benzene, m. p. 51°, b. p. 231. $C_6H_5(C_5H_{11})$, Amyl-benzene, etc.			
$C_{12}H_{18}$	$C_6(CH_3)_6$, Hexamethyl-benzene, m. p. 164°, b. p. 264. $C_6H_3(C_2H_5)_3$, Triethyl-benzene, etc.			

The most important of the benzene hydrocarbons are shown arranged in tabular form on the opposite page.

Benzene, C_6H_6, was discovered by Faraday in 1825, and detected in coal-tar by Hofmann in 1845. It is practically always obtained from the light oil of tar by taking the purified fraction boiling at 83°–85° and chilling it, when the benzene will crystallize out from the adhering portions of higher homologues. It is also obtainable from illuminating gas, or perfectly pure by distilling benzoic acid with lime. It has a melting point of 5.2°, and a boiling point of 80°. Sp. gr. 0.876 at 25° C. It burns with a luminous but smoky flame. It is an excellent solvent for fats, resins, iodine, sulphur, and phosphorus. Commercial benzene generally contains thiophene, and hence gives the indophenin reaction (see p. 614). Is used on a large scale as the starting-point for the manufacture of aniline and other technical products of value in the color industry.

Toluene (Methyl-benzene), $C_6H_5.CH_3$, is formed by the distillation of certain resins, as Tolu balsam (whence the name), dragon's-blood, etc. Is generally obtained along with benzene in the light oil of tar. It can also be made synthetically, as mentioned under general modes of formation (see p. 623). It is very similar to benzene, and when obtained from coal-tar is often contaminated with thiotolene (methyl-thiophene). Toluene boils at 110°, and is still liquid at —28°. Oxidized by nitric or chromic acid it yields benzoic acid. Is less poisonous, taken internally, than benzene. It is changed into benzoic acid in the organisms, and eliminated from the system as hippuric acid.

Xylenes (Dimethyl-benzenes), $C_6H_4.(CH_3)_2$.—The xylene of coal-tar is a mixture of the three isomers, meta-xylene making up 70 to 85 per cent. of it. The boiling points lie so close (142°, 139°, 137°) that they cannot be separated by fractional distillation. As *m*-xylene is oxidized more slowly than its isomers, it can be separated in this way. The others are separated by converting them into sulphonic compounds. When oxidized they yield the corresponding isomeric phthalic acids.

Ethyl-benzene, $C_6H_5.C_2H_5$, has been made synthetically from brombenzene and ethyl iodide in the presence of $AlCl_3$. Boils at 134°. When oxidized yields benzoic acid.

Mesitylene (1 : 3 : 5 Trimethyl-benzene), $C_6H_3(CH_3)_3$, is contained in coal-tar along with the other two isomeric trimethyl-benzenes. It can also be prepared from acetone or allylene (see page 618). It is a liquid of agreeable odor. Nitric acid oxidizes the side-groups one by one, producing successively a monobasic, a dibasic, and a tribasic acid.

Cumene (Isopropyl-benzene), $C_6H_5(C_3H_7)$, is produced by the distillation of cumic acid with lime as well as synthetically. Boils at 153°.

Durene (Tetramethyl-benzene), $C_6H_2(CH_3)_4$, has been found in coal-tar, and can be made from toluene and methyl chloride in the presence of $AlCl_3$. It is a solid, melting at 79°, and possesses a camphor-like odor.

Cymene (Methyl-propyl-benzene), $C_6H_4(CH_3)(C_3H_7)$.—It is found in Roman cumin oil, as well as in eucalyptus and thyme oils, and results upon heating camphor with P_2O_5 and P_2S_5. It is a liquid of agreeable odor, boiling at 176°.

2. **Unsaturated Hydrocarbons.**—The unsaturated hydrocarbons of the aromatic series are formed by the entrance of the benzene radicles (phenyl) into the unsaturated hydrocarbons of the methane series. Thus, by the replacement of a hydrogen atom of ethylene, $CH_2 = CH_2$, we obtain $C_6H_5.CH = CH_2$, Phenyl-ethylene or Styrene, and by the replacement of a hydrogen atom in acetylene, $CH \equiv CH$, we obtain $C_6H_5.C \equiv CH$, Phenyl-acetylene.

Styrene (Phenyl-ethylene), $C_6H_5.CH = CH_2$, is found in storax (**Styrax**, U.S.P.), from the bark of *Liquidambar orientalis*, and in small amount in coal-tar. May be made synthetically by passing a mixture of benzene and ethylene through red-hot tubes, or by the heating of cinnamic acid with water to 200°. Aromatic-smelling liquid, boiling at 144°. It is optically inactive.

Phenyl-acetylene, $C_6H_5.C \equiv CH$, may be prepared by heating styrene bromide, $C_8H_8Br_2$, with potash: $C_8H_8Br_2 + 2KOH = C_8H_6 + 2HBr + 2H_2O$; also by the splitting off of CO_2 from phenyl-propiolic acid, $C_6H_5.C \equiv C.COOH$. Pleasant smelling liquid, boiling at 139°. Shows its character as an acetylene derivative by combining with silver and cuprous solutions to form explosive metallic compounds.

3. **Hydrogen Addition Compounds of the Benzene Series.**—We have already stated that benzene and its homologues, by prolonged treatment with HI under pressure, can be made to take up six hydrogen atoms. The compound so formed from benzene is C_6H_{12} and the molecule shows six CH_2 groups in a closed chain, hence the name *hexamethylene*. This hydrocarbon and its homologues have sometimes been called the "naphthenes," and, although isomeric with the olefines, differ from them notably. For instance, they are not attacked by alkaline permanganate solution, do not dissolve in sulphuric acid, and are not able to add on bromine. Hydrogenation of benzene and its homologues by hydrogen in the presence of heated, finely divided metallic nickel also yields hexahydro benzene and its homologues. They are found in considerable quantity in Russian petroleum, and in smaller amount in other oils. They very readily yield to oxidizing agents, and give up the six atoms of extra hydrogen.

II. THE HALOGEN DERIVATIVES OF THE BENZENE HYDROCARBONS.

The halogen derivatives of these hydrocarbons are formed by substitution. With benzene, these derivatives are entirely analogous to the halogen substitution derivatives of methane and its homologues, $C_6H_5.Cl$, monochlor-benzene or phenyl chloride, being the analogue of $CH_3.Cl$, monochlor-methane or methyl chloride, or C_2H_5Cl, monochlor-ethane or ethyl chloride.

With toluene and the higher members of the benzene series, however, we have the possibility of the replacement of the hydrogen of the side-group as well as the hydrogen of the nucleus, giving rise to a great number of isomers. The halogen atoms which are attached to the nucleus are much more firmly held than those which enter in the side-group only. Ammonia and oxidizing agents will attack and eliminate the chlorine of the side-group, but not affect that contained in the nucleus. This action of oxidizing agents is so distinctly different as to serve to distinguish whether the chlorine is present in the one position or the other.

SUMMARY OF HALOID SUBSTITUTION PRODUCTS.

C_6H_5Cl, Chloro-benzene, b. p. 133°.	C_6H_5Br, Bromo-benzene, b. p. 154°.	C_6H_5I, Iodo-benzene, b. p. 185°.
$C_6H_4Cl_2$, Dichloro-benzenes.	$C_6H_4Br_2$, Dibromo-benzenes.	Diiodo-benzenes.
o-179°, *m*- 172°, *p*- 173°.	*o*- 224°, *m*- 219°, *p*- 219°.	

$C_6H_3Cl_3$, Trichloro-benzenes, three isomers.
$C_6H_2Cl_4$, Tetrachloro-benzenes, three isomers.
C_6HCl_5, Pentachloro-benzene.
C_6Cl_6, Hexachloro-benzene, m. p. 226°, b. p. 332°.

$C_6H_4Cl(CH_3)$	Isomeric	with	$C_6H_5.CH_2Cl$.
Chloro-toluenes, three isomers . .	"	"	Benzyl chloride, b. p. 179°.
$C_6H_3Cl_2(CH_3)$	"	"	$C_6H_5.CHCl_2$.
Dichloro-toluenes, six isomers . .	"	"	Benzal chloride, b. p. 206°.
—— ——			$C_6H_5.CCl_3$.
—— ——			Benzo-trichloride, b. p. 213°.
$C_6H_3Cl(CH_3)_2$	"	"	$C_6H_4(CH_3)CH_2Cl$.
Chloro-xylenes, six isomers . . .	"	"	Xylyl chlorides.

Modes of Formation.—Chlorine and bromine acting upon benzene readily yield monochloro- and monobromo-benzene. A further substitution takes place especially easily in the presence of iodine. This acts as a carrier of chlorine or bromine, and by its presence aids in the introduction of these elements.

In the homologues of benzene, if the chlorination takes place in the cold, the chlorine enters the nucleus; if at a boiling temperature, it enters the side-group.

The action of phosphorus pentachloride upon phenols and aromatic alcohols also serves to form the halogen derivatives.

The nitro or primary amido compounds of the benzene hydrocarbons may also be converted into halogen compounds by first converting them into the diazo compounds, and then boiling these with cuprous chloride:

$$C_6H_5.N{=}N.Cl \;=\; C_6H_5Cl \;+\; N_2.$$

$$\left.\begin{array}{l}\textit{Monochloro-benzene},\ C_6H_5Cl,\\ \textit{Monobromo-benzene},\ C_6H_5Br,\\ \textit{Monoiodo-benzene},\ C_6H_5I,\end{array}\right\}\ \text{are all colorless liquids of peculiar,}$$

aromatic odor. The boiling points have been given in the table.

Benzyl Chloride, $C_6H_5.CH_2Cl$, is formed by the action of chlorine upon toluene at a boiling temperature. When oxidized it yields benzoic acid

This reaction, together with the fact that prolonged boiling with water or potassium carbonate solution changes it into benzyl alcohol, $C_6H_5.$-CH_2OH, shows that the chlorine is present in the side-group. Colorless liquid, boiling at 179°. It is used on a large scale for the manufacture of benzoic aldehyde (oil of bitter almonds).

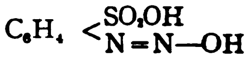
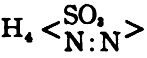
Benzal Chloride, $C_6H_5.CHCl_2$, is produced by the further chlorination of boiling toluene, also from benzoic aldehyde by the action of PCl_5. It is used in the manufacture of benzaldehyde and benzoic acid. When heated with water or sulphuric acid, or, as is done on a large scale, with water and calcium hydroxide, the benzal chloride is changed into the aldehyde, $C_6H_5CHCl_2 + H_2O = C_6H_5.CHO + 2HCl$.

Benzo-trichloride, $C_6H_5.CCl_3$, sometimes termed Phenyl-chloroform, is used on a large scale for the manufacture of artificial benzoic acid. For this purpose it is heated with water under pressure:

$$C_6H_5.CCl_3 \quad + \quad 2H_2O \quad = \quad C_6H_5.COOH \quad + \quad 3HCl.$$

III. SULPHONIC DERIVATIVES.

The sulphonic acids of the aromatic series, like those mentioned under the methane derivatives, contain the monad group HSO_3, but are much more readily formed. They result from the action of strong or fuming sulphuric acid upon a great variety of aromatic compounds, and play quite an important part in the technical application of the benzene derivatives, and latterly in the manufacture of synthetic compounds of medicinal value. Thus we may have the following classes of sulphonic acid derivatives:

1. Sulphonic acids of the hydrocarbons, as benzene-sulphonic acid, $C_6H_5HSO_3$.
2. Sulphonic acids of the phenols, as phenol-sulphonic acid, $C_6H_4(OH)HSO_3$.
3. Sulphonic acids of the amines, as amido-benzene-sulphonic acid, $C_6H_4(NH_2)HSO_3$.
4. Sulphonic acids of the diazo compounds, as  $C_6H_4<\genfrac{}{}{0pt}{}{SO_2OH}{N=N-OH}$ diazo-benzene-sulphonic acid and  $C_6H_4<\genfrac{}{}{0pt}{}{SO_2}{N:N}>$, diazo benzene-sulphonic anhydride.
5. Sulphonic acids of the azo compounds, as azo-benzene-sulphonic acid, $C_6H_5.N:N-C_6H_4HSO_3$.
6. Sulphonic acids of the hydrazines, as phenyl-hydrazine-sulphonic acid, $C_6H_5.NH-NH-HSO_3$.

In general, these sulphonic acids and their salts are very stable compounds, mostly soluble in water, difficultly soluble in alcohol.

When fused with caustic potash or soda, they yield phenols and sulphites, $C_6H_5.NaSO_3 + NaOH = C_6H_5.OH + Na_2SO_3$.

When distilled with potassium cyanide, they yield cyanides or nitriles.

When heated with fuming hydrochloric acid or with water under pressure, they regenerate the same hydrocarbons from which they were originally formed $C_6H_5.HSO_3 + H_2O = C_6H_6 + H_2SO_4$.

Benzene-monosulphonic Acid, $C_6H_5.HSO_3$, is obtained by heating benzene with concentrated sulphuric acid. The excess of sulphuric acid is removed by addition of barium or lead carbonate, as both the barium and lead salts of the sulphonic acid are soluble. It forms small, crystalline leaflets, deliquescing in the air, and easily soluble in water. Because of the fact stated above, that when fused with caustic alkalies it yields phenol, it is of importance in the manufacture of synthetic carbolic acid.

Benzene-disulphonic Acids, $C_6H_4(HSO_3)_2$.—Three isomers are obtainable. The meta compound when fused with caustic alkali yields the diatomic phenol, resorcin. (See Resorcin, p. 642.)

Toluene-sulphonic Acids, $C_6H_4(CH_3)HSO_3$, exist in three isomeric modifications.

Xylene-sulphonic Acids, $C_6H_3(CH_3)_2HSO_3$.—The different isomers of this substance are utilized to separate the isomeric xylenes. (See p. 624.)

The higher homologues of benzene, except hexamethyl-benzene, are all capable of yielding sulphonic acids.

The sulphonic acids of the several classes of benzene derivatives will be mentioned, when of sufficient importance, under the different groups of compounds.

IV. NITRO DERIVATIVES.

By the action of the strong nitric acid upon the aromatic hydrocarbons, derivatives in which one or more hydrogen atoms are replaced by the monad group, NO_2, are formed. These are mostly soluble in the strong nitrating acid, and are thrown out of solution on dilution with water. Thus, from benzene we have $C_6H_6 + NO_2.OH = C_6H_5.NO_2 + H_2O$, and from toluene $C_6H_5.CH_3 + NO_2OH = C_6H_4(CH_3)NO_2 + HOH$. When more than one such replacement takes place, we distinguish by the names mononitro-benzene, dinitro-benzene, trinitro-benzene, etc.

In all these cases the NO_2 group attaches itself to the nucleus, and not to the side-group. Whether one or more such replacements shall take place is dependent upon the strength of the acid and the length of time of its action.

The nitro compounds are mostly pale yellowish liquids, distilling undecomposed in a current of steam, or, in the case of the higher derivatives, yellowish needles or prisms. They are heavier than water, and insoluble therein, but generally soluble in alcohol, ether, and glacial acetic acid. All the nitro compounds are reduced in acid solution by the action of nascent hydrogen, forming the corresponding amido compounds. This may be effected by the action of tin and hydrochloric acid, stannous chloride and hydrochloric acid, or iron and acetic acid. Thus, $C_6H_5.NO_2 + H_6 = C_6H_5.NH_2 + 2H_2O$ and $C_6H_4(NO_2)_2 + H_{12} = C_6H_4(NH_2)_2 + 4H_2O$.

The nitro compounds are of very great technical importance as necessary steps in the manufacture of aniline and similar amido compounds.

Nitro-benzene, $C_6H_5.NO_2$, is formed by adding benzene gradually to well-cooled fuming nitric acid as long as it seems to dissolve. After some standing the nitro-benzene is separated by the addition of water, washed with water and dilute caustic soda, and purified by distilling in a current of steam. It forms a light yellowish liquid smelling strongly of bitter almonds, boiling at 206°, and crystallizing in needles at 3°. It is manufactured on a large scale as a step in the manufacture of aniline, and, pharmaceutically, under the name of "mirbane oil," as a basis of toilet preparations, soaps, etc., because of its characteristic odor. It is poisonous.

Dinitro-benzenes, $C_6H_4(NO_2)_2$, are formed when benzene is added to a mixture of equal volumes of concentrated nitric and sulphuric acids and the mixture heated to boiling. All three isomers are solid and crystallizable.

Nitro-toluenes, $C_6H_4(CH_3)NO_2$.—When toluene is acted upon by strong nitric acid, the ortho- and para- nitro-toluenes are formed, the meta compound being absent, although obtainable by indirect means. By boiling with fuming nitric acid the nitro-toluenes are changed into dinitrotoluenes and by continuing the nitration with fresh acid we obtain *trinitrotoluene*, a solid melting at 81° C., which is now largely used as a substitute for picric acid in filling explosive shells, being much more stable than the latter.

The presence of a halogen atom replacing an atom of hydrogen in the benzene nucleus does not interfere with the nitration, so that compound derivatives are easily formed. Thus, chloro-benzene is readily nitrated, and yields three isomeric chloronitro-benzenes.

A derivative of this character is trinitrochloro-benzene, $C_6H_2(NO_2)_3$.-Cl, which acts like an acid chloride, and corresponds to $C_6H_2(NO_2)_3OH$, the so-called "picric acid" (see Trinitro-phenol, or Picric Acid).

V. AMIDO DERIVATIVES OF THE BENZENE HYDROCARBONS.

In studying these compounds it is necessary to remember that they can be looked at from two points of view: first, as benzene in which one or more atoms of hydrogen of the nucleus are replaced by the group NH_2, or as ammonia in which one or more hydrogen atoms are replaced by the radical C_6H_5, or similar aromatic hydrocarbon radical. Thus, C_6H_5-NH_2 is called amido-benzene when looked at from the first point of view, or phenylamine when looked at from the second point of view, and considered as analogous to methylamine, $CH_3.NH_2$. Moreover, just as we had secondary and tertiary amines like dimethylamine and trimethylamine, so we have diphenylamine and triphenylamine. We have, also, the classes of monamines and diamines according as one or two molecules of ammonia are taken as the basis of replacement. The amido group NH_2 can also replace hydrogen of the side-group in the homologues of benzene.

In the accompanying tables we have indicated first the primary amines, which, containing the group NH_2, may also be called amido compounds, and then compared with these the secondary and tertiary amines, containing NH and N respectively, combined with aromatic radicals.

I. TABLE OF PRIMARY AMINES. AROMATIC AMIDO-DERIVATIVES.

From Benzene.	From Toluene.	From Xylene.	From Pseudocumene.
$C_6H_5.NH_2$, Aniline, b. p. 183°.	$C_6H_4(CH_3).NH_2$, Toluidines: *o*- b. p. 199°, *m*- 200°, *p*- 198°.	$C_6H_3(CH_3)_2.NH_2$, Xylidines; six isomers.	$C_6H_2(CH_3)_3NH_2$, Pseudocumidine.
$C_6H_4(NO_2).NH_2$, Nitranilines.	$C_6H_5.(CH_2.NH_2)$, Benzylamine. $C_6H_5.(CH_2.CH_2.NH_2)$, Phenethylamine.		
$C_6H_4(NH_2)_2$, Phenylenediamine.	$C_6H_3(CH_3)(NH_2)_2$, Toluylenediamine.		
$C_6H_3(NH_2)_3$, Triamido-benzene.			

II. TABLE OF SECONDARY AND TERTIARY AMINES.

Secondary.	Tertiary.
$(C_6H_5)_2.NH$, Diphenylamine.	$(C_6H_5)_3N$, Triphenylamine.
Basic Substituted Amines.	
$C_6H_5.NH.CH_3$, Methyl-aniline. $C_6H_5.NH.C_2H_5$, Ethyl-aniline. $(C_6H_5)_2N.NO$, Nitrosodiphenylamine.	$C_6H_5.N(CH_3)_2$, Dimethyl-aniline. $C_6H_5N(C_2H_5)_2$, Diethyl-aniline. $C_6H_4(NO).N(CH_3)_2$, Nitrosodimethylaniline.
Acid Substituted Amines (Anilids).	
$C_6H_5NH(C_2H_3O)$, Acetanilid. $(C_6H_5.NH)_2CO$, Carbanilid. $(C_6H_5NH)(NH_2)CS$, Phenyl-sulphurea.	$C_6H_5.N(CH_3)(C_2H_3O)$, Methyl-acetanilid. $(C_6H_5.N)CO$, Phenyl-cyanate $(C_6H_5N)CS$, Phenyl mustard oil.

1. **Primary Monamines.**—This most important class is formed most readily by the reduction of the corresponding compounds in acid solution, as already mentioned. This is the process used in the technical manu-

facture of aniline and its homologues. If a dinitro compound is taken we may obtain by partial reduction a nitro-amido compound, such as nitraniline. Primary monamines, with the NH_2 groups in the side-chain, like benzylamine, are formed differently. These result from the action of ammonia upon such halogen derivatives as contain the halogen in the side-group: $C_6H_5.CH_2Cl + NH_3 = C_6H_5.CH_2NH_2 + HCl$.

The determination as to whether the amido group may be attached to the nucleus or to the side-group can be had by one of two reactions: first, only those with the amido group in the side-chain result by the action of ammonia upon a haloid derivative of a hydrocarbon; second, only the primary amines with the NH_2 group in the nucleus are changed by nitrous acid into diazo compounds, according to the reaction.

$$\underset{\text{Aniline Hydrochloride.}}{C_6H_5NH_2.HCl} + HNO_2 = \underset{\text{Diazo-Benzene Chloride.}}{C_6H_5{-}N{=}N{-}Cl} + 2H_2O.$$

Two other characteristic and important reactions for primary amines may be mentioned. By the action of acids or acid anhydrides upon these amines the hydrogen of the NH_2 group is replaced by an acid radical. These compounds are called anilids:

$$\underset{\text{Aniline.}}{C_6H_5NH_2} + \underset{\text{Acetic Acid.}}{CH_3COOH} = \underset{\text{Acetanilid.}}{C_6H_5NH(CH_3CO)} + H_2O.$$

With chloroform and alcoholic potash solution the primary amines of the benzene series, just as those of the methane series, yield the fearful-smelling carbylamines (isonitriles):

$$C_6H_5NH_2 + CHCl_3 + 3KOH = C_6H_5{-}NC + 3KCl + 3H_2O.$$

Aniline (Amido-benzene or Phenylamine), $C_6H_5.NH_2$, was first obtained in 1826 from the dry distillation of indigo (Portuguese *anil*). It is also contained in coal-tar and in bone-oil. Colorless, oily liquid, turning yellow or brown on exposure to the air. Possesses a weak but peculiar odor. Boils at 182°, and solidifies at —8°. It has no action upon litmus, but is a weak base. It is poisonous, and is a good solvent for many compounds like indigo and sulphur. Unites like ammonia by direct addition to acids to form salts like $C_6H_5.NH_2.HCl$ and $(C_6H_5NH_2)_2.H_2SO_4$.

Small quantities of aniline in solution are recognized by the action of a solution of bleaching powder, which gives a violet color transient in character. A solution of aniline in concentrated sulphuric acid is first colored red and then deep blue by a grain of potassium bichromate. A solution of $K_2Cr_2O_7$, on the other hand, in acid solution of aniline sulphate produces a dark-green color, which in the end gives a precipitate of aniline black. The aqueous solution of aniline sulphate colors paper pulp made from wood-fibre intensely yellow. This is used as a test for wood-pulp in paper.

Substituted Anilines.—The modification of the aniline molecule may arise from the replacement of hydrogen of the nucleus by replacing groups, or by the replacement of the hydrogen in the amido group NH_2, (*a*) *Substituted Anilines with Replacement in the Nucleus.*—We may have according to theory three isomeric chloro-, bromo-, or iodo-anilines. These are of no present importance. We may have also three isomeric *Nitranilines*, $C_6H_4(NO_2)NH_2$. These all crystallize in yellow needles or prisms, readily soluble in alcohol, but only slightly soluble in water. They go into the phenylenediamines, $C_6H_4(NH_2)_2$, on reduction. They are also converted into nitrophenols when boiled with alkalies, ammonia being liberated.

Amido-benzene-sulphonic Acids, $C_6H_4(HSO_3).NH_2$.—By heating aniline with fuming sulphuric acid, as well as by the heating of aniline sulphate to 185° to 200°, the para acid, known as *Sulphanilic Acid*, is formed. It crystallizes with one molecule of water in somewhat difficultly soluble rhombic tablets. The meta acid, known as *Metanilic Acid*, finds application, as well as the sulphanilic acid, in the manufacture of azo dye-colors.

(*b*) *Substituted Anilines with Basic Groups in Side-Chain.*—By the action of aniline hydrochloride and an alcohol we have formed such compounds as:

Methyl-aniline, $C_6H_5.NH(CH_3)$, which is lighter than water, and has an odor like that of aniline, but stronger and more aromatic.

Dimethyl-aniline, $C_6H_5.N(CH_3)_2$, is an oil of sharp odor, solidifying at 0.5° and boiling at 192.6°. When oxidized with mild oxidizing agents it is changed into methyl violet, one of the aniline dyes. With benzotrichloride, $C_6H_5.CCl_3$, **dimethyl-** aniline reacts to form malachite green.

(*c*) *Substituted Anilines with Acid Groups in Side-Chain.*—These are also known as *Anilids*. They are formed by the action of acid anhydrides or acid chlorides upon aniline.

Formanilid, $C_6H_5.NH(HCO)$, is obtained by the rapid distillation of 93 parts of aniline with 126 parts of crystallized or 90 parts of dehydrated oxalic acid: $C_2O_4H_2 + C_6H_5.NH_2 = H_2O + CO_2 + C_6H_5NH(HCO)$.

It forms colorless crystals, melting at 46°, tolerably easily soluble in water, easily soluble in alcohol. Is decomposed by dilute acids. Used for both external and internal use, as a local anæsthetic or as an antipyretic.

Acetanilid, $C_6H_5.NH(C_2H_3O)$ (**Acetanilidum, U.S.P.**).—100 parts of pure aniline and 100 parts of glacial acetic acid are boiled in a round-bottomed flask provided with inverted condenser for from one to two days, until a drop taken out for testing perfectly solidifies on cooling, or until a drop added to dilute caustic soda solution shows no free aniline. It is then fractionally distilled. When the water produced in the reaction has distilled off, the temperature, as shown by the thermometer, rises rapidly, and the Liebig condenser is changed for a straight glass tube, not cooled in any way, as otherwise the acetanilid solidifying in the tube would cause stoppage. The pure substance distils at 295°, and solidifies on cooling. It may be recrystallized out of boiling water. It forms colorless, odorless scales, neutral to test-paper, melting at 113°, and boiling, as said, at 295°. Difficultly soluble in cold water, more readily in hot water, readily in alcohol and ether. Is decomposed by hydrochloric acid into aniline and acetic acid. Heated with dry zinc chloride to 250°-270° it yields "flavaniline," $C_{16}H_{14}N_2$, a dye-stuff, dissolving in hydrochloric acid with moss-green color. First introduced under the name of "antifebrin," and largely used as an antipyretic and antineuralgic. In some cases it has been used for external use as an antiseptic.

Para-bromacetanilid, $C_6H_4BrNH(C_2H_3O)$, has been used in medicine under the name of "antisepsin" or "asepsin."

Methyl-acetanilid (Exalgin), $C_6H_5.N(CH_3)(C_2H_3O)$, is best made by the acetylating of monomethyl-aniline by a method analogous to that described for acetanilid. Forms large crystalline needles, difficultly soluble in cold water, easily soluble both in dilute and concentrated alcohol. Has been used as an antineuralgic.

Benzanilid, $C_6H_5.NH(C_6H_5CO)$, is formed by the action of benzoic anhydride or benzoyl chloride upon aniline. Colorless, pearly, lustrous scales, distilling without decomposition. Insoluble in water, moderately soluble in cold alcohol, more readily in hot alcohol. Used as an antipyretic.

Gallanilid, $C_6H_5.NH[C_6H_2(OH)_3CO]$.—Made by heating gallic acid with an excess of aniline for an hour to 150°. The pure compound fuses at about 205°, and is difficultly soluble in cold water, more readily soluble in hot water, soluble in alcohol and ether. Has been used instead of pyrogallol in skin diseases for external application.

Toluidines, $C_6H_4(CH_3)NH_2$.—The three toluidines are formed by the reduction of the three nitro-toluenes. Para-toluidine, which is solid, and ortho-toluidine, which is liquid, are both present in coal-tar. In manufacturing commercial aniline by the reduction of commercial nitrobenzene, there is always formed a mixture of the two toluidines with aniline, as the original benzene is contaminated with toluene.

Xylidines, $C_6H_3(CH_3)_2NH_2$.—The six possible isomeric xylidines are all known. The technical xylidine contains several isomers, and is largely used for the manufacture of azo dye-stuffs.

Benzylamine, $C_6H_5CH_2.NH_2$, is isomeric with the toluidines. A colorless, basic liquid, boiling undecomposed. Formed most readily by heating benzyl chloride, $C_6H_5.CH_2Cl$, with acetamide, $NH_2(C_2H_3O)$, when the acetyl derivative is formed, from which the base may be obtained.

2. **Secondary Monamines.**—We have, as the first representative of this class:

Diphenylamine, $(C_6H_5)_2.NH$, which is obtained technically by heating aniline hydrochloride with aniline under pressure:

$$C_6H_5NH_2.HCl + C_6H_5.NH_2 = C_6H_5.NH—C_6H_5 + NH_4Cl.$$

It forms white scales, with an agreeable odor of flowers, and a burning aromatic taste; hardly soluble in water, easily soluble in alcohol, ether, and petroleum naphtha. A solution of diphenylamine in concentrated sulphuric acid is colored intensely blue by traces of nitric or nitrous acids, and hence is used for this purpose in water analysis.

The hexanitro derivative of diphenylamine, $C_{12}H_5(NO_2)_6N$, acts as a weak acid. Its ammonia salt is a yellow dye-stuff, known as "aurantia." Methyl-aniline and acetanilid and related compounds already considered may also be ranked as secondary monamines.

3. **Tertiary Monamines.**—The only compound to mention here is: *Triphenylamine*, $N(C_6H_5)_3$.—It forms large leaflets, melting at 127°.

4. **Diamines and Triamines.**—The diamines may be formed by several reactions, the simplest of which is the reduction of the dinitro compounds. The three isomeric compounds may be distinguished from each other by characteristic reactions; thus, the meta diamines with nitrous acid give rise to a class of yellowish-brown azo dye-stuffs:

$$\underset{\text{Metaphenylene-diamines.}}{2C_6H_4(NH_2)_2} + HNO_2 = \underset{\text{Bismarck Brown.}}{C_{12}H_{13}N_5} + 2H_2O;$$

and the paradiamines when reduced with H_2S and then oxidized yield violet or blue sulphur-containing dye-stuffs of the methylene-blue class.

Metaphenylene-diamine, $C_6H_4\left\{\begin{matrix}NH_2\ (1)\\ NH_2\ (3)\end{matrix}\right.$, forms crystals melting at 63° and boiling at 276°–277°; difficultly soluble in water, easily in alcohol and ether. As traces of nitrous acid produce the reaction given above with the formation of a yellow dye, it constitutes a very delicate test for nitrous acid.

Paraphenylene-diamine, $C_6H_4\left\{\begin{matrix}NH_2\ (1)\\ NH_2\ (4)\end{matrix}\right.$, forms tablets fusing at 140° and boiling at 267°. When oxidized with ferric chloride or manganese oxide and sulphuric acid, quinone, $C_6H_4O_2$, is formed.

Triamido-benzene, $C_6H_3(NH_2)_3$, and *Tetramido-benzene*, $C_6H_2(NH_2)_4$, are representatives of triamines and tetramines respectively.

More special mention of the important dye-colors which are derived from the amines will be found under triphenyl-methane in a later section.

VI. DIAZO AND AZO COMPOUNDS. HYDRAZINES.

Both the diazo and the azo compounds contain the dyad group—N=N—. In the diazo compounds this group links together a hydrocarbon radical and an acid, in the azo compounds it links together two hydrocarbon radicals, as $C_6H_5—N=N—Cl$, diazo-benzene chloride. and $C_6H_5—N=N—C_6H_5$, azo-benzene.

1. **Diazo Compounds.**—This class is of very great scientific and technical interest, and its study has led to the discovery of the very numerous group of azo dye-colors, compounds formed by the reaction of the diazo bodies with the phenols and the amines.

To understand these diazo bodies let us compare the action of nitrous acid upon the primary amines of the methane series and the benzene series respectively. The former are converted into alcohols without the formation of intermediate products, according to the reaction:

$$C_2H_5.NH_2 + NOOH = C_2H_5.OH + N_2 + H_2O$$

The latter can undergo an analogous change, but there result in their case well-characterized intermediate products, these so-called diazo compounds. Thus:

$$\begin{array}{l} C_6H_5.N\vdots H_2.H\vdots NO_3 = C_6H_5.N{=}N.NO_3 + 2H_2O. \\ \quad N\vdots O_2H\vdots \end{array}$$

Diazo-benzene Nitrate.

This reaction is carried out in the cold, in fact in a carefully-cooled solution. If the solution is warmed, the reaction goes on to the end result indicated with the other class of amines and a phenol is formed:

$$C_6H_5.N{=}N.NO_3 + H.OH = C_6H_5.OH + N_2 + HNO_3.$$

Just as the salts of the primary monamines when treated with nitrous acid yield the diazo compounds, so when primary diamines are treated with nitrous acid we obtain *tetrazo compounds*, also of great value as dyestuffs, particularly for cotton dyeing.

Besides the reaction whereby on heating in solution the diazo compounds decompose with the formation of a phenol, we have a second equally important one. When their salts are heated with alcohol they are changed into the corresponding hydrocarbons with liberation of nitrogen:

$$C_6H_5.N{=}N.Cl + C_2H_5OH = C_6H_6 + N_2 + HCl + C_2H_4O.$$

By means of these two reactions it is possible to change from an amido compound into either a phenol or back to the original hydrocarbon. Hence their great importance in the synthetic work of organic chemistry. The salts of the diazo compounds are mostly colorless crystalline bodies, which are explosive in dry condition and decompose on strong heating of their aqueous solutions.

Diazo-benzene Chloride, $C_6H_5.N{=}N.Cl$.—Stable only in solution.

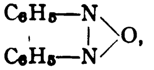
Diazo-benzene Nitrate, $C_6H_5N{=}N.NO_3$.—Colorless, needles, very explosive.

Diazo-benzene Sulphate, $C_6H_5N{=}N.HSO_4$.—Prisms which explode at 160°.

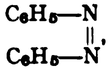
The free *diazo-benzene*, $C_6H_5N{=}N{-}(OH)$, is a heavy oil of yellow color and aromatic odor, which decomposes easily with liberation of nitrogen.

2. **Azo Compounds.**—While the reduction of nitro compounds in acid solution leads to the aromatic amines, the use of alkaline reducing agents, such as sodium amalgam, zinc-dust and caustic soda, and potash and alcohol, gives rise to intermediate products. The connection of these with the starting-point nitro-benzene and the end product aniline is shown in the following formulas:

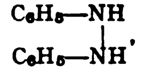
$C_6H_5.NO_2$,



Azoxy-benzene.



Azo-benzene.



Hydrazo-benzene.

$C_6H_5.NH_2$.

These three intermediate classes are usually grouped together under the general name of azo compounds.

From azo-benzene, $C_6H_5—N=N—C_6H_5$, may be obtained two important classes of colored derivatives, which are of great value under the name of *azo dye-colors*. By the introduction of the amido group in the place of a hydrogen atom we obtain the amido-azo compounds like $C_6H_5.N=N.C_6H_4NH_2$, amido-azo-benzene; by the introduction of the hydroxyl group in the place of a hydrogen atom we obtain oxyazo compounds like $C_6H_5.N=N—C_6H_4(OH)$, oxyazo-benzene. These are formed respectively, by the action of an amine upon the diazo compounds and the action of a phenol upon the same.

Most of these azo dyes are insoluble in water, but all can be converted by the action of strong sulphuric acid into the corresponding sulphonic acids, and both these and their alkaline salts are soluble in water.

The dyes which are derivatives of amidoazo-benzene are termed "Chrysoïdines," and those which are derivatives of oxyazo-benzene are termed "Tropæölines."

3. **Hydrazines.**—The aromatic hydrazines, like those in the methane series, are derivatives of hydrazine, $NH_2—NH_2$, formed by the replacement of the hydrogen atoms by alcohol radicals.

Phenyl-hydrazine, $C_6H_5.NH—NH_2$, the most important of the class of hydrazines, is prepared by the reduction of diazo-benzene chloride:

$$C_6H_5.N=N.Cl + H_4 = C_6H_5.NH—NH_2.HCl.$$

The base itself fuses at 18° to a colorless oil, insoluble in water, soluble in alcohol and ether, which distils undecomposed at 233°. Forms crystallizable salts. Phenyl-hydrazine is a powerful reducing agent, reducing Fehling's solution even in the cold. Its reaction with aceto-acetic ether to form phenyl-methyl-pyrazolon, as the most important step in the manufacture of "antipyrin," has already been mentioned (see Antipyrin, p. 614). Its most general use, however, is as a reagent, as it combines with aldehydes and ketones, and hence with the sugars, to form crystalline compounds known as *hydrazones* and *osazones*. Phenyl-hydrazine itself is poisonous.

VII. PHENOLS AND THEIR DERIVATIVES AND QUINONES.

The hydroxyl derivatives of the methane series of hydrocarbons were all called alcohols, although the distinction was made of primary, secondary, and tertiary alcohols. In the case of benzene and its homologues, we must distinguish between the case where the OH group replaces a hydrogen atom of the nucleus and where it replaces a hydrogen atom of the side-group. In the former case the compounds are called *phenols*, and in the latter *aromatic alcohols*. As the latter contain the group $—CH_2.OH$ characteristic of primary alcohols (see p. 533), they can be oxidized to aldehydes and acids, while the former, which are more likely tertiary alcohols, cannot be oxidized without entire decomposition of the molecule

According to the number of the OH groups introduced in place of hydrogen of the nucleus, we have monatomic, diatomic, triatomic, etc., phenols.

TABULAR VIEW OF THE MORE IMPORTANT PHENOLS.

Monatomic.	Diatomic.	Triatomic.
$C_6H_5.OH$, Phenol, m. p. 42°, b. p. 181°.	$C_6H_4(OH)_2$, Dioxy-benzenes: *o*- = Pyrocatechin, 104°–245°; *m*- =Resorcin, 118°–280°; *p*- = Hydroquinone, 169°.	$C_6H_3(OH_3)$, Trioxybenzenes: *v*- = Pyrogallol, 115°–210°; *a*- = Oxyhydroquinone, 140.5°; *s*- = Phloroglucin, 217°.
$C_6H_4(CH_3).OH$, Cresols, *o*-31°–188°, *m*-3°–201°, *p*-36°–198°.	$C_6H_3(CH_3).(OH)_2$, Dioxytoluenes: 1:3 : 5 = Orcin, 107°–288°; 1 : 3 : 4 = Homopyrocatechin.	$C_6H_2(CH_3)(OH)_3$, Methyl-pyrogallol.
$C_6H_3(CH_3)_2OH$, Xylenols.	$C_6H_2(CH_3)_2(OH)_2$, Xylorcin.	
$C_6H_2(CH_3)_3OH$, Pseudo-cumenols.	$C_6H(CH_3)_3.(OH)_2$. Mesorcin.	
$C_6H(CH_3)_4.OH$, Durenols. Isomeric with these are: $C_6H_3(CH_3)(C_3H_7).OH$, Thymol, Carvacrol.	Tetratomic Phenols.	Hexatomic Phenols.
$C_6(CH_3)_5OH$, Penta-methyl-phenol.	$C_6H_2(OH)_4$, Tetraoxybenzene.	$C_6(OH)_6$, Hexaoxybenzene.

The phenols in chemical character stand between the true alcohols and the organic acids. They combine to form mixed ethers, like anisol, $C_6H_5.OCH_3$, or esters, like phenyl-sulphuric acid, $C_6H_5{-}OSO_3H$. At the same time they have the character of weak acids, and form salts with the metals, like $C_6H_5.ONa$, sodium phenol. The acid character is notably increased by the entrance of NO_2 groups, as in trinitro-phenol (picric acid), $C_6H_2(NO_2)_3.OH$.

Phenols are formed by the dry distillation of many organic substances. Thus, phenol and cresol and their homologues are found in coal-tar and in various wood-tars. They are also formed artificially by numerous reactions, among which may be mentioned:

1. By the fusion of the sulpho acids of the aromatic hydrocarbons with caustic potash, $C_6H_5HSO_3 + 2KOH = C_6H_5.OH + K_2SO_3 + H_2O$.

2. By the action of nitrous acid upon the amido compounds and boiling the diazo compounds which first form with water. The two reactions are:

(*a*) $C_6H_5NH_2HCl + HNO_2 = C_6H_5N{=}N{-}Cl + 2H_2O$.
(*b*) $C_6H_5.N{=}N.Cl + H_2O = C_6H_5.OH + N_2 + HCl$.

3. By the dry distillation of the aromatic phenol-acids (oxyacids) either with or without lime:

$$\underset{\text{Gallic Acid.}}{C_6H_2(OH)_3.COOH} = \underset{\text{Pyrogallol.}}{C_6H_3(OH)_3} + CO_2.$$

Among the most characteristic reactions of the phenols may be mentioned:

1. The formation of the several classes of derivatives already referred to, in which the H of the hydroxyl is replaced,—viz., phenolates, phenol-ethers, and phenol-esters.

2. The formation of substitution compounds in which hydrogen of the nucleus is replaced by chlorine, bromine, nitro, or sulphonic group.

3. The sodium and potassium phenolates unite with CO_2, when heated under pressure, to form salts of oxyacids:

$$\underset{\text{Sodium Phenol.}}{C_6H_5ONa} + CO_2 = \underset{\text{Sodium Salicylate.}}{C_6H_4(OH)COONa.}$$

4. Many phenols give characteristic colors when ferric chloride is added to their neutral solutions. Thus, with ferric chloride phenol and resorcin give a violet color, pyrocatechin a green color, orcin a blue-violet, and pyrogallol a red color.

1. **Monatomic Phenols.**—From benzene but one monatomic phenol is derived.

Phenol, $C_6H_5.OH$ (**Phenol**, U.S.P.), was discovered in 1834 in coal-tar. It is found in the urine of herbivora and of man (as phenyl-sulphuric acid), in castoreum, in bone oil, and in coal- and wood tar. It forms colorless, crystalline needles, fusing at 42°, and boiling at 181°. A small percentage of water liquefies the crystals and keeps it in liquid condition (**Phenol Liquefactum**, U.S.P.). It is soluble in 12 parts of water at ordinary temperatures, easily soluble in hot water, in alcohol, ether, glycerin, fixed oils, potash, and ammonia; has a strong and characteristic odor, burning taste, and caustic action on the skin. It is a strong antiseptic, even in the impure state, when it contains considerable cresols and higher phenols. Ferric chloride colors it even in dilute solution violet. Bromine water causes a white precipitate of tribrom-phenol. It unites with the alkalies and other bases to form the so-called "carbolates," as $C_6H_5.ONa$.

Both chlorine and bromine readily form substitution compounds with phenol, such as *Trichlor-phenol*, $C_6H_2Cl_3.OH$, and *Tribrom-phenol*, $C_6H_2Br_3.OH$. Both of these are distinguished by their antiseptic and healing power, and have been recommended in medicine. The former is a gas of sharp, penetrating odor, and the latter is a white, crystalline solid, melting at 95°. The bismuth compound of tribrom-phenol is also used as an antiseptic dressing under the name of "xeroform."

Nitro Phenols.—Mono- and dinitro-phenols are known, but the only important compound to note is **Trinitro phenol**, U.S.P., known also as picric acid. This is formed by the action of fuming nitric acid upon many organic substances such as indigo, silk, leather, wool, etc. It is ordinarily prepared by the nitration of phenol in the presence of strong sulphuric acid. It crystallizes out of water or alcohol in pale-yellow scales, and out of ether in prismatic needles, which have a bitter taste. It melts at 122.5°, and can be sublimed without decomposition, but on rapid heating it is instantly decomposed with slight explosion. It is an important yellow dye and is used to fill explosive shells. Its salts are beautifully crystallized, but very explosive when heated or struck. The potassium and ammonium salts are used in various explosive mixtures. Picric acid also forms well-crystallized addition compounds with many of the higher hydrocarbons, as naphthalene and anthracene, and with alkaloids.

Amido Phenols are formed by the reduction of the corresponding nitro phenols. From para-amido-phenol, $C_6H_4(OH)NH_2$, several important derivatives are obtained. The ethyl ethers of the amido-phenols are called "phenetidins." From the para-amido-phenol just mentioned we obtain then para-phenetidin, $C_6H_4\left\{\begin{matrix}NH_2\\OC_2H_5\end{matrix}\right.$. When this is treated with glacial acetic acid the acetyl group is introduced, and we obtain *acetpara-phenetidin*, (**Acetphenetidinum**, U.S.P.), $C_6H_4\left\{\begin{matrix}OC_2H_5\\NH(C_2H_3O)\end{matrix}\right.$ which was first brought into medical use under the name of "phenacetin." It forms white, lustrous crystals, without odor and almost without taste, melting at 135°. It is difficultly soluble in cold water, more readily soluble in alcohol. Phenacetin is one of the best known of the newer antipyretics and antineuralgics.

An important amino-phenol derivative is *arsenphenolamine hydrochloride* $\begin{matrix}AS—C_6H_3.OH.NH_2.HCl\\ \| \\ AS—C_6H_3.OH.NH_2.HCl\end{matrix}+2H_2O$, known as *salvarsan* or "606," introduced by Ehrlich as a specific for syphilis.

Phenol-sulphonic Acids are formed by the action of concentrated sulphuric acid upon phenol at low temperatures. The ortho-phenol-sulphonic acid is used in 33⅓ per cent. solution as an antiseptic, under the name of "aseptol" or "sozolic acid." On keeping, it gradually changes into the isomeric para-phenol-sulphonic acid, which change is also readily effected by heating its solutions. The para acid yields well-crystallized salts, two of which are well known in medicine. The sodium salt, $C_6H_4\left\{\begin{matrix}OH\\SO_3Na\end{matrix}\right.+2H_2O$ (**Sodii Phenolsulphonas**, U.S.P.), forms colorless, rhombic prisms, odorless, and with a cooling, saline and slightly bitter taste. The zinc salt $(C_6H_5O.SO_3)_2Zn+8H_2O$ (**Zinci Phenolsulphonas**, U.S.P.), forms colorless, tabular efflorescent crystals. By the action of a mixture of potassium iodide and iodate upon the para-phenol-sulphonic acid is obtained the potassium salt of di-iodo-para-phenol-sulphonic acid, which, along with other salts of the same acid, has been introduced into medicine under the name of "soziodol" compounds. They are used as antiseptics and substitutes for iodoform for external use.

Anisol (phenyl-methyl ether), $C_6H_5.OCH_3$, and *Phenetol* (phenyl-ethyl ether), $C_6H_5.OC_2H_5$, are obtained by heating phenol and caustic potash with either methyl or ethyl iodide in alcoholic solution. They are liquids of ethereal odor, the former boiling at 152°, and the latter at 172°.

Cresols, $C_6H_4(CH_3)OH$ (**Cresol**, U.S.P.), are the first homologues of phenol. All three of these compounds are present in coal-tar, and are also contained in the tar from pine and beech wood. Crude carbolic acid always contains a mixture of these, known technically as "cresylic acids." The official cresol is "a mixture of the three isomeric cresols obtained from coal-tar, freed from phenol, hydrocarbons and water." The addition of soaps increases the solubility of the cresols, hence the use of mixtures like **Liquor cresolis compositus**, U.S.P., and such preparations as *lysol*, *creolin*, *cresolin*, etc., which are of this kind. Ortho-cresol is found in the form of its sulphuric ester in the urine of horses; para-cresol is produced by the decay of albumin (tyrosin), and is found in human urine. Its dinitro compound is a golden yellow dye, which is used as ammonium or potassium salt, under the name of "Victoria orange." Meta-cresol is said to be the most powerful antiseptic, exceeding phenol in power, but is much more poisonous. A derivative of this latter is the tri-iodo-meta-cresol, $C_6HI_3(CH_3)OH$, introduced into medicine under the name of "losophan." Several of the amido phenols and amido cresols find application as photographic developing agents. Para-amido-phenol is known as "rhodinal," methyl-*p*-amido cresol as "amidol," and the salts of the same as "metol."

Thymol, U.S.P., is para-propyl-meta-cresol, $C_6H_3.\overset{1}{C}H_3.\overset{3}{O}H.\overset{4}{C}_3H_7$. It is a phenol found naturally occurring in a number of essential oils. It forms large, colorless, translucent crystals with an aromatic, thyme-like odor and pungent, aromatic taste. It melts at 50°–51°, and boils at 228°–230°. When triturated with equal quantities of camphor, menthol, or chloral hydrate, it liquefies. It is difficultly soluble in water, readily soluble in alcohol, ether, or chloroform. A derivative of thymol is dithymol di-iodide, $C_{20}H_{24}O_2I_2$ (**Thymolis Iodidum**, U.S.P.), which was first introduced into medicine under the name of "aristol." It is a light, chocolate-colored powder, almost without odor or taste, and is used as a substitute for iodoform.

Isomeric with thymol is *carvacrol*, which is para-propyl-ortho-cresol, $C_6H_3.\overset{1}{C}H_3.\overset{2}{O}H.\overset{4}{C}_3H_7$. It is present in oil of *Origanum hirtum*, and may be prepared by heating camphor with iodine.

Xylenols, $C_6H_3(CH_3)_2OH$.—Of the six possible isomers, *m*-xylenol is found in the creosote of beech-wood tar.

2. Diatomic Phenols.—These compounds containing two hydroxyl groups are formed by methods analogous to those given for the monatomic phenols, especially by the method of fusion of the sulphonic acids with potash.

Pyrocatechin (or Catechol) $C_6H_4(OH)_2$, is the ortho compound. It was first formed by the dry distillation of catechin (mimosa catechu), whence the name. It is present in small amounts in human urine, and is formed by the dry distillation of wood, by heating cane sugar, cellulose, and starch with water to 200°–280°. It is also formed by the fusion of many resins with potash. It crystallizes in short, rhombic prisms, which can be sublimed, and are readily soluble in water, alcohol, and ether. The aqueous solution is colored green with ferric chloride and then violet by ammonia. It possesses reducing properties, causing reduction of silver nitrate even in the cold. Its monomethyl-ether, $C_6H_4\left\{\begin{matrix}OH\\ OCH_3\end{matrix}\right.$, is *guaiacol* (**Guaiacol,** U.S.P.), and its dimethyl-ether, $C_6H_4\left\{\begin{matrix}OCH_3\\ OCH_3\end{matrix}\right.$, is *veratrol*. The first of these forms the main constituent of the beech-wood creosote (**Creosotum,** U.S.P.), making up from 60-90 per cent. of the same. The guaiacol is now obtained pure from the creosote as well as made synthetically from either catechol by methylating, or from ortho-anisidin by diazotizing and boiling, and introduced into medicine in various preparations as a remedy in phthisis. It forms a colorless, somewhat refractive liquid, of strong aromatic, not unpleasant odor, boils at 205°, and has a sp. gr. 1.140. It is difficultly soluble in water, easily soluble in alcohol and ether.

Its carbonate $(C_7H_7O)_2CO_3$ (**Guaiacolis Carbonas,** (U.S.P.), is obtained by the action of carbonyl chloride upon sodium guaiacolate, and is also used in medicine. A mixture of the carbonates of the various constituents of creosote, chiefly guaiacol and creosol, is also official (**Creosoti Carbonas,** U.S.P).

Resorcin (or Resorcinol), $C_6H_4(OH)_2$, is the meta compound and is official (**Resorcinol,** U.S.P.). It is obtained on fusing various resins (galbanum, asafœtida, ammoniac, etc.) with potash. Commercially it is obtained by fusing mixed benzene-disulphonic acids with soda. It forms colorless or faintly reddish needles, with a faint, peculiar odor, and a disagreeable, sweetish and pungent taste. It melts at 119° and volatilizes at a higher heat. It is soluble in water, alcohol, and ether, and reduces an aqueous solution of silver nitrate when warmed and an alkaline solution in the cold. It gives a dark-violet color with ferric chloride solution. Nitrous acid converts it into a nitroso derivative, $C_6H_4O_2(NO)_2$, the iron salt of which is used in cotton-dyeing under the name of "solid green." Fused with phthalic anhydride it yields fluoresceïn (see phthaleïn dyes), which dissolves in caustic soda with a green fluorescence. Resorcin is used in medicine as an antiseptic and on a large scale in the manufacture of fluoresceïn and eosin dye-colors.

Hydroquinone (or Quinol) $C_6H_4(OH)_2$, is the para-dioxy-benzene. It is prepared by the dry distillation of quinic acid, or its oxidation by means of lead dioxide, by the reduction of quinone, $C_6H_4O_2$, and by the decomposition of the glucoside arbutin. Commercially, it is made by oxidizing aniline with chromic acid mixture. It forms small monoclinic plates, fusing at 169°, readily soluble in hot water, alcohol, and ether. It reduces silver nitrate solution on heating, and Fehling's solution even in the cold. Its alkaline solutions are active reducing agents, and are used in photography as the basis of developing solutions.

Orcinol, $C_6H_3(CH_3)(OH)_2$, is a dioxy-toluene. It is found in many lichens (*Rocella tinctoria, Lecanora,* etc.). It is formed when aloes are fused with caustic potash, and can be made synthetically from toluene, by fusing *m*-dibrom-toluene with potash at 280°. It crystallizes in colorless prisms, which turn red. The ammoniacal solution absorbs oxygen from the air, and yields *orceïn,* $C_7H_7NO_3$, the chief constituent of commercial archil dye. Related to this latter coloring matter is also *litmus,* the well-known blue vegetable color.

Homo-*pyrocatechol,* $C_6H_3(CH_3)(OH)_2$, is an isomeric dioxytoluene. Its methyl-ether is *creosol,* $C_6H_3(CH_3), \left\{ \begin{matrix} OH, \\ OCH_3, \end{matrix} \right.$ one of the chief constituents, along with guaiacol, of the creosote of beech-wood tar.

Eugenol, $C_6H_3(OH)(OCH_3)C_3H_5$, 4:3:1 (**Eugenol,** U.S.P.), the chief constituent of oil of cloves, is the methyl-ether of allyl-dioxybenzene, an unsaturated phenol, $C_6H_3(OH)_2(CH_2.CH = CH_2)$.

Safrol, found in oils of sassafras and camphor; is the methylene-ether of the same allyl-dioxy-benzene.

An important derived diphenol compound is *dihydroxydiamino-arsenobenzene,* or as it is more commonly known, "Salvarsan," introduced into medical practice by Ehrlich in 1910.

3. **Triatomic Phenols.**—Of the three isomeric trioxy-benzenes, the most important is *Pyrogallol,* $C_6H_3(OH)_3$, 1:2:3 (**Pyrogallol,** U.S.P.). It is obtained by heating gallic acid with water under pressure: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$. It forms light, white, shining laminæ, odorless, and with a bitter taste. It becomes darker on exposure to air and light. It is soluble in water, alcohol, and ether. Its solutions, especially when alkaline, absorb oxygen from the air and turn brown in color. Because of this reaction it is used in gas analysis to absorb free oxygen from gaseous mixtures. This reducing power is also recognized with silver, gold, and mercury solutions. It is largely used in photography as a developer because of this power of reduction of silver salts, Pyrogallol also combines with phthalic anhydride to form the dye-color "galleïn."

Phloroglucinol, $C_6H_3(OH)_3$, an isomeric trioxy-benzene, is produced in the decomposition of phloretin, a glucoside, and by the fusion of a number of resins (such as gamboge, dragon's blood, catechu, and kino) with caustic potash. It is also obtained synthetically by the fusion of benzene-trisulphonic acid with potash. It forms large prisms, which sublime without decomposition, melting at 218°. With ferric chloride it gives a dark-violet coloration. Phloroglucinol colors a pine shaving moistened with hydrochloric acid, red, and is used for the detection of lignin or wood-fibre in paper, etc.

Oxyhydroquinone, $C_6H_3(OH)_3$, the third isomeric trioxy-benzene, results from the fusion of hydroquinone with potash.

4. **Tetratomic Phenols.**—A tetroxy-benzene, $C_6H_2(OH)_4$, has been prepared from succino-succinic ether. It crystallizes in yellow needles, and is stable when pure.

5. **Pentatomic Phenols.**—As hexahydro derivatives of a pentatomic phenol, $C_6H(OH)_5$, we must include several compounds which at one time were considered to be pentatomic alcohols, or to belong to the carbohydrates.

Quercitol, $C_6H(OH)_5.H_6$.—A sweet-tasting crystalline principle extracted from the oak. It forms colorless monoclinic crystals, melting at 235°.

Pinitol, $C_6H(OH)_5.H_6$, is found in the exudation of the California pine (*Pinus lambertiana*). It forms colorless crystals, easily soluble in water, and fusing at over 150°.

Inosite (Phaseomannite), $C_6H_{12}O_6 + 2H_2O$, is found in small amount in the muscular tissue, in the heart, lungs, liver, spleen, kidneys, and brain; the urine also contains inosite after abundant water drinking.

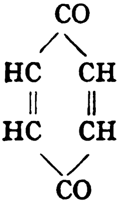
It is also contained in plants, as green beans, peas, lentils, and grape juice. It crystallizes in rhombic plates, which crumble in the air. Soluble in water, insoluble in alcohol. Melts at 210°. It has no reducing power, nor is it fermentable.

6. **Hexatomic Phenols.**—We have a derivative of the normal hexoxy-benzene, $C_6(OH)_6$, in the so-called potassium carbon monoxide, formed in the distillation of metallic potassium, which has the formula $C_6(OK)_6$. The phenol itself has also been prepared synthetically. It forms small, grayish-white needles, which acquire a reddish color on exposure to the air. They are not fusible, but decompose at about 200°.

Phenose is a hexatomic phenol of hexahydro-benzene, and has the formula $C_6H_6(OH)_6$. It has been obtained by the action of soda solution upon the hypochlorous acid addition product of benzene, $C_6H_6\left\{\begin{matrix}Cl_3\\(OH)_3\end{matrix}\right.$. It is an amorphous, readily soluble, and deliquescent substance. It is much like the glucoses, has a sweet taste, and reduces Fehling's solution, but is not capable of fermentation.

7. **Quinones.**—This term is applied to a class of benzene derivatives in which two hydrogen atoms seem to be replaced by two oxygen atoms. Not only benzene, but especially the condensed aromatic hydrocarbons, naphthalene, anthracene, phenanthrene, chrysene, etc., when oxidized by chromic acid in glacial acetic acid solution yield quinones. They are formed also by the oxidation of a number of derivatives of benzene in which the replacing groups occupy the para position. Thus, hydroquinone (paradioxy-benzene), sulphanilic acid (*p*-amido-benzene-sulphonic acid), and phenylene-diamine, as well as phenol and aniline, all yield quinone when oxidized by chromic acid.

The constitution of quinone, $C_6H_4O_2$, is expressed by the formula:



. According to this formula quinone would be a ketone, not of benzene itself, but of a dihydro-benzene. This view brings it into analogy with anthraquinone and the other higher quinones which are known to be diketones.

Quinone (Benzo-quinone), $C_6H_4O_2$, is made most readily by oxidizing aniline sulphate with potassium chromate and sulphuric acid. The quinone so formed is shaken out with ether. Yellow prisms melting at 115.7° and subliming. It has a chlorine-like odor, is difficultly soluble in cold water, more readily soluble in hot water, as well as in alcohol and ether. It is easily converted into hydroquinone by reducing agents like SO_2 or HI.

By chlorinating quinone, or by the action of potassium chlorate and hydrochloric acid upon phenol, we obtain *tetrachlor-quinone* (chloranil), $C_6Cl_4O_2$. As reducing agents convert it readily into tetrachlorhydroquinone, it is used as an oxidizing agent in the manufacture of aniline colors, as with methyl-violet. Several of the homologues of quinone may also be mentioned, as Tolu-quinone, $C_6H_3(O_2)(CH_3)$, Xylo-quinone, $C_6H_2(O_2)(CH_3)_2$, and Thymo-quinone, $C_6H_2(O_2)\begin{cases}CH_3\\C_3H_7\end{cases}$.

VIII. AROMATIC ALCOHOLS, ALDEHYDES, AND KETONES.

1. Aromatic Alcohols.—The aromatic alcohols differ, as before stated, from the phenols in that the OH has replaced hydrogen in the side-group instead of hydrogen in the nucleus. They may be, and often are, isomeric with phenols, as benzyl alcohol, $C_6H_5.CH_2OH$, and cresol, $C_6H_4(CH)_3OH$.

The comparison of the formula of benzyl alcohol with that of the alcohols of the methane series will make its nature clearer:

$H.CH_2OH$	$CH_3.CH_2OH$	$C_6H_5.CH_2OH$.
Methyl Alcohol.	Ethyl Alcohol.	Benzyl Alcohol.

It is seen here that the single hydrogen of methyl alcohol is replaced by the radical methyl in the second formula, and by the radical phenyl, C_6H_5, in the third formula. Benzyl alcohol is therefore sometimes called phenyl-carbinol.

Just as in the methane series of alcohols we have primary, secondary, and tertiary, so we may have primary, secondary, and tertiary aromatic alcohols, as

$C_6H_5.CH_2OH$	Primary alcohol.
$(C_6H_5)_2CH.OH$ and $C_6H_5.CHOH.CH_3$	Secondary "
$(C_6H_5)_3.C(OH)$	Tertiary "

Diatomic and triatomic alcohols likewise can be formed, as $C_6H_4(CH_2.OH)_2$, toluylene alcohols, and $C_9H_9(OH)_3$, phenyl-glycerin.

The strongest analogy of these aromatic alcohols with the corresponding compounds in the methane series is found in the similarity in the effect of oxidizing agents. The primary aromatic alcohols yield aldehydes and monobasic acids, and the secondary yield ketones. Ethers, esters, mercaptans, amines, etc., are also formed in strict analogy to those already studied under the methane series. By the entrance of the phenyl group into unsaturated fatty alcohols we also obtain unsaturated aromatic alcohols analogous to other unsaturated compounds.

Benzyl Alcohol, $C_6H_5.CH_2OH$, is found as benzoic and cinnamic esters in Peru and Tolu balsams, and is made from benzyl chloride, $C_6H_5CH_2.Cl$, by boiling it for a time with water, or by the action of potash solution upon its aldehyde, $C_6H_5.COH$:

$$2C_6H_5.COH + KOH = C_6H_5.CH_2OH + C_6H_5.COOK.$$

Benzaldehyde. Benzyl Alcohol. Potassium Benzoate.

Benzyl alcohol is a colorless liquid of weak aromatic odor, boiling at 206.5°. It is not very soluble in water. When oxidized it yields first benzaldehyde, $C_6H_5.COH$, and then benzoic acid, $C_6H_5.COOH$.

Tolyl Alcohols, $C_6H_4(CH_3)CH_2OH$.—All three isomeric varieties have been obtained.

Phenyl-methyl Carbinol, $C_6H_5.CHOH.CH_3$, is a secondary alcohol obtained by the action of sodium amalgam upon the corresponding ketone, $C_6H_5.CO.CH_3$ (acetophenone), and on careful oxidation reproduces this compound.

Phenyl-propyl Alcohol (Hydrocinnamyl Alcohol), $C_6H_5.CH_2.CH_2.CH_2.OH$, is obtained from cinnamyl alcohol by reduction. It exists as cinnamic ester in storax. Closely related to this is the unsaturated aromatic alcohol known as

Cinnamyl Alcohol (Styrene), $C_6H_5.CH{=}CH.CH_2OH$.—This occurs as cinnamic ester under the name of styracine in storax resin (**Styrax**, U.S.P.). It crystallizes in shining needles, is sparingly soluble in water, and possesses a hyacinth-like odor. It melts at 33° and distils at 250°. On careful oxidation it yields cinnamic acid; more energetically oxidized it yields benzoic acid.

2. **Aromatic Aldehydes.**—These correspond in all their general properties with the aldehydes of the methane series.

Benzaldehyde, $C_6H_5.COH$ (**Benzaldehydum**, U.S.P.).—This compound was at one time exclusively obtained by the decomposition of the glucoside amygdalin of the bitter almond in the presence of emulsin and other ferments, according to the reaction $C_{20}H_{27}NO_{11} + 2H_2O = C_6H_5.COH + 2C_6H_{12}O_6 + HCN$. It is now mostly made artificially by the oxidation of the chlorine derivatives of toluene:

$$2C_6H_5CH_2Cl + C_6H_5CHCl_2 + 2MnO_2 = 3C_6H_5.COH + 2MnCl_2 + H_2O,$$

Benzyl Chloride. Benzal Chloride. Benzaldehyde.

or by heating benzal chloride with milk of lime under pressure. This reaction has already been noted under benzal chloride (see p. 628).

Benzaldehyde is a colorless, strongly-refracting liquid of pleasant bitter-almond odor and burning aromatic taste. Boils at 179°, and has a sp. gr. of 1.045 at 25° C. It is only slightly soluble in water, but is easily soluble in alcohol and ether. Its behavior shows in many ways its character as an aldehyde. It is easily oxidized to the corresponding acid; it reduces silver solutions with the formation of a metallic mirror; it may be reduced to a primary alcohol; it forms a crystalline compound with sodium bisulphite; it reacts with hydroxylamine and phenyl-hydrazine. A reaction which is distinct and quite characteristic of it as an aromatic aldehyde is its power to unite to form condensation products. Thus, we are able to effect the synthesis of cinnamic acid by the condensation of benzaldehyde and sodium acetate, $C_6H_5.COH + CH_3COONa = C_6H_5CH : CH.COONa + H_2O$.

Nitro-benzaldehydes, $C_6H_4(NO_2).COH$.—Of these isomers the ortho compound is of especial interest, as by its means artificial indigo has been made, the aldehyde condensing with acetone to form a compound which is decomposed by caustic soda into indigo and acetic acid.

Cumic Aldehyde (Cuminol), $C_6H_4(C_3H_7).COH$.—This is an isopropyl-benzaldehyde. It occurs together with cymene, $C_{10}H_{14}$, in Roman caraway oil and in oil of water hemlock (*Cicuta virosa*). It possesses an aromatic odor, and boils at 235°.

Cinnamic Aldehyde, $C_6H_5.CH = CH.COH$. This unsaturated aldehyde is the chief constituent of the essential oils of cinnamon and cassia, and can be isolated from them by means of its sodium bisulphate compound. It may also be made synthetically by saturating a mixture of benzaldehyde and acetaldehyde with hydrochloric acid gas, when condensation takes place: $C_6H_5.COH + CH_3.COH = C_6H_5.CH:CH.COH + H_2O$.

It is a colorless, aromatic oil which boils at 250° and distils in a current of steam. When exposed to the air it oxidizes to cinnamic acid.

3. **Aromatic Ketones.**—The ketones which correspond to secondary aromatic alcohols are in all respects analogous to the corresponding ketones of the methane series. They may be formed by analogous methods: either by the oxidation of the secondary alcohols, or by the distillation of the lime salts of the aromatic acids.

Aceto-phenone (Phenyl-methyl Ketone, Hypnone), $C_6H_5.CO.CH_3$, is the simplest representative of this class. It is formed by the distillation of a mixture of calcium acetate and benzoate taken in molecular proportions:

$$(C_6H_5.COO)_2Ca + (CH_3.COO)_2Ca = 2CaCO_3 + 2C_6H_5.CO.CH_3.$$

It is a colorless, oily liquid, boiling at 210°, and crystallizing at 14° in large leaflets, which then melt at 20°. It has a peculiar aromatic odor, is difficultly soluble in water, easily soluble in alcohol, ether, chloroform, and fatty oils. When oxidized it yields benzoic acid and carbon dioxide. It has been introduced into medicine as an hypnotic, replacing chloral hydrate and paraldehyde. The name "hypnone" has been given it in this connection.

Phenyl-ethyl Ketone and *Phenyl-propyl Ketone* are also known. The ketone corresponding to benzoic acid, $C_6H_5CO.C_6H_5$, and known as diphenyl ketone, or benzo-phenone, will be mentioned later under diphenyl-methane. The diatomic and triatomic phenols also react with glacial acetic acid in the presence of zinc chloride to produce a class of ketones known as keto-phenols.

Gallaceto-phenone, $C_6H_2(OH)_3.COCH_3$, is formed by the reaction between pyrogallol and glacial acetic acid in the presence of zinc chloride. It forms a dirty-flesh-colored crystalline powder, difficultly soluble in cold water, easily soluble in hot water, alcohol, or ether, and in glycerin. It melts at 170°. It is used in medicine as a substitute for pyrogallol, being relatively non-poisonous, and at the same time strongly antiseptic against micro-organisms.

IX. Phenol Alcohols and Phenol Aldehydes.

1. **Phenol Alcohols.**—These compounds, as the name indicates, partake of both phenol and aromatic alcohol character; that is, they must contain at least two OH groups, one of which (the phenolic OH) is directly attached to the nucleus, and the other (the alcoholic OH) is contained in the side group, which will then be CH_2OH. The empirical formulas of the phenol alcohols will always differ by one additional oxygen atom from the aromatic alcohols to which they correspond. Hence they are often called "oxy alcohols."

Oxy-benzyl Alcohols, $C_6H_4(OH)CH_2OH$.—Of the three isomeric compounds of this formula the ortho compound is best known. It is *Saligenin*, or salicyl alcohol, which results when the glucoside salicin is decomposed by emulsin or dilute acids: $C_{13}H_{18}O_7 + H_2O = C_6H_4(OH)$-$CH_2OH + C_6H_{12}O_6$.

It forms pearly tablets soluble in hot water, alcohol, and ether, melting at 82°, and subliming near 100°. It yields salicylic acid when oxidized.

Anisyl Alcohol, $C_6H_4(OCH_3)CH_2OH$, is the methyl ether of the *p*-oxybenzyl alcohol, and is obtained from anisic aldehyde by alcoholic potassium hydroxide. It crystallizes in needles, melting at 25° and boiling at 259° without decomposition. When oxidized it yields anisic aldehyde and acid.

Vanillin Alcohol, $C_6H_3\left\{\begin{array}{l}OH\\OCH_3\\CH_2OH\end{array}\right.$, and *Piperonyl Alcohol*, $C_6H_3\left\{\begin{array}{l}\left.\begin{array}{l}O\\O\end{array}\right>CH_2\\CH_2OH\end{array}\right.$, are formed from their aldehydes vanillin and piperonal by acting on their solutions with sodium amalgam. They are derivatives of the hypothetical prototcatechuy' alcohol, $C_6H_3\left\{\begin{array}{l}OH\\OH\\CH_2OH\end{array}\right.$, as yet unknown.

Vanillin alcohol crystallizes in colorless prisms which melt at 115° and dissolve easily in hot water and alcohol. Piperonyl alcohol forms long prisms melting at 57°, and is difficultly soluble in water.

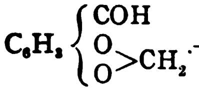
2. Phenol Aldehydes (Oxy Aldehydes).—The phenol aldehydes contain besides the aldehyde group COH the phenolic OH, and show the characters of both aldehydes and phenols, the latter being, however, subordinate. Besides their formation by oxidizing the corresponding alcohols, we have an interesting synthetic method. This consists in the action of chloroform and alkali upon phenols, as: $C_6H_5.OH + CHCl_3 + 4KOH = C_6H_4 \left\{ \begin{array}{l} OK \\ COH \end{array} \right. + 3KCl + 3H_2O$.

Salicyl Aldehyde, $C_6H_4(OH)COH$.—This is the *ortho-oxybenzaldehyde*. It occurs in the volatile oils of different varities of *Spiræa*. It is also obtained by the oxidation of saligenin and salicin, and by the synthetic reaction given above. It is an oil with pleasant aromatic odor, solidifying at 20° and boiling at 196°. It is easily soluble in water, and ferric chloride produces a violet color when added to its solutions. On oxidation it yields salicylic acid. When heated with sodium acetate and acetic anhydride, it undergoes condensation analogous to that mentioned under benzaldehyde, and yields coumarin.

Anisic Aldehyde, $C_6H_4(OCH_3)COH$, is formed in the oxidation of various essential oils (anise, fennel, etc.) with dilute nitric acid or chromic acid mixture. It is a colorless oil, boiling at 248°, with an agreeable odor of flowering hawthorn. On exposure to the air it oxidizes readily to anisic acid, and should therefore be kept in well-stoppered bottles. It is readily soluble in alcohol, and is used in perfumery and in soaps.

Protocatechuic Aldehyde, $C_6H_3(OH)_2COH$.—This compound, the parent substance of vanillin and piperonal, was first obtained from the latter. It may be prepared synthetically from pyrocatechin by the chloroform reaction, or from its ethers, vanillin, isovanillin, and piperonal, by heating them with dilute hydrochloric acid to 200°. It forms crystals soluble in water and melting at 150°. It reduces silver solutions with formation of a mirror. Ferric chloride colors its aqueous solution a deep green.

Vanillin (Methyl-protocatechuic Aldehyde), $C_6H_3 \left\{ \begin{array}{l} CHO \\ OCH_3 \\ OH \end{array} \right.$, **Vanillinum**, U.S.P., is the odoriferous principle of the vanilla bean, which contains from 2 to 2½ per cent., and is found also in many crude beet-sugars, in asparagus, asafœtida, and in small amount in the woody tissue of many plants. It was first made artificially by Tiemann and Haarmann by oxidizing coniferin, $C_6H_3(OCH_3)(OH)C_3H_4.OH$, a glucoside contained in the cambial juice of the *Coniferæ*, with chromic acid. It is also formed synthetically together with an isomeric aldehyde (isovanillin) when guaiacol is acted upon with chloroform and alkali, and by oxidizing eugenol from oil of cloves, which latter method is the present commercial one. Vanillin crystallizes in needles, and is soluble in water, alcohol, ether, carbon disulphide, and chloroform. It melts at 80° and boils at 285°. Heated with HCl to 180° it decomposes into methyl chloride and protocatechuic aldehyde. Ferric chloride colors its solution blue.

Piperonal (Heliotropine), **C_6H_3**  $C_6H_3\begin{cases}COH\\ O\\ O\end{cases}\!\!>CH_2$.—This is the methylene ether of protocatechuic aldehyde. It is obtained by oxidizing piperic acid. Forms small, colorless, shining crystals smelling of coumarin and difficultly soluble in water, but readily soluble in alcohol, ether, vaseline, and glycerin. Melts at 37° and boils at 263°. Is largely used in perfumery as artificial heliotropine.

X. AROMATIC ACIDS AND PHENOL ACIDS.

The aromatic acids, like the fatty acids and other acids of the methane series, contain one or more carboxylic groups, COOH, in this case linked either directly or indirectly with the phenyl group or the benzene nucleus. This group COOH, of course, pre-supposes the side-group CH_3, from which it is formed by oxidation.

TABLE OF AROMATIC ACIDS AND PHENOL ACIDS.

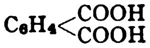
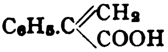
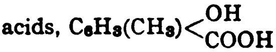
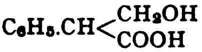
Monobasic Saturated Acids:	Melting Point.
Benzoic acid, $C_6H_5.COOH$	121°
Phenylacetic acid, $C_6H_5.CH_2.COOH$	76°
Toluic acids, $C_6H_4(CH_3).COOH$	*o-* 102° *m-* 110° *p-* 180°
Hydrocinnamic acid, $C_6H_5.CH_2.CH_2.COOH$	49°
Mesitylenic acid,	166°
$C_6H_3(CH_3)_2COOH$	126°
Xylylic acids,	163°
Cumic acid, $C_6H_4(C_3H_7)COOH$	116°
Polybasic Saturated Acids:	
Phthalic acids,  $C_6H_4<^{COOH}_{COOH}$	*o-* 213° *m-* 300°+ *p-* ——
Trimesic acid, $C_6H_3(COOH)_3$	300°
Pyromellitic acid, $C_6H_2(COOH)_4$	264°
Benzene-penta-carboxylic acid, $C_6H(COOH)_5$	——
Mellitic acid, $C_6(COOH)_6$	——
Unsaturated Acids:	
Cinnamic acid, $C_6H_5.CH{=}CH.COOH$	133°
Atropic acid,  $C_6H_5.C\begin{matrix}{\diagup\!\!\diagup}CH_2\\ \diagdown COOH\end{matrix}$	106°
Phenyl-propiolic acid $C_6H_5.C{\equiv}C.COOH$	136°

TABLE OF AROMATIC ACIDS AND PHENOL ACIDS.

(*Continued.*)

	Melting Point.
Phenol Acids and Alcohol Acids:	
Salicylic acid, $C_6H_4(OH)COOH$	155°
m- and *p-* oxybenzoic acids, $C_6H_4(OH)COOH$	*m-* 200° *p-* 210°
Anisic acid, $C_6H_4(OCH_3)COOH$	184°
Oxytoluylic acids,  $C_6H_3(CH_3)<^{OH}_{COOH}$	——
Melilotic acid, $C_6H_4(OH)CH_2.CH_2.COOH$	128°
Mandelic acid, $C_6H_5.CHOH.COOH$	118°
Tropic acid,  $C_6H_5.CH<^{CH_2OH}_{COOH}$	117°
Protocatechuic acid, $C_6H_3(OH)_2COOH$	199°
Vanillic acid, $C_6H_3(OH)(OCH_3).COOH$	207°
Orsellinic acid, $C_6H_2(CH_3)(OH)_2COOH$	176°
Gallic acid, $C_6H_2(OH)_3.COOH$	222°
Tannic acid, $C_{14}H_{10}O_9$	——
Quinic acid, $C_6H.H_6(OH)_4COOH$	162°
Unsaturated Phenol Acids:	
Coumaric acid, $C_6H_4(OH)CH{=}CH.COOH$	*o-* 208° *p-* 206°
Caffeic acid, $C_6H_3(OH)_2CH{=}CH.COOH$	——

1. **Monobasic Saturated Acids.**—These may be formed by the oxidation of the homologues of benzene, the side-group being changed. Of course the oxidation of the corresponding primary aromatic alcohol may also serve for their formation, as well as the saponification of the cyanides or nitriles of the hydrocarbons (see p. 610). The aromatic acids may undergo in general the same reactions and yield similar classes of products as the fatty acids.

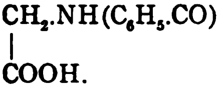
Benzoic Acid, $C_6H_5.COOH$ (**Acidum Benzoicum,** U.S.P.), was discovered in 1608 in gum benzoin, and prepared from urine by Scheele in 1785. It occurs in the free state in a number of resins and balsams, as gum benzoin, Peru balsam, Tolu balsam, dragon's blood, and in certain plants. In the urine, especially of carnivorous animals, it occurs as hippuric acid. It is produced on the oxidation of all hydrocarbons, alcohols, aldehydes, ketones, ketonic acids, etc., which are derived from benzene by replacing one atom by a monovalent side-chain. It is prepared practically either by sublimation from the gum-resin (*acidum ex resina*), or by the decomposition of hippuric acid (*acidum ex urina*), or synthetically starting from toluene (*acidum ex toluole*). The reaction for this latter production, $C_6H_5CCl_3 + 2H_2O = C_6H_5.COOH + 3HCl$, has already been referred to (see p. 628).

Benzoic acid forms white, lustrous scales, melting at 121°, boiling at 250°, and subliming in a current of steam. The vapors have a peculiar odor, exciting to sneezing and coughing. It is difficultly soluble in cold water, readily soluble in hot water, alcohol, benzene, and petroleum ether.

Of the metallic benzoates we have, as official compounds, **Ammonii Benzoas,** U.S.P., $NH_4C_7H_5O_2$, and **Sodii Benzoas,** U.S.P., $NaC_7H_5O_2$. The lithia, mercury and bismuth benzoates have also been used in medicine. Both the methyl and the ethyl esters of benzoic acid, $C_6H_5.COOCH_3$ and $C_6H_5.COOC_2H_5$ respectively, are known as pleasant-smelling aromatic liquids, the latter especially, under the name of "benzoic ether," being used in some artificial fruit essences. *Benzyl benzoate,* $C_6H_5.$-$COOC_7H_7$, has been used in medicine.

Other derivatives of benzoic acid are: benzoyl chloride, $C_6H_5.COCl$, benzonitrile (or phenyl cyanide), $C_6H_5.CN$, benzoic anhydride, $(C_6H_5$-$CO)_2O$, benzamide, $C_6H_5.CONH_2$, and benzanilid, $C_6H_5.CO.NHC_6H_5$. This latter compound is the analogue of acetanilid, and has been introduced into medicine as an antipyretic possessing some advantages over acetanilid. *Benzoyl peroxide,* $(C_6H_5.CO)_2O_2$, and *benzoyl-acetyl peroxide,* $\left.\begin{matrix}C_6H_5CO\\CH_3CO\end{matrix}\right\}O_2$ have also been used in medicine as antiseptics, the latter under the name of "acetozone."

An important derivative of benzoic acid, and at the same time one of the commercial sources of it, is *hippuric acid* (benzoyl-glycocoll),



$$\begin{array}{l}CH_2.NH(C_6H_5.CO)\\ |\\ COOH.\end{array}$$

This compound is obtained from the urine of the herbivora, and in case benzoic acid or compounds capable of yielding it by oxidation are taken internally, from human urine as well. It may be formed artificially by the reaction of benzoyl chloride and glycocoll in the presence of caustic alkali:

$$C_6H_5.COCl + CH_2(NH_2)COOH = C_6H_5CO.NH.CH_2COOH + HCl.$$

It forms rhombic prisms, melting at 187.5°; difficultly soluble in cold water, easily soluble in hot water and alcohol, but insoluble in petroleum, ether, and benzene. By boiling with acids or alkalies, as well as by putrefactive decomposition, it is decomposed again into benzoic acid and glycocoll. Of the substituted benzoic acids, such as nitrobenzoic, amidobenzoic, and sulphobenzoic acid and derivatives from them, two compounds may be mentioned: *o*-amidobenzoic acid, known also as *anthranilic acid,* which is obtained when indigo is boiled with caustic potash solution; and is now manufactured on a large scale as a step in the manufacture of artificial indigo (see p. 662), and the anhydride of *o*-sulphamid-benzoic acid, which is known commercially as *saccharine* (**Benzosulphinidum,** U.S.P.). This compound, although chemically in no way related to the sugars, possesses an extraordinary sweet taste, and is some 500 times sweeter than cane sugar. To prepare it, *o*-toluene sulphonic acid, $C_6H_4(CH_3)SO_3H$, is changed into *o*-toluene-sulphochloride, $C_6H_4(CH_3)$ SO_2Cl, and this by the action of ammonia into the sulphamide,

$C_6H_4(CH_3)SO_2NH_2$. This on oxidation, yields *o*-sulphamid-benzoic acid, $C_6H_4\left\{\begin{matrix}COOH\\ SO_2NH_2\end{matrix}\right.$, of which "saccharine" is the anhydride, $C_6H_4\left\{\begin{matrix}CO\\ SO_2\end{matrix}\right.>NH$. It forms a white, crystalline powder, fusing at 220° with partial decomposition. It is used for sweetening foods, etc., for diabetic patients where the carbohydrates cannot be allowed. Fused with caustic potash it yields salicylic acid. As this original saccharine is difficultly soluble in water, the sodium salt of the *o*-sulphamid-benzoic acid, $C_6H_4\left\{\begin{matrix}COONa\\ SO_2NH_2\end{matrix}\right.$, is also used and is now official (**Sodii Benzosulphinidum**, U.S.P.).

Toluic Acids, $C_6H_4(CH_3)COOH$.—The three toluic acids can be prepared from the three xylenes. Isomeric with them is

Phenyl-acetic Acid, $C_6H_5.CH_2COOH$.—This, as the name indicates, is a phenylated acetic acid. It may be formed synthetically by the saponification of benzyl cyanide, $C_6H_5.CH_2CN$. It forms also in the putrefaction of albuminoids and of wool. It forms scales, melting at 76.5° and boiling at 265.5°.

Xylylic Acids, $C_6H_3(CH_3)_2COOH$.—Of these six are possible and four are known. Isomeric with them are the phenyl-propionic acids, of which there are two: *a-Phenyl-propionic Acid* (Hydratropic Acid), CH_3-—$CH(C_6H_5).COOH$, and *β-Phenylpropionic Acid* (Hydrocinnamic Acid), $CH_2(C_6H_5).CH_2.COOH$. Of these the latter is the most important. It is formed by the action of sodium amalgam upon cinnamic acid, and from the decay of albuminous matter. It forms fine needles, melting at 47° and boiling at 280°.

Cumic Acid (*p*-Isopropyl-benzoic Acid), $C_6H_4(C_3H_7)COOH$, is obtained by oxidizing Roman oil of cumin with potassium permanganate. It also results from the oxidation of cymene in the animal organism. It crystallizes in plates, and yields cumene when distilled with lime.

2. Polybasic Saturated Acids.—By the oxidation of two or more of the side-groups in the homologues of benzene, polybasic acids are obtained.

Phthalic Acids (Benzene-dicarboxylic Acids), $C_6H_4(COOH)_2$.—We have here three isomers: orthophthalic acid, isophthalic acid, and terephthalic acid. The first is in all respects the most important. It forms when orthoxylene is oxidized by nitric acid or potassium permanganate (not by chromic acid, however, which decomposes it) or from any ortho-di-derivative of benzene. It is made on a large scale by the oxidation of naphthalene, either by first forming the tetrachlor-naphthalene, $C_{10}H_8Cl_4$, and then oxidizing this with nitric acid, or by heating naphthalene with very concentrated sulphuric acid in the presence of mercuric sulphate as oxygen carrier, as now done in connection with the manufacture of artificial indigo. It crystallizes in short prisms or plates, melting at 184°; readily soluble in water, alcohol, and ether. When heated above its melting point, it readily loses water and yields the anhydride. Distilled with lime it loses CO_2 and yields benzene.

Phthalic Anhydride, $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right>O$.—This compound is obtained by sublimation in long, white prisms, melting at 128° and boiling at 284°. When heated with the phenols it yields a series of compounds known as "phthaleïns," such as phenolphthaleïn, resorcinphthaleïn (fluorescein), etc. These will be referred to again under Triphenyl-methane and derivatives.

Terphthalic Acid is the para compound. It results from the oxidation of *p*-xylene, cymene, etc., and especially of oil of turpentine or oil of cumin.

Benzene-tricarboxylic Acids, $C_6H_3(COOH)_3$.—Three isomers are known: trimesic acid obtained by the oxidation of mesitylene; trimellitic acid, obtained by the oxidation of colophony; and hemimellitic acid.

Benzene-tetracarboxylic Acids, $C_6H_2(COOH)_4$.—Of this formula are pyromellitic acid, prehnitic acid, and mellophanic acid.

Benzene-pentacarboxylic Acid, $C_6H(COOH)_5$.—But one acid of this formula is possible and it has been obtained.

Benzene-hexacarboxylic Acid, $C_6(COOH)_6$.—The aluminum salt of this acid occurs as the mineral mellilite (or honey-stone) in peat and lignite deposits. The acid may also be formed by the oxidation of lignite or graphite with potassium permanganate. It forms fine, silky needles of great stability, easily soluble in water and alcohol. When distilled with lime it yields benzene.

3. **Unsaturated Aromatic Acids.**—It will be remembered that, besides the saturated aromatic hydrocarbons consisting of benzene and its homologues, we mentioned unsaturated hydrocarbons, such as phenyl-ethylene and phenyl-acetylene (see p. 626). From these are derived alcohols, aldehydes, and acids after the same manner as from the saturated hydrocarbons. Thus, from styrene (phenyl-ethylene), $C_6H_5.CH{=}CH_2$, is derived cinnamyl alcohol, $C_6H_5.CH{=}CH.CH_2OH$, cinnamic aldehyde, $C_6H_5.CH{=}CH.CHO$, and lastly *Cinnamic Acid*, $C_6H_5.CH{=}CH.COOH$. This acid occurs in Peru and Tolu balsams and in storax (both free and as cinnamic esters). It may also be prepared synthetically as previously mentioned (see p. 647), by the condensation of benzaldehyde and acetic anhydride in the presence of a dehydrating agent like dry sodium acetate:

$$C_6H_5.CH\boxed{O + H_2}CHCOOH = C_6H_5CH{=}CH{-}COOH + H_2O.$$

It crystallizes in prisms, melting at 133° and boiling at 300°–304°. It is difficultly soluble in water, more readily in alcohol, and easily in ether. It can be sublimed, and is volatile in a current of steam. As an unsaturated acid it can add on halogens, haloid acids, and hypochlorous acid. Isomeric with cinnamic acid is

Atropic Acid, $CH_2{=}C{<}\begin{matrix}C_6H_5\\COOH\end{matrix}$. This acid is a decomposition product of the alkaloid atropine, which when boiled with acids or alkalies breaks up into atropic acid, $C_9H_8O_2$, and the base tropine, $C_8H_{15}NO$.

Phenyl-propiolic Acid, $C_6H_5C{\equiv}C.COOH$.—This acid bears the same relation to the unsaturated hydrocarbon phenyl-acetylene that cinnamic acid does to phenyl-ethylene or styrene. It may be formed synthetically by the addition of bromine to ethyl cinnamate, and decomposing the dibromide thus formed with alcoholic potash. Its most important derivative is the *o-nitro-phenyl-propiolic acid*, $C_6H_4(NO_2)—C{\equiv}C.COOH$, which heated with reducing agents goes over into indigo blue (see Indigo).

4. **Phenol Acids.**—These compounds are also known as oxy-acids, as their empirical formulas show one or more atoms of oxygen in excess of the corresponding aromatic acid. Thus, benzoic acid is $C_7H_6O_2$, while salicylic (oxybenzoic) acid is $C_7H_6O_3$. In them there is at least one OH group attached directly to the benzene nucleus, and giving to the compound the phenol character, while at the same time they contain the carboxyl group COOH and act as acids. These phenol acids may form with bases two classes of salts, in one of which the H of the acid group alone is replaced by metal, and in the other of which the H of the phenol group is also replaced. Thus, we have from salicylic acid both $C_6H_4\left\{\begin{matrix}OH\\COONa\end{matrix}\right.$ (neutral sodium salicylate) and $C_6H_4\left\{\begin{matrix}ONa\\COONa\end{matrix}\right.$ (basic sodium salicylate). The first salt is not acted upon by carbonic acid, the second, like the salt of a phenol, is decomposed in aqueous solution by CO_2, and changed into the first compound.

Oxybenzoic Acids, $C_6H_4\left\{\begin{matrix}OH\\COOH\end{matrix}\right.$.—Of the three isomers the most important is the ortho acid, which is **Acidum Salicylicum**, U.S.P This is found in the blossoms of *Spiræa ulmaria* and as methyl ester in oils of wintergreen and birch. Also obtained by the oxidation of saligenin (see p. 648), and by fusing coumarin, indigo, ortho-cresol, etc., with caustic potash. Synthetically it is now made by the process of Kolbe as improved by Schmidt; acting upon sodium-phenol with CO_2 in closed vessels at a temperature of 130°:

$$\begin{aligned} C_6H_5ONa + CO_2 &= C_6H_5—O—COONa. \\ C_6H_5—O—COONa &= C_6H_4(OH)COONa. \end{aligned}$$

There is formed in this case at first an ether-like compound, sodium-phenol carbonate, and this then by molecule rearrangement passes into sodium salicylate. At a somewhat higher temperature only half the phenol used is converted into salicylic acid, the basic sodium salt is formed, and the other half of the phenol distils off unchanged.

Salicylic acid crystallizes in fine needles, fusing at 156°–157°, and volatile in a current of steam. It is difficultly soluble in cold water, and more readily soluble in hot water, easily soluble in chloroform, alcohol, and ether. Ferric chloride produces a violet color in its aqueous solutions.

The salts of salicylic acid which are official are **Ammonii Salicylas, U.S.P., Sodii Salicylas**, U.S.P., **Strontii Salicylas**, U.S.P., **Hydrargyri Salicylas**, U.S.P., and **Bismuthi Subsalicylas**, U.S.P.

Of the esters of salicylic acid, two are official: **Methylis Salicylas**, U.S.P., the artificial or synthetic methyl salicylate, used in perfumery and in flavoring, and *Phenyl Salicylate* or *Salol* (**Phenylis Salicylas**, U.S.P.) which is extensively used in medicine. It is made by the action of salicylic acid upon phenol in the presence of acid chlorides like $POCl_3$ or $COCl_2$. It is a white, crystalline powder, odorless, and almost tasteless. It melts at 42°–43°, and is almost insoluble in water, but soluble in alcohol, ether, chloroform, and fixed or volatile oils. Its alcoholic solution gives a violet color with ferric chloride. It is saponified by caustic soda with liberation of salicylic acid, and the odor of free phenol. It is used mainly as an antirheumatic, but also in some cases as an antipyretic and antiseptic.

Both *m-cresol salicylate* and *p-cresol salicylate*, $C_6H_4(OH)COO(C_6H_4\text{-}CH_3)$, have been proposed as substitutes for salol, liberating the isomeric cresols instead of phenol when saponified.

A substitution derivative of salicylic acid that has been introduced into medicine is *di-iodosalicylic acid*, $C_6H_2I_2(OH)COOH$, prepared by the action of iodine and iodic acid upon salicylic acid in alcoholic solution. It has been used as an analgesic, antipyretic, and antiseptic. The sodium salt of this acid is also used in the same way.

Acetyl-salicylic Acid, $C_6H_4.OC_2H_3O.COOH$, was first introduced under the name of "aspirin," and the methyl-oxymethyl ester of salicylic acid under the name of "mesotan." The former is extensively used.

Under the name of "salophen" there has been introduced into medicine acetyl-amido-phenol salicylate, $C_6H_4(OH)COO.(C_6H_4NH.COCH_3)$. This compound contains about 51 per cent. of salicylic acid. It is claimed for it that when decomposed in the intestines it yields salicylic acid with antiseptic properties and acetyl-para-amido-phenol with antipyretic properties and can therefore replace salol to advantage. Both the meta- and the para-oxybenzoic acids are known, the latter being obtained when resins like gum benzoin, dragon's blood, and aloes, as well as tyrosine, are fused with caustic potash.

Anisic Acid, $C_6H_4(OCH_3)COOH$, is the phenol ether of the *p*-oxybenzoic acid. It also results from the oxidation of anisol (see p. 641). It forms rhombic prisms, melting at 184°.

Hydro-cumaric Acids, $C_6H_4(OH).CH_2.CH_2COOH$.—Of the several isomeric acids of this formula, the ortho-acid, known also as "melilotic acid," occurs in *Melilotus officinalis*, and results from the reduction of coumarin. The para variety, on the other hand, is produced by the decay of tyrosine.

Tyrosine, $C_6H_4(OH).CH_2.CH(NH_2).COOH$.—This amido acid (see p. 561), which crystallizes in fine silky needles, is found in old cheese (τυρός) in the pancreatic gland, in diseased liver, in beet-root molasses, etc., and results from albumin, horn, silk, and similar substances on boiling these with sulphuric acid or from their decay. It is also found in human urine in cases of acute phosphorus poisoning. It has been made also synthetically from phenyl-acetaldehyde.

Isomeric with several of these monobasic phenol acids are several alcohol acids in which we have alcoholic OH in one side-chain and the carboxyl group COOH in another.

Mandelic Acid (Phenyl-glycollic Acid), $C_6H_5.CH(OH).COOH$, results upon heating amygdalin with hydrochloric acid, and is made synthetically by saponifying benzaldehyde cyanhydrin, $C_6H_5.COH.HCN$. Mandelic acid is interesting as entering into the formation of the artificial alkaloid homatropine (see Alkaloids).

Tropic Acid, $C_6H_5.CH\left\{\begin{matrix}CH_2OH\\COOH\end{matrix}\right.$, is formed by the breaking up of atropine and hyoscyamine under the influence of baryta water, the products being tropic acid, $C_9H_{10}O_3$, and tropine, $C_8H_{15}NO$. Tropic acid has also been made synthetically. Prolonged boiling with baryta water changes it into atropic acid (see p. 654).

Protocatechuic Acid, $C_6H_3(OH)_2COOH$, contains two phenol OH groups and the one COOH group. It is obtained by fusing various resins, such as catechu, benzoin, dragon's blood, asafœtida, and others, with potash. It may be prepared synthetically by heating pyrocatechin with carbonate of ammonia. It forms lustrous needles, melting at 199°, soluble in warm water and alcohol, insoluble in benzene. It reduces ammoniacal silver solution but not Fehling's solution. The solution is colored green by ferric chloride, turning to blue after addition of Na_2CO_3. Putrefactive decomposition changes it into pyrocatechin, $C_6H_4(OH)_2$ and CO_2.

Vanillic Acid, $C_6H_3\left\{\begin{matrix}OH\\OCH_3\end{matrix}\right\}COOH$, is the monomethyl ether of protocatechuic acid. It results from the oxidation of vanillin or coniferin. Forms needles, melting at 207°, and capable of subliming.

Veratric Acid, $C_6H_3(OCH_3)_2.COOH$, is the dimethyl ether. It occurs in sabadilla seeds (*Veratrum sabadilla*). A homologue of protocatechuic acid is *orsellinic acid*, $C_6H_2(CH_3)(OH)_2COOH$, which is found in many lichens, both free and as an ester, erythrin (see p. 541).

Gallic Acid, $C_6H_2(OH)_3COOH$ (**Acidum Gallicum**, U.S.P.), is found naturally in nutgalls, in tea, in sumac, and in other plants, and is made synthetically by several reactions. It can readily be prepared from the tannin of nutgalls by the action of dilute acids or by the change due to mould growths. It forms silky needles, fusing at 220° to 240°, and is soluble in hot water, alcohol, and ether. Is decomposed by dry distillation into pyrogallol and carbon dioxide: $C_6H_2(OH)_3COOH = C_6H_3(OH)_3 + CO_2$.

It reduces Fehling's solution, is colored blue-black with ferric chloride, but is not precipitated by lead acetate. With potasium cyanide it gives a red color, and with iodine in the presence of inorganic salts a purplish red color.

Among the salts of gallic acid may be mentioned the *basic bismuth gallate* (or subgallate), $C_6H_2(OH)_3COOBi(OH)_2$, (**Bismuthi Subgallas,** U.S.P.). This compound, discovered in 1841 by Bley, has recently been brought forward as a substitute for iodoform in skin diseases. It forms a saffron-yellow powder, insoluble in water, alcohol, or ether, but soluble in dilute acids.

Closely related to gallic acid and occurring with it in the several natural sources mentioned, is an alteration product of it:

Gallotannic Acid, (Digallic Acid) $C_{14}H_{10}O_9$ (**Acidum Tannicum, U.S.P.**).—It is found in gall-nuts to the amount of 60–65 per cent. as well as in sumac, tea, etc. It is best prepared by extracting powdered nut-galls with commercial ether or with acetone. It is a light-yellowish powder, or in scales or spongy masses, nearly odorless, and with a strongly astringent taste. It is soluble in water, difficultly soluble in absolute alcohol, and insoluble in absolute ether, benzene, and carbon disulphide. When boiled with dilute acids or alkalies it takes up a molecule of water and yields 2 molecules of gallic acid. The aqueous solution is colored dark-blue by ferric chloride. Tannin has an affinity for the animal hide and for gelatin, and is abstracted from its solution by these substances, the product in the former case being leather.

Acetyl-tannin has been introduced into medicine under the name of "tannigen," and *methylene-ditannin* under the name of "tannoform."

The salts of tannic acid, or the tannates, are amorphous. The iron salt is the basis of the "nutgall ink," the ferric tannate being kept in suspension by the addition of some gum to the aqueous liquid.

Gallotannic acid is but one of a large series of related tannins which are named according to their sources. The classification proposed by Prof. Trimble and generally accepted is as follows:

Group *a*. Gallotannic acid, Chestnut-wood tannin, Chestnut-bark tannin, Pomegranate-bark tannin, and Sumac tannin.

Group *b*. Oak-bark tannin, Mangrove tannin, Canaigre tannin, Rhatany tannin, Kino tannin, Catechu tannin, Tormentil tannin.

In addition to these not classified may be mentioned Mori-tannic acid (from *Morus tinctoria*), Caffe-tannic acid (in coffee), Cinchona-tannic acid (in cinchona bark), etc. It has been supposed that a number of these exist in the plants as glucosides, and only show the distinctive characters on the breaking up of this original combination, but all recent investigations indicate that there is no chemical combination of the tannin with glucose.

Quinic Acid, $C_6H.H_6(OH)_4COOH$, is a hexahydro-tetroxy-benzoic acid. It is found in quinine bark, in coffee beans, and meadow hay. Forms prismatic crystals, fusing at 161.6°, and soluble in water. When oxidized yields quinone and hydroquinone, and fused with caustic potash yields protocatechuic acid. The action of reducing agents converts it into benzoic acid:

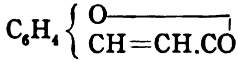
$$C_7H_{12}O_6 + H_2 = C_7H_6O_2 + 4H_2O.$$

Several of the salts of quinic acid are used in medicine, such as "sidonal," the *quinate of piperazine* and "chinotropin," the *quinate of urotropine* (hexamethylene tetramine).

5. Unsaturated Phenol Acids.—These acids, like the unsaturated alcohols and aldehydes, contain an unsaturated side-group with a COOH, and at the same time one or more phenol groups OH.

Coumaric Acid (Oxycinnamic Acid), $C_6H_4(OH).CH{=}CH.COOH$.—The ortho-coumaric acid is found in sweet clover (*Melilotus officinalis*), and is made synthetically by several reactions, the most interesting of which is the condensation of salicyl-aldehyde with acetic anhydride in the presence of acetate of soda:

$$C_6H_4(OH)CHO + (CH_3CO)_2O = C_6H_4(OH)CH{=}CH.COOH + C_2H_4O_2.$$

It forms needles melting at 207°–208°, and subliming when heated. The acid very readily loses a molecule of water and yields the anhydride *Coumarin*,  $C_6H_4\left\{\begin{array}{l}O\text{——————}\\CH{=}CH.CO\end{array}\right.$. It is found in Tonka beans (the seeds of *Dipterix odorata*), in woodruff (*Asperula odorata*), and other vegetable sources. It may be formed by the synthesis given above for coumaric acid, and in small quantity when malic acid is heated with phenol and sulphuric acid. Forms shining prisms, melting at 67° and boiling at 290°. It is powerfully aromatic, and is employed in perfumery and to impart an aroma to certain wines. It is scarcely soluble in cold water, but soluble in hot water, alcohol, and ether.

Caffeic Acid (Dioxycinnamic Acid), $C_6H_3(OH)_2CH{=}CH.COOH$, is obtained by the decomposition of the caffe-tannic acid of coffee beans. It may also be formed synthetically by the condensation of protocatechuic aldehyde with acetic anhydride.

Ferulaïc Acid is the methyl derivative of caffeic acid. It is found in asafœtida, and may be made synthetically from vanillin (methyl-protocatechuic aldehyde) and acetic anhydride.

Umbellic Acid is an isomer of caffeic acid. Its anhydride is *umbelliferon*, which bears the same relation to this acid that coumarin does to coumaric acid.

Anhydrides of trioxy-cinnamic acids, or, as they may also be termed, dioxy-coumarins, are *Æsculetin* and *Daphnetin*, the products of the decomposition of the glucosides Æsculin and Daphnin.

CHAPTER VII.

AROMATIC COMPOUNDS WITH MORE THAN ONE NUCLEUS.

Two classes are here to be distinguished: compounds in which the several benzene nuclei are joined together without condensation, and compounds in which two or more benzene nuclei have condensed together to form a new and distinctive nucleus or grouping.

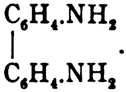
I. COMPOUNDS WITH UNCONDENSED NUCLEI. (ISOCYCLIC COMPOUNDS).

1. **Diphenyl Group.**—Just as the action of sodium on methyl iodide in ethereal solution by withdrawing the iodine causes the two methyl groups to unite to form ethane, $CH_3—CH_3$, so the action of sodium on brom-benzene in ethereal solution causes the two phenyl groups to unite to form

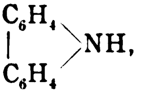
Diphenyl, $C_6H_5.C_6H_5$.—It is also formed when the vapor of benzene or benzoic acid is led through a red-hot tube, and is contained in coal-tar. White, lustrous scales, fusing at 71° and boiling at 254°. When oxidized it yields benzoic acid.

The usual replacing groups OH, NO_2, NH_2, HSO_3, and CH_3 may replace hydrogen in the diphenyl formula, and isomeric compounds are formed according to the position of the replacing group.

Among the most important of the diphenyl derivatives may be mentioned

Di-p-amido-diphenyl (Benzidine),  $\begin{array}{l}C_6H_4.NH_2\\ |\\ C_6H_4.NH_2\end{array}$. It is obtained by reducing the corresponding nitro compound of diphenyl. It is a diatomic base which crystallizes in colorless, silky plates, readily soluble in hot water and alcohol, and melting at 122°. It is of great importance in the color industry, since its diazo compounds react with phenols and amines to form a valuable class of dyes, which are used on cotton without previous mordanting. These are known collectively as "benzidine dyes."

By the action of hydrofluoric acid upon benzidine is obtained *difluor-diphenyl*,  $\begin{array}{l}C_6H_4F\\ |\\ C_6H_4F\end{array}$, which has been introduced into medicine under the name of "antitussin."

Carbazole,  $\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\!\!>NH$, is the imide of diphenyl. It is contained in coal-tar and in crude anthracene, and may be obtained also by passing diphenylamine (see p. 634) through red-hot tubes.

Hexoxy-diphenyl, $C_{12}H_4(OH)_6$, which dissolves in potash with violet-blue color, is the mother-substance of *Cærulignone* (or Cedriret), C_{16}-

$H_{16}O_6$, a violet-colored compound which is formed when crude pyroligneous acid is purified with chromate of potash, and also from the oxidation of the dimethyl-pyrogallol of beech-wood tar. It crystallizes in fine, steel-gray needles, soluble in concentrated sulphuric acid with fine blue color.

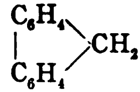
2. **Diphenyl-methane Group.**—The replacement of one hydrogen in methane by phenyl, C_6H_5, gives us phenyl-methane, which we have already considered as methyl-benzene, or toluene; the replacement of two or three hydrogen atoms by phenyl groups gives us diphenyl-methane and triphenyl-methane compounds, which, therefore, bear a simple relation to toluene. Thus, we have,

$$C\left\{\begin{array}{l}H\\H\\H\\H\end{array}\right. . \qquad C\left\{\begin{array}{l}C_6H_5\\H\\H\\H\end{array}\right. . \qquad C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\H\\H\end{array}\right. , \qquad C\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_5\\H\end{array}\right. .$$

Methane. Phenyl-methane, or toluene. Diphenyl-methane. Triphenyl-methane.

Diphenyl-methane, $C_6H_5.CH_2.C_6H_5$, is obtained by the action of benzyl chloride upon benzene in the presence of aluminum chloride or zinc-dust. It forms long, colorless needles, which smell of oranges. Fusing point 26°–27°.

Benzophenone (Diphenyl-ketone), $C_6H_5.CO.C_6H_5$, may be obtained by oxidizing diphenyl-methane with chromic acid, or more simply by distilling benzoic acid with lime. This reaction shows it to be the counterpart of acetone obtained by distilling acetate of lime. Colorless crystals, insoluble in water, soluble in alcohol. It is dimorphous and may crystallize in rhombic prisms, fusing at 49°, or in rhombohedra, fusing at 27°.



Fluorene (Diphenylene-methane), $\begin{array}{l}C_6H_4\diagdown\\ \,|\qquad\;\; \rangle CH_2\\C_6H_4\diagup\end{array}$, is contained in coal-tar, and crystallizes in colorless plates with a violet fluorescence. It melts at 113° and boils at 295°.

3. **Triphenyl-methane Group.**—Triphenyl-methane, $CH(C_6H_5)_3$, and its homologues, diphenyl-tolyl-methane, $CH\left\{\begin{array}{l}C_6H_5\\C_6H_5\\C_6H_4.CH_3\end{array}\right.$, and phenyl-ditolyl-methane, $CH\left\{\begin{array}{l}C_6H_5\\C_6H_4.CH_3\\C_6H_4.CH_3\end{array}\right.$, are of especial importance as being the mother-substances of the great majority of the so-called "aniline dyes."

Triphenyl-methane can be made synthetically by a variety of reactions. Thus, by the action of benzal chloride on benzene in the presence of Al_2Cl_6 we have

$$C_6H_5.CHCl_2 + 2C_6H_6 = CH(C_6H_5)_3 + 2HCl,$$

or from chloroform and benzene in the presence of aluminum chloride,

$$CHCl_3 + 3C_6H_6 = CH(C_6H_5)_3 + 3HCl.$$

It forms white, prismatic crystals, soluble in hot alcohol and ether, fusing at 92.5° and boiling at 359°.

Triphenyl-carbinol, $(C_6H_5)_3.C(OH)$, may be prepared by oxidizing triphenyl-methane with chromic acid.

Fuming nitric acid acting upon triphenyl-methane produces *trinitro-triphenyl-methane*, $(C_6H_4.NO_2)_3CH$, and this oxidized gives *trinitro-triphenyl-carbinol*, $(C_6H_4NO_2)_3.C(OH)$. The corresponding amido compounds $(C_6H_4NH_2)_3CH$ and $(C_6H_4NH_2)_3C(OH)$ are known as "para-leucaniline" and "para-rosaniline" respectively, and are the starting-points of the aniline color manufacture.

In practice para-rosaniline is obtained by the oxidation of a mixture of 1 molecule of para-toluidine and 2 molecules of aniline, by means of arsenic acid or nitro-benzene.

TRIPHENYL-METHANE DYE-COLORS.

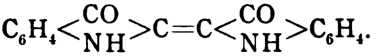
From triphenyl-methane may be derived the four groups of dye-colors which follow, and these, which, in distinction from the nitro dye-colors, the azo dye-colors, or the naphthalene and anthracene dye-colors, are called the triphenyl-methane colors, are the "aniline colors" in the narrower sense of the word. These groups are:

(*a*) The Malachite Green group (Diamido derivatives of Triphenyl-methane)
(*b*) The Rosaniline group (Triamido derivatives of Triphenyl-methane).
(*c*) The Rosolic Acid group (Oxy derivatives of Triphenyl-methane).
(*d*) The Phthaleïn group (derivatives of Triphenyl-methane-carboxylic acid).

Phenol-phthaleïn forms colorless needles, fusing at 250°–253°, which are insoluble in water, soluble in alcohol. Alkalies also dissolve it with red color, which the slightest excess of acid causes to disappear. Hence used as an indicator in alkalimetry. **Phenol phthalinum**, U.S.P.

4. **The Indigo Group.**—In the Indigo plant (*Indigofera tinctoria*), as well as in woad (*Isatis tinctoria*) and other plants, is present a glucoside, *Indican*, which by its decomposition, which takes place by a spontaneous fermentation when the plant is cut, yields "Indigo blue" along with a sugar-like substance known as "indiglucin."

Indigo (Indigotin or Indigo Blue), $C_{16}H_{10}N_2O_2$, has now been made synthetically by a variety of methods, and its molecular constitution is clearly understood. Its formula is



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C{=}C{<}\genfrac{}{}{0pt}{}{CO}{NH}{>}C_6H_4.$$

Its synthesis from *o*-nitro phenyl-propiolic acid (see p. 655) has already been referred to, the reaction in this case being $2C_6H_4(NO_2).C{\equiv}C.COOH + 4H = C_{16}H_{10}N_2O_2 + 2CO_2 + 2H_2O$, the reducing agent in this case being either grape-sugar in alkaline solution or an alkaline xanthogenate.

A later synthesis of different character consists in fusing together phenyl-glycocoll with caustic potash out of excess of air, when "indigo white" is formed, which by oxidation at once changes into indigo blue. The commercially practical synthesis, however, which is now being carried out on a large scale in Germany requires as the two important materials anthranilic acid (see p. 652) and monochloracetic acid. The former is made from naphthalene by first forming phthalic acid, and from this phthalimide, which treated with alkaline bromine solution yields anthranilic acid; the latter by the reaction of chlorine and glacial acetic acid. The reaction is:

$$C_6H_4{<}\begin{matrix}NH\,\vdots\,H + Cl\\COOH\end{matrix}\,H_2C.COOH = C_6H_4{<}\begin{matrix}NH.H_2C.COOH\\COOH\end{matrix}$$

The phenylglycocoll-*o*-carboxylic acid on fusion with caustic soda is transformed into indoxyl $C_6H_4{<}\begin{matrix}NH\\C(OH)\end{matrix}{\gg}CH$, which in alkaline solution is converted by atmospheric oxidation into indigo.

Indigo can be obtained from solution in aniline in blue crystals with a coppery-red lustre. It is insoluble in water, alcohol, and ether, but soluble in hot aniline, chloroform, petroleum naphtha, fusel oil, and nitrobenzene. It dissolves in cold sulphuric acid without change, but on heating, the indigo-sulphonic acids are formed. Oxidizing agents like fusing alkalies change it into salicylic and anthranilic acids. Reducing agents change it into indigo white. Indigo has been used from the earliest times for dyeing purposes, being brought from the East Indies

Indigo White, $C_{16}H_{12}N_2O_2$, results from the reduction of indigo blue.

Sulphonic Acids of Indigo.—Indigo, when treated with fuming sulphuric acid, is converted into a mixture of Indigo-monosulphonic and Indigo-disulphonic Acids, $C_{16}H_9(SO_3H)N_2O_2$ and $C_{16}H_8(SO_3H)_2N_2O_2$ respectively. When the strong acid solution is diluted with water, the first of these is precipitated, insoluble in dilute acids, although soluble in pure water. The second remains dissolved in the dilute acid solution. Its sodium salt comes into commerce as "**Indigo-carmine,**" or soluble **indigo-color,** and is official (**Sodii Indigotindisulphonas,** U.S.P.).

Isatin, $C_8H_5NO_2\left(\text{or } C_6H_4{<}\begin{matrix}CO\\N\end{matrix}{\gg}C(OH)\right)$, is formed by the oxidation of indigo with nitric acid. It forms yellowish-red prisms, soluble in hot water and alcohol, fusing at 200°–201°. When dissolved in excess of concentrated sulphuric acid, it gives a blue color with thiophene or benzene containing thiophene (see Thiophene, p. 614).

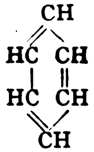
By reduction of isatin are obtained *dioxindol*, *oxindol*, and *indol*.

Indoxyl, $C_8H_7NO\left(\text{or } C_6H_4{<}\begin{matrix}C(OH)\\NH\end{matrix}{\gg}CH\right)$, is found in the form of its sulphonic acid in normal urine in small amount, and, under pathological conditions (stoppage of the intestine), in larger amount. Yields indigo when oxidized. Indoxyl may be tested for in the urine by adding strong hydrochloric acid and a few drops of chlorinated soda as an oxidizing agent, when the blue color of indigo will be obtained.

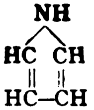
The underlying substance of the whole indigo group is

Indol, $C_6H_4{<}\begin{matrix}CH\\NH\end{matrix}{\gg}CH$.—This substance is obtained readily from albuminoids by the action of bacteria, by the pancreatic fermentation and by fusion with caustic potash. It has also been made synthetically by heating *o*-nitrocinnamic acid with potash and iron filings, by heating aniline with monochloracetaldehyde, and by other reactions. It forms lustrous white leaflets, melting at 52° and readily volatile with steam. It has the peculiar odor of fæces.

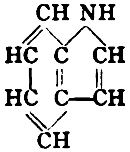
Indol can be considered as the condensation product of a benzene nucleus and a pyrrol nucleus, as illustrated by the structural formulas:



Benzene.



Pyrrol.



Indol.

In this formula, two carbon atoms are common to both the benzene and the pyrrol nuclei. We shall have examples of similar condensation of two or more benzene nuclei in the formulas of naphthalene and anthracene.

Skatol, (β-methylindol), $C_6H_4<\begin{smallmatrix}C(CH_3)\\NH\end{smallmatrix}>CH$, is found in the fæces and is formed from albumin by fusion with potash or by the action of bacteria, generally accompanied by indol. It may also be made synthetically from propionaldehyde and phenyl-hydrazine. It forms white, lustrous leaflets, melting at 95° and boiling at 265°–266°, and possessing a strong odor of fæces. A pine chip, moistened with an alcoholic skatol solution and then dipped in cold, strong hydrochloric acid, is colored first cherry-red and then dark violet.

II. COMPOUNDS WITH TWO CONDENSED BENZENE NUCLEI.

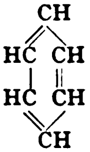
(ISOCYCLIC COMPOUNDS.)

In the higher-boiling portions of coal-tar occur hydrocarbons still richer relatively in carbon than benzene,—that is, containing relatively less hydrogen for a given number of carbon atoms. While the general formula of benzene and its homologues was C_nH_{2n-6}, these hydrocarbons belong mainly in two series, possessing the general formulas C_nH_{2n-12} and C_nH_{2n-18} respectively. These hydrocarbons not only belong to the closed-chain or cyclic hydrocarbons, but they bear a close relationship to benzene, and are, in fact, derivatives of it. This is seen, for instance, in the fact that naphthalene, the representative of the formula C_nH_{2n-12} when oxidized yields phthalic acid, and anthracene, the representative of the formula C_nH_{2n-18}, when oxidized yields benzoic acid.

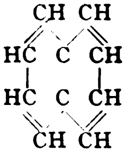
1. Naphthalene Series. (General formula, C_nH_{2n-12}.)

Naphthalene, $C_{10}H_8$ (**Naphthalenum**, U.S.P.), is a product of destructive distillation of many organic compounds, being formed when ethylene, acetylene, alcohol, ether, acetic acid, camphor, etc., are decomposed by heat, as in passing through a red-hot tube. Is mainly extracted from coal-tar, of which it is an abundant constituent. It forms white lustrous scales, melting at 79.2° and boiling at 218°, but volatile in a current of steam. Is insoluble in water, soluble in hot alcohol and ether. Naphthalene has a strong and characteristic coal-tar odor. It is used as an antiseptic and disinfectant, and as a substitute for camphor as a preservative against moths (hence the designation "coal-tar camphor"), and on a large scale for the manufacture of phthalic acid and numerous derivatives used in the dye-color industry, and for carburetting illuminating gas.

The constitution of naphthalene has been established by a study of its decompositions and is illustrated by the following graphic formulas:



Benzene.

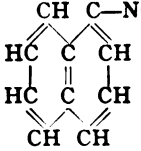


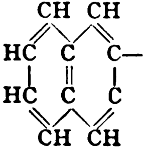
Naphthalene.

In this formula, two benzene nuclei are considered to have condensed, two atoms of carbon being held in common by the two parts which have united. This gives us 10 atoms of carbon, of which only 8, however, are free to attach hydrogen, hence the formula $C_{10}H_8$.

2. Addition Compounds of Naphthalene.—Naphthalene takes up hydrogen far more readily than benzene does, and forms first *naphthalene dihydride*, $C_{10}H_8.H_2$, and *naphthalene tetrahydride*, $C_{10}H_8.H_4$. By more intense action of hydriodic acid and phosphorus the second benzene nucleus is also attacked, and a *hexahydride*, $C_{10}H_8.H_6$, and finally a *dekahydride*, $C_{10}H_8.H_{10}$, are formed. It also yields chlorine addition products more readily than benzene does, such as *naphthalene dichloride*, $C_{10}H_8.Cl_2$, and *naphthalene tetrachloride*, $C_{10}H_8.Cl_4$. This latter is manufactured on a large scale by the action of potassium chlorate and hydrochloric acid upon naphthalene, and is then oxidized by the aid of nitric acid, yielding phthalic acid as a product (see p. 653).

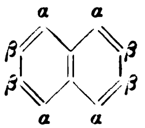
3. Substitution Derivatives of Naphthalene.—In speaking of benzene it was stated (see p. 619) that in the case of mono-substitution compounds it mattered not which H atom of the benzene molecule was considered to have been replaced. In the case of naphthalene we find that there are two mono-chlornaphthalenes, two mono-nitronaphthalenes, etc. The reason of this is apparent on examining the structural formula of naphthalene. It will be seen that in the accompanying two cases represented the replacement in the one formula is of hydrogen attached to a carbon adjacent to one of the two linking carbons, and in the other formula is of a hydrogen not adjacent to either of these linking carbon atoms:





The first of these compounds is called α-nitronaphthalene and the second β-nitronaphthalene.

There are four positions the replacing group may take in the case of the α derivative, and four positions in the case of the β derivative. Thus, in the formula we have represented the several cases for both α derivatives and β derivatives.



The halogen derivatives of naphthalene possess only slight interest. The α- and β-nitronaphthalenes are chiefly important as furnishing by their reduction the corresponding naphthylamines. These are the counterpart of aniline and its homologues in the benzene series. They find a large application in the manufacture of azo dye-colors.

Both naphthylamines are reducible by sodium in alcoholic solution to tetrahydro-addition compounds. The second of these, tetrahydro β-naphthylamine, has been introduced into medicine under the name of "thermin." It is a clear, colorless liquid of a piperidine-like odor, and of so energetic basic properties that it forms a stable salt with carbonic acid. It has a mydriatic action, and at the same time raises the temperature of the body quite appreciably. The salt used is the hydrochlorate.

The two naphthalene-monosulphonic acids are also important, both for the manufacture of dye-colors and because by their fusion with caustic alkali they yield the two naphthols.

The naphthols, $C_{10}H_7.OH$, are the simple hydroxyl derivatives—or, in other words, are the phenols—of the naphthalene series. Both are found in coal-tar. *α-naphthol* may be obtained from α-naphthylamine by means of the diazo compound or upon fusing α-naphthalene-sulphonic acid with alkalies. Both reactions are analogous to those used for the preparation of phenol (see p. 638). It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles, and has the odor of phenol. It melts at 95° and boils at 278°–280°.

A nitro derivative of α-naphthol that has been used largely in the dyeing industry is *dinitro-α-naphthol*, $C_{10}H_5(NO_2)_2.OH$. The sodium and calcium salts have been known as "Martius yellow" (naphthalene yellow). They are, however, difficultly soluble, and have been replaced by the corresponding sulphonate, $C_{10}H_4(NO_2)_2\left\{\begin{matrix}OK\\SO_3K\end{matrix}\right.$, which is known as "naphthol yellow."

β-Naphthol (**Betanaphthol,** U.S.P.).—Fuming sulphuric acid acting upon naphthalene at 80°–90° produces α-naphthalene-sulphonic acid chiefly, but at 200° β-naphthalene-sulphonic acid is the chief product. The sodium salt of this acid is fused with caustic soda, and the result is β-naphthol-sodium. From this the official compound is liberated by the addition of hydrochloric acid. It forms colorless, silky scales or crystalline powder of a weak phenol-like odor and sharp taste. It fuses at 122° and boils at 286°. Alkalies produce a bluish-violet fluorescence; ferric chloride produces a greenish color. β-naphthol is soluble in alcohol, ether, benzene, chloroform, oils, and alkalies.

It is quite analogous in chemical properties to phenol or carbolic acid. It is largely used for external application as an antiseptic; taken internally it is a poison. β-naphthol should be free from contamination with α-naphthol, as this is quite poisonous. The ferric chloride test above mentioned serves to distinguish them; with α-naphthol a violet color is obtained.

β-Naphthol-Bismuth (**Bismuthi Beta Naphthol, U.S.P.**) **is a compound** of varying composition.

β-Naphthol ethyl ether, $C_{10}H_7(OC_2H_5)$ is known as "nerolin" and has an odor similar to orange flowers. It is used in perfumery.

Amido-naphthol monosulphonate of sodium is used as a photographic developer under the name of "Eikonogen."

β-Naphthyl-salicylate (Betol), $C_6H_4(OH)COOC_{10}H_7$.—This compound is the counterpart of salol, which is phenyl salicylate. It forms a pure white powder of lustrous crystals, melting at 95°. It is difficultly soluble in both cold and hot water, easily soluble in boiling alcohol, ether, benzene, and warm linseed oil. Its therapeutic action is almost the same as that of salol, decomposing in the intestine into salicyclic acid and β-naphthol.

β-Naphthol-α-monosulphonate of Calcium (Asaprol or Abrastol).—It has been recommended for internal administration in case of rheumatism, gout, etc., and is used as a food preservative.

Dioxynaphthalenes, $C_{10}H_6(OH)_2$, the counterparts of the diatomic phenols, are also known. Similarly corresponding to quinone, $C_6H_4O_2$, are the α- and *β-naphthoquinones*, $C_{10}H_6O_2$. These are produced directly by the oxidation of naphthalene with chromic acid.

Both the hydroxyl group, OH, and the quinone group, O_2, may exist in the same molecule. We have an *oxynaphthoquinone*, $C_{10}H_5(OH)O_2$, and a *dioxynaphthoquinone*, $C_{10}H_4(OH)_2O_2$. This latter is known as "naphthazarine" (or alizarine black), a valuable dye-color.

Homologues of naphthalene, such as α- and *β-methyl-naphthalenes*, are found in coal-tar. From these are derived the *naphthoic acids*, $C_{10}H_7.COOH$, just as benzoic acid is derived from toluene or methylbenzene, and corresponding to the oxybenzoic acids (such as salicylic acid) we have α- and *β-oxynaphthoic acids*. Of these the former has been used in medicine as an antiseptic of very similar character to salicylic acid.

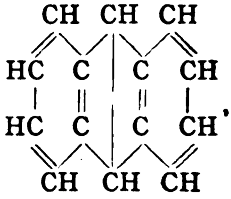
III. COMPOUNDS WITH THREE CONDENSED NUCLEI.

(ISOCYCLIC COMPOUNDS.)

Under the general formula C_nH_{2n-18} we have two hydrocarbons of the composition $C_{14}H_{10}$, besides homologues of these. These hydrocarbons are anthracene and phenanthrene, and both occur in coal-tar.

1. **Anthracene and its Derivatives.**—Anthracene is a product of destructive distillation of organic material, such as coal-tar, petroleum,

turpentine oil, etc., and can be made synthetically from a variety of sources. Its structural formula is considered to be



in which formula we have two benzene residues, C_6H_4, united by the group C_2H_2 as the middle nucleus. This group, C_2H_2, with the equivalence four, links together the two parts in the manner expressed by the full structural formula given above, or sometimes expressed $C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4$. That the two CH groups which join together the two benzene nuclei are also linked with each other by a single bond is indicated by several reactions, among which may be mentioned the formation of anthracene from benzene and tetrabromethane in the presence of aluminum chloride:

$$2C_6H_6 + \begin{matrix}CHBr_2\\|\\CHBr_2\end{matrix} = C_6H_4\left\langle\begin{matrix}CH\\|\\CH\end{matrix}\right\rangle C_6H_4 + 4HBr.$$

It is obtained from the fraction of the coal-tar boiling above 300° and known as the "green oil" (or anthracene oil) by chilling this and pressing out the crude anthracene in cakes of greenish-yellow color. The pure hydrocarbon forms colorless plates of white color with blue fluorescence. It fuses at 213° and boils above 360°. With picric acid it forms an addition compound, crystallizing in beautiful red needles. It is difficultly soluble in alcohol and ether, readily soluble in hot benzene or toluene. When oxidized it yields *anthraquinone*, while reducing agents change it to *anthracenehydride*, $C_6H_4<\begin{matrix}CH_2\\CH_2\end{matrix}>C_6H_4$, and on prolonged action to *anthracene hexahydride*, $C_{14}H_{16}$, and ultimately to *anthracene perhydride*, $C_{14}H_{24}$.

The chief uses of anthracene are in the preparation of alizarine and similar artificial dye-colors.

Anthraquinone, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4$, is readily obtained by the oxidation of anthracene by chromic acid in glacial acetic acid and by the distillation of calcium benzoate:

$$(C_6H_5.COO)_2Ca = C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_4 + CaO + H_2O.$$

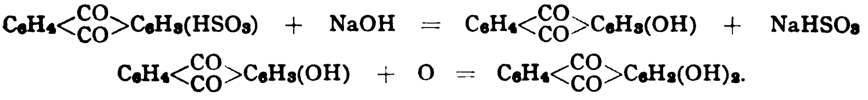
It forms yellow prisms, soluble in hot benzene or glacial acetic acid, fusing at 277°, and boiling at over 360°. By distillation in contact with zinc-dust it yields anthracene again. Fused at high temperatures with caustic potash it yields benzoic acid. By heating with strong sulphuric acid it is made to yield sulphonic acids, such as *anthraquinone-monosulphonic acid*, $C_6H_4<\substack{CO\\CO}>C_6H_3(HSO_3)$, and *anthraquinone-disulphonic acids*, $C_{14}H_6(HSO_3)_2O_2$. These sulphonic acids are of great technical importance as being steps in the synthetic formation of alizarine.

Oxyanthraquinones are formed when hydrogen of the anthraquinone formula is replaced by OH groups. Thus, *mono-oxyanthraquinone* is $C_{14}H_7(OH)O_2$, and *dioxyanthraquinone* is $C_{14}H_6(OH)_2O_2$. Of this latter there are a number of isomers, of which the most important is alizarine. *Trioxyanthraquinones*, $C_{14}H_5(OH)_3O_2$, are also obtained, of which anthragallol and purpurine are the most important. The methods for the formation of these very important technical compounds will be noted later.

Alizarine (Ortho-dioxyanthraquinone), $C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2$, is found in madder-root (*Rubia tinctorum*), where it results from the decomposition of a glucoside, rubianic acid (ruberythric acid). It has been known from early historic times, and was used in the East for the cotton and damask dyeing known as "Turkey red."

Since 1867, when Graebe and Liebermann first effected its synthesis from anthracene, it has been made artificially in a variety of ways. Thus, the first synthesis was from anthracene, by the action of bromine upon the anthraquinone, and then fusing the dibromanthraquinone with caustic potash.

This first synthesis was soon superseded by that involving the use of fuming sulphuric acid. The mono- and disulphonic acids when fused with caustic alkali should yield by theory the corresponding oxyanthraquinones. It is found, however, in practice, that oxygen is always absorbed from the air, and that the monosulphonic acid when fused yields a mixture of mono- and di-oxyanthraquinones, and the disulphonic acid yields a mixture of di- and tri-oxyanthraquinones. Chlorate of potash is, therefore, added in practice to facilitate their partial oxidation and to complete the change. The reactions then for the manufacture of alizarine are:

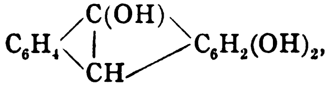


$$C_6H_4<\substack{CO\\CO}>C_6H_3(HSO_3) + NaOH = C_6H_4<\substack{CO\\CO}>C_6H_3(OH) + NaHSO_3$$

$$C_6H_4<\substack{CO\\CO}>C_6H_3(OH) + O = C_6H_4<\substack{CO\\CO}>C_6H_2(OH)_2.$$

Of course as an excess of the fused alkali is present, the alizarine, as formed, becomes sodium alizarate, $C_6H_4<\substack{CO\\CO}>C_6H_2(ONa)_2$, which is soluble in water with rich purple color. From this solution, on addition of hydrochloric acid, the alizarine is precipitated as a tawny-yellow powder, which generally comes into commerce in the moist state as a 10-per-cent. or 20-per-cent. paste.

Alizarine crystallizes in fine red prisms or needles, which melt at 289°, and can be sublimed. It is readily soluble in alcohol and ether, combines with a violet or purple color with alkalies, and forms various colored insoluble compounds or "lakes" with metallic oxides, the ones of chief importance being those of aluminum and tin (red), the iron (violet-black), and the lime (reddish-blue). The finest color obtained with alizarine, known as "Turkey red," is produced by mordanting the materials with acetate of alumina and treating them with a sulphonated castor oil, known as "Turkey red oil," before applying the alizarine

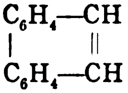
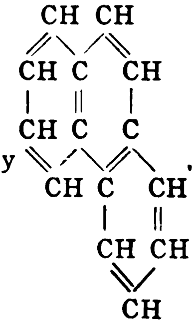
By the reduction of alizarine with ammonia and zinc-dust is formed *desoxyalizarine*,  $C_6H_4\left<\begin{array}{c}C(OH)\\ | \\ CH\end{array}\right>C_6H_2(OH)_2$, which, under the name of "anthrarobin," has been used in medicine as a non-poisonous substitute for chrysarobin and chrysophanic acid.

Purpurine (Trioxyanthraquinone), $C_{14}H_5(OH)_3O_2$.—This dye is found along with alizarine in madder-root, and is also prepared artificially.

A homologue of anthracene is also found in coal-tar,—viz., *Methyl-anthracene*, $C_{14}H_9(CH_3)$. It is capable of analogous reactions, yielding a quinone and hydroxyl derivatives of the same. The name of one of the latter is *Chrysophanic Acid* (Dioxy-methyl-anthraquinone), $C_{14}H_5(CH_3)(OH)_2O_2$. It is found in certain lichens, in yellow dock (*Rumex*), in senna, and in rhubarb. It crystallizes in golden-yellow prisms or needles, melting at 162°, and soluble in alcohol, ether, or benzene. Alkalies also dissolve it, forming dark-red solutions. When distilled over zinc-dust it yields methyl-anthracene.

Chrysarobinum, U.S.P., which is found in Goa and araroba powder, has the formula $C_{30}H_{26}O_7$, and bears the same relation to chrysophanic acid that anthrarobin does to alizarine. It readily yields chrysophanic acid by its oxidation. It forms yellow scales or needles, melting at 170°–178°, is insoluble in water and ammonia, soluble in alkalies, with yellow color which gradually turns red, as on exposure to the air chrysophanic acid is formed. It is used like anthrarobin for external application in skin diseases.

Emodin (Trioxy-methyl-anthraquinone), $C_{15}H_{10}O_5$, occurs with chrysophanic acid in the bark of wild cherry and in rhubarb-root. When distilled with zinc-dust it also yields methyl-anthracene. It forms orange-red crystals, melting at 245°–250°.

2. Phenanthrene, $C_{14}H_{10}$, is an isomer of anthracene, and is also found in coal-tar. Its structural formula differs from that of anthracene, and is represented as  $\begin{array}{l}C_6H_4—CH\\ |\qquad\ \ \|\\ C_6H_4—CH\end{array}$ or more fully , in which formula is shown the condensation of three benzene nuclei, the middle one having two carbon atoms jointly with each of the side nuclei. It crystallizes in colorless, lustrous scales, melting at 99° and boiling at 340°. It may be separated from anthracene by fractional distillation, followed by repeated crystallization from alcohol, in which it is much more soluble than anthracene. It forms a crystalline compound with picric acid, crystallizing from benzene in yellow needles, melting at 145°, and soluble in hot alcohol without decomposition.

Phenanthrenquinone, $C_{14}H_8O_2$, is obtained by oxidizing phenanthrene by chromic acid mixture. It crystallizes in dark orange-yellow prisms, melting at 198°. When ignited with soda-lime it yields diphenyl, $(C_6H_5)_2$, in almost the theoretical proportions, whereas anthraquinone gives benzene when similarly treated.

The phenanthrene molecule is contained in the alkaloid morphine, as when this latter is distilled with zinc-dust phenanthrene is obtained.

COMPOUNDS CONTAINING NITROGEN IN THE BENZENE NUCLEUS.

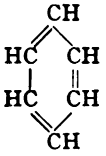
(HETEROCYCLIC COMPOUNDS.)

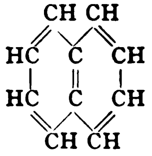
By the replacement of one triad group, CH, in the benzene molecule by the element nitrogen we obtain *Pyridine*, C_5H_5N.

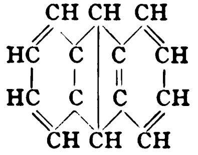
By the replacement of one triad group, CH, in the naphthalene molecule by the element nitrogen we obtain *Quinoline*, C_9H_7N.

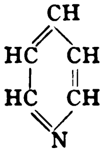
By the replacement of one triad group, CH, in the anthracene molecule by the element nitrogen we obtain *Acridine*, $C_{13}H_9N$.

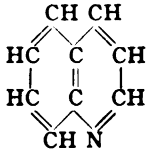
The relations of these nitrogenous bases to the parent hydrocarbons is shown clearly by a comparison of the graphic formulas:

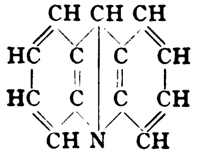

Benzene.


Naphthalene.


Anthracene.


Pyridine.


Quinoline.


Acridine.

1. **Pyridine Bases.**—Pyridine, C_5H_5N, and several of its homologues are found in coal-tar and in the animal oils (Dippel's oil) obtained by the distillation of bones. They are also found in the products of the distillation of bituminous shales. Except that they are strong bases, they bear a great analogy to the aromatic hydrocarbons, and give rise to similar derivatives. Thus, they form acids, which when distilled with lime yield the pyridine again just as the aromatic acids yield benzene. This is seen in the comparison of reactions:

$C_6H_5.COOH = C_6H_6 + CO_2.$ (Benzoic Acid. Benzene.)

$C_5H_4NCOOH = C_5H_5N + CO_2.$ (Pyridine Carboxylic Acid. Pyridine.)

Hydrogen addition compounds form here just as in the case of benzene, and even more readily:

$$\underset{\text{Pyridine.}}{C_5H_5N} + H_6 = \underset{\substack{\text{Hexahydro-pyridine}\\ \text{(or Piperidine.)}}}{C_5H_5N.H_6.}$$

Pyridine and its homologues may be built up synthetically by several reactions, among which the simplest is that whereby the aldehydes of the fatty series when treated with ammonia are made to yield these bases:

$$\underset{\text{Acetaldehyde.}}{4C_2H_4O} + NH_3 = \underset{\substack{\text{Collidine}\\ \text{(Trimethyl-pyridine).}}}{C_8H_{11}N} + 4H_2O.$$

More generally, however, they are obtained as decomposition products from more complex substances. Thus, both pyridine and quinoline bases are the products of the distillation of many alkaloids, such as quinine, cinchonine, and strychnine, with potash, and the carboxylic acids of these bases from the oxidation of the same alkaloids. The relationship of the alkaloids to pyridine and quinoline will be referred to later under the individual alkaloids.

Because of the existence of the one nitrogen atom in the benzene nucleus we may have three isomeric mono-substitution derivatives, according to the position of the replacing group with reference to this nitrogen atom. Where the same replacing group enters twice in place of two hydrogen atoms of the nucleus we may have six isomeric derivatives.

Pyridine, C_5H_5N, may be obtained from coal-tar or in a pure state by distilling its carboxylic acid with lime. It is also present in commercial ammonia, and has been identified in tobacco-smoke. Colorless liquid, with penetrating, characteristic odor, boiling at 115°. Is readily miscible with water. By adding metallic sodium to its hot alcoholic solution hydrogen is taken up and hexahydropyridine or piperidine is formed.

It is very stable and is not at all affected by nitric acid or oxidizing agents, and only by sulphuric acid at high temperatures.

It is a strong base, throwing the hydroxides of aluminum, chromium, and iron out of the solutions of the salts of these metals. It has been used in medicine as a remedy for asthma.

By the action of metallic sodium pyridine is polymerized, forming *dipyridine*, $C_{10}H_{10}N_2$, together with a compound analogous to diphenyl (see p. 636), known as *dipyridyl*, $C_{10}H_8N_2$.

Methyl-pyridines, $C_5H_4(CH_3)N$.—The three isomeric methyl-pyridines, known also as "picolines," are found in coal-tar. The β-compound may also be prepared from acroleïn-ammonia, or from strychnine, by distilling with lime. Liquids of unpleasant, penetrating odor.

Ethyl- and *Propyl-pyridines* are both known. The latter, we shall see, bears a close relation to the natural alkaloid conine. Thus, conyrine, $C_8H_{11}N$, which is obtained on heating conine with zinc-dust, and which yields conine again when treated with HI, is α-normal-propyl-pyridine.

Dimethyl-pyridines, $C_5H_3(CH_3)_2N$.—In bone-oil and tar-oil three isomeric compounds of this formula, known also as "lutidines," have been found.

Trimethyl-pyridines, $C_5H_2(CH_3)_3N$.—These compounds, known as "collidines," are found in bone-oil and obtained from cinchonine by heating with potash.

Pyridine-carboxylic Acids.—While pyridine itself is quite stable and resists the action of oxidizing agents, its homologues, like those of benzene, are very readily oxidized, yielding the corresponding carboxylic acids. Three mono-carboxylic acids, $C_5H_4N.COOH$, are known,—viz., α acid—*picolinic acid*, melting at 135°; β acid—*nicotinic acid*, melting at 231°; and γ acid—*isonicotinic acid*, melting at 309°. These acids may be obtained by the oxidation of the α-, β-, and γ-picolines respectively with potassium permanganate. The β acid is also obtained by the oxidation of the alkaloid nicotine by different oxidizing agents. On heating with lime the above acids yield pyridine, just as benzoic acid yields benzene under similar conditions.

Of the six possible di-carboxylic acids, $C_5H_3N.(COOH)_2$, all are known. The only ones requiring mention are *quinolinic acid*, obtained by the oxidation of quinoline and *cinchomeronic acid*, the chief product of the oxidation of quinine by nitric acid, as well as from cinchonine along with other products. Of the pyridine-tricarboxylic acid, $C_5H_2N(COOH)_3$, two may also be mentioned: hydroxycinchomeronic acid, obtained from quinine, quinidine, and cinchonidine by boiling with an alkaline solution of potassium permanganate, and *berberonic acid*, obtained from berberine when oxidized by nitric acid.

Oxypyridines, $C_5H_4(OH)N$, correspond to the phenols and give a yellow or red coloration with ferric chloride. Isomeric bodies which correspond to the ketones may also be formed which are called *pyridones*.

Eucaine β. **(Beta Eucainæ Hydrochloridum, U.S.P.)**.—$C_{15}H_{20}O_2.NH.HCl$ is the hydrochloride of benzoyl-trimethyl-oxy piperidine. It forms a colorless crystalline powder of neutral reaction and is used as a local anæsthetic instead of cocaine.

Hydrogen-addition Products of Pyridine.—Just as benzene, C_6H_6, is capable of taking up six hydrogen atoms and yielding hexahydrobenzene, $C_6H_6.H_6$, so pyridine may take up six hydrogen atoms and yield hexahydropyridine or *piperidine*, $C_5H_5N.H_6$. This compound, in addition to being produced synthetically, as above mentioned, is obtained by the decomposition of the alkaloid piperine of pepper, which, under the influence of alcoholic potash, splits into piperidine and piperic acid. An important synthesis of piperidine is also that from pentamethylene-diamine, as shown:

$$CH_2<\begin{matrix}CH_2-CH_2-NH_2\\CH_2-CH_2-NH_2\end{matrix} = CH_2<\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}>NH + NH_3.$$

Pentamethylene-diamine. = Piperidine. + Ammonia.

Piperidine is a colorless liquid, boiling at 106°, easily soluble in water and alcohol, and of a peculiar peppery odor. It is a strong base, and forms crystallized salts.

Two of the natural alkaloids may be mentioned here, as they are hydrogen-addition derivatives of pyridine.

Conine, $C_8H_{17}N$, is *dextro-rotatory a-normal propyl-piperidine*, $C_5H_{10}N(C_3H_7)$. This is the poisonous principle of the hemlock (*Conium maculatum*), and is found chiefly in the seeds. Colorless liquid, of stupefying odor, boiling at 166°. Easily soluble in ether and alcohol, more difficultly in water. It has been made synthetically by Ladenburg from α-allyl-pyridine, which, reduced by sodium in alcoholic solution, yields an optically inactive, normal propyl-piperidine, and this by the crystallization of its tartrate is split into a dextro-rotatory variety (the true conine) and a lævo-rotatory variety. Hydrogen iodide reduces it at a high heat to normal octane, C_8H_{18}, while nitric acid oxidizes it to butyric acid.

Piperidine, as well as conine, can be methylated, and the products are known as methyl-piperidine and methyl-conine. The latter is also found in the hemlock with conine.

Nicotine, $C_{10}H_{14}N_2$, the alkaloid of tobacco, contains a pyridine nucleus combined with a modified pyrrol nucleus. It exists in the tobacco plant combined with malic and citric acids. Pure nicotine is a colorless, oily liquid, turning brown in the air; soluble in water, alcohol, and ether, of stupefying odor, and boiling at 250° with decomposition. It is intensely poisonous. When oxidized yields nicotinic (β-pyridine-carboxylic) acid, and by loss of hydrogen dipyridyl, $(C_5H_4N)_2$.

Tropine, the decomposition product of the alkaloids atropine and hyoscyamine, is also a hydrogenated pyridine derivative.

Cocaine and *Ecgonine*, its decomposition product, are similarly derivatives of these hydrogenated pyridines.

2. Quinoline Bases.—By the dry distillation of organic substances, such as bituminous coal and bones, is produced a series of bases known by this name. The same bases are also obtained in the distillation of quinine and cinchonine with potash. A number of synthetic methods have also been found for their preparation, of which may be mentioned:

(*a*) By heating acroleïn-aniline quinoline is formed, just as the heating of acroleïn-ammonia yields pyridine.

(*b*) By the oxidation of allylaniline with heated oxide of lead:

$$C_6H_5.NH(C_3H_5) + O_2 = C_9H_7N + 2H_2O.$$

(*c*) By heating aniline with glycerol, concentrated sulphuric acid, and nitrobenzene. This method (discovered by Skraup) is that now employed for the manufacture of quinoline. 24 parts of nitrobenzene. 38 parts of aniline, 120 parts of glycerol, and 100 parts of concentrated sulphuric acid are taken and heated, at first carefully, and then for several hours with inverted condenser. The mixture is now diluted with water, and the nitrobenzene distilled off. Caustic soda is then added to strong alkaline reaction, and the quinoline distilled off in a current of steam. In this reaction the sulphuric acid first dehydrates the glycerol, producing acroleïn, which then unites with the aniline to form the quinoline molecule with the elimination of hydrogen. The nitrobenzene furnishes the oxygen to combine with this hydrogen, and is itself reduced to aniline. The reactions may be summarized thus:

$$2C_6H_5.NH_2 + C_6H_5.NO_2 + 3C_3H_8O_3 = 3C_9H_7N + 11H_2O.$$

By using the homologues of acroleïn in the first of these methods instead of acroleïn we obtain the homologues of quinoline, as methyl-quinoline (quinaldine), dimethyl-quinoline, etc.

The constitution of the quinoline molecule has already been referred to and illustrated. That it contains the benzene nucleus is shown by its syntheses from aniline and nitrobenzene; that it contains a pyridine nucleus joined with this is shown by the fact that, when oxidized by potassium permanganate, quinoline yields pyridine-dicarboxylic (cinchomeronic) acid.

Quinoline, C_9H_7N, is a pale yellowish liquid with considerable refractive power and a characteristic aromatic odor. It boils at 237°, and has a specific gravity of 1.084. Only slightly soluble in water, easily soluble in alcohol, ether, chloroform, and petroleum benzine. It is darkened in color on exposure to light. It is a base, and forms a series of crystallizable and deliquescent salts. Among these may be mentioned:

Quinoline Tartrate, $3C_9H_7N.4(C_4H_6O_6)$.—This salt forms white, rhombic needles, which have a slight odor of bitter-almond oil, and taste sharp and peppermint-like. It is permanent in air, and fuses at 125°. It is moderately soluble in water, more difficultly soluble in alcohol, and almost insoluble in ether. It has been used in medicine as an antiseptic and antipyretic.

Quinoline Salicylate, $C_9H_7N.C_7H_6O_3$, forms a whitish, crystalline powder, not very soluble in water, easily soluble in alcohol, ether, benzene, vaseline, fats, and glycerin. It is used in medicine as the tartrate, and in similar amounts.

Homologues of Quinoline.—The methyl group may replace H in either the benzene nucleus or the pyridine nucleus of the quinoline molecule. The compounds so obtained are isomeric. Thus, the compound obtained by the replacement of a hydrogen atom of the pyridine nucleus by methyl is known as *quinaldine*, and is found in coal-tar. When oxidized by chromic acid it yields quinoline-carboxylic acid. On the other hand, the compound obtained by the replacement of a hydrogen atom of the benzene nucleus by methyl is known as *Toluquinoline*, and has only been obtained synthetically. When oxidized it yields pyridine-dicarboxylic acid. By heating quinaldine with phthalic anhydride and chloride of zinc is obtained a phthaleïn of the composition $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}CH.C_9H_6N$. It is known as "quinoline yellow," and is insoluble in water, and difficultly soluble in alcohol. On sulphonation with fuming sulphuric acid is obtained a disulphonic acid, the sodium salt of which is known as "soluble quinoline yellow."

Oxy-quinolines.—Those derivatives which have the OH group replacing hydrogen of the benzene nucleus have a phenol-like character, and unite with diazo salts to form azo dye-colors. On the other hand, those oxy-quinolines which contain the OH group in the pyridine nucleus are called *carbostyriles*.

Hydrogen Addition Compounds.—Nascent hydrogen from tin and hydrochloric acid produces *dihydro-quinoline*, C_9H_9N, melting at 161°, and a liquid *tetrahydro-quinoline*, $C_9H_{11}N$, boiling at 245°. By the action of methyl iodide upon this latter is obtained *methyl-tetrahydro-quinoline*, the acid sulphate of which was introduced into medicine as an artificial febrifuge under the name of "kairoline." The hydrochlorate of ethyl-oxytetrahydro-quinoline was known as "kairine A," and that of methyl-oxytetrahydro-quinoline as "kairine M." They were, perhaps, the first of the artificial febrifuges, but are no longer in use, being accompanied by injurious after-effects.

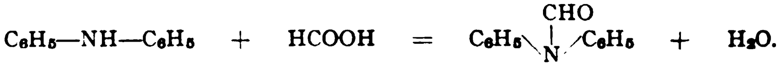
Isomeric with the methyl-oxytetrahydro-quinoline, $C_9H_9(OH)N.CH_3$, is the base *tetrahydro-paraquinanisol*, $C_9H_{10}(OCH_3)N$, the sulphate and tartrate of which were introduced into medicine under the name of thalline," because of the emerald-green color produced in its solution by ferric chloride. It was used as an antipyretic, antiseptic, and antifermentative.

Other quinoline derivatives that have been proposed for use in medicine are "diaptherine," a compound of one molecule of orthophenol-sulphonic acid (aseptol) with two molecules of ortho-oxy-quinoline; "analgene," *ethyoxy-ana-monobenzoyl-amido-quinoline*, $C_9H_5(OC_2H_5)$.-$NH.COC_6H_5.N$, recommended as a febrifuge and antineuralgic; and "orexine," the hydrochloride of phenyldihydro-quinazoline, $C_{14}H_{12}N_2$.-$HCl + 2H_2O$, which has been recommended as a stomachic and stimulant to digestion.

Quinoline-carboxylic Acids.—Among the mono-carboxylic acids of the formula $C_9H_6N.COOH$ may be mentioned *quinaldinic acid*, obtained by oxidizing quinaldine and *cinchoninic acid*, obtained by oxidizing cinchonine with potassium permanganate or nitric acid. When distilled with lime it yields quinoline.

Kynurenic Acid is an oxy-quinoline-carboxylic acid. It occurs in the urine of dogs. *Quininic Acid*, $C_9H_5(OCH_3)N.COOH$, is the methyl-phenol ether of another oxy-quinoline-carboxylic acid. It is obtained by oxidizing quinine and quinidine with chromic acid in sulphuric acid solution. Quinoline-dicarboxylic acids, $C_9H_5N(COOH)_2$, are also known.

3. **Acridine and its Derivatives.**—Acridine, $C_{13}H_9N$, has already been explained and its relationship to anthracene stated (see p. 671). It is found in coal-tar and in the crude anthracene extracted therefrom. It has been made synthetically from diphenylamine, formic acid, and zinc chloride:



$$C_6H_5\text{—}NH\text{—}C_6H_5 \quad + \quad HCOOH \quad = \quad C_6H_5\diagdown\overset{\overset{CHO}{|}}{N}\diagup C_6H_5 \quad + \quad H_2O.$$

Diphenylamine + Formic Acid = Formyl-diphenylamine.

This compound then breaks up into acridine and water:

$$C_6H_5\diagdown\overset{CHO}{\underset{N}{|}}\diagup C_6H_5 = C_6H_4{<}\overset{CH}{\underset{N}{|}}{>}C_6H_4 + H_2O.$$

Acridine.

It forms colorless needles or scales, fusing at 107°–111°. Scarcely soluble in water, easily soluble in ether, alcohol, benzene, carbon disulphide, etc. It is a base, and dissolves in dilute acid with a beautiful green fluorescence. Acridine irritates the skin and mucous membranes, whence the name. Among its derivatives are several important dye-colors, such as *chrysaniline,* which is the nitrate of diamido-phenylacridine, and *benzoflavine,* which is an isomer of the other.

SIX-MEMBERED CYCLIC COMPOUNDS CONTAINING OXYGEN (HETEROCYCLIC COMPOUNDS.)

a. Pyrone (coumalin), $O{<}\genfrac{}{}{0pt}{}{CO-CH}{CH=CH}{>}CH$, is a colorless neutral liquid, boiling at 209° and having an odor similar to caraway seeds. It is produced by heating coumalic acid.

b. Pyrone (pyrocomane), $O{<}\genfrac{}{}{0pt}{}{CH=CH}{CH=CH}{>}CO$, forms colorless neutral crystals which melt at 32°. The pyrones and their derivatives on warming with NH_3 are converted into pyridones (see p. 673), when the oxygen of the ring is replaced by $=NH$.

The properties of many pyrones are peculiar because, although of neutral reaction, they form salts with acids by addition similar to ammonia. On account of this analogy to ammonium salts, the compounds are called *oxonium* salts and the oxygen atom of the ring is supposed to act as tetravalent.

Coumanic acid and *coumalic acid,* both $C_5H_3(COOH)O_2$, are pyrone-carboxyl acids.

Chelidonic acid, $C_5H_2(COOH)_2O_2$, is pyrone dicarboxyl acid and occurs in *chelidonium majus.*

Meconic acid, $C_5H(OH)(COOH)_2O_2$, is oxy-pyrone dicarboxylic acid and occurs in opium (see p. 690).

CHAPTER VIII.

THE ALKALOIDS AND PTOMAINES.

THE term alkaloid has been applied to a number of physiologically active principles occurring in the vegetable kingdom, and this common occurrence was emphasized more than any general chemical character. It is true it was recognized that they were nitrogenous, and that they acted as derived ammonias in their method of forming salts, but for a long time nothing more definite could be said with regard to their chemical nature. It is now recognized that, while the great majority of these are derivatives of the basic compounds pyridine and quinoline, just noticed in the preceding pages, there are also methane derivatives among them, as caffeine and theobromine, which belong to the purin group, and that, besides the occurrence of these important bases in the plant kingdom, substances answering to many of the alkaloidal tests are produced in the decay of animal tissue, giving rise to the so-called "cadaveric alkaloids," or ptomaines. It remains true of all these classes, however, that we have to do with derived ammonias, either amines or amides, and this feature, together with their physiological activity, must be taken to constitute the basis of their claim to the name alkaloid, whether synthetically formed, or found in the vegetable or animal kingdom only. The termination *ine* has been made uniform for them as expressing their basic character and their derivation from ammonia.

Classification of the Alkaloids.—Leaving the animal alkaloids for subsequent consideration, we find that the vegetable alkaloids may be divided into two classes: those which are liquid and volatile, and those which are solid and non-volatile. At the same time we find that with this physical distinction corresponds a difference in chemical composition,—viz., the liquid alkaloids do not contain oxygen, while the solid alkaloids are oxygenated bases. As the liquid alkaloids are very limited in number, no further grouping is necessary for them. For the solid alkaloids it will be found convenient to group them in addition according to the order or family of plants in which related alkaloids are found.

Extraction of Alkaloids from the Plants.—The vegetable alkaloid does not ordinarily exist in the plant in a free state. It is most generally present as a salt, often an acid salt of some organic acid, such as malic or tannic acid. We have also some as salts of organic acids peculiar to the particular plant, such as meconic acid in opium, quinic acid in cinchona bark, and igasuric acid in *nux vomica*. Inorganic acids are also occasionally found in combination with the alkaloids, as in opium, where the morphine is combined as sulphate. While most of these naturally occurring alkaloidal salts are soluble in water, others, such as the tannates, are not, so that for their extraction from the plants dilute acids are generally used. At times, though, the alkaloid is liberated from its combination in aqueous infusion by the aid of lime or magnesia, and then extracted by ether, chloroform, or alcohol. The extraction is also accomplished at times by alcohol used directly upon finely powdered or comminuted plant, as most of the alkaloidal salts are easily soluble in it. In this case the solvent is removed by gentle evaporation or distillation before proceeding to further purification of the alkaloid.

Alkaloidal Reagents.—Under this head we may consider the two classes,—those which act as *precipitants*, and those which give distinctive *color-tests*. Among the precipitants we note, first, *tannic acid*. The tannates of the alkaloids are mostly difficultly soluble in cold water, so that the addition of tannic acid precipitates them from aqueous solution of either free alkaloid or its salt even quite dilute; the precipitates are soluble in excess of the tannic acid, and in other acids and alcohol; often, indeed, in hot water. Second, the haloid salts of mercury and some other metals tend to form difficultly soluble precipitates with the alkaloids. Thus, *corrosive sublimate* alone, or *potassium iodohydrargyrate* (Mayer's reagent), together with the corresponding double salts, *potassium cadmium iodide* (Marmé's reagent) and *potassium bismuth iodide* (Dragendorff's reagent), all have the power of precipitating in greater or less degree the alkaloids in the form of a double salt. Indeed, *iodized iodide of potassium* (Bouchardat's or Wagner's reagent) will produce insoluble precipitates with the great majority of alkaloids. Third, *picric acid* (Hager's reagent) precipitates a number of the alkaloids, such as the cinchona bases, from solution of the salts or the free bases. Fourth, *phosphomolybdic acid* (Sonnenschein's reagent) and *phosphotungstic acid* (Scheibler's reagent) are available as precipitants for the great majority of alkaloids. Fifth, neutral *potassium chromate*, as well as the *bichromate*, precipitates from the concentrated aqueous solutions of their salts most of the alkaloids in the form of difficultly soluble chromates. From dilute solutions, however, the neutral chromate precipitates often the free alkaloid. Sixth, both *gold chloride* and *platinic chloride* form well-crystallized double salts with many of the alkaloids, which serve for their separation and purification.

The color-tests with alkaloids are at times very strong, but are not sufficiently distinctive or exclusive in character to be depended upon for decisive determination of the alkaloids. They are easily interfered with in most cases by the presence of a third substance, and can only be of value when compared with the same test applied to a sample of the same alkaloid of known purity. These color-reactions are thus classified by A. H. Allen:* (1) Those produced by dehydrating agents, such as strong sulphuric acid, phosphoric oxide, and zinc chloride; (2) those given by oxidizing agents not of themselves yielding colors, such as nitric acid, chlorine, bromine, and bleaching powder; or sulphuric acid and oxidizing agents, such as potassium chlorate, perchlorate, and

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* Com. Org. Anal., vol. iii., Part ii., p. 44.

permanganate; (3) those given by oxidizing agents which themselves yield a colored product by reduction, such as iodic acid and reagents containing chromic, molybdic, tungstic, and vanadic acids; (4) and colorations produced by certain special reagents, such as ferric chloride, hydrochloric acid, sulphuric acid and sugar, etc.

The most important and characteristic of these color-tests will be given later under the heads of the individual alkaloids.

DETECTION AND EXTRACTION OF THE ALKALOIDS FROM MIXTURES.

1. **Method of Stas and Otto.**—The first general process for the extraction of the alkaloids from various complicated mixtures in which they may occur was that of Stas as modified by Otto in 1856. The material supposed to contain the alkaloids is extracted by alcohol with the addition of tartaric acid, and the residue obtained by the careful evaporation of this liquor is shaken with ether. The portion insoluble in ether is now made alkaline and again shaken with ether. The alkaline solution containing soda is then treated with ammonium chloride. and shaken with amyl alcohol. The solution containing ammonium chloride is evaporated and extracted with strong alcohol, This method of Stas and Otto was next modified by Rodgers and Girdwood, who employed chloroform instead of ether, and by Uslar and Erdmann, who recommended the use of amyl alcohol.

2. **Method of Dragendorff.**—This method is the most comprehensive one as yet proposed, and is in most general use. It is given in outline: The material to be investigated is extracted with dilute sulphuric acid. The extract which contains the alkaloids as sulphate is evaporated and precipitated with alcohol. It is then filtered and the alcoholic filtrate evaporated. The acid solution is then extracted in succession with petroleum ether, benzene, and chloroform. The portion undissolved is made alkaline with ammonia and then extracted in succession with petroleum ether, benzene, chloroform, and amyl alcohol. Seven extractions are thus made, which may be tabulated as follows:

I. Extractions from acid solutions:
  - (*a*) With petroleum ether: piperine, and, in addition, carbolic, salicylic, and picric acids.
  - (*b*) With benzene: cantharidin and digitalin, berberine and colchicine.
  - (*c*) With chloroform: narcotine, picrotoxin, and digitaleïn.

II. Extractions from alkaline solutions:
  - (*a*) With petroleum ether: nicotine, conine, quinine, and some strychnine.
  - (*b*) With benzene: quinine, atropine, cocaïne, strychnine, brucine, veratrine, and thebaïne.
  - (*c*) With chloroform: a little morphine, papaverine.
  - (*d*) With amyl alcohol: morphine, solanine, narceïne.

3. **Sonnenschein's Method.**—In this method the material is acidified with dilute hydrochloric acid, and then phosphomolybdic acid is added,

which precipitates all the alkaloids. The precipitate is warmed with baryta water, when the volatile alkaloids may be distilled off. The solution, after filtering off the barium precipitates, is freed from barium by addition of carbon dioxide, and the aqueous solution is then investigated by the methods of either Stas-Otto or Dragendorff. The objection to this method is that the treatment with barium hydrate may cause decomposition in some of the active principles present.

4. **Method of Brieger.**—This is chiefly for the separation of the ptomaïnes if present in a suspected mixture. The solution is treated with hydrochloric acid to convert the bases into chlorides, and then, after a preliminary clarifying of the solution, if necessary, with lead acetate, the ptomaines are precipitated with mercuric chloride solution. Most of these bases are thus thrown out (tetanine is an exception), and, after suspending the mixture in water and freeing it from mercury by hydrogen sulphide, the ptomaïnes are obtained in the form of double salts with gold and platinic chlorides, and tested by experiments upon animals.

The special description of the more important alkaloids can now be taken up on the basis of the simple classification before made.

VOLATILE ALKALOIDS.

As the simplest of the naturally occurring alkaloids may be mentioned *methylamine* and *trimethylamine*, both of which are found at times in the vegetable kingdom, as well as in the products of decomposition of animal tissues. They have already been noted and their varied occurrence detailed (see p. 580).

Piperidine, $C_5H_5N.H_6$, has been found naturally occurring in pepper as a decomposition-product of piperine. It has already been described under the name of hexahydropyridine (see p. 673).

Conine, $C_8H_{17}N$ [or $C_5H_{10}(C_3H_7)N$].—This has also been referred to as α-normal-propyl-piperidine, or rather the dextro-rotatory variety of the same, having been made synthetically by Ladenburg.

Conine is the poisonous alkaloid of the hemlock (*Conium maculatum*) and is an oily liquid of a peculiar repulsive odor. It is colorless when freshly prepared, but becomes yellow and ultimately resinoid on keeping. It is soluble in about 90 parts of water, and is readily dissolved by alcohol, acetone, amylic alcohol, ether, chloroform, petroleum ether, and benzene. It is a strong base and neutralizes acids perfectly. By the treatment of conine with chromic-acid mixture, normal butyric acid is produced. The reaction may be employed as a test for conine, as butyric acid is readily recognized by its odor.

Associated with conine in the conium are the following less important bases: *Conhydrine*, $C_8H_{17}NO$; *pseudo-conhydrine*, isomeric with the former; *methylconine*, $C_9H_{19}N$, and *coniceine* $C_8H_{15}N$ (the latter being *tetrahydropropyl-pyridine*).

Conine is an extremely powerful paralytic poison, which acts on the motor nerves; one drop is a distinctly poisonous dose, while ten drops may be fatal.

Nicotine, $C_{10}H_{14}N_2$.—This alkaloid has been referred to and stated to be hexa-hydro-dipyridyl. It is the poisonous principle of tobacco, in which it exists combined with malic and citric acids in amounts ranging from about 1 per cent. to 7 per cent. of the dry leaf. The nicotine is a colorless, oily liquid of sp. gr. 1.011 at 15°, which on prolonged exposure to air becomes yellow and ultimately resinous. It has a strong and unpleasant odor, recalling that of tobacco, a sharp, caustic taste, and is intensely poisonous. It is soluble in water and alcohol, but is extracted from its aqueous, alkaline solutions by agitation with ether, chloroform, benzene, amyl alcohol, or petroleum naphtha. Nicotine is precipitated by Mayer's reagent from very dilute solutions. On adding mercuric chloride to a solution of nicotine, a white, crystalline precipitate is produced, soluble in dilute hydrochloric or acetic acid. This is the most characteristic reaction of nicotine. From conine, nicotine is distinguished by its odor, by being heavier instead of lighter than water, and by its reactions with mercuric chloride, platinic chloride (yellowish-crystalline precipitate), and picric acid (yellow, amorphous precipitate turning crystalline). The poisonous effects of tobacco when taken into the stomach, it is agreed, are entirely due to the nicotine. When tobacco is smoked, the greater part of the nicotine is converted into pyridine and other decomposition-products; some, however, escapes decomposition, as Melsens has proved the presence of unchanged nicotine in tobacco smoke in a proportion equal to about one-seventh of that present in the original tobacco. Vohl and Eulenberg have concluded from their experiments that the intense action of tobacco smoke on the nervous system is not due to nicotine at all, but to the presence of the bases of the pyridine series.

Piturine, $C_{12}H_{16}N_2$.—The volatile alkaloid of pituri (the dried leaves of *Duboisia Hopwoodii*, a shrub growing in Australia) was regarded by Petit as identical with nicotine, but its individual character was established by Liversidge. In chemical characters and physiological effects it bears a close resemblance to nicotine, but can be distinguished by gently warming it with hydrochloric acid. Nicotine so heated turns violet, while piturine does not change at all.

Lobeline is the active principle of *Lobelia inflata*, or Indian tobacco. Paschkis and Smita obtained the alkaloid as a viscous oil with an odor at once resembling honey and tobacco.

Sparteine, $C_{15}H_{26}N_2$, is obtained from the coarsely-powdered leaves and branches of broom (*Spartium scoparium*). It is a colorless, oily liquid, boiling at 287°. When oxidized with potassium permanganate it yields a volatile acid, together with a non-volatile, pyridine-carboxylic acid, which distilled with lime yields pyridine. Its sulphate, $C_{15}H_{26}N_2.H_2SO_4 + 5H_2O$ (**Sparteinæ Sulphas**, U.S.P.) forms a colorless crystalline powder soluble in water and alcohol, insoluble in ether and chloroform.

Spigeline is the active principle of *Spigelia Marylandica*, or "pink-root." It was obtained as a volatile alkaloid on distilling the root with milk of lime.

NON-VOLATILE ALKALOIDS.

1. **The Belladonna Alkaloid Group.**—A series of natural alkaloids exists in the plants of the family *Solanaceæ*, and have been named atropine and belladonine, from the *Atropa belladonna*, hyoscyamine and hyoscine, from *Hyoscyamus niger* and scopolamine from *Scopola*

Carniolica. These alkaloids all contain a methylated-pyrrol ring in combination with a piperidine ring, which general structure is also true of the coca alkaloids ecgonine and cocaine. All of solanaceæ bases are distinguished by a remarkable power of dilating the pupil, and hence are often termed the "mydriatic alkaloids." The two bases, atropine, and hyoscyamine, are isomeric, and hyoscyamine, it is found, is converted into atropine by prolonged heating above its fusing point or by the action of alkalies. Hyoscine and scopolamine are chemically identical, although from different sources.

Atropine (Daturine), $C_{17}H_{23}NO_3$ (**Atropina,** U.S.P.), belongs to the class of tropeïnes, or compounds of the base *tropine*, $C_8H_{15}NO$. When the natural alkaloid is heated with hydrochloric acid or baryta water, it is decomposed (saponified) according to the reaction:

$$\underset{\text{Atropine.}}{C_{17}H_{23}NO_3} + H_2O = \underset{\text{Tropine.}}{C_8H_{15}NO} + \underset{\text{Tropic Acid.}}{C_9H_{10}O_3}.$$

The preferable method of effecting the saponification of these alkaloids is to heat the alkaloid with saturated baryta water to 60° or 80° for a few hours. When the hydrolysis is effected by an acid, especially concentrated hydrochloric acid, the tropic acid loses the elements of water, and atropic acid, $C_9H_8O_2$, results. On the other hand, the tropic acid and tropine resulting from the hydrolysis of either atropine or hyoscyamine, when heated together at 100° with dilute hydrochloric acid, regenerate atropine.

Pure atropine forms white, rhombic crystals, without odor, having a bitter, acrid taste. It melts when pure at 115.8°, but the commercial article containing hyoscyamine melts at a lower temperature. It is difficultly soluble in cold water, easily soluble in alcohol, ether, and chloroform. It is optically inactive, although a dextro-rotatory and a lævo-rotatory variety can be obtained synthetically. It is a powerful poison, producing delirium and convulsions.

Of its salts the sulphate is the most important (**Atropinæ Sulphas,** U.S.P.), but the borate and valerate are also used in ophthalmic surgery.

Hyoscyamine (Duboisine), $C_{17}H_{23}NO_3$, occurs with atropine in *Altropa belladonna*, and with hyoscine in the several species of *Hyoscyamus*. It is isomeric with atropine, and is readily converted into it. Ladenburg holds that the inactive atropine stands to the active hyoscyamine in the same relation as racemic acid stands to lævo-tartaric acid. It forms slender, colorless needles, melting at 108.5°. It shows an optical rotation of —29°. When decomposed by baryta water it yields the same products as atropine.

Of its salts the hydrobromine (**Hyoscyaminæ Hydrobromidum,** U.S.P.) is official.

Hyoscine, $C_{17}H_{21}NO_4$, is an amorphous base occurring with hyoscyamine in henbane. It is more rapid and powerful in its mydriatic effects than either atropine or hyoscyamine. Of its salts one only is official (**Hyoscinæ Hydrobromidum,** U.S.P.).

Scopolamine, $C_{17}H_{21}NO_4$, from *Scopola Carniolica*, is, as before stated, identical with hyoscine. When boiled with bases, it splits up into atropic acid, $C_9H_8O_2$, and scopoline (oxytropine) $C_8H_{13}NO_2$. Its hydrobromide (**Scopolaminæ Hydrobromidum,** U.S.P.) is official.

Artificial Tropeïnes.—When tropine, $C_8H_{15}NO$, is treated with certain acid chlorides, like benzoyl chloride, or evaporated to dryness with the acids referred to, together with dilute hydrochloric acid, we have formed esters of the base tropine with the several acid radicals. Thus, we have formed *benzoyl-tropeïne*, *salicyl-tropeïne*, and, with mandelic acid (see p. 657), *homatropine*, $C_{16}H_{21}NO_3$. The last-mentioned artificial alkaloid has the formula of a lower homologue of atropine, and has the same mydriatic action, which, however, is shorter in its duration. The homatropine crystallizes from absolute ether in prisms, which melt at 98°, and are very deliquescent. Its hydrobromide is official as **Homatropinæ Hydrobromidum,** U.S.P.

2. **The Coca Alkaloids.**—The leaves of *Erythroxylon coca* and related species contain a number of alkaloids, all of which appear to be derivatives of *ecgonine*, $C_9H_{15}NO_3$. This base is a carboxylic acid of tropine, $C_8H_{15}NO$. When heated with baryta, it splits into carbon dioxide and isotropine. The coca leaves contain some 9 bases, of which the one medicinally important is *cocaine* (benzoyl-ecgonine methyl ester), $C_{17}H_{21}NO_4$. Cocaine may be extracted from the plant, but as separation from the accompanying alkaloids and products of hydrolysis is difficult, Liebermann has proposed a synthetic method which avoids these difficulties and at the same time utilizes the amorphous by-products. The mixed bases are boiled with hydrochloric acid, whereby they all suffer hydrolysis with formation of ecgonine; then by passing dry hydrochloric acid into a solution of ecgonine hydrochloride in methyl alcohol, the hydrochloride of ecgonine methyl-ester is formed, which, on concentrating the alcoholic solution, crystallizes out in prisms. Cocaine is formed when this compound is heated on the water-bath with an equal weight of benzoyl chloride until the mixture becomes homogeneous and the evolution of hydrochloric acid ceases. The melted mass is poured into water and separated from the insoluble benzoic acid, when the cocaine is precipitated by ammonia and recrystallized from alcohol. The artificial alkaloid possesses all the properties of the natural cocaine.

Cocaine (**Cocaina,** U.S.P.) crystallizes from alcohol in colorless, monoclinic prisms, melting at 98°. It is very slightly soluble in water, but readily soluble in alcohol, ether, chloroform, benzene, petroleum spirit, and carbon disulphide. Cocaine is lævo-rotatory. Its chief use in medicine is as a local anæsthetic.

Cocaine Hydrochloride, $C_{17}H_{21}NO_4.HCl$ (**Cocainæ Hydrochloridum,** U.S.P.).—It forms colorless, transparent crystals of a saline taste and producing upon the tongue a tingling sensation followed by a numbness of some minutes' duration. It is readily soluble in water and alcohol, difficultly soluble in ether. At 191°C. it melts with partial sublimation.

3. The Cinchona Alkaloids.—The barks of the *Cinchona Calisaya*, *Cinchona officinalis*, and of hybrids of these, are, according to the U. S. Pharmacopœia, the sources of quinine and its associated alkaloids, containing not less than 5 per cent. of total alkaloids, of which 2.5 per cent. is quinine. The maximum percentage of quinine seems to have been reached in the *Cinchona Ledgeriana*, grown in Java in 1876, which yielded 13.25 per cent. of quinine. These barks contain some 32 natural alkaloids, and in the processes of extraction and purification some 8 additional bases are formed by alteration of the naturally occurring ones.

The list of naturally occurring cinchona alkaloids, as given by A. H. Allen, on the authority of Paul and Cownley, is as follows:

I. *Cinchonine class:*
Paricine, $C_{16}H_{18}N_2O$.
Cinchotine, $C_{19}H_{24}N_2O$.
Cinchonamine, "
Hydrocinchonine, "
Hydrocinchonidine, "
Cinchonine, $C_{19}H_{22}N_2O$.
Cinchonidine, "
Homocinchonidine, "
Cinchonicine, "
Paytine, $C_{21}H_{24}N_2O$
Paytamine, "

II. *Quinamine class:*
Quinamine, $C_{19}H_{24}N_2O_2$.
Conquinamine, "
Javanine, ——.
Cupreine, $C_{19}H_{22}N_2O_2$.

III. *Quinine class:*
Hydroquinine, $C_{20}H_{26}N_2O_2$.
Hydroquinidine, "
Quinine, $C_{20}H_{24}N_2O_2$.
Quinidine, "
Quinicine, "

IV. *Cusconine class:*
Chairamine, $C_{22}H_{26}N_2O_4$.
Conchairamine, "
Chairamidine, "
Conchairamidine, "
Concusconine, "
Aricine, $C_{23}H_{26}N_2O_4$.
Cusconine, $C_{23}H_{26}N_2O_4$.
Cusconidine, "
Cuscamine, ——.
Cuscamidine, ——.

V. *Anhydro-bases:*
Dicinchonicine, $C_{38}H_{44}N_4O_2$.
Diquinicine, $C_{40}H_{46}N_4O_3$.

Of all this list, however, four stand out as more important, of which three are represented among official compounds. These four are *quinine* and *quinidine*, which are isomers with the formula $C_{20}H_{24}N_2O_2$, and *cinchonine* and *cinchonidine*, isomers with the formula, $C_{19}H_{22}N_2O$.

These alkaloids are derivatives of a quinoline and a complicated piperidine ring, as is shown by an examination of certain of their oxidation products which prove to be carboxylic acids of quinoline (see p. 676).

In the free state these alkaloids are colorless or slightly yellowish solids, fusible but not volatile without decomposition. They are generally but slightly soluble in water, but more readily soluble in alcohol, and generally quite soluble in ether and chloroform. When soluble in these last two liquids, they may be removed from their ammoniacal solutions by agitation with ether or chloroform, but these solvents will not remove them from an aqueous solution acidified with sulphuric or hydrochloric acid. The anhydrous sulphates of several of the cinchona alkaloids, however, are soluble in chloroform, and still more readily in a mixture of chloroform and absolute alcohol. Solutions of some of the cinchona alkaloids in excess of dilute sulphuric acid exhibit a strong blue fluorescence which is visible even in very dilute liquids. This fluorescence is destroyed by adding an excess of chloride of sodium or other haloid salt.

The solutions of the cinchona alkaloids all show optical activity, quinine and cinchonidine being lævo-rotatory and cinchonine and quinidine being dextro-rotatory.

The sulphates of several of the cinchona bases possess the property of combining with iodine, forming "iodosulphates." Some of these, as herapathite (quinine iodosulphate), have the power of polarizing light like tourmaline (see p. 110).

Certain of the cinchona bases give a deep-green coloration when their solutions are treated with chlorine or bromine water and ammonia is subsequently added, a reaction known as the "thalleioquin test."

Quinine, $C_{20}H_{24}N_2O_2 + 3H_2O$ (**Quinina,** U.S.P.), is the most important of these bases, and apparently possesses the most powerfully febrifuge properties. The free base may be obtained either anhydrous, as a white, flaky, amorphous powder, melting at 174.9°, and readily becoming resinous, or as a crystalline powder containing 3 molecules of water of crystallization. It then melts at 57° and loses its water gradually, the last disappearing at 125°. It is odorless and has an intensely bitter taste. It is very sparingly soluble in water, readily soluble in alcohol and anhydrous ether, in chloroform, benzene, petroleum naphtha, and carbon disulphide, the anhydrous base being in all cases more readily soluble than the hydrate. The reactions for quinine which are more distinctive are: First, the strong blue fluorescence which its solutions in dilute sulphuric acid exhibit; even the salts with haloid acids show this when an excess of dilute sulphuric acid is added. Quinidine will also show this fluorescence, but neither cinchonine and its isomers nor cupreine show it. Second, a solution of quinine, as nearly neutral as possible, is treated with either chlorine or bromine, and then with excess of ammonia, when a green substance called "thalleioquin" is produced. In concentrated solutions a precipitate is formed, and in dilute ones a deep-green coloration only. The thalleioquin reaction is also given by quinidine and cupreine, but not by cinchonine and its isomers. It is prevented by morphine. Third, on adding tincture of iodine to a solution of acid sulphate of quinine in dilute alcohol, a compound is produced known as *Herapathite*, of the composition $4C_{20}H_{24}N_2O_2,3H_2SO_4,2HI,I_4 + 3H_2O$. This body, also called "iodo-sulphate of quinine," is the type of a series of similar compounds formed by the action of iodine on the sulphates of the cinchona bases. It is only slightly soluble in water or dilute alcohol, but is soluble in boiling alcohol of 92 per cent., and is deposited on cooling in tabular crystals which are dichroic, and, as before stated, when in thin sections have the power of polarizing light Herapathite is reconverted into quinine sulphate by treatment with sulphurous acid, thiosulphates, hydrogen sulphide, and other reducing agents. As the iodosulphate of quinine is much less soluble than the corresponding compounds of the other cinchona bases, it has been proposed by de Vrij as a basis for the determination of quinine.

While the complete synthesis of quinine has not as yet been effected, it has been made from the accompanying alkaloid cupreine of the *Cinchona cuprea.* When cupreine in methyl alcohol solution is treated with metallic sodium and methyl chloride in a sealed tube under pressure, the following reaction takes place:

$$\underset{\text{Cupreine-sodium.}}{C_{19}H_{21}N_2O.ONa} + CH_3Cl = NaCl + \underset{\text{Quinine.}}{C_{19}H_{21}N_2O.OCH_3}.$$

It is necessary to note that the cinchona bases form two classes of sulphates,—viz., neutral sulphates, with the general formula $R_2H_2SO_4$, and acid or bisulphates, with the formula RH_2SO_4. The former of these have a neutral reaction to litmus and methyl orange, and are in general sparingly soluble in water, while the second class are generally readily soluble.

Quinine Sulphate, $(C_{20}H_{24}N_2O_2)_2H_2SO_4.7H_2O$ (**Quininæ Sulphas,** U.S.P.).—This, the staple salt of quinine, is generally made on a large scale direct from the cinchona barks.

The official sulphate forms loose, white, needle-like crystals of a somewhat silky lustre, which, however, is easily impaired by its tendency to lose water of crystallization and effloresce superficially. It is odorless, but of a persistent, very bitter taste.

Quinine Acid Sulphate, $C_{20}H_{24}N_2O_2,H_2SO_4.7H_2O$ (**Quininæ Bisulphas,** U.S.P.), is readily formed by dissolving quinine sulphate in the calculated amount of dilute sulphuric acid. It forms colorless, transparent, rhombic crystals of a bitter taste. It is soluble in 8.5 parts of water, forming a solution which fluoresces strongly blue and shows acid reaction. It loses its water of crystallization at 100° C., and at 160° it melts with decomposition.

Quinine Hydrobromide, $C_{20}H_{24}N_2O_2,HBr.H_2O$ (**Quininæ Hydrobromidum,** U.S.P.), forms light, white, silky needles, odorless, but with very bitter taste. It is soluble in 40 parts of water at 25°. The salt is neutral or faintly alkaline. The aqueous solution when acidulated with sulphuric acid shows a fine blue fluorescence.

Quinine Hydrochloride, $C_{20}H_{24}N_2,HCl.2H_2O$ (**Quininæ Hydrochloridum,** U.S.P.), forms white, silky, asbestos-like crystals which become anhydrous at 120°. It is soluble in 18 parts of water at 25° and in 0.6 parts of alcohol. The dilute, aqueous solution shows some little fluorescence, which becomes stronger on adding dilute sulphuric acid.

Quinine Dihydrochloride, $C_{20}H_{24}O_2N_2.2HCl$ (**Quininæ Dihydrochloridum,** U.S.P.), forms a white powder, odorless and with a very bitter taste. *Quinine and Urea Hydrochloride,* $C_{20}H_{24}O_2N_2.HClCO(NH_2)_2.HCl + 5H_2O$ (**Quininæ et Ureæ Hydrochloridum,** U.S P.), is also official.

Quinine Salicylate, $C_{20}H_{24}N_2O_2.C_7H_6O_3 + H_2O$ (**Quininæ Salicylas,** U.S.P.), forms colorless needles permanent in the air, assuming a pink color on keeping.

Quinine Tannate (**Quininæ Tannas,** U.S.P.), a compound of somewhat varying composition, is also official.

Ferri et Quininæ Citras, U.S.P., is an official scale preparation. Several of the esters of quinine have also been introduced lately into medicine. The neutral carbonate of quinine as "aristochin," the ethyl carbonic ester as "euchinin," and the salicylate as "saloquinine."

Quinidine (Conquinine), $C_{20}H_{24}N_2O_2$, is an isomer of quinine, and occurs frequently in cinchona barks. It is present to a considerable extent in commercial "quinoidine" (chinoidine). The free base crystallizes from alcohol in large, monoclinic, efflorescing needles, containing 2½ molecules of water. It gives the thalleioquin reaction like quinine and shows a blue fluorescence in dilute sulphuric-acid solution, but is dextro-rotatory and is sparingly soluble in ether, two points of difference.

Quinidine Sulphate $(C_{20}H_{24}N_2O_2)_2H_2SO_4.2H_2O$, crystallizes in white, silky needles or prisms, which require 100 parts of water or 8 parts of alcohol for solution. This salt differs from the sulphates of the other cinchona alkaloids in requiring a temperature of 120° to render it anhydrous, and in readily taking up the water again in moist air.

Cinchonine, $C_{19}H_{22}N_2O$.—This base is invariably present in cinchona barks. When the bases are crystallized from alcohol, the cinchonine, being the least soluble, deposits first. It crystallizes in anhydrous, shining prisms, or needles, which melt at 255°. It is almost insoluble in cold water, requiring 3760 parts at 15° and 3500 parts at a boiling temperature, and is difficultly soluble in alcohol and ether, the best solvent being amyl alcohol or a mixture of amyl alcohol and chloroform. It does not give the thalleioquin reaction, its dilute sulphuric acid solutions do not fluoresce blue, and it is dextro-rotatory, which characters, together with its difficult solubility in ether, distinguish it from quinine. When heated to a high temperature with an alkali, cinchonine yields quinoline, C_9H_7N, together with other products.

Cinchonine Sulphate $(C_{19}H_{22}N_2O)_2H_2SO_4.2H_2O$ (**Cinchoninæ Sulphas,** U.S.P.), forms short, hard, and shining, monoclinic prisms. Soluble in 60 parts of water at 25°, with a weak, alkaline reaction. Loses its water of crystallization at 100°, and melts with partial decomposition at 198.5°.

Cinchonidine, $C_{19}H_{22}N_2O$, is contained in several species of cinchona, but is especially characteristic of the red bark of *C. succirubra.* It is lævo-rotatory, but is not fluorescent in its solutions and does not give the thalleioquin reaction.

Cinchonidine Sulphate $(C_{19}H_{22}N_2O)_2H_2SO_4.3H_2O$ (**Cinchonidinæ Sulphas,** U.S.P.).—The official salt is that which crystallizes from a hot and concentrated aqueous solution, while from moderately concentrated aqueous solutions crystallizes a salt with 6 molecules of water. The official sulphate forms silky, acicular crystals, slightly efflorescing on exposure to dry air. It is soluble at 25° in 63 parts of water, and in 1.42 parts of boiling water. It is almost insoluble in chloroform and ether.

Quinoidine is the name given to the resinous mixture of amorphous alkaloids left in the mother liquor after the extraction of the crystalline bases.

Phenyl cinchonic acid, $C_6H_5C_9H_5N(COOH)$ **(Acidum Phenylcinchoninicum,** U.S.P.), forms colorless needles or a white micro crystalline powder.

4. **The Strychnos Alkaloids.**—The varies species of *Strychnos* contain certain alkaloids of intensely poisonous properties, which contain a condensed quinoline-piperidine ring. Of these, two have been specially investigated, strychnine and brucine. Both of them occur in the seeds of the *Strychnos nux vomica* in combination with lactic and igasuric acids, and in the bark of the same. A third base, *igasurine*, supposed to exist in nux vomica, has been shown by Shenstone to be merely a mixture of strychnine and brucine. The seeds of *Strychnos Ignatiæ*, commonly called "St. Ignatius' beans," also contain strychnine and brucine, and are employed for the manufacture of the alkaloids. The decoction of the root-bark of *Strychnos Tieute*, or "deadly upas tree" of Java, evaporated to an extract, is the chief ingredient of the arrow-poison "upas-tieute." It contains strychnine and brucine.

Strychnine, $C_{21}H_{22}N_2O_2$ (**Strychninæ**, U.S.P.).—The alkaloid may be prepared from the several sources above mentioned. Strychnine forms colorless, transparent crystals, odorless, and having an intensely bitter taste perceptible even in very dilute (1 in 700,000) solution. It is very difficultly soluble in water, moderately soluble in alcohol, more readily in chloroform, and almost insoluble in ether. Strychnine melts at 268°. Its solutions are lævo-rotatory. It dissolves without color in strong mineral acids. Its solution in strong sulphuric acid, however, is changed by a small fragment of potassium dichromate,* yielding a blue color, changing to purplish-blue, violet, purplish-red, cherry-red, and finally orange-yellow.

Strychnine may be separated from brucine by taking advantage of the insolubility of its ferrocyanide, the corresponding compound of brucine being readily soluble.

Strychnine Nitrate, $C_{21}H_{22}N_2O_2.HNO_3$ (**Strychninæ Nitras**, U.S.P.), forms colorless glistering needles with an intensely bitter taste. Decomposed when heated without melting.

Strychnine Sulphate, $(C_{21}H_{22}N_2O_2)_2H_2SO_4.5H_2O$ (**Strychninæ Sulphas**, U.S.P.), forms colorless, prismatic crystals, with an intensely bitter taste, efflorescing in dry air, soluble in water and alcohol, almost insoluble in ether. The salt loses its water of crystallization at 110° and fuses at 200°.

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*Allen prefers manganese dioxide as an oxidizing agent for this reaction, as the play of colors is well developed and the change of tints more gradual than with the other oxidizing compounds.

Brucine, $C_{23}H_{26}N_2O_4$.—This second alkaloid of *Nux vomica, St. Ignatius' beans*, and false angustura bark seems chemically to be a dimethoxy-strychnine. It is obtained in bitter, white crystalline powder or groups of prismatic needles. It is more soluble than strychnine in water, and very soluble in alcohol. Brucine is a weaker base than strychnine and is not so poisonous. When treated with concentrated sulphuric acid and oxidizing agents it does not give the color reactions seen with strychnine. On the other hand, with nitric acid of 1.42 sp. gr., brucine gives a blood-red color, which on heating becomes yellowish-red and yellow.

5. The Opium Alkaloids.—Opium contains, besides the two different compounds *meconoisin*, $C_8H_{10}O_2$, and *meconin*, $C_{10}H_{10}O_4$, a series of alkaloids which occur for the most part combined with *meconic acid*. Several of these, (papaverine, narcotine, and narceine) are isoquinoline derivatives, but the others are phenanthrene-morpholine compounds. The complete list of the opium alkaloids thus far recognized is:

Morphine, $C_{17}H_{19}NO_3$.
Codeine, $C_{18}H_{21}NO_3$.
Thebaine, $C_{19}H_{21}NO_3$.
Papaverine, $C_{20}H_{21}NO_4$.
Meconidine, $C_{21}H_{23}NO_4$.
Codamine, $C_{20}H_{25}NO_4$.
Laudanine, $C_{20}H_{25}NO_4$.
Laudanosine, $C_{21}H_{27}NO_4$.
Lanthopine, $C_{23}H_{25}NO_4$.
Protopine, $C_{20}H_{19}NO_5$.
Cryptopine, $C_{21}H_{23}NO_5$.
Rhœadine, $C_{21}H_{21}NO_6$.
Narcotine, $C_{22}H_{23}NO_7$.
Oxynarcotine, $C_{22}H_{23}NO_8$.
Narceine, $C_{23}H_{29}NO_9$.
Pseudomorphine, $C_{34}H_{36}N_2O_6$
Gnoscopine, $C_{34}H_{36}N_2O_{11}$.
Tritopine, $C_{42}H_{54}N_2O_7$.
Hydrocotamine, $C_{12}H_{15}NO_3$.

Of these bases, morphine is always present in opium in largest amount (10 to 14 per cent.). The amount of narcotine present ranges from 4 to 8 per cent., that of papaverine from 0.5 to 1 per cent., that of codeine from 0.2 to 0.8 per cent., that of thebaine from 0.2 to 0.5 per cent., and that of narceine from 0.1 to 0.4 per cent. The other bases are less important, and are found in relatively small amount. Besides these bases opium contains some resin and caoutchouc-like bodies, fat, wax, gum, coloring matter, inorganic salts, and water.

Opium, U.S.P., is the concrete, milky exudation obtained by incising the unripe capsules of *Papaver somniferum* Linné (nat. ord. *Papaveraceæ*), yielding in its normal moist condition not less than 9 per cent. of "crystallized morphine," when assayed by the official process. The opium used for pharmaceutical purposes is mainly the Smyrna or Turkey opium, the Persian and East Indian varieties being, however, worked on a large scale for the extraction of alkaloids.

Morphine, $C_{17}H_{19}NO_3 + H_2O$ (**Morphina,** U.S.P.), forms "colorless or white, shining, prismatic crystals or fine needles or a crystalline powder, odorless, and having a bitter taste, permanent in the air." It loses its water of crystallization at 100° C. It is difficultly soluble in water, somewhat more soluble in alcohol, insoluble in ether and benzene. Its aqueous solutions are lævo-rotatory.

Morphine when distilled with zinc-dust yields pyridine, quinoline, pyrrol, and phenanthrene.

It contains two OH groups, of which one seems to be phenolic, and the other alcoholic in character. In Codeine (methylmorphine) the hydrogen of the phenols OH has been replaced and in methyl-codeine, the hydrogen of the alcoholic OH also.

Of the salts of morphine the following are official: **Morphinæ Hydrochloridum,** U.S.P., $C_{17}H_{19}NO_3.HCl + 3H_2O$, and **Morphinæ Sulphas,** $(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$.

By acetylization of morphine is obtained *Diacetyl Morphine* (**Diacetylmorphina,** U.S.P.) a white crystalline powder melting at 171.5° C. The hydrochloride is also official (**Diacetylmorphinæ Hydrochloridum,** U.S.P.), forming a white crystalline powder melting at about 230° C.

When morphine or its hydrochloride is heated to 140°–150° in a sealed tube with a large excess of strong hydrochloric acid, or with zinc chloride at 110°, it is converted into the hydrochloride of *apomorphine,* the formula of which differs from that of morphine by the elements of water.

The hydrochloride (**Apomorphinæ Hydrochloridum,** U.S.P.), $C_{17}H_{17}NO_2.HCl$, forms minute grayish-white, acicular crystals, without odor, and of a faintly bitter taste, and acquiring a greenish tint on exposure to air and light. It is moderately soluble in water and alcohol, only slightly soluble in ether or chloroform. Codeine, $C_{18}H_{21}NO_3$, when treated in a similar way with hydrochloric acid, yields first $C_{18}H_{20}ClNO_2$, and then splits off methyl chloride and leaves apomorphine, $C_{17}H_{17}NO_2$.

Codeine (**Codeina,** U.S.P.), is morphine methyl-ester, $C_{17}H_{17}NO(OH)OCH_3$, and has been made synthetically by heating morphine with methyl iodide.

Two of the codeine salts are also official (**Codeinæ Phosphas,** U.S.P.), $C_{18}.H_{21}NO_3.H_3PO_4 + 2H_2O$; and (**Codeinæ Sulphas,** U.S.P.) $(C_{18}H_{21}NO_3)_2H_2SO4 + 5H_2O$. The hydrochloride of the ethyl ester of morphine is (**Aethylomorphinæ Hydrochloridum,** U.S.P.).

Narceine, $C_{23}H_{29}NO_9$, crystallizes with $2H_2O$ in long, white prisms or needles. The anhydrous base melts, according to Merck, at 170°–171°. It has powerful hypnotic properties.

Narcotine, $C_{22}H_{23}NO_7$, crystallizes from alcohol or ether in colorless needles or prisms, melting at 170°. When hydrolyzed it yields *Cotamine,* $C_{12}H_{13}NO_3$, the hydrochloride of which is official (**Cotaminæ Hydrochloridicum,** U.S.P.).

Papaverine, $C_{20}H_{21}NO_4$, is a weak base of feebly narcotic properties.

Thebaine, $C_{19}H_{21}NO_3$.—It crystallizes from strong alcohol in needles, which melt at 193°. It has a sharp and styptic taste, and is a powerful tetanic poison, producing symptoms resembling those of strychnine.

6. **Aconite Bases.**—*Aconitum napellus* (monk's-hood or wolf's-bane), *Aconitum ferox,* and *A. Fischeri* (Japanese aconite) contain a number of related alkalies which, according to C. R. Alder Wright, are esters either

of benzoic acid or of a derivative of this acid. Thus, when heated with water alone, each of the *crystalline* bases undergoes saponification, with formation of benzoic acid or a derivative thereof, together with a new amorphous base which generally has a far less physiological activity than the crystalline alkaloid from which it is derived.

These crystalline alkaloids, together with the products of their hydrolysis, are:

Crystalline Base.	Amorphous Base.	Acid.
Aconitine, $C_{33}H_{45}NO_{12}$ (from *A. napellus*).	Aconine, $C_{26}H_{41}NO_{11}$.	Benzoic acid, $C_7H_6O_2$.
Picraconitine, $C_{31}H_{45}NO_{10}$ (from *A. paniculatum?*).	Picraconine, $C_{24}H_{41}NO_9$.	Benzoic acid, $C_7H_6O_2$.
Japaconitine, $C_{66}H_{88}N_2O_{21}$ (from *A. Fischeri*).	Japaconine, $2C_{26}H_{41}NO_{10}$.	Benzoic acid. $2C_7H_6O_2$.
Pseudaconitine, $C_{36}H_{49}NO_{12}$ (from *A. ferox*).	Pseudaconine, $C_{27}H_{41}NO_9$.	Veratric acid (dimethyl-protocatechuic acid), $C_9H_{10}O_4$.

7. **Veratrum Alkaloids.**—In the *Veratrum viride* and *V. album* are contained several alkaloids which have been the subject of repeated studies. The most recent views indicate the existence of the following:

Jervine, $C_{12}H_{22}NO_2$.—Melts at 237.7° and is slightly lævo-rotatory.

Veratroidine (Rubijervine), $C_{32}H_{53}NO_9$.—Melts at 149.2° and is optically inactive.

Pseudojervine, $C_{29}H_{49}NO_{12}$.—Melts at 259.1° and is optically inactive.

Protoveratrine, $C_{32}H_{51}NO_{11}$.—Melts with charring at 245°–250°.

Protoveratridine, $C_{26}H_{45}NO_8$.—Melts at 265°; non-poisonous.

8. **Additional Alkaloids.**—*Berberine*, $C_{20}H_{17}NO_4.5\frac{1}{2}H_2O$, is found in the root of *Berberis vulgaris* and *Hydrastis canadensis*. It forms yellow needles, melting at 120°. When fused with caustic potash it yields quinoline. Associated with it in *Hydrastis canadensis* is the alkaloid *Hydrastine*, $C_{21}H_{21}NO_6$, (**Hydrastina**, U.S.P.), which forms colorless prisms melting at 131°.

Its hydrochloride, $C_{21}H_{21}O_6N.HCl$, is also official, as **Hydrastinæ Hydrochloridum**, U.S.P.

By the action of oxidizing agents hydrastine is split up into *hydrastinine*, $C_{11}H_{11}NO_2$ and *opianic acid*, $C_{10}H_{10}O_5$. The hydrochloride of hydrastinine (**Hydrastininæ Hydrochloridum**, U.S.P.), is official.

Colchine, $C_{22}H_{25}NO_6$ (**Colchicina**, U.S.P.), is obtained from colchicum seed. It forms pale yellow leaflets or powder turning darker on exposure to light. It has a peculiar odor of damp hay and a very bitter taste.

From Ipecac is obtained the alkaloid *Emetine*, of which the hydrochloride, $C_{30}H_{84}N_2O_4.2HCl$, is official (**Emetinæ Hydrochloridum**, U.S.P.).

Physostigmine, $C_{15}H_{21}N_3O_2$, is found in *Physostigma venenosum* (Calabar bean). It forms colorless or pinkish crystals, only slightly soluble in water, soluble in alcohol and ether. One of its salts is now official, **Physostigminæ Salicylas,** U.S.P.

Pilocarpine, $C_{11}H_{16}N_2O_2$, is an alkaloid found in the several varieties of *Pilocarpus.* It is a crystalline alkaloid first found in Jaborandi leaves, but since made synthetically by Hardy and Calmels from β-pyridine-α-lactic acid by first forming pilocarpidine, $C_{10}H_{14}N_2O_2$, and then converting this by the action of methyl iodide into pilocarpine. Two of its salts are official, **Pilocarpinæ Hydrochloridum,** U.S.P., and **Pilocarpinæ Nitras,** U.S.P.

Piperine, $C_{17}H_{19}NO_3$, is obtained from the black and white pepper, in which it is found to the amount of from 7 to 9 per cent. It is a weak alkaloidal base, forming pale yellowish crystals, melting at 130°. When heated with alcoholic potash it is decomposed into *Piperidine,* $C_6H_{11}N_4$, and *Piperic acid,* $C_{12}H_{10}O_4$.

The first of these compounds has already been noticed as hexahydropyridine (see p. 673), and the second is related to the oxyacids of the benzene series, and yields piperonal (see p. 650) by its oxidation.

Piperine can be made synthetically by the action of piperidine on the acid chloride, $C_{12}H_9O_3Cl$.

Pelletierine Tannate (**Pelletierinæ Tannas,** U.S.P.) is a mixture of tannates of several alkaloids obtained from Pomegranate.

ANIMAL ALKALOIDS, PTOMAINES, AND LEUCOMAINES.

While it was pointed out as far back as 1820 that symptoms of poisoning would be developed by introducing into an animal products of decomposing and putrefying organic matter, it has only been since 1870, when the Italian Selmi published his studies on cadaveric poisons, that the subject has been fully appreciated. He gave the name of "ptomaines" to these poisonous products of putrefaction. In 1884, Poehl, of St. Petersburg, in the report of a commission appointed to investigate the subject, stated the following conclusions:

1. Putrefaction, fermentation, and other as yet indefinite alterations of albuminous substances are accompanied by the generation of alkaloid-like bodies,—ptomaines.

2. These ptomaines may be fixed or volatile, fluid or solid, amorphous or crystalline. They show an alkaline reaction, and form salts with the acids like the alkaloids.

3. Some ptomaines are tasteless or odorless; others possess an intense bitter taste or aromatic, sweetish odor. Others, again, evolve a cadaveric odor, or resemble conine or nicotine. They are optically inactive bodies. Their color reactions are as various as those of the vegetal alkaloids and often simulate them.

Gautier, in 1881, announced the presence of toxic alkaloids in the excretions of animals, and gave to them the name of "leucomaines." His explanation of their occurrence is as follows: "While four-fifths of the products of animal combustion are aërobic formations, the remaining part of the combustion of the animal economy takes place at the expense of the tissues and is anaërobic, oxygen taking no part in it. In a normal condition of the body a very small proportion of muscular leucomaines is found in urine. But if the air that reaches the blood be diminished in quantity, or if the proportion of hæmoglobin be dimished, as in chlorosis or anæmia, or if substances be introduced into the blood which prevent hæmatosis, substances of the character of leucomaines or ptomaines accumulate in the blood."

Nitrogenous substances not alkaloids, which are still poisonous are also formed. These have been named "toxalbumens" or "albumoses."

Among the non-oxygenated liquid ptomaines may be enumerated:

Dimethylamine, Triethylamine, Propylamine (see p. 580). These are monamines.

In the class of diamines (see p. 581) we have: *Putrescine,* $C_4H_{12}N_2$ (tetramethylene-diamine), *Cadaverine,* $C_5H_{14}N_2$ (penta-methylene-diamine). These have both been described on p. 581. Isomeric with the last is *Neuridine,* a non-poisonous ptomaine from the decomposition of flesh.

Hydrocollidine, $C_{11}H_{13}N$, is a very poisonous ptomaine found by Gautier in decomposing horse-flesh. *Collidine,* $C_8H_{11}N$ (tri-methyl-pyridine), and *Parvoline,* $C_9H_{13}N$ (tetramethyl-pyridine), are also found as ptomaines.

Tyrotoxicon, $C_6H_5N_2$, found in putrid cheese and in milk and cream after undergoing certain putrefactive changes, also belongs to the non-oxygenated ptomaines. It has the composition of the diazo-benzene radical $C_6H_5.N{=}N—$.

Among the more important oxygenated ptomaines we may mention:

Neurine, $C_5H_{13}NO$, and *Choline,* $C_5H_{15}NO_2$, are both derived ammonium hydroxides, and are described on p. 557. They are both quite poisonous. *Muscarine,* $C_5H_{15}NO_3$, first obtained from the fungus *Agaricus Muscarius,* was found by Brieger in decomposing flesh. *Gadinine,* $C_7H_{16}NO_2$, was found in putrid fish. *Mytilotoxine,* $C_6H_{15}NO_2$, was obtained from poisonous mussels.

CHAPTER IX.

THE TERPENES AND THEIR DERIVATIVES.

I. THE TERPENES.

THE terpenes are hydrocarbons of the formula $(C_5H_8)_x$. Both they and the camphors, which are oxygenated derivatives, show a close relationship to the aromatic hydrocarbons, as common camphor, $C_{10}H_{16}O$, by the action of certain dehydrating agents yields cymene, $C_{10}H_{14}$, and terpenes of the formula $C_{10}H_{16}$ when heated with iodine are oxidized and yield the same hydrocarbon, $C_{10}H_{14}$. We may therefore consider the terpenes as hydrogen addition compounds of benzene hydrocarbons.

Characteristic Reactions.—Besides the production of cymene by oxidation, we have other distinctive reactions. The terpenes of the formula $C_{10}H_{16}$ may add on one or two molecules of a haloid acid (HCl,HBr,HI) or the corresponding amount of bromine, showing that they are unsaturated and that their molecules contain either one or two double linkings of carbon atoms. Many terpenes also form characteristic compounds with nitrous acid, called *nitrosites*, such as $C_{10}H_{16}N_2O_3$. These are crystalline compounds, and may be availed of for the separation of many terpenes. Most terpenes also combine with *nitrosylchloride*, NOCl, forming *nitrosochloride-terpenes*. These also are crystalline compounds, which combine with organic bases like benzylamine and piperidine to form *nitrolamines*.

Some terpenes form with water crystalline hydrates, as terpinhydrate, $C_{10}H_{16}(H_2O)_2 + H_2O$. This combination takes place especially in the presence of dilute nitric acid and alcohol. The terpenes frequently polymerize by heating under pressure or by shaking with concentrated sulphuric acid.

Many terpenes are optically active. Frequently a lævo-rotatory and a dextro-rotatory modification of the same terpene may be obtained, which, when mixed, yield an optically inactive variety.

The terpenes and essential oils have an antiseptic action.

Classification of Terpenes.—Based upon the differences in chemical formulas, as controlled by molecular weight determinations and analysis of derivatives, we may divide the whole class of terpenes into:

1. *Hemiterpenes*, C_5H_8, such as isoprene, which by polymerization yields dipentene, $C_{10}H_{16}$, belonging to the next group.
2. *Terpenes*, $C_{10}H_{16}$. These are the compounds to which in the narrower sense belongs the class name.
3. *Sesquiterpenes,* $C_{15}H_{24}$, such as cedrene and cadinene.
4. *Diterpenes,* $C_{20}H_{32}$, include colophene.
5. *Folyterpenes* $(C_{10}H_{16})_x$, include the polymerized hydrocarbons of caoutchouc and gutta-percha.

Based on the formation of the addition compounds before referred to, due to their unsaturated character, we may divide the special terpenes of the formula $C_{10}H_{16}$ into two groups:

1. Such as are able to combine with but one molecule of haloid acid, leaving out of consideration cases of polymerization. This group, which therefore contains only one double linking in the molecule, has been called by Baeyer the *camphane* group. It includes pinene and camphene.

2. Such as are able to combine with two molecules of haloid acid, and therefore contain two double linkings in the molecule. This group has been called the *terpane* group, and includes dipentene, sylvestrene, right and left rotatory limonene, terpinolene, terpinene, and phellandrene.

The characters of these terpenes and their addition compounds may be thus given in tabular form:

Terpene.	Melting Point.	Boiling Point.	Melting Point of Bromides.	Melting Point of Hydrochlorides.	Melting Point of Nitrosites.
Pinene . . .	Liquid	159°–160°	Liquid	$C_{10}H_{16}+HCl$, 125°	132°
Camphene. .	49°	160°–161°	"	$C_{10}H_{16}+HCl$, unstable	
±Limonene . .	Liquid	177°–178°	$C_{10}H_{16}Br_4$, 104°	$C_{10}H_{16}+2HCl$, 50°	
Dipentene. .	"	178°	$C_{10}H_{16}Br_4$, 125°	$C_{10}H_{16}+2HCl$, 50°	
Sylvestrene .	"	176°–177°	$C_{10}H_{16}Br_4$, 135°	$C_{10}H_{16}+2HCl$, 72°	
Terpinolene .	"	185°–190°	$C_{10}H_{16}Br_4$, 116°	$C_{10}H_{16}+2HCl$, 50°	
Terpinene . .	"	180°	. . . . . .	. . . .	155°
Phellandrene	"	170°	. . . . .	. . . .	

Description of the Individual Terpenes.—Pinene, $C_{10}H_{16}$, is the chief constituent of the American and French oils of turpentine as well as of juniper oil and eucalyptus oil. Along with sylvestrene and dipentene it makes up the Russian and Swedish turpentine oils.

Oil of Turpentine (**Oleum Terebinthinæ,** U.S.P.) is distilled from the oleo-resin (crude or virgin turpentine) obtained from *Pinus palustris* (*australis*). The European turpentine is chiefly obtained from *Pinus sylvestris* and *Pinus maritima;* Venice turpentine from *Larix Europœa;* the Strassburg turpentine from *Pinus picea;* Canadian turpentine or Canada balsam from *Abies balsamea.*

The oleo-resin is distilled with steam, whereby the terpenes distil over, leaving as a residue *colophony* resin, which accompanied the essential oil in the original exudation.

The crude oil may be further rectified according to the Pharmacopœial process by distilling after treatment with sodium hydroxide solution. It then forms a "colorless liquid, having a characteristic odor and taste, both of which become stronger and less pleasant by age and exposure to the air." Sp. gr. 0.860 to 0.870. It boils when rectified at

160°. It is almost insoluble in water, easily soluble in alcohol and ether. It dissolves resin, caoutchouc, sulphur, phosphorus, etc. Turpentine oil, like many other mixtures of terpenes, readily absorbs oxygen, and hydrogen dioxide is formed. The oil is then capable of turning guaiacum tincture blue, liberating iodine from potassium iodide, and producing other reactions characteristic of ozone and hydrogen dioxide. Strong nitric acid inflames the oil, but oxidized by dilute acid, it yields acids of both the methane series, like butyric, propionic, acetic, and oxalic, and the benzene series like terepthalic and para-toluic. Treated with bromine or iodine it yields cymene.

The American and Russian turpentine oils are right-rotatory, the French, German, and Venetian oils are left-rotatory. These differences are due to the existence of the right and left rotatory varieties of pinene. Inactive pinene may be obtained by heating the pinene nitrosochloride with aniline, whereby NOCl is split off.

Very considerable quantities of "wood turpentine" are now obtained from the so-called "lightwood" or stumps and dead wood of the pine trees.

This is worked by steam distillation or solvent processes or in connection with the production of wood pulp by the alkali process. An average of 9½ gallons of turpentine per cord of wood is stated to be obtained.

It differs from the true gum turpentine in composition, being more complex, and contains a higher percentage of unpolymerizable oil.

Pinene unites with one molecule of HCl to form *Pinene hydrochloride,* $C_{10}H_{17}Cl$, a white solid, melting at 125°, and resembling camphor in appearance and odor, whence the name "artificial camphor." It is insoluble in water, soluble in alcohol. When heated with soaps or weak alkali it splits off hydrochloric acid again and leaves camphene, $C_{10}H_{16}$.

When turpentine oil stands in contact with water, especially in the presence of nitric acid and alcohol, it unites with three molecules of water to form a hydrate, $C_{10}H_{18}(OH)_2 + H_2O$, known as *Terpin Hydrate* (**Terpini Hydras,** U.S.P.). This is in colorless rhombic prisms of slightly aromatic and somewhat bitter taste, melting at 116°–117°. The anhydrous *terpin,* $C_{10}H_{18}(OH)_2$, obtained in this fusion, or by drying over sulphuric acid, has somewhat of a glycol (or diatomic alcohol) character. When distilled with dilute sulphuric acid it loses a molecule of water and yields *terpineol,* $C_{10}H_{17}(OH)$, an oil of hyacinthine odor which is used in medicine. Still further heating changes it into a mixture of dipentene, terpinene, and terpinolene, all terpenes of the formula $C_{10}H_{16}$.

When sulphuric acid is allowed to stand in contact with oil of turpentine, and the mixture, after a day's standing, is heated to boiling, the oil is changed into an optically inactive mixture of terpenes known as *Terebene* (**Terebenum,** U.S.P.). The Pharmacopœia states that terebene "consists of dipentene and other hydrocarbons." The Pharmacopœia gives the boiling point as 160°–172°.

Camphene may be obtained, as already mentioned, by the decomposition of pinene hydrochloride by soap, or with alcoholic potash, also from bornyl chloride, $C_{10}H_{17}Cl$. It exists as dextro- and lævo-camphene.

Camphene forms a solid crystalline mass, fusing at 49°, and smelling of turpentine and camphor. It is more stable than pinene, but it is oxidized by chromic acid mixture to common camphor. The addition-compound formed with one molecule of HCl is unstable.

Limonene.—The dextro-limonene, known also as *hesperidene, citrene,* or *carvene,* is almost the exclusive constituent of oil of orange-peel, and the chief constituent of oils of dill, caraway, and erigeron. Mixed with pinene it forms lemon oil. It boils at 175°, and forms a tetrabromide, $C_{10}H_{16}Br_4$, fusing at 104°, and dextro-rotatory in character. It is readily changed into inactive limonene or dipentene.

Lævo-limonene is found, according to some authorities, along with lævo-pinene in oil of Norway spruce, although Drs. Bertram and Walbaum, of Schimmel & Co.'s laboratory, state that the limonene of this oil is inactive. The dextro- and lævo-limonene tetrabromides, both fusing at 104°, unite to form a dipentene tetrabromide fusing at 125°.

Dipentene (*Cinene* or *inactive Limonene*) is found in cajuput and camphor oils along with cineol. It is formed from pinene, camphene, limonene, etc., by heating these for several hours to 250°–270°. It is also formed from pinene under the influence of dilute alcoholic sulphuric acid, from terpin hydrate by the splitting off of water, from isoprene by polymerization, from caoutchouc by distillation along with isoprene, and in other ways. It forms a pleasant-smelling liquid with an odor of lemons, boiling at 175°–176°. It readily forms a dihydrochloride and a tetrabromide, both of which have been given in the table (see p. 696). It is more stable than pinene. Its nitrosochloride, by the splitting off of hydrochloric acid, yields a nitrosodipentene, known also as inactive *carvoxime,* fusing at 93°.

Sylvestrene is the dextro-rotatory constituent of Swedish and Russian turpentine oils. It boils at 175°, and is one of the most stable of the terpenes. With acetic anhydride and concentrated sulphuric acid it yields a fine blue color. Its dihydrochloride fuses at 72°, and is dextro-rotatory.

Terpinolene is very similar to dipentene.

Terpinene.—This and the preceding terpene both result from the isomerization of pinene and limonene (see Terpin Hydrate, p. 697). Terpinene forms a nitrosite.

Phellandrene is found in a dextro-rotatory variety in oil of water-fennel, and in a lævo-rotatory variety in oil of *Eucalyptus amygdalina.* It unites readily with nitrous acid to form a solid nitrosite. It is one of the least stable of the terpenes, and readily changes into dipentene, and when treated with alcoholic hydrochloric acid into terpinene.

Sesquiterpenes, $C_{15}H_{24}$.—Hydrocarbons of this formula occur in oils of cubebs and patchouly, and may also be obtained synthetically by the heating of the unsaturated hydrocarbon valerylene, C_5H_8, to 250°–260° under pressure, or by the action of concentrated sulphuric acid upon it. They are all liquid.

Diterpenes, $C_{20}H_{32}$.—Such hydrocarbons are found in copaiba balsam, and are formed by the superheating of turpentine oil. *Colophene,* the residue formed in the manufacture of terebene, is also of this class. It is a thick oil, boiling at 318°.

Polyterpenes, $(C_{10}H_{16})_x$.—These may be obtained by the polymerization of oil of turpentine under the influence of antimony trichloride. They boil at over 250°, and are lævo-rotatory. The terpenes of caoutchouc and gutta-percha probably belong in this class also.

Caoutchouc is the solidified, milky juice of certain tropical trees (*Euphorbiaceæ, Asclepiadaceæ, Apocynaceæ*). This juice is a vegetable emulsion in which the caoutchouc is suspended in minute globules. This emulsion is coagulated by heat or by the addition of alum and salt solutions. The caoutchouc, at first tough and elastic, on keeping tends to become hard and brittle. To prevent this it is treated with sulphur, the process being known as "vulcanizing." This causes it to retain its elasticity and strength, but it then becomes insoluble in the carbon disulphide, chloroform, and benzene, which dissolve the untreated rubber. When destructively distilled it yields isoprene, C_5H_8, and dipentene, $C_{10}H_{16}$.

Rubber has in recent years been made synthetically by the polymerization of butadiene, C_4H_6, isoprene, C_5H_8, and their homologues. This polymerization is effected by the action of metallic sodium at low temperatures, by the action of heat and by other methods. As yet these processes are not in commercial use.

Gutta-Percha (from *Isonandra gutta*) is also obtained as a milky juice, which can be coagulated and kneaded into lumps. It forms then a fibrous mass looking like leather clippings cemented together. At ordinary temperatures it is hard and somewhat elastic, but becomes soft when heated. When distilled it yields polyterpenes, but these seem always to be accompanied by oxidation products. It can also be vulcanized by treatment with sulphur.

Chicle (Balata) is the milky juice from *Sapota Muelleri,* and is obtained extensively from Mexico and Central America. It is in properties intermediate between caoutchouc and gutta-percha. It is used in large amounts as a basis of chewing-gum.

II. The Camphors.

The camphors are oxygenated derivatives. Of their relationship to cymene and the terpenes mention has already been made. Many of them contain an hydroxyl group, as is shown by their reaction with acids to form esters. These are largely secondary and tertiary alcohols, and like the latter (see Amylene Hydrate), under the influence of dehydrating agents split up into hydrocarbons and water. Carvone, $C_{10}H_{14}O$, and Japan camphor, $C_{10}H_{16}O$, appear, however, to be ketones. Of the camphors the most important are:

Japan Camphor, $C_{10}H_{16}O$ (**Camphora,** U.S.P.), is obtained by distilling with steam the wood of the camphor-tree (*Cinnamomum Camphora*). It may be obtained synthetically from both borneol and camphene by oxidation.

Camphor has also been obtained on a commercial scale within a few years from oil of turpentine. By the action of anhydrous oxalic acid upon the turpentine is formed pinyl oxalate and pinyl formate. By distillation with steam in the presence of an alkali the pinyl oxalate is converted into camphor while the formate is changed into borneol. The white pulverulent mixture of the two is at once submitted to oxidation in order to change the borneol into camphor. The yield in camphor is from 25 to 30 per cent. of the turpentine used. The product is either optically inactive or has a very slight dextro-rotation.

Camphor forms colorless, translucent, and readily sublimable crystals of a tough consistence, of characteristic odor, melting at 175° and boiling at 204°. It has a crystalline structure, and is readily pulverized in the presence of a little alcohol, ether, or chloroform. It is sparingly soluble in water, but is soluble in alcohol, ether, chloroform, carbon disulphide, benzine, and fixed and volatile oils. It is inflammable and burns with a luminous, smoky flame. Its sp. gr. is 0.990. The natural camphor is dextro-rotatory; the artificial camphor is dextro- or lævo-rotatory according to the character of the camphene from which it is prepared or inactive when produced from bornyl esters. Under the influence of phosphoric oxide it splits off water, yielding cymene. Heated with iodine it yields carvacrol (see p. 641). As camphor combines with both hydroxylamine and phenyl-hydrazine, it is of ketone character. This is also shown by its relation to the secondary alcohol borneol.

By the action of bromine in proper proportion upon camphor we obtain a bromine substitution compound known as *Monobromated Camphor,* $C_{10}H_{15}BrO$ (**Camphora Monobromata,** U.S.P.). This forms "colorless, prismatic needles, with a mild, camphoraceous odor and taste, permanent in the air, unaffected by light, and neutral to litmus paper." It melts at 76° and sublimes at a slightly higher temperature.

By the oxidation of camphor with boiling nitric acid is obtained *Camphoric acid,* $C_8H_{14}(COOH)_2$ (**Acidum Camphoricum,** U.S.P.), which forms colorless prismatic crystals melting at 187°, difficultly soluble in water, easily soluble in alcohol.

Isomeric with camphor are *pinol,* obtained artificially from pinene, and *absinthol,* contained in oil of wormwood. *Fenchone* from oil of fennel, *thujone* (*tanacetone*), from oils of thuja root and tansy, and *pulegone,* from oil of pennyroyal, are also ketones of the formula $C_{10}H_{16}O$.

Borneol, $C_{10}H_{18}O$.—Borneol (or Borneo camphor) has been found in the wood of *Dryobalanops aromatica,* and is contained also chiefly in the form of esters in the oils of rosemary, Spanish thyme, valerian, citronella, and the different pine oils. Borneol forms crystals melting at 203°–204° and boiling at 212°, and possessing an odor recalling patchouly and ambergris. When common camphor is reduced by metallic sodium, the product, commercially known as borneol, is a mixture of true borneol and *iso-borneol.* This latter melts at 212°, and has more the odor of tansy and sage. Among the esters of borneol may be mentioned *bornyl acetate,* found in the pine-needle oils, and *bornyl formate* and *bornyl valerate,* found in oil of valerian.

Isomeric with borneol are *cineol* (*eucalyptol*) (**Eucalyptol,** U.S.P.) found in oils of cajuput, camphor, lavender, rosemary, wormseed, eucalyptus, etc., and *terpineol,* found in oils of cajuput and Japanese valerian, and made synthetically, along with cineol, from terpin.

Isomeric with borneol are also *linalool* and *geraniol,* two monatomic unsaturated alcohols, which either by themselves or through their esters play a very important part in the composition of many of the essential oils.

Linalool, $C_{10}H_{17}OH$, is the essential and fragrant constituent of oil of linaloe, and is found either free or in the form of esters in oils of lavender, bergamot, petit grains, spike, and coriander. It is a colorless, fragrant liquid of sp. gr. 0.78, and boiling at 197°–198°. It forms a perfectly clear solution with 2 volumes or more of 70-per cent. alcohol. Its most important esters are *linaloyl acetate* (known as bergamiol and constituting one of the chief constituents of bergamot oil) and *linaloyl formate.*

Geraniol, $C_{10}H_{17}OH$, is the chief constituent of the true geranium oils and of the Turkish geranium or Palmarosa oil. It has also been shown to be the chief constituent of the liquid portion of the oil of rose, and it occurs in addition in oils of citronella, oil of lavender flowers, and one of the eucalyptus oils. It is a colorless liquid with a fragrant rose-like odor, sp. gr. 0.882 to 0.885, and boils at 230°. One part of geraniol requires from 12 to 15 volumes of 50-per-cent. alcohol to form a clear solution. Its most important esters are the *geranyl acetate* and *geranyl formate.*

Both linalool and geraniol when oxidized with chromic acid mixture yield the same aldehyde citral.

Citral, $C_{10}H_{16}O$.—This compound is present to the amount of about 7.5 per cent. in oil of lemon, to which it gives its characteristic odor. It is a golden-yellow liquid of sp. gr. 0.899, and boils at 116° under a pressure of 16 mm., or, when perfectly pure, at 228°–229° under ordinary pressure without decomposition.

Closely related to citral is another aldehyde-like body, *Citronellal,* $C_{10}H_{18}O$. This is found in oil of *Eucalyptus maculata,* in oil of citronella, and in small amount in oil of lemon. It is a colorless liquid with an agreeable odor, sp. gr. 0.880, and distilling between 205° and 210° with slight decomposition.

Menthol, $C_{10}H_{20}O$ (**Menthol,** U.S.P.), is the most valuable constituent of the several varieties of peppermint oil. It "forms colorless, acicular crystals, having a strong and pure odor of peppermint, and a warm, aromatic taste, followed by a sensation of cold, when air is drawn into the mouth. It melts at 43° C. to a colorless liquid, boils at 212°, and volatilizes slowly at the ordinary temperature. Its alcoholic solution deviates polarized light to the left." Menthol is a secondary alcohol. When oxidized with chromic acid mixture it yields a ketone, *menthone,* $C_{10}H_{18}O$, which also occurs naturally in the peppermint oil. Menthol also forms esters, such as *methyl formate, menthyl acetate,* and *menthyl iso-valerate.* Of these the latter two are found naturally in the peppermint oil. By the action of dehydrating agents menthol is converted into the hydrocarbon *menthene,* $C_{10}H_{18}$, which boils at 167°.

III. The Essential Oils.

By the distillation of the blossoms, flowers, and fruit of many plants with steam is obtained a class of products known as the *essential* or *volatile oils*. They are distinguished both by physical and chemical differences from the *fixed* or *fatty oils*. These latter (see p. 574) are largely mixtures of the glycerin esters of the fatty acids, often containing, in addition, the fat acids in the free state. While the essential oils show some variations in their chemical composition, they are in the main mixtures of terpenes and camphors, although esters of these latter occur and in a few instances we have aldehydes and ketones.

The fixed oils belong in the aliphatic or methane series of derivatives, while the essential oils all show cyclic or aromatic derivatives among their constituents. The essential oils also show a tendency to absorb oxygen on prolonged exposure to the air and to form resinous products.

Physically the essential oils are characterized by their entire volatility without residue, while the fatty oils are decomposed by heat before volatilization can be completed, and yield acrolein and similar products of decomposition.

The specific gravity of the essential oils is generally less than that of water, and hence they separate on its surface in the product of the steam distillation. They are only very slightly soluble in water, but easily soluble in strong alcohol, chloroform, ether, benzene, and fatty oils. They leave a transient spot only upon paper, while the fixed oils leave a permanent "grease-spot."

The extraction of the essential oils from the plants containing them may be effected:

1. By *distillation*, usually with steam, although in rare cases without. A Florentine receiver is frequently employed to collect the distillate, and by this means the separation of the light, oily layer from the accompanying water is effected.

2. By *expression*. This is followed in cases where the oil is abundant and readily separable, as with oil of lemon, orange peel, etc.

3. By *extraction with solvents*. This solvent may be a liquid fat, as in the case of maceration, a solid fat, as in the case of *enfleurage*, or a volatile solvent, as in the extraction of fine or costly perfumes.

The official essential oils and their proximate chemical composition are as follows:

Oleum Amygdalæ Amaræ, U.S.P. (Oil of Bitter Almond), is a clear, yellowish, thin, and strongly refractive liquid, with a characteristic odor and a bitter, burning taste. Its sp. gr. is from 1.045–1.060, and it boils at 180°. It is essentially benzaldehyde, $C_6H_5.COH$, with from 1.5 to 4 per cent. of hydrocyanic acid, and has resulted from the decomposition of the amygdalin of the bitter almond under the influence of the ferment emulsin. (For reaction see p. 710.) Benzaldehyde combines, on standing with hydrocyanic acid, to form the cyanhydrin or nitrile of mandelic acid, $C_6H_5.CH(OH).CN$, a body having the sp. gr. 1.124, and this is, therefore, often contained in oil of bitter almonds.

Oleum Anisi, U.S.P. (Oil of Anise), is "a colorless or pale yellow, strongly refractive liquid, having the characteristic odor of anise, and a sweetish mildly aromatic taste. At a temperature usually 15° it solidifies to a white, crystalline mass." Over 90 per cent. of the oil consists of ***anethol*** (methoxy-propenyl-benzene), $C_6H_4\left\{\begin{matrix}OCH_3\\C_3H_5\end{matrix}\right.$, the residue containing the isomeric compound ***methyl chavicol.***

Oleum Aurantii, U.S.P. (Oil of Sweet Orange), is obtained by expression from the fresh peel of the Sweet Orange. The chief constituent is the terpene limonene. Oil of sweet orange also contains a small amount of *citral* (*geranial*) and a lower boiling aldehyde.

Oleum Cadinum, U.S.P. (Oil of Cade), is a product of the dry distillation of the wood of *Juniperus Oxycedrus.* It is a brownish liquid of a tarry odor and an empyreumatic, burning taste. The oil contains phenols and a sesquiterpene termed *cadinene,* boiling at 274°–275°.

Oleum Cajuput, U.S.P. (Oil of Cajuput).—A thin, colorless or yellowish liquid with an agreeable camphoraceous odor and an aromatic bitter taste. It contains cineol (cajuputol), terpineol, terpenyl acetate, and one or more terpenes.

Oleum Cari, U.S.P. (Oil of Caraway), is distilled from the fruit of *Carum Carvi.* The oil contains dextro-rotatory limonene (formerly known as *carvene*) and dextro-rotatory *carvone.* This body is chemically a ketone of the composition $C_{10}H_{14}O$, and is a liquid boiling at 224°.

Oleum Caryophylli, U.S.P. (Oil of Cloves), is "a colorless or pale yellow, thin liquid, becoming darker and thicker by age and exposure to the air, having a strongly aromatic odor of cloves, and a pungent and spicy taste." The oil contains *eugenol* (oxy-methoxy-allyl-benzene, $C_6H_3\left\{\begin{matrix}C_3H_5\\OCH_3\\OH\end{matrix}\right)$(**Eugenol,** U.S.P.), to the amount of from 80 to 90 per cent., methyl alcohol, furfurol, and a sesquiterpene termed *caryophyllene,* which boils at 255°. Eugenol, the chief constituent, forms a colorless liquid with the odor and taste of cloves. It is also found in other essential oils, such as pimenta, bay, Ceylon cinnamon, sassafras, and camphor.

Oleum Cassiæ, U.S.P. (Oil of Cinnamon or Oil of Cassia).—"A yellowish or brownish liquid, becoming darker and thicker by age and exposure to the air, having the characteristic odor of cinnamon." It consists chiefly of *cinnamic aldehyde,* $C_8H_7.COH$, (**Cinnaldehydum,** U.S.P.) with some *cinnamyl acetate,* $C_9H_9.C_2H_3O_2$. The amount of cinnamic aldehyde should not be less than 75 per cent.

Oleum Chenopodii, U.S.P. (Oil of Chenopodium, or American Wormseed), is a yellowish liquid, with a penetrating odor, and pungent, bitterish taste. It is stated to contain a terpene, $C_{10}H_{16}$, and a body of the formula $C_{10}H_{18}O$.

Oleum Coriandri, U.S.P. (Oil of Coriander), is distilled from the fruit of ***Coriandrum sativum.*** The oil contains linalol (formerly known as *coriandrol*) and pinene.

Oleum Cubebæ, U.S.P. (Oil of Cubeb), is "a colorless, pale greenish or yellowish liquid, having the characteristic odor of cubeb, and a warm, camphoraceous, aromatic taste." The oil consists chiefly of *cadinene,* $C_{15}H_{24}$, with some dipentene, and when old, or distilled from old fruit, contains *cubeb camphor,* $C_{15}H_{24}.H_2O$.

Oleum Eucalypti, U.S.P. (Oil of Eucalyptus), is "a colorless or slightly yellowish liquid, having a characteristic, aromatic, somewhat camphoraceous odor, and a pungent, spicy, and cooling taste." The oil from the *E. globulus* contains cineol (eucalyptol), dextro-rotatory pinene, small amounts of valeric, butyric, and caproic aldehydes, and ethyl and amyl alcohols. The oil from *E. oleosa* (which is also included as an official source of eucalyptus oil) contains cineol and cuminol. Both of these eucalyptus oils have strongly antiseptic properties due to the cineol (eucalyptol) contained in them.

Oleum Fœniculi, U.S.P. (Oil of Fennel), is distilled from the fruit of *Fœniculum capillaceum.* It contains pinene, phellandrene, dipentene, limonene, *fenchone,* $C_{10}H_{16}O$, and anethol, $C_{10}H_{12}O$, the latter usually in amounts of about 60 per cent. The higher the temperature at which the crystals of anethol separate the better the quality of the oil. Oil of fennel from different sources may differ, and one or more of the above named constituents may be absent.

Oleum Juniperi, U.S.P. (Oil of Juniper).—It may vary in optical properties, and show either dextro-rotatory, lævo-rotatory, or inactive character. It consists chiefly of pinene, with some cadienne, $C_{15}H_{24}$, and an undetermined substance called *juniper-camphor,* to which the peculiar juniper-like odor and taste are due.

Oleum Lavendulæ, U.S.P. (Oil of Lavender.)—The oil contains linalool, linaloyl acetate, geraniol, and a very small amount of cineol.

Oleum Limonis, U.S.P. (Oil of Lemon), is obtained by expression from fresh lemon peel, the rind of the recent fruit of *Citrus Limonum*. It contains a small amount of pinene with dextro-rotatory limonene, about 7 per cent. of *citral* (see p. 701), and a small amount of citronellal.

Oleum Menthæ Piperitæ, U.S.P. (Oil of Peppermint).—"A colorless liquid having the characteristic strong odor of peppermint, and a strongly aromatic, pungent taste, followed by a sensation of cold when air is drawn into the mouth."

The results of an investigation conducted in the laboratory of Fritsche Bros. at Garfield, N. J., show that the composition of American peppermint oil is quite complex, the following constituents having been noted:

Acetaldehyde.
Amyl alcohol.
Isovaleraldehyde.
Isovaleric acid.
Dimethyl-sulphide
Pinene.
Phellandrene.
A lactone, $C_{10}H_{16}O_2$.
Limonene.
Cineol.
Menthone.
Menthol.
Menthyl acetate.
Menthyl isovalerate.
Cadinene.

Oleum Menthæ Viridis, U.S.P. (Oil of Spearmint), is distilled from the fresh herb of *Mentha viridis*. The oil contains lævo-rotatory carvone and lævo-rotatory limonene, with possibly some lævo-rotatory pinene.

Oleum Myristicæ, U.S.P. (Oil of Nutmeg), is distilled from nutmeg, the seed of *Myristica fragrans* deprived of its testa. It consists chiefly of pinene, with probably some dipentene, also *myristicol*, $C_{10}H_{16}O$, and *myristicin*, $C_{12}H_{14}O_3$.

Oleum Picis Liquidæ Rectificatum, U.S.P. (Rectified Oil of Tar). A volatile oil distilled from tar.

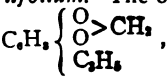
Oleum Pimentæ, U.S.P. (Oil of Pimenta or Oil of Allspice).—It is distilled from pimenta, the nearly ripe fruit of *Pimenta officinalis*. The oil contains eugenol and a sesquiterpene, $C_{15}H_{24}$.

Oleum Pini Pumilionis, U.S.P. (Oil of Dwarf Pine Needles). A volatile oil distilled from the fresh leaves of *Pinus montana*.

Oleum Rosæ, U.S.P. (Oil of Rose), is distilled from the fresh flowers of *Rosa damascena*. Oil of rose when slowly cooled to between 16° and 21° becomes a transparent solid, interspersed with numerous slender scale-like crystals. The liquid fragrant portion of the oil consists for the most part of an alcoholic body of the composition $C_{10}H_{18}O$, which at first was called *rhodinol*, but is now recognized as geraniol (see p. 701). Along with this is some *citronellol*, $C_{10}H_{20}O$. The solid crystallizable portion, or so-called "stearopten," of the oil is odorless when pure, and consists of a mixture of several hydrocarbons, one of which melts at from 35.5° to 36.5°, and has the composition $C_{20}H_{42}$.

Oleum Rosmarini, U.S.P. (Oil of Rosemary), is "a colorless or pale yellow, limpid liquid, having the characteristic, pungent odor of rosemary, and a warm, somewhat camphoraceous taste." The oil contains pinene, cineol, borneol, and camphor.

Oleum Santali, U.S.P. (Oil of Santal or Sandal-wood), is distilled from the wood of *Santalum album*. The East Indian or official oil of sandal contains, according to Chapoteaut, an aldehyde body called *santalal*, $C_{15}H_{24}O$, boiling at 300°, together with an alcoholic body, *santalol*, $C_{15}H_{26}O$, which boils at 310°, and is converted by phosphoric oxide into *santalene*, $C_{15}H_{24}$, boiling at 260°.

Oleum Sassafras, U.S.P. (Oil of Sassafras), is distilled from the bark of the root of *Sassafras variifolium*. The oil consists chiefly of *safrol* (methylene ester of allyl-dioxybenzene),  $C_6H_3\begin{cases} O \\ O \end{cases}\!>CH_2 \; C_3H_5$, (**Safrolum,** U.S.P.), a colorless liquid, boiling at from 232° to 233°, together with a very small amount of eugenol, camphor, and the two terpenes, pinene and phellandrene.

Oleum Sinapis Volatile, U.S.P. (Volatile Oil of Mustard), is obtained from black mustard, the seed of *Brassica nigra*, by maceration with water and subsequent distillation. It consists chiefly of allyl isosulphocyanate, $CS{=}N(C_3H_5)$, with traces of carbon disulphide. These products result from the decomposition of the glucoside *sinigrin* (see chapter on Glucosides) under the influence of a naturally occurring ferment myrosin.

Mustard oil is also made artificially by treating allyl iodide with alcoholic solution of potassium sulphocyanate. The resulting allyl-sulphocyanate is changed into the isomeric allyl-isosulphocyanate by heating it to its boiling point. The carbon disulphide seems to be an invariable product of secondary decomposition.

Oleum Terebinthinæ, U.S.P. (Oil of Turpentine), has already been described under Pinene (see p. 696).

Oleum Thymi, U.S.P. (Oil of Thyme), is distilled from the leaves and flowering tops of *Thymus vulgaris*. Its most important constituent is thymol (methylpropylphenol), $C_6H_3 . \begin{cases} CH_3 \\ C_3H_7 \\ OH \end{cases}$ (see p. 641). In some oils the isomeric compound carvacrol replaces the thymol in whole or part. The oil also contains pinene, cymene, linalool, and small amounts of bornyl esters.

IV. THE RESINS.

The resins seem to be products of the oxidation of the terpenes. They occur in many essential oils, and seem to form from the hydrocarbons when some of the essential oils are exposed for a time to the air. Unlike the camphors, they are not volatile without decomposition, and, instead of showing the characters of alcohols, aldehydes, and ketones, they are often acids or acid anhydrides.

The most recent investigations seem to show that the chief constituents of the resins are the *resin esters, resin acids,* and in different aromatic compounds *resenes* of which little is known. The resin esters contain peculiar alcohols, the *resinols,* which are colorless, and *resino-tannols* which are colored, and give the tannin reaction.

They may be divided conveniently into at least three groups,—viz., Hard or True Resins, Oleo-resins and Balsams, and Gum-resins.

1. **Hard or True Resins.**—These are solids, fusible but not volatile, and soluble in one or more of the following solvents: alcohol, ether, chloroform, carbon disulphide, fixed oils, volatile oils, fixed alkalies, and ammonia. When soluble in the alkalies it is because of their acid character, and a resin soap is formed. These resins are found either as exudations from plants, when they are generally dissolved in volatile oils, or they may be contained in the cells, ducts, or upon the surface of the plants. Among the hard resins may be enumerated:

Colophonium (Colophony or Common Rosin).—This is obtained from the oleo-resin of the *Coniferæ,* and is the residue when the volatile oil (see *Oleum Terebinthinæ,* p. 696) is distilled off. It forms a yellowish or brown brittle mass, with glossy fracture, melting at about 100°, and soluble in the liquids named above. It is chiefly composed of *abietic anhydride,* $C_{44}H_{62}O_4$, which in the presence of dilute alcohol is converted into abietic acid. Readily saponifiable when mixed with fats, and hence used largely in the manufacture of rosin soaps (see p. 577). Rosin by destructive distillation yields "rosin spirit" and "rosin oil," the latter of which is used extensively in the manufacture of printer's ink.

Dammar (from *Dammara orientalis* and *D. australis*).—The East Indian dammar is an exudation; the New Zealand dammar, known also as "Kauri resin," is found fossil as well as of present formation. The resin is harder than colophony; only partially soluble in alcohol, more soluble in ether, chloroform, and benzene. About 1 per cent. of resin acid only is present. The chief use is for varnishes.

Copal, which is found fossil in Zanzibar and on the West Coast of Africa, is the hardest of these resins, and is especially valuable for the manufacture of varnishes.

Amber (a fossil resin from *Picea succinifera*) is found along the shores of the Baltic and other localities. It melts at 287.5°, giving off succinic acid, and at a higher heat, volatile acids and empyreumatic oil of amber.

Lac Resin is an exudation resulting from the puncture of trees by the female insect *Coccus lacca*. The "stick-lac" forms thin branches covered with a brown-red resin; "seed-lac" is in somewhat rounded fragments detached from the twigs; "shellac" is the purified resin solidified in thin layers of amber to brown color.

Guaiac Resin is an exudation from the bark of the *Guaiacum officinale* or melted out of the heart wood by heat. Its alcoholic solution is colored blue on the addition of ferric chloride, chlorine, chromic acid, and other oxidizing agents. The resin fused with caustic potash yields protocatechuic acid. Destructively distilled, it yields guaiacol, creosol (see p. 643), and other products.

Dragon's Blood is a red resin obtained as an exudation from the fruit of *Calamus draco*, growing in Sumatra, Borneo, and adjacent islands. It may contain benzoic and cinnamic acids in small amounts. It is used in colored varnishes and various preparations.

Mastic (Mastiche) is obtained as an exudation from incisions in the bark of *Pistacia lentiscus*, and is collected in the island of Scio. It contains from 1 to 2 per cent. of volatile oil, together with two resins. It is used for cements and varnishes.

Sandarac is also obtained as an exudation. Is chiefly used for varnishes of the alcohol or spirit class.

Benzoïn (from *Styrax Benzoïn*) is obtained from Sumatra, Java, and Siam. It has an aromatic, acrid taste and an agreeable balsamic odor, and contains from 12 to 20 or 24 per cent. of benzoic acid, cinnamic acid, and several resins, which, fused with caustic potash, yield paraoxybenzoic acid, protocatechuic acid, and pyrocatechin.

Xanthorrhœa Resin (Acaroid or Botany Bay Resin) is obtained in Australia from *Xanthorrhœa hastilis*. It contains benzoic acid, some cinnamic acid, and resins. Is used in the preparation of varnishes.

2. **Oleo-resin and Balsams.**—The oleo-resins are mixtures of resins and volatile oils. Those liquid or soft products which contain benzoic and cinnamic acids, in addition to the resin, are generally given the special designation of balsams.

Turpentines (*Terebinthinæ*).—Under this heading may be included the oleo-resins known as common or American turpentine (from *Pinus australis* and *P. tæda*), French or Bordeaux turpentine (from *P. maritima*), Canada balsam (from *Abies balsamea*), Strassburg turpentine (from *Abies pectinata*), Venice turpentine (from *Larix Europæa*), and Russian turpentine (from *Pinus sylvestris* and *P. Ledebourii*). The composition of these several natural mixtures has already been stated under *Oleum Terebinthinæ* (see p. 696).

Burgundy Pitch and *Canada Pitch* (Hemlock Pitch) are both natural oleo-resins, the former exuding from incisions in the *Abies excelsa*, and the latter from *Tsuga Canadensis*.

Wood Tar (**Pix Liquida,** U.S.P.), on the other hand, is a product of the destructive distillation of the wood of the different species of *Pinus*. It is a very complex mixture, containing pyroligneous acid, acetone, and methyl alcohol, toluene and several of its homologues, naphthalene, pyrene, chrysene, paraffin, phenols, and their esters.

Juniper Tar (see Oil of Cade, p. 703) and *Birch Tar* are similar products of destructive distillation.

Copaiba Balsam (**Copaiba,** U.S.P.) is the oleo-resin of *Copaiba Langsdorfii*, and contains, besides the sesquiterpene *caryophyllene*, resins, of which one, *copaivic acid*, $C_{20}H_{30}O$, is crystalline.

Elemi is an oleo-resin exuding from incisions in *Canarium commune*, in the Philippine Islands. It contains, besides volatile oil, a mixture of resins (breïn, amyrin, bryoïden, breïdin, and elemic acid).

Gurjun Balsam (Wood Oil) is a liquid exudation from the species of *Dipterocarpus*, and contains volatile oil, said to be identical with oil of copaiba, and resin.

Peru Balsam (**Balsamum Peruvianum,** U.S.P.) is of a syrupy consistence and reddish-brown color, with a balsamic and smoky odor. The oily liquid which separates on agitation with caustic potash, called cinnamein, is made up of benzyl alcohol, benzyl benzoate, and benzyl cinnamate. The resin, which is admixed with the oil, yields by dry distillation benzoic and cinnamic acids, styrene, and toluene, together with styracine (cinnamyl cinnamate).

Tolu Balsam (**Balsamum Tolutanum,** U.S.P.) is a balsam obtained from *Toluifera Balsamum*, a tree growing in Venezuela and New Granada. The balsam is at first semi-solid, but becomes harder by age. It contains benzyl benzoate and cinnamate, free benzoic and cinnamic acids, *tolene*, $C_{10}H_{16}$, and two resins, which make up over 80 per cent. of the balsam.

Liquidambar (Sweet Gum) is an exudation from *Liquidambar styraciflua*. It is a thick brownish-yellow liquid or solid resin. It contains a mixture of cinnamic esters, the hydrocarbon styrol (or cinnamene), C_8H_8, and two resins known as α-storesin and β-storesin.

Storax (**Styrax,** U.S.P.) is a balsam obtained from *Liquidambar orientalis*. The principal constituent is *storesin*, $C_{36}H_{55}(OH)_3$, and its cinnamic ester. Several other esters of cinnamic acid, a little vanillin, and styrol or cinnamene are the other constituents.

3. **Gum-resins.**—These are milky exudations from plants, and contain gum which is wholly or partly soluble in water and resin soluble in alcohol. Many gum-resins also contain essential oil. Of this class are *Asafetida* (**Asafœtida,** U.S.P.). It is a gum-resin obtained from the root of *Ferula fœtida.* It contains from 3 to 9 per cent. of volatile oil (containing sulphur), 20 to 30 per cent. of gum, and 50 to 70 per cent. of resin. This latter contains a little ferulaic acid (see p. 659), on dry distillation yields umbelliferon, and fused with caustic potash gives resorcin and protocatechuic acid.

Galbanum is a gum-resin brought from Persia. It contains from 6 to 9 per cent. of volatile oil, gum, and from 60 to 66 per cent. of resin. This latter also yields umbelliferon, $C_9H_6O_3$, on distillation, and resorcin on fusion with caustic potash. *Sagapenum* is a very closely-related gum-resin.

Ammoniac.—A gum-resin obtained from *Dorema ammoniacum.* It contains volatile oil (free from sulphur), gum, and resin. It does not yield umbelliferon on distillation, but does yield resorcin and protocatechuic acid on fusion with caustic potash.

Olibanum (or Frankincense) is a gum-resin exuding from the several species of *Boswellia* in Eastern Africa and Southern Arabia. It contains from 4 to 7 per cent. of essential oil, from 56 to 72 per cent. of resin, and about 30 per cent. of gum. When burned it develops a strongly aromatic odor.

Myrrh (**Myrrha,** U.S.P.) is a gum-resin exuding from the *Commiphora Myrrha* in Eastern Africa and Southwestern Arabia. It contains from 2 to 4 per cent. of volatile oil, from 25 to 40 per cent. of resin, and from 40 to 60 per cent. of gum. Fused with caustic potash the resin yields pyrocatechin and protocatechuic acids. It is used extensively in the form of tincture and powders.

Bdellium is a gum-resin very similar in character to myrrh.

Gambouge (**Cambogia,** U.S.P.) is a gum-resin exuding as a milky juice from incisions in *Garcinia Hanburii,* and is collected in bamboo joints, and comes into commerce in cylindrical pieces. It forms a yellow emulsion with water. It contains 16 to 26 per cent. of gum, 66 to 80 per cent. of resin or *cambogic acid,* and about 4 per cent. of wax.

Euphorbium is an exudation from incisions in the stem of the *Euphorbia resinifera* from Morocco. It contains 18 per cent. of gum, 38 per cent. of resin, some starch, malates, and ash.

Scammony is a milky juice collected in Western Asia from the *Convolvulus Scammonia.* It forms a greenish emulsion with water. It contains from 75 to 90 per cent. of resin, known as *scammonin,* $C_{34}H_{56}O_{16}$, identical with the *orizabin* of *Ipomea orizabensis,* and converted by alkalies into scammonic acid, which is soluble in water. The rest of the drug is gum, soluble in water.

CHAPTER X.

GLUCOSIDES—BITTER AND NEUTRAL PRINCIPLES.

I. GLUCOSIDES.

UNDER this name have been grouped a number of compounds, occurring mainly in the vegetable kingdom, that under the influence of dilute acids or ferments are split up into component parts, of which glucose or a related carbohydrate always is one. The glucosides appear to be, not esters, but ethers, which, under the treatment above referred to, take up the elements of water, and then yield the glucose and other products.

While sharing this method of decomposition in common they show in other respects a wide divergence. Thus, solanin is a nitrogenous base, and is thus at once an alkaloid and a glucoside, while other glucosides like myronic acid, are of well-defined acid character. The most of the glucosides, however, are neutral bodies, although they frequently combine with metallic oxides, such as lead and mercuric oxides. They are usually soluble in water and in alcohol, often insoluble in ether, and generally crystallizable. On heating with concentrated sulphuric acid and the bile acids, the glucosides give, like the sugars, the Pettenkofer bile reaction,—viz., a deep-red color. Alkaline copper solution is reduced by most, but not all, of the glucosides. Ammoniacal silver solution is reduced by glucosides, as by cane-sugar and mannitol, only after the addition of caustic alkali. Many glucosides are optically active, most of them showing a lævo-rotatory character. This rotatory power does not, however, correspond in any way to that of the sugar, which is obtained by the decomposition of the glucoside.

Glucosides, as a rule, are not decomposed by pure water, even on boiling or heating under pressure, but dilute acids readily effect the decomposition, sulphuric and hydrochloric being chiefly used. Alkalies may also effect the decomposition, although baryta water is better adapted, as the stronger alkali generally acts upon the sugar liberated, decomposing or altering it. The splitting up of the glucosides is, however, often best effected by the action of the ferments, which may act at the ordinary or only slightly elevated temperature. Among such ferments may be mentioned *emulsin*, an albuminoid found in the almond; *myrosin*, found in mustard-seed; and the ferment contained in the saliva.

For the extraction of glucosides from the plant it frequently suffices to extract with water or alcohol, and to crystallize the glucoside from the concentrated extracts after decolorizing with animal charcoal; or after defecating the decoction from the plant with neutral acetate of lead, which does not affect the glucoside as a rule, the addition of basic lead acetate will precipitate it in the form of a weak combination readily decomposed by hydrogen sulphide. Tanret has proposed still another procedure. After leaving a finely pulverized plant material in contact with milk of lime for 24 hours, he extracts with distilled water in a displacement apparatus, and precipitates these extraction liquors with a concentrated solution of sodium chloride; the precipitate is dried, preferably in vacuo, and extracted with chloroform, which dissolves the glucoside, which can then be crystallized out.

The first successful synthesis of a natural glucoside was accomplished by Arthur Michael in 1879, who caused acetochlorhydrose (obtained by the action of acetyl chloride upon glucose) to act upon the potassium compound of salicyl-aldehyde in alcoholic solution, when helicin was formed, and this, by the action of sodium amalgam, was converted into salicin. The same synthesis led to the formation of populin (benzoyl-salicin), and the corresponding reaction of acetochlorhydrose upon the potassium compound of methyl-hydroquinone led to the synthesis of methyl-arbutin, another naturally occurring glucoside. A newer and much more generally applicable method for the synthesis of the glucosides has been announced* by Emil Fischer. He finds when glucose and other sugars of the monosaccharide class (see p. 583) are dissolved in an alcohol, and hydrochloric acid gas is passed in, there forms a glucoside or mixed ether with the elimination of water. This reaction seems to be available for all the alcohols; in the case of glucose it has been proved with methyl, ethyl, propyl, isopropyl, amyl, allyl, and benzyl alcohols, as also with ethylene glycol and glycerol. It may even be employed for the hydroxy-acids (alcohol-acids), as was proved by the preparation of lactic glucoside. Where the sugar is completely insoluble in the alcohol, which is the case with many compounds of the aromatic and terpene series, in place of glucose, acetochlorhydrose, or pentacetyl-glucose, may be employed, as both are soluble in ether, benzene and chloroform. As the bioses (cane- and milk-sugar and maltose) are hydrolyzed by hydrochloric acid, they cannot be converted in this way into glucoside-like compounds. These new artificial glucosides, like the natural ones, are unattacked by boiling alkalies, Fehling's solution and phenyl-hydrazine; if, however, they be heated with dilute acids they are readily hydrolyzed into their components. They are likewise hydrolyzed by the invertase of yeast.

The glucosides which are of more especial pharmaceutical or medical importance are the following:

Amygdalin, $C_{20}H_{27}NO_{11}.3H_2O$, is found in bitter almonds and in the kernels of fruit. It is extracted by alcohol from the compacted cake of the almond after the oil has been pressed out. It forms a white, crystalline powder, of slightly bitter taste, melting at 200°. When boiled with dilute acids, or when the aqueous extract of the bitter almond is digested at 25°–35°, it is decomposed according to the reaction:

$$C_{20}H_{27}NO_{11} + 2H_2O = C_7H_6O + CNH + 2C_6H_{12}O_6.$$

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*Berichte der Chem. Ges., 1893, 2400.

the products being benzaldehyde, hydrocyanic acid, and dextrose. In the latter case the decomposition is brought about by the *emulsin*, or soluble ferment, which occurs in both the sweet and the bitter almond.

Æsculin, $C_{15}H_{16}O_9.1\frac{1}{2}H_2O$, is found in the bark of the horse-chestnut. It forms prisms of a bitter taste, melting at 160°, and is decomposed by boiling with dilute acids or by emulsin into *glucose* and *æsculetin* (dioxycoumarin):

$$C_{15}H_{16}O_9 + H_2O = C_6H_{12}O_6 + C_9H_6O_4.$$

Arbutin, $C_{12}H_{16}O_7.\frac{1}{2}H_2O$, and *Methyl-arbutin*, $C_{13}H_{18}O_7$, are contained in *Arbutus Uva-ursi* and *Chimaphila umbellata* and other ericaceous plants. Both are bitter, crystallizable, principles, separable only with difficulty. Both are decomposed by dilute acids or emulsin, the former into glucose and hydroquinone, and the latter into glucose and methyl-hydroquinone.

Carminic Acid, $C_{17}H_{18}O_{10}$, is the coloring constituent of cochineal (the dried female insect *Coccus cacti*), and the essential constituent of the commercial "carmine," obtained by extracting the cochineal with water and precipitating with alum. It is an amorphous, purplish-red mass, soluble in water and alcohol, which on boiling with dilute acids is decomposed as follows:

$$C_{17}H_{18}O_{10} + 2H_2O = \underset{\text{Carmine-red.}}{C_{11}H_{12}O_7} + \underset{\text{Carmine-sugar.}}{C_6H_{10}O_5.}$$

Cerebrin is a nitrogenous glucoside contained in brain- and nerve-tissue. On boiling with dilute sulphuric acid it yields galactose (cerebrose).

Chitin, $C_{15}H_{26}N_2O_{10}$, is another animal glucoside found in the outer shells of the *Crustaceæ*. It is an amorphous substance, which when boiled with strong hydrochloric acid is decomposed into *acetic acid* and *glycosamine*, $C_6H_{11}O_5.NH_2$.

Coniferin, $C_{16}H_{22}O_8.2H_2O$, is a glucoside found in the cambial juice of the *Coniferæ* and in the woody tissue of the sugar-cane. It is decomposed by emulsin into *glucose* and *coniferyl-alcohol*, according to the reaction:

$$C_{16}H_{22}O_8 + H_2O = C_{10}H_{12}O_3 + C_6H_{12}O_6.$$

When oxidized with chromic acid mixture coniferin yields vanillin (see p. 649). On the other hand, if oxidized by weaker agents, like potassium permanganate, the coniferin is changed into *gluco-vanillic acid*, $C_{14}H_{18}O_9$, and *gluco-vanillin*, $C_{14}H_{18}O_8$. By the action of emulsin or dilute mineral acids, these artificial glucosides are split up into glucose and vanillic acid, or vanillin, as the case may be.

Convolvulin, $C_{34}H_{56}O_{16}$, and *Jalapin*, $C_{31}H_{50}O_{16}$, are two glucosides contained in jalap resin, the former chiefly obtained from *Ipomœa orizabensis* (Mexican male jalap), and the latter from *Ipomœa Jalapa*. When jalap resin is boiled with dilute sulphuric acid some time and filtered, we obtain a mixture of *jalapinol*, $C_{13}H_{24}O_3$, and *convolvulinol*, $C_{16}H_{30}O_3$,

Digitalin.—The leaves of the foxglove (*Digitalis purpurea*) yield several medicinally active principles which are glucosides, but the true composition of which seems still to be a matter of controversy.

The French or crystalline preparation, difficultly soluble in alcohol, seems to consist chiefly of *digitoxin*, $C_{21}H_{32}O_7$, which is not a glucoside. On the other hand, the German preparation is amorphous and easily soluble in alcohol. It contains *digitonin*, $C_{31}H_{52}O_{17}$, *digitaleïn*, $C_{22}H_{38}O_9$, and *digitalin*, $(C_5H_8O_2)_n$. The first of these breaks up on boiling with dilute acids into sugar and two compounds, *digitoresin* and *digitoneïn;* the second and the third both break up into glucose and *digitaliresin*.

Frangulin, $C_{21}H_{20}O_{10}$, is a glucoside found in the bark of *Rhamnus frangula*. It is decomposed on hydrolysis into rhamnose, $C_6H_{12}O_5$, and *emodin* (trioxymethyl-anthraquinone, $C_{15}H_{10}O_5$.

Glycyrrhizin, $C_{44}H_{63}NO_{18}$, is found in liquorice-root (*Glycyrrhiza glabra*) as the acid ammonium salt, $C_{44}H_{62}(NH_4)NO_{18}$. The salt is obtained in yellowish scales, the free glycyrrhizic acid in a gelatinous mass. It is decomposed on boiling with acids into *glycyrrhetin*, $C_{32}H_{47}NO_4$, and *parasaccharic acid*, $C_6H_{10}O_8$.

Helicin, $C_{13}H_{16}O_7$, is an oxidation product of salicin. It is split up by the action of dilute acids or emulsin into salicylic aldehyde, $C_6H_4\left\{\begin{matrix}OH\\COH\end{matrix}\right.$, and dextrose. $C_6H_{12}O_6$. Its synthesis by Michael has already been described.

Helleborin, $C_{36}H_{42}O_6$, and *Helleboreïn*, $C_{26}H_{44}O_{15}$, are glucosides occurring in the roots of black hellebore (*Helleborus niger*) and green hellebore (*H. viridis*).

Indican, $C_{26}H_{31}NO_{17}$, is a glucoside found in woad (*Isatis tinctoria*). It is decomposed by heating with dilute acids into *indiglucin*, $C_6H_{10}O_6$, and indigo-blue, C_8H_5NO. The reaction, however, is not a complete one, as other side-products are obtained. The so-called "indican" found in the urine at times is indoxylsulphuric acid (see p. 663).

Jalapin $C_{34}H_{56}O_{16}$, in *Jalap* resin, splits into glucose and jalapinolic acid $C_{16}H_{30}O_3$.

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, is found in black mustard-seed as the potassium salt. The free acid is unstable. The potassium salt is decomposed by a ferment, *myrosin*, which is found mainly in the white mustard-seeds, according to the reaction:

$$C_{10}H_{18}NS_2O_{10}K \ = \ C_6H_{12}O_6 \ + \ KHSO_4 \ + \ C_3H_5.NCS,$$

the products being dextrose, acid potassium sulphate and allylisosulphocyanate (mustard oil).

Phloridzin, $C_{21}H_{24}O_{10}.2H_2O$, is a glucoside found in the root-bark of the apple-, pear-, plum-, and cherry-tree. It forms silky needles, fusing at 106°–108°. It is decomposed by dilute acids into glucose and *phloretin*, $C_{15}H_{14}O_5$. This latter decomposition product appears to occur also ready formed in the root-bark of the apple-tree.

Populin, $C_{20}H_{22}O_8$ or $C_{13}H_{17}(C_6H_5CO)O_7$, is benzoyl-salicin, and is found along with salicin in the bark and leaves of *Populus tremula*. When heated with dilute mineral acids it is split into glucose, benzoic acid, and saligenin. It is made synthetically from salicin by treatment with benzoyl-chloride.

Quercitrin, $C_{36}H_{38}O_{20}.3H_2O$, is a glucoside contained as the coloring principle of quercitron bark (from *Quercus tinctoria*). When boiled with dilute acids it splits up into *quercetin*, $C_{24}H_{16}O_{11}$, and *isodulcitol*, $C_6H_{14}O_6$.

Ruberythric Acid, $C_{26}H_{28}O_{14}$, is the constituent of the madder-root, which by its decomposition yields alizarine, the reaction being:

$$C_{26}H_{28}O_{14} + 2H_2O = C_{14}H_8O_4 + 2C_6H_{12}O_6.$$

The purpurine of madder-root appears also to be a decomposition product of another glucoside occurring naturally in the root.

Salicin, $C_{13}H_{18}O_7$, is the glucoside of the willow-bark, and is contained as well in the young twigs and the leaves of the tree. It is also contained in the poplar and in castoreum. Its artificial production from helicin has already been mentioned. When heated with dilute acids, or treated with emulsin, it is decomposed into dextrose and *saligenin* (*o*-oxybenzyl alcohol, $C_6H_4\left\{\begin{matrix}OH\\CH_2OH\end{matrix}\right)$.

Saponin (Senegin), $C_{19}H_{30}O_{10}$, is found in many plants, as *Saponaria officinalis*, **Senega**, U.S.P., **Quillaja**, U.S.P., and others. It forms a a powder, which dissolves in water to form a frothy liquid. On boiling with water it is decomposed into glucose and *sapogenin*, $C_{14}H_{22}O_2$, which crystallizes and is insoluble in water.

Sinalbin, $C_{30}H_{44}N_2S_2O_{16}$, is a glucoside found in the white mustard seed. It is decomposed by the ferment myrosin found in the same seeds into glucose, sinalbin-sulphocyanate (or sinalbin-mustard oil), $C_7H_7O.NCS$, and acid sulphate of sinapin, $C_{16}H_{24}NO_5.HSO_4$.

Solanin, $C_{42}H_{75}NO_{15}$, is a poisonous alkaloid-like glucoside found in the Solanum species and in potato-sprouts. It forms crystalline needles, melting at 235°. It is decomposed by dilute acids into dextrose and solanidin, $C_{26}H_{41}NO_2$.

Xanthorhamnin (Rhamnin), $C_{48}H_{66}O_{29}$, is the coloring matter of *Rhamnus infectoria* and *R. tinctoria*, and of the so-called Persian berries from the same. On heating with dilute acids the glucoside is decomposed into *isodulcitol*, $C_6H_{14}O_6$, and *rhamnetin*, $C_{12}H_{10}O_5$.

II. BITTER PRINCIPLES AND NEUTRAL BODIES.

In this class we include a number of bitter principles, sometimes crystallizable, sometimes resinous, the chemical nature of which is not as yet sufficiently settled to allow of their classification under the proper heads, and some vegetable coloring principles found in the natural dyewoods which are equally undetermined as to their chemical relationship. The more important will be enumerated in alphabetical order.

Alkannin, $C_{15}H_{14}O_4$, is contained in alkanna root (*Anchusa tinctoria*). It forms a brownish-red mass, which dissolves in alkalies with blue color. Distilled with zinc-dust it yields methyl-anthracene.

Aloin, $C_{17}H_{18}O_7.\frac{1}{2}H_2O$, is the active constituent of aloës. It crystallizes in yellowish needles and has a bitter taste. Distilled with zinc-dust it yields anthracene. The benzene solution of aloin, when heated with ammonia, gives a violet-red color.

Bixin, $C_{28}H_{34}O_5$, is obtained from "orlean," the fruit of *Bixa orellana*. It forms reddish scales melting at 175°–176°. It is still extensively used in dyeing, as it colors animal and vegetable fibres yellow without the aid of mordants. It is also well known under the name of "annatto" in its use in butter-color and the coloring of cheese.

Brasilin, $C_{16}H_{14}O_5$, is obtained from Brazil wood (*Peltophorum dubium*). It forms amber-yellow crystals, which dissolve in alkalies with carmine color. The red color is developed by oxidation and is due to the formation of *brasileïn*, $C_{16}H_{12}O_5$. When fused with potassium hydroxide it yields resorcin. It is also used extensively in dyeing on wool and cotton.

Cantharidin, $C_{10}H_{12}O_4$, is found in Spanish flies (*Lytta vesicatoria*). It forms tablets melting at 218°. When heated with phosphorus penta-sulphide it yields *o*-xylol. When cantharidin is heated with alkalies it takes up the elements of water and forms *cantharidic acid*, $C_{10}H_{14}O_5$, an unstable acid, the potassium salt of which is used in medicine.

Chlorophyll is the name given to the green coloring matter of fresh vegetation. It appears to be a mixture of a yellow coloring matter, *xanthophyll*, and a blue coloring matter, *cyanophyll*. A crystalline product is also obtained, *chlorophyllan*, which by reduction with zinc-dust yields the original chlorophyll.

Cotoïn, $C_{22}H_{18}O_6$, is obtained from the coto bark of Bolivia. Forms pale-yellow crystals melting at 130°. When fused with caustic potash or heated with concentrated hydrochloric acid to 140°, benzoic acid is split off.

Cubebin, $C_{10}H_{10}O_3$, is obtained from cubeb, the unripe fruit of *Piper Cubeba*. It forms small needles melting at 125°. When oxidized by nitric acid it yields oxalic and picric acids; when fused with caustic potash it yields acetic and protocatechuic acids.

Curcumin, $C_{14}H_{14}O_4$, is the coloring principle of the turmeric root (*Curcuma tinctoria*). It forms yellow prisms melting at 178°. It is changed to a reddish-brown by alkalies, whence its use as an indicator for alkalies. It is used somewhat for dyeing in compound colors.

Biliary Pigments.—In the bile and bilary calculi are found several pigments of definite composition. The best known are *bilirubin*, $C_{16}H_{18}N_2O_3$; *biliverdin*, $C_{16}H_{18}N_2O_4$,; *bilifuscin*, $C_{16}H_{20}N_2O_4$; and *biliprasin*, $C_{16}H_{22}N_2O_6$. These biliary pigments may be recognized by Gmelin's test, in which nitric acid containing nitrous acid is added, when colors changing from green to bluish, violet, red, and yellowish-red are produced. Bilirubin forms an insoluble calcium compound which is found in biliary calculi.

Hæmatoxylin, $C_{16}H_{14}O_6 \cdot 3H_2O$, is the coloring principle of logwood (*Hæmatoxylon campechianum*). It forms colorless crystals, turning red on exposure to light. Its solution is dextro-rotatory, and reduces Fehling's solution; it is dissolved by ammonia solution with a purplish color. This solution absorbs oxygen from the air, and then deposits *hæmateïn*, $C_{16}H_{12}O_6$. Logwood and its extracts are used extensively in dyeing and calico-printing and other applications.

Litmus, as well as *Orseille* (or Archil), results from the fermentation of colorless compounds contained in certain lichens. The coloring matter of litmus appears to be *azolitmin*, $C_7H_7NO_4$, while that of orseille extract is *orceïn*, $C_7H_7NO_3$. Litmus acts like a weak acid, the salts of which are blue (the potassium compound existing in the commercial litmus), and which, when set free by acids, is reddish in color. Hence the use of litmus as an indicator.

Picrotoxin, $C_{30}H_{34}O_{13}$, is contained in the seed of *Anamirta paniculata*. It crystallizes in needles melting at 201°; is very bitter and poisonous.

Protagon, $C_{160}H_{308}N_5PO_{35}$, is found in the brain. It is soluble in warm alcohol, from which it separates on cooling in fine crystals. It is decomposed on boiling with baryta water into *cerebrin* (see p. 711) and the decomposition products of *lecithin* (*neurin* [see p. 581], *glycerin-phosphoric acid*, and *fatty acids*).

Quassin, $C_{32}H_{42}O_{10}$, is the bitter principle of quassia-wood (*Picræna excelsa*). It forms colorless leaflets, with an extremely bitter taste. Its aqueous solution reduces Fehling's solution, and is precipitated by tannin.

Santalin, $C_{15}H_{14}O_5$, is the coloring principle of Red Saunders, from *Pterocarpus santalinus*. It forms reddish prisms melting at 104°. Soluble in alcohol with blood-red color, in alkalies with violet color. It is used along with the related woods (bar-wood and cam-wood) in dyeing.

Santonin, $C_{15}H_{18}O_3$ (**Santoninum**, U.S.P.), is the active principle of wormseed (*Artemisia pauciflora*). It forms colorless prismatic crystals fusing at 170°. It is the anhydride of *santonic acid*, $C_{15}H_{20}O_4$, into which it is readily converted by bases.

CHAPTER XI.

TISSUE-FORMING SUBSTANCES, OR PROTEID MATTER.

The living plant or animal, no matter how elementary its structure, is largely composed of cells, of which the invariable organic constituents are proteids. In plant tissue the proteids share their importance with cellulose and its alteration products, but in the animal tissue they are so fundamentally important that it has well been said "that they are indispensable constituents of every living active, animal tissue, and indissolubly connected with every manifestation of animal activity."

The proteids of the animal body all come, directly or indirectly, from vegetable sources, the nitrogenous or proteid principles of which form an important element in our food. By the action of certain ferments present in the alimentary juices (p. 596) all proteids are capable of being converted into closely-allied bodies called peptones, which, after absorption, are capable of reconversion into proteids. Not all the proteids of the food are so reconverted, however, or go to the building up of wasting proteid tissues and organs; much undergoes decomposition, producing carbon dioxide, water, and simpler nitrogen compounds like urea, $CO(NH_2)_2$.

The various proteids are highly complex compounds of very high molecular weight and unknown constitution, containing carbon, hydrogen, oxygen, nitrogen, and sulphur, and in some cases phosphorus and iron, in percentage composition ranging within the following limits:

C.	H.	N.	S.	O.	P.
From 50.6 per cent.	6.9	15.2	0.3	20.9	0.00
to 54.5 "	7.3	17.6	2.2	23.5	0.85

In addition to these constituents, the proteids, no matter how carefully purified, usually leave when ignited a small quantity of mineral matter, composed chiefly of alkaline chlorides and phosphates.

All of the proteids are optically active, and their solutions are all lævorotatory in varying degree.

Only certain of the proteids are soluble in water; they are all soluble, however, especially with the aid of heat, in concentrated acetic acid, and in solutions of the alkali hydroxides; they are insoluble in cold absolute alcohol and in ether.

CHEMICAL REACTIONS OF THE PROTEIDS.

I. PRECIPITATION REACTIONS.

Slightly acid (especially acetic acid) albumin solutions are *coagulated* on heating, and this change is hastened by the presence of salts such as sodium chloride. The temperature of coagulation differs for the different proteids, and hence can be used for their identification and separation. On addition of *dilute nitric acid* most proteids give a precipitate of yellow *xanthoproteic acid*; peptones, however, do not give the reactions. *Potassium ferrocyanide* in the presence of an excess of dilute acetic acid precipitates proteids. From acetic acid solution proteids are also precipitated by adding *sodium chloride* and neutral salts of the alkalies to saturation. *Trichloracetic acid* will precipitate most proteids quantitatively from solution; peptones, however, constitute an exception. Most of the *alkaloidal precipitants* (see p. 679). will also precipitate proteid compounds.

II. Color Reactions.

The albuminoids, if present, cause the solution to take a yellow color on addition of *concentrated nitric acid*, constituting the "xanthoproteic reaction," *Millon's reagent*,* added to a solution containing even a trace of a proteid, and the mixture heated, causes a purple-red coloration. A mixture of 1 volume of concentrated sulphuric acid and 2 volumes of glacial acetic acid, when heated, causes proteids to assume a violet-red color. Glue, however, does not show this change. This is known as "Adamkiewicz's reaction." Many proteids, treated with sodium hydroxide and a few drops of copper-sulphate solution, show in the cold a reddish-violet color. This develops most readily with peptones; with other proteids heat must be applied. It is known as the "Biuret reaction." If albumin is precipitated with alcohol and washed with ether, it gives a deep violet color when heated with hydrochloric acid. This is "Liebermann's reaction."

III. Products of Decomposition and Digestive Action on Proteids.

1. **Action of Heat alone.**—When submitted to dry distillation the proteids yield the product known as Dippel's oil (see p. 671), which contains ammonium salts of the fatty acids, like butyric, valeric, and caproic, amines of the radicals of the paraffin series, like methylamine, etc., aromatic compounds like aniline and phenol, and, lastly, the pyridine and quinoline bases.

2. **Action of Oxidizing Agents.**—Manganese dioxide and sulphuric acid or potassium bichromate and sulphuric acid acting upon the proteids produce cyanides, aldehydes, and acids of both the aromatic and the fatty groups. Nitric acid, as before stated, produces at first xanthoproteic acid, and by continued action oxybenzoic and paraoxybenzoic acids. Chlorine acting upon proteids produces, among other products, fumaric and oxalic acids. Bromine and water, when heated with proteids under pressure, cause the formation of carbon dioxide, aspartic, oxalic, and bromacetic acids, leucine, bromoform, bromanil, and other products.

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* Millon's reagent is made by dissolving 1 part by weight of mercury in 2 parts of nitric acid of specific gravity 1.42, and, after complete solution, diluting each volume of the liquid with two volumes of water.

3. **Action of Strong Acids and Caustic Alkalies.**—Prolonged boiling with sulphuric and hydrochloric acid, and fusion with caustic alkalies give rise to practically the same products, among which are ammonia, acetic and valeric acids, amido-acids like leucine (see p. 561) and tryosine, and indol and skatol (see p. 664).

4. **Action of Dilute Mineral Acids.**—Under the influence of dilute sulphuric acid (or hydrochloric acid in the presence of stannous chloride) hydrolysis ensues and a variety of products are obtained. Among these we have belonging to the class of methane derivatives leucine, aspartic acid, glutamic acid, and furfurol, and to the class of benzene derivatives tryosine (see p. 656) and phenyl-amido-propionic acid.

5. **Decomposition under the Influence of Putrefactive Ferment.**—Reference was made to the decomposition of albuminoid matter under the influence of bacteria (see p. 598). The first effect on the albuminoids is a peptonization and then a formation of products such as have been just mentioned under the two preceding cases of decomposition. In this case ammonia and hydrogen sulphide are also among the products of decomposition. In the putrefaction of gelatin or glue, instead of tyrosine, we have glycocoll as the product. Under certain pathological conditions this putrefactive change of albuminoids may take place in the intestines.

6. **Digestive Action on Proteids.**—In general, the effect of digestive action is to change proteids under the influence of enzymes into albumoses and peptones. In the digestive action of the stomach little true peptone is formed, but much albumose, while in the action of the pancreas the opposite result takes place. Very energetic action of the pancreatic ferment (see p. 596) changes the hemipeptones still further into amido-acids like tyrosine and leucine.

CLASSIFICATION OF PROTEID COMPOUNDS.

As the constitution of these compounds is still so entirely obscure, it is not possible to establish more than a provisional grouping of them. The scheme generally accepted by the best authorities is as follows:

I. **True Albuminoids,** including: 1, *Albumins;* 2, *Globulins;* 3, *Alkali-albuminates and Acid-albuminates;* 4, *Coagulated Albuminoids;* 5, *Albumoses and Peptones.*

II. **Nucleo-albumins.**

III. **Proteids,** including: 1, *Glucoproteids* (*α*, *Mucins and Mucoids,* and *β*, *Hyalogens*); 2, *Chromoproteids* (*Hæmoglobins*).

IV. **Gelatinoids,** including: 1, *Keratins;* 2, *Collagen and Glue;* 3. *Elastin;* and 4, *Amyloid* (*Lardacein*).

I. TRUE ALBUMINOIDS.

These are free from phosphorus or contain it as calcium phosphate only; are readily peptonized (with the exception of the peptones, of course); yield, when decomposed by acids or allowed to putrefy, amido-acids; soluble in dilute alkalies and acids (with the exception of the coagulated albuminoids). They occur in animal and vegetable tissues and liquid secretions.

1. **Albumins.**—These are soluble in water, dilute acids, and alkalies. The aqueous solution coagulates on heating in case neutral salts like sodium chloride or magnesium sulphate are present. If freed from salts (by precipitation of the insoluble copper compound and treatment of this with strong potassium hydroxide) they do not coagulate on boiling. The solution may be completely precipitated by saturating it with ammonium sulphate or with sodium chloride followed by acetic acid. As varieties of this class we may mention:

Serum Albumin occurring in the blood, chyle, and lymph. Its solutions show a specific rotatory power of —56°, and are coagulable at temperatures of from 50° to 90°, according to the solvent.

Egg Albumin is found in the white of egg. Its specific rotatory power is —35.5°, and its temperature of coagulation about 56°. White of egg contains about 12 per cent. of albumin, and may be evaporated in thin films at ordinary temperatures without losing its transparency or solubility in water.

Muscle Albumin exists in several varieties, coagulating at about 47°.

Milk Albumin (lactalbumin) is found in milk of various animals in amount from 0.5 to 1 per cent. and remains in the whey after the coagulation of the casein by rennet. Its point of coagulation ranges from 72° to 84°.

2. **Globulins.**—These are insoluble in water, but soluble in dilute solutions of salts like sodium chloride, ammonium chloride, and sodium sulphate. The solutions coagulate on boiling, and are completely precipitated by saturation with ammonium sulphate. With the exception of vitellin, they are precipitated by saturating the solution with common salt. As varieties we have:

Vitellin.—Obtained from the yoke of egg (**Vitellus,** U.S.P.), by extracting the fats and cholesterin with ether, dissolving the white residue in common salt solution, and, after filtration, precipitating by the addition of water. It is difficult to free it from the lecithine which accompanies it in the egg yoke. It coagulates at about 75° and is lævo-rotatory.

Plant vitellins are also obtained from beans, peas, almonds, white mustard, and corn. The aleurone grains, obtained from Brazil-nuts and other sources, seem to represent a crystalline albuminoid or a compound of an albuminoid with magnesia.

Crystallin, from the crystalline lens of the eye, is probably identical with vitellin.

Myosin is the product of the clotting of muscle plasma. It coagulates in 10 per cent. sodium chloride solution at 55°–56°. The substance in the plasma generating the myosin is called *myosinogen.*

Plant myosins are also found in vegetable protoplasm.

Fibrinogen is found in blood plasma, in chyle, lymph, and serous fluids, and at times in transudations. In the clotting of blood it is converted into *fibrin*. This change takes place under the influence of a soluble fibrin ferment acting in the presence of neutral salts. It coagulates in 10 per cent. salt solution at 55°.

Serum Globulin (Paraglobulin or Fibrino-plastin) is found in blood plasma and blood serum, as well as in chyle, lymph, and serous fluids. It is incompletely precipitated by saturating the fluid with common salt. Its temperature of coagulation when in 10 per cent. sodium chloride solution is 75°.

3. **Alkali-albuminates and Acid-albuminates.**—Albuminoids are converted more or less rapidly by the action of alkalies and acids into the two classes above named.

The acid albuminates form jelly-like masses which, while not readily soluble in pure water, dissolve easily in acidified water. These acid solutions do not coagulate on boiling, but are precipitated by neutralization or adding neutral salts to the solution.

Syntonin is an acid albuminate prepared by the action of 0.1 per cent. hydrochloric acid upon muscle globulin. Frequently the whole class of acid albuminates are termed "syntonins."

The alkali-albuminates are not mere solutions of the albuminoids in alkali, but show a difference in percentage composition from the albuminoids from which they have been formed. This is because the alkali acts upon the albuminoid sufficiently to cause a splitting off of the nitrogen as ammonia and a loss of sulphur due to the formation of alkali sulphide.

Lieberkühn's Alkali-albuminate is a gelatinous mass insoluble in pure water, but soluble in dilute alkalies, which is obtained by the action of strong potassium hydroxide solution upon egg albumin.

4. **Coagulated Albuminoids.**—These are formed by heating the neutral or slightly acid solutions of albumins and globulins. Prolonged action of strong alcohol also causes coagulation of proteids. The coagulated albuminoids are insoluble in water, dilute acids, and alkalies. By the action of the gastric or the pancreatic juice they are converted into peptones at the temperature of the body, and then go into solution. The coagulation of albuminoids must be distinguished from precipitation by neutralization or the addition of salts. In the latter case the precipitate still retains the properties possessed by the body when in solution; in the case of coagulation it is no longer capable of being changed back into the original proteid material.

Fibrin is formed by the action of the fibrin ferment upon fibrinogen (see p. 719). It is a white, elastic solid made up of fibre bundles.

Gluten results probably by the action of an enzyme (the gluten ferment) upon the globulin material of the flour. Gluten is, however, believed to be a mixture of *gluten-fibrin, gliadin* (vegetable glue), and *mucedin.*

5. **Albumoses and Peptones.**—Pepsin (see p. 596), in dilute hydrochloric acid solution and trypsin (see p. 596), in alkaline solution both have the power of "peptonizing" proteids. If the peptone solution so obtained be freed from unchanged albumin by coagulation and neutralization, we can in the filtrate precipitate the albumoses by saturating with ammonium sulphate, while the peptones remain in solution. The albumoses are probably the first products of the action of enzymes upon

proteids, and the continuance of the action changes them into peptones. Besides the difference in solubility in ammonium sulphate just stated, we may distinguish between the two classes also by the addition of potassium ferrocyanide to acetic acid solution, albumoses being precipitated and peptones not, or the addition of common salt to saturation of the acetic acid solution, when albumoses are precipitated while peptones are not. At least two kinds of albumoses are to be distinguished: *anti-albumose* and *hemi-albumose,* to each of which corresponds a peptone, named therefore *anti-peptone* and *hemi-peptone* respectively. The first of these peptones cannot be further changed, while the latter (hemi-peptone) is changed by trypsin into leucine and tyrosine.

As already stated (see p. 716), the peptones, after absorption into the blood, are capable of reconversion into proteids or tissue-forming material.

The formation of poisonous albumoses, or "toxalbumens," as a product of decomposition of proteid matter in the body has already been referred to (see p. 694).

II. Nucleo-albumins.

These contain phosphorus, and, at times, also iron. They are decomposed by artificial digestion with pepsin into peptones and *nucleïns.*

1. **Vitellin,** previously described under the globulins, may belong here, as by the pepsin digestion a nucleïn is separated from it.

2. **Casein** is found only in the milk of mammalia. It is insoluble in water, soluble in dilute alkali and in an excess of hydrochloric or sulphuric acid. The caseins of cow's milk and human milk show, however, slight differences of solubility, as well as in the appearance of the precipitate obtained by the addition of dilute acids.

Casein is not coagulated by heat alone, a film forming in this case. The ferment rennin (see p. 596), however, readily coagulates it in the presence of the accompanying calcium phosphate, as do gastric and pancreatic juice; but in milk freed from the salts normally present, rennin will not cause the formation of a curd.

The artificial digestive action of pepsin and hydrochloric acid decomposes casein at the temperature of the blood into peptone and nucleïn.

Other nucleo-albumins are found in the synovial fluid, in the kidneys, and in urine.

Nucleïns.—These are bodies containing phosphorus which are closely related to the albuminoids, and are either found in animal and vegetable cells, or are formed by the decomposition of nucleo-albumins under the influence of pepsin and hydrochloric acid. They are insoluble in alcohol and ether, scarcely soluble in water, but easily soluble in dilute alkalies. By boiling with alkali they lose their phosphorus, which splits off as alkali phosphate. Dilute mineral acids split off at ordinary temperatures metaphosphoric acid from certain nucleïns, as in the yolk of egg and yeast. By boiling the nucleïn of yeast with dilute acids xanthine, hypoxanthine, and adenin (see p. 607) are formed.

III. PROTEIDS.

The proteids are broken up by appropriate reagents into the two classes albuminoid and non-albuminoid compounds (carbohydrates or coloring matters). According to the character of these latter products, they may therefore be divided into two groups, *Glucoproteids* and *Chromo-proteids*.

1. **Glucoproteids.**—These yield on decomposition with dilute acids, along with albuminoids, reducing compounds of the class of carbohydrates, or substances easily convertible into reducing carbohydrates.

(*a*) **Mucins and Mucoids.**—The mucins are precipitated from their solutions by acetic acid, and the precipitates so obtained are not soluble in excess of the precipitant. When boiled with dilute mineral acids they yield reducing substances The solutions of the true mucins are ropy in character. Those glucoproteids which form ropy solutions but are not precipitated by acetic acid, have been named mucoids. Mucins and mucoids are found in the submaxillary gland and the submaxillary saliva, in the mucous glands of the air-passages and of the intestines, in the umbilical cord, and in the sinews and tendons.

(*b*) **Hyalogens.**—These are little-investigated substances which are found in the skeletons of lower forms of animal life. By the action of alkalies they are changed into *hyalines*, from which, by more complete decomposition, reducing compounds (possibly carbohydrates) are obtained.

2. **Chromoproteids.**—These compounds break up into albumin and coloring matter. The most important representatives of this class are the *Hæmoglobins*, or coloring matters of the blood. The parent substance of these compounds is *Oxyhæmoglobin*, as the compound of hæmoglobin with oxygen which occurs in arterial blood is called. To prepare it defibrinated blood is treated with ten times its volume of a salt solution (made by adding 1 volume of saturated salt solution to 10 volumes of water). The blood-corpuscles which settle out are freed from the salt solution by pouring this off; 2 volumes of water are added, and it is then shaken with an equal amount of ether. The ethereal layer is poured off and the aqueous layer filtered. The filtrate is precipitated by the addition of $\frac{1}{4}$ its volume of alcohol, and allowed to stand at a temperature of —5°. The composition of the oxyhæmoglobin crystals from the blood of different animals varies slightly, but the average composition is expressed by the formula $C_{600}H_{960}N_{154}FeS_3O_{179}$. Oxyhæmoglobin obtained from the blood of man and the majority of the lower animals crystallizes in prisms or rhombic plates of a beautiful blood-red color. The crystals are soluble in water, and the solution, if not too concentrated, shows two absorption bands between the lines D and E of the spectrum, which are visible with a dilution of even $\frac{1}{10000}$. At a temperature of from 60° to 70° oxyhæmoglobin splits up into albumin and hæmatin. One molecule of oxygen is held loosely combined in oxyhæmoglobin, and is given off in a vacuum or may be displaced by inert gases like nitrogen. The resulting compound is *reduced hæmoglobin*, which is present in venous blood, and results also from the putrefactive decomposition of oxyhæmoglobin. Its aqueous solution shows a broad absorption band between D and E. Hæmoglobin, by absorption of oxygen in the lungs, is changed into oxyhæmoglobin. It also combines even more readily with certain other gases, such as carbon monoxide, nitrogen dioxide, and

hydrogen cyanide. *Carbon-monoxide-hæmoglobin* is a compound of 1 molecule of CO and 1 molecule of hæmoglobin. Its aqueous solution also shows absorption bands in the spectroscope which differ in position from those of oxyhæmoglobin, being nearer the violet end of the spectrum. It may also be distinguished from oxyhæmoglobin, according to Hoppe-Seyler's test, by adding an equal volume of sodium hydroxide solution of 1.3 sp. gr. The carbon monoxide compound is changed hereby to a clear red color, while ordinary blood is changed to a brownish mass.

Hæmatin, $C_{34}H_{35}N_4FeO_5$, is the colored decomposition product of the hæmoglobin. It is formed by the action of acids upon the blood, and by the decomposition of hæmin by an alkali hydroxide. It is an amorphous, brownish-black powder, insoluble in water, alcohol, and ether, easily soluble in alkalies. Its alkaline solution shows a single broad absorption band extending from between C and D to near E of the spectrum. The acid solution shows several narrow bands, instead of the broad band just mentioned. Hæmatin forms a crystalline hydrochloride, $C_{34}H_{35}N_4FeO_5.HCl$, known as *Hæmin.* These crystals are often obtained in examining dried blood-spots. The dried matter supposed to be blood is warmed in a watch-crystal with common salt and glacial acetic-acid. On evaporating the solution on a water-bath characteristic crystals of hæmin are obtained. Hæmin forms a crystalline powder of silky lustre and bluish-black color, which is insoluble in water, alcohol, and ether, but soluble in dilute alkali, acidified alcohol, and hot glacial acetic acid.

By the action of concentrated sulphuric acid upon hæmatin in the presence of oxygen is formed *hæmoporphyrin*, and, by the action of the same acid upon hæmatin in the absence of oxygen, *hæmatolin*, both of which substances are free from iron.

IV. GELATINOIDS.

We include here several groups of insoluble substances, which are attacked with difficulty by digestive ferments, and differ, therefore, from the other tissue-forming materials.

1. **Keratins** (or horny substances).—These compounds are found in the epithelial tissues, nails, hair, horns, and hoofs, and in feathers. They contain carbon, hydrogen, oxygen, nitrogen, and sulphur, the percentage of the last-named element varying considerably and being very loosely combined. These keratins are insoluble in water, alcohol, ether, dilute acids, and alkalies. They are hardly attacked by digestive ferments, but are decomposed by boiling with water under pressure, hydrogen sulphide being evolved. When boiled with strong acids, leucine, tyrosine, and aspartic acid are formed.

Keratin, when prepared from feathers, forms a brownish-yellow powder, soluble in concentrated acetic acid, alkalies, and ammonia, which has been recommended for coating pills, so as to enable them to withstand the digestive liquids of the stomach, and to act only when in the intestines.

Neurokeratin is a variety which has been isolated from the nerves and brain-tissue

Spongin is the substance of the common bath-sponge. When decomposed by acids it yields tyrosine, leucine, and glycocoll.

Silk consists of *fibroïn*, $C_{15}H_{23}N_5O_6$, which is covered with an alteration product known as *sericin* (or silk-glue), $C_{15}H_{25}N_5O_8$. The latter is easily removed by warm soap-water, and its solution so obtained constitutes the "boiled-off" liquor of the silk-dyer. Fibroïn is decomposed by acids, yielding glycocoll, alanine, leucine, and tyrosine.

Cerebrin and *Chitin*, which may be included here, have already been described (see p. 687).

2. **Collagen.**—The white fibres of connective tissues (sinews and tendons) are mainly composed of a substance now generally termed collagen. Its most important reaction is the change into *gelatin* when boiled with water. Bones also contain a substance, *osseïn*, which undergoes a similar change. The solutions obtained in these cases "gelatinize" or set to a jelly-like mass on cooling, and this, if carefully dried, forms the commercial gelatin, or *glue*. Solutions of gelatin are precipitated by a number of alkaloidal reagents (see p. 679). Pepsin or trypsin converts gelatin into gelatine-peptones, and certain micro-organisms have also the power of liquefying and decomposing it. When decomposed by acids gelatin yields ammonia, glycocoll, leucine, and glutamic acid, but not tyrosine or iodol.

Hoffmeister has found that by heating gelatin for some time to 130° it loses about 0.755 per cent. of water, and becomes converted into a body in all respects identical with collagen. He therefore considers that collagen is simply the anhydride of gelatin, and ascribes to them the formulas $C_{102}H_{151}N_{31}O_{39}$ for gelatin, and $C_{102}H_{149}N_{31}O_{38}$ for collagen.

Chondrin, formerly considered to be the gelatigenous material of tissues, is now considered to be a mixture of gelatin with chondromucoid and chondroitic acid.

3. **Elastin.**—When connective tissue is treated with acetic acid the white fibres swell up and become transparent, whilst the elastic fibres remain unaltered, and can be seen very distinctly. Prolonged boiling with water also decomposes the collagen of the white fibres and leaves the elastin. So far as is known elastin is not soluble in any liquid which does not decompose it. It is soluble in boiling potassium hydroxide, in cold concentrated sulphuric acid, and in concentrated nitric acid. It is also gradually dissolved when digested with pepsin and trypsin. With sulphuric acid it yields leucine, but no tyrosine.

4. **Amyloid** (Lardaceïn) is a proteid substance found under pathological conditions in the liver, spleen, kidneys, and intestines. It forms small grains somewhat resembling starch granules, whence the name. It is acted upon by pepsin and hydrochloric acid with great difficulty. When dissolved in alkalies it yields an alkali-albuminate, and with concentrated hydrochloric acid yields an acid-albuminate. It is colored reddish-brown with iodine, and violet with iodine and sulphuric acid.

CHAPTER XII.

ELECTROLYSIS AND ITS APPLICATIONS.

Conditions of Electrolysis.—The substance to be electrolyzed must be in a liquid condition, obtained either by solution or by liquefaction. It must be a conductor, and a compound resolvable under the influence of the current into ions of opposite electric charge. Increase of temperature increases electric conductivity and electrolytic action in fluids, while with metals the reverse is the case. When electrolysis is employed for the deposition of metals, as in electroplating, the rapidity of action greatly influences the structure of the deposited metal. The metallic elements separate at the cathode, hence are electro-positive, while the non-metals collect at the anode, and are therefore electronegative. When pure, water resists the electrolytic action of the strongest currents; however, when slightly acidulated with sulphuric or hydrochloric acid, resistance is reduced and decomposition takes place readily. Since water is employed as the solvent in solutions of chemicals, their electrolysis involves the simultaneous decomposition of the water. This important factor must not be overlooked.

Action of Electrolytes on the Electrode.—The material of which the electrodes are composed depends largely upon the nature of the work to be performed. Such metals as copper, mercury, lead, nickel, and iron are employed in special cases, while carbon (retort carbon), where applicable, is more generally used because of its cheapness and comparative resistance to the destructive action of certain gases evolved and the compounds formed. Platinum, while it resists to the greatest extent the corrosive action of acids, gases, and alkalies, is too expensive for commercial use. We find carbon employed in the electrolytic preparation of caustic alkalies, metallic sodium, chlorinated soda, potassium chlorate, etc., while examples of the former class may be cited in the following: in the electric refining of copper, the impure metal forms the anode, while a thin strip of pure metal serves as the cathode, upon which the metal is deposited; in electroplating with such metals as gold, silver, and nickel, the anode is of the same material as we wish to deposit on the base metal which is attached to the cathode; by employing mercury as the cathode, amalgams with such metals as barium, sodium, lithium, etc., may be obtained; metallic calcium, strontium, etc., may be obtained by placing saturated solutions of their salts in a porous earthenware cup in which a strip of amalgamated platinum is suspended as the negative pole, while this is set into a graphite crucible containing hydrochloric acid, which serves as the positive electrode. Further instances will be found under the various applications of the current.

Faraday's Law and Electro-Chemical Equivalents.—In studying the quantitative results of electrolytic action Faraday arrived at conclusions which are now summarized and known as Faraday's law and are fundamental for all calculations in connection with electro-chemical work. This law is thus stated by Helmholtz: "The same quantity of electricity passing through an electrolyte either sets free or transfers to other combinations always the same number of valencies." As hydrogen is the basis of our comparison of valence, we naturally turn to this for a basis of electro-chemical comparison. It has been found by experiment that the passage of one *coulomb* (one ampere × one second) of electricity through water liberates .000010384 gram of hydrogen. The quantity .000010384 is therefore called the *Electro-chemical Equivalent* of hydrogen. A current the strength of which is C (amperes) will liberate C × .000010384 gram of hydrogen per second. The "electro-chemical equivalents" of other elements can be easily calculated if their "chemical equivalent" (atomic weight divided by valence) is known. The following table* giving these several values will be found to be useful in connection with all work on electrolysis.

TABLE OF ELECTRO-CHEMICAL EQUIVALENTS, Etc.

Elements.	Atomic Weight.	Valency.	Chemical Equivalent.	Electro-chemical Equivalent (Grams per Coulomb).
Electro-positive:				
Hydrogen	1	1	1	0.000010384
Potassium	39.03	1	39.03	0.0004053
Sodium	23	1	23	0.0002388
Gold	196.2	3	65.4	0.0006791
Silver	107.67	1	107.67	0.0011181
Copper (cupric)	63.18	2	31.59	0.0003281
" (cuprous)	63.18	1	63.18	0.0006562
Mercury (mercuric)	199.8	2	99.9	0.0010374
,, (mercurous)	199.8	1	199.8	0.0020748
Tin (stannic)	117.8	4	29.45	0.0003058
" (stannous)	117.8	2	58.9	0.0006116
Iron (Ferric)	55.9	3	18.64	0.0001935
" (Ferrous)	55.9	2	27.95	0.0002902
Nickel	58.6	2	29.3	0.0003043
Zinc	64.9	2	32.45	0.00033698
Lead	206.4	2	103.2	0.0010716
Electro-negative:				
Oxygen	15.96	2	7.98	0.00008286
Chlorine	35.37	1	35.37	0.0003673
Iodine	126.54	1	126.54	0.0013140
Bromine	79.76	1	79.76	0.0008282
Nitrogen	14.01	3	4.67	0.00004849

Electro-Chemical Analysis.—Metals may be deposited quantitatively from their solutions by means of electrolysis, and, when carried

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* From S. P. Thompson's "Elementary Lessons in Electricity and Magnetism," page 228

out under proper precautions, this method may be extended to the quantitative separation of different metals, based on their comparative electro-positive affinities. The solution containing the metal or metals is placed in a beaker containing two platinum electrodes, connected with a low-voltage current. The anode is usually a wire spiral while for a cathode a strip of platinum foil may be used. In some instances a platinum dish may be used as cathode and at the same time the container for the fluid; the metal is deposited on the sides of the platinum dish, which, after washing and drying, is weighed. The least electro-positive metal is deposited first because of its proportionate weakest chemical affinity; stronger ones follow on increasing the strength of the current. The dilution of the solution, the relative time of electrolytic action, and the strength of the current are all important factors in the successive separation of different metals from mixtures of metallic salts. The student is referred to special works on this subject.

Electrotyping.—This consists in depositing by electrolysis a layer of copper over moulds, for the purpose of reproducing engraved surfaces, also of type. In printing of books, periodicals, maps, illustrations, etc., electrotypes are made from the pages or forms after they have been set up by the printer; these reproductions are then employed for printing, and may be preserved for subsequent use. They are made by taking impressions of the type or wood-cuts by means of a press on plates composed of a mixture of beeswax, turpentine and graphite, and, after trimming, the surface is brushed over with finely powdered graphite, which affords the conducting surface. These impressions are hung from copper hooks, and form the cathode, in a vat containing a strong solution of copper sulphate acidulated with sulphuric acid, and a plate of copper forms the anode. Usually two hours' immersion, using a dynamo current, is sufficient to give a coating of the desired thickness. The copper coating is then removed from the moulds, and the reverse surface filled with solder, so as to give it the necessary rigidity, after which the plates are mounted on wooden blocks.

Electroplating is the electrolytic deposition of one metal upon another. The chief metals employed for this purpose are gold, silver, nickel, copper, platinum, and such alloys as brass and German silver. For plating purposes a vat of enamelled cast iron or stoneware is used, and as anode one or more plates of the same metal which is to be deposited. These plates may be suspended from hooks of the same material. However, copper is usually employed. The articles to be plated, after scouring and washing to remove all greasy matter, are immersed in an acid bath, to rid the surface of all traces of oxide; then they are suspended in the plating solution from copper rods, and serve as the cathode. The current employed is furnished by either a dynamo or a battery, and varies in voltage according to the metal deposited. For example, in nickel-plating we begin with 5 volts, gradually decreasing the current to 1 volt; for silver-plating 3 volts are employed, with a strength of 50 amperes per square meter of cathodic surface; in gold-plating the E.M.F.

should not exceed 1 volt and the current strength 10 amperes per square meter of cathodic surface. The time of immersion varies according to the metal to be plated, the metal deposited, and the thickness of the desired deposit. For nickel-plating with a battery current the time is from two to six hours, for silver from eight to twelve hours, while gold requires but a few minutes' immersion.

Heavy platings should be avoided because of their tendency to peel. The metals to be deposited in electroplating are usually employed as double cyanides with sodium or potassium, which may be made by adding to a diluted solution of the metallic salt a solution of potassium cyanide until the precipitated metallic cyanide redissolves. Before such base metals as zinc, pewter, etc., can be plated with nickel or silver they are given a light coating of copper, in order to secure adhesion of the plating metal. In silver-plating the metal is first amalgamated by immersing in a bath of mercuric oxide and water acidulated with sulphuric acid.

Electrolytic Refining of Metals.—This process of electrolytic refining of crude smelted metals, although of wide application, has as yet been chiefly restricted to the refinement of copper. In a vat containing a solution of copper sulphate are suspended anodes which consist of thick plates of the crude copper, while the cathodes are very thin plates of the pure metal. By means of a dynamo current thick layers of the pure metal are deposited from the solution on the cathode, while the liberated acid unites with the crude copper of the anode and keeps up the supply of sulphate as long as any metal remains. The foreign impurities with metals are deposited in the bottom of the vat.

Stimulated by the war demand, the production of the electrolytic copper refineries of this country in 1917 is estimated to have been 2,350,000,000 pounds.

The demand for high-grade zinc for cartridge brass early in the war put a premium on the purity of zinc and gave a great impetus to the development of electrolytic zinc. Earlier difficulties with the spongy nature of the deposit have been overcome and several hundred tons of pure electrolytic zinc are now being made per day in Montana. Electrolytic nickel is also being produced of a purity of 99.8 per cent. on a commercial scale.

The recovery of metallic tin from scrap tin plate is another application of electrolytic refining that has developed in recent years. It takes place in alkaline solution and the tin goes into solution as an alkaline stannate.

The electrolytic refining of silver and its separation from gold and platinum contained in the silver bullion is also very extensively practiced and is replacing the method of "parting" by nitric acid.

PROCESSES INVOLVING ELECTROLYSIS.

Electrolysis of the Alkali Chlorides.—In the electrolysis of the alkali chlorides a number of primary and secondary reactions take place which introduce difficulties to be considered when the isolation of but one product is desired. The possible reactions are as follows:

1. Electrolysis of alkali chlorides, with formation of caustic alkalies, chlorine, and hydrogen.

(*a*) $2NaCl = Na_2 + Cl_2$
(*b*) $Na_2 + 2H_2O = 2NaOH + H_2$.

2. Electrolysis of the caustic alkali formed, with liberation of hydrogen and oxygen.

(*a*) $2NaOH = Na_2 + O_2 + H_2$.
(*b*) $Na_2 + 2H_2O = 2NaOH + H_2$.

3. Formation of alkali hypochlorites through the action of chlorine on caustic alkalies (generated in Reaction 1).

$$2Cl + 2NaOH = NaClO + NaCl + H_2O.$$

4. Formation of chlorates through decompositon of hypochlorites.

$$3NaClO = NaClO_3 + 2NaCl.$$

5. Electrolysis of hypochlorites, with formation of caustic alkali, hydrogen, hypochlorous acid, and oxygen.

(*a*) $2NaClO = Na_2 + Cl_2 + O_2$.
(*b*) $2Na + 2H_2O = 2NaOH + H_2$.
(*c*) $H_2O + Cl_2 + O = (HClO)_2$.

6. Electrolysis of chlorates, with formation of caustic alkali, hydrogen, chloric acid, and oxygen.

(*a*) $2KClO_3 = K_2 + Cl_2 + 3O_2$.
(*b*) $K_2 + 2H_2O = 2KOH + H_2$.
(*c*) $H_2O + Cl_2 + O_5 = (HClO_3)_2$.

7. Reduction of hypochlorites, which diffuse to the cathode, to chlorides.

$$NaClO + H_2 = H_2O + NaCl.$$

8. Reduction of chlorates, which diffuse to the cathode, to chlorides.

$$KClO_3 + 3H_2 = KCl + 3H_2O.$$

According to the construction of the various forms of apparatus for the electrolysis of alkali chlorides, we have two classes: the one arranges for the separation of the products of the anode and cathode by means of a diaphragm, while the second utilizes mercury as a cathode without the intervention of a diaphragm. Examples of the first class will be found in the electrolytic manufacture of arsenic, antimony, potassium chlorate, and all the various organic syntheses, while the manufacture of the caustic alkalies is a notable example of the application of the second class.

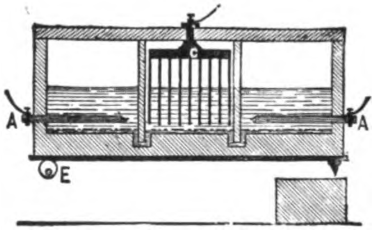
Electrolytic Preparation of Hypochlorites (Bleaching Liquid).—If a solution of an alkali chloride—for example, sodium chloride—be electrolyzed, chlorine will be liberated at the anode and sodium at the cathode. This latter reacts immediately with the water present, forming sodium hydroxide, and liberates hydrogen (Reaction 1). The chlorine now reacts on the sodium hydoxide, with the production of sodium hypochlorite (Reaction 3). A 10 per cent. solution of sodium chloride, after electrolytic treatment, will contain somewhat over 2 per cent. of hypochlorite and about 0.6 per cent. of chlorate, while the rest consists of unchanged chloride. This fluid is preferable for bleaching because it is far less destructive than calcium hypochlorite and more readily removed by washing.

Electrolytic Preparation of Chlorates.—A moderately concentrated solution of potassium or sodium chloride is employed as electrolyte, to which from 1 to 5 per cent. of sodium (or potassium) carbonate is added. A small amount of potassium or sodium dichromate is also added to prevent cathodic reduction of the chlorate as formed. In the construction of the apparatus care is taken that the alkali hydroxide liberated around the cathode shall be exposed to the action of the chlorine liberated from the anode, while the temperature of the fluid is kept above 50° C., which decomposes at once all hypochlorites formed (Reaction 4). The cathodes are either of iron or nickel, while the anodes are of platinum or carbon. The formation reactions involved are 1, 3, and 4, while 4 and 8 show the losses due to regeneration of the chloride.

In the case of the potassium chlorate formation this salt crystallizes out from the solution on cooling, leaving potassium chloride in solution; in the case of sodium chlorate, it remains in solution while sodium chloride crystallizes out first.

Electrolytic Preparation of Caustic Alkalies and Chlorine.—The electrolysis of alkaline chlorides for the production of alkaline hydroxide and chlorine is practically always carried out in aqueous solution at present, as the electrolysis of the fused sodium chloride carried out for a time by the Acker Company at Niagara Falls has been given up. The cells for electrolysis of aqueous solution are either the mercury cells with movable diaphragm like the Castner cell, or those with fixed diaphragm. The Castner cell is illustrated in Fig. 143. The operation is carried on in a tank which is divided into three compartments; the outside ones contain the sodium or potassium chloride brine and the carbon anodes, A, A, while the inside one contains the iron cathode, C. Through this inside compartment a continuous supply of water flows, which takes up the caustic alkali produced and is conducted off into collecting tanks. The partitions are open below, just reaching to the surface of a layer of mercury which covers the entire bottom of the tank. The alkali metal (K or Na) liberated amalgamates at once with the mercury, which, through the rocking of the tank by means of the cam, E, passes into the centre compartment, where it acts as the anode during the passage of the current to the iron cathode, C; the metallic sodium (or K) of the amalgam is thereby liberated, which, reacting with the water present, gives rise to sodium (or K) hydroxide and hydrogen gas. From the two end compartments a current of chlorine gas is evolved which may be further utilized. The lye obtained from the middle (cathode) chamber contains about 20 per cent. of caustic soda (or KOH), which, when evaporated, yields a product 99.5 per cent. pure.

Fig. 143.



Castner's electrolytic tank.

Of the cells using a porous diaphragm the most successful have been the Macdonald cell, the Hargreaves-Bird cell, and the Townsend cell. The diaphragm is usually of asbestos cloth or asbestos reinforced by cement and must be strong enough to stand the disintegrating action of chorine and yet be porous enough for the passage of the current. Still more recent are the Nelson cell and the Allen-Moore cell, which are very efficient diaphragm cells.

Electrolytic Preparation of Persulphates.—A cold saturated solution of ammonium sulphate is placed in a porous cell as anode liquid and a mixture of equal volumes of sulphuric acid and water in an outer beaker glass as cathode liquid. A platinum wire spiral serves as anode and a coil of lead tubing through which ice water circulates, is made the cathode. After passage of the current for several hours the ammonium persulphate which has separated out in crystalline form in the anode cell is filtered through glass wool placed in a funnel, and dried on a porous tile. The potassium persulphate is similarly prepared, but is less soluble than the ammonium salt.

Electrolytic Extraction of Gold.—According to Siemens's process the powdered ore or tailings are extracted with a potassium cyanide solution, which is electrolyzed. Lead plates (or more recently lead shavings) are utilized as cathodes, while iron plates serve as anodes; the gold is deposited on the surface of the former, which are periodically removed, melted and the gold separated. The iron plates are gradually dissolved by the lye, giving rise to Prussian blue, which can be converted back to cyanide.

Electrolytic Preparation of White Lead.—In a wooden vat provided with a porous diaphragm is suspended an anode of lead and a cathode of copper, while the electrolyte is a solution of sodium nitrate. Through the action of the current, nitric acid is liberated at the anode, which dissolves a corresponding amount of lead, forming a solution of lead nitrate, while at the cathode metallic sodium is liberated, which decomposes in the water to sodium hydroxide. These two salts react, with the production of lead hydroxide, which is allowed to digest with a solution of sodium bicarbonate, forming neutral lead carbonate. The sodium nitrate formed as by-product again electrolyzes, as above described. The sodium hydroxide formed in the last reaction is utilized for the production of bicarbonate by passing through it a current of carbonic acid gas. The reactions are as follows:

1. $NaNO_3 + H_2O = NaOH + HNO_3$.
2. $2HNO_3 + Pb = Pb(NO_3)_2 + H_2$; or,

2a $2NaNO_3 + 2H_2O + Pb = (2NaO\bar{H} + H_2) + [PbO_2(+\overset{+}{N}O_2)_2]$

3. $Pb(NO_3) + 2NaOH = Pb(OH)_2 + 2NaNO_3$.
4. $Pb(OH)_2 + NaHCO_3 = PbCO_3 + NaOH + H_2O$.

Electrolytic Production of Mineral Pigments.—By the use of various metals as cathodes under varying conditions, a number of other pigments have been prepared, as *cadmium yellow* (CdS), *vermilion* (HgS), and *Scheele's green* ($CuHAsO_3$).

Ozone.—Ozone is a well-known oxidizing and bleaching agent and has many commercial applications. Its preparation is carried out on a large scale by employing a series of ozonizing tubes. The Siemens form (see p. 194) consists of a glass tube, covered outside with tin-foil; inside of this is a smaller tube, coated with foil on its inner side. A current of oxygen is made to pass between the two tubes. The two foil coatings are connected with the poles of an induction coil the tension of which is about 13,000 volts and the interruptions from 200 to 300 per second. As a bleaching agent, it is rapid in its action, and is not so destructive as chlorine or the hypochlorites. Ozone is used as a disinfectant; also for destroying the fusel oil and aging spirits, and for aging wood for musical instruments. The micro-organisms, ammonia, and nitrites present in contaminated water may be destroyed by this agent and a perfectly sterile water obtained by its aid. Ozone is used for purifying and whitening starch and dextrin.

Prussian Blue, prepared from potassium ferrocyanide and a ferrous salt, is suspended in water containing from 1 to 20 per cent. of a mineral acid, and placed in the anode chamber of an electrolytic apparatus. Through the action of the current various shades of blue may be obtained, and by prolonging electrolytic action a dark green product results.

PROCESSES INVOLVING THE ELECTRIC FURNACE.

I. Electrolysis at High Temperatures.

In these processes, the current acts at an extremely high temperature on a fused mass containing the chlorides, hydroxides, or oxides of the metal to be extracted, the arrangement of the furnace varying somewhat in each case. The metals extracted by such processes on a commercial scale are potassium, sodium, magnesium and aluminum (for descriptions of these processes, see under their respective headings in the chapters on Chemistry). Other elements which can be prepared thermo-electrically are boron, silicon, chromium, cobalt, wolfram, manganese, molybdenum, uranium, vanadium and titanium.

II. Manufacturing Processes with Electric Furnace.

Thermo-Electric Preparation of the Carbides.—Through the agency of the electric furnace most metals have been made to combine with carbon to form carbides and in many cases these compounds are more readily attainable than the pure metals themselves. The carbides are of the greatest value in metallurgy, owing to the influence they exert upon the hardness, tenacity, fusibility, and malleability of metals, as illustrated in the case of iron. To chemists the carbides have opened up new fields and possibilities. They are produced by heating the metallic oxides or carbonates with coke in a furnace, which consists of two blocks of limestone or burnt lime, hollowed out in the middle and securely fitted together. The carbon electrodes which pass in at the sides carry a current of 110 volts and from 1000 to 2000 ampères. Among the more important carbides are those of silicium and calcium. The former is made by fusing together sand (SiO_2), sodium chloride, and coke, and is more commonly known as carborundum (SiC) (see p. 294). Because of its extreme hardness carborundum is used for grinding and polishing. Calcium carbide (CaC_2) is obtained by fusing together calcium carbonate and coke, and is extensively used for preparing acetylene gas, which is used as an illuminating agent (see p. 298), and as a step in the manufacture of calcium cyanamide (see p. 611).

The carbides of Li, Na, K, Ca, Ba, and Sr are decomposed by water, yielding acetylene  $\left(\begin{matrix}CH\\ |||\\ CH\end{matrix}\right)$.

Aluminum and beryllium carbides react with water, yielding methane (CH_4). Manganese carbide yields, in addition, hydrogen gas.

The carbides of lanthanum, yttrium, and thorium give, with water, a mixture of acetylene, ethylene, menthane, and hydrogen.

Manufacture of Steel in Electric Furnace.—The perfect control of temperature in the electric resistance furnace has made it possible to produce superior steel for steel casting in this way. The development of the electric steel production in the United States since the outbreak of the present war has been phenomenal. In 1913 there was produced in the United States 30,180 tons of electric steel; in 1917 the production is estimated to have been 750,000 tons.

Manufacture of Ferro-alloys.—Of more importance than electric steel is the production of ferro-alloys. Practically all of these except ferromanganese are made in the electric furnace, and a constantly increasing proportion of the ferromanganese is being made in the electric furnace rather than by the older blast furnace process. These ferro-alloys, especially ferromanganese, silicon and ferrosilicon, ferrochrome, ferronickel, ferrovanadium, ferrotitanium and ferrotungsten are of prime importance in the production of high-grade steel either as deoxidizers in the manufacture of the steel or as an addition material in the manufacture of an alloy steel. Many alloy steels are of special importance in the manufacture of automobiles and auto-trucks.

Electro-thermic Preparation of Phosphorus.—According to the Parker process, calcium phosphate is mixed with charcoal and sand and placed in an electric furnace, so constructed that a current of coal-gas can be passed through while being heated. It is also provided with a tubular outlet, in order that the vaporized phosphorus may be carried off and condensed. The heat is generated by an electric arc. Before turning on the current, all air is driven out of the apparatus by means of coal-gas, and while in operation this current of gas serves to force the vapors of phosphorus over into a copper vessel containing water. Another method consists in the simultaneous preparation of calcium carbide, in which tricalcic phosphate is heated in the electric furnace, with an excess of charcoal, according to the equation:

$$Ca_3(PO_4)_2 + 14C = P_2 + 3CaC_2 + 8CO.$$

Electro-thermic phosphorus is pure white and of excellent quality.

Electro-thermic Production of Carbon Disulphide.—Carbon disulphide made by the reaction of sulphur upon glowing carbon is now made almost exclusively by the aid of the electric furnace. The interior furnace of fire-clay or iron, within which the electric arc is maintained between carbon electrodes, is surrounded by an outer shell of metal into which the cold sulphur is fed. This is melted near the base by the radiated heat, and, being admitted through valves, rises and comes in contact with the carbon arc. The vapor of the carbon disulphide formed is drawn off at the top of the furnace and condensed. The operation of the furnace is continuous.

ELECTROLYSIS APPLIED TO ORGANIC COMPOUNDS.

The application of the electric current in the decomposition and synthesis of organic compounds has as yet received but comparatively limited study, yet a number of important synthetic products can be prepared electrolytically on the industrial scale. Among the organic compounds which break up most readily are the acids, or still more so their salts. For example, sodium acetate will decompose as follows:

$$2CH_3.COONa = C_2H_6 + 2CO_2 + Na_2.$$
$$Na_2 + 2H_2O = 2NaOH + H_2.$$

The hydrogen of the carboxyl group is liberated at the negative pole, while carbon dioxide and a hydrocarbon separate at the positive.

Acetic Acid from Acetylene.—By subjecting acetylene to an anodic oxidation with the aid of an acid electrolyte containing a quicksilver salt, it is converted into acetic acid with almost quantitative yield. The process is being carried out on an extensive scale at present because of the demand for glacial acetic acid.

Iodoform may be prepared by the electrolytic action of the current upon a mixture of alcohol (aldehyde or acetone) and an aqueous solution of an alkali or alkali earth iodide mixed with an alkaline carbonate. The reaction, in part, is as follows:

$$CH_3.CH_2OH + 10I + H_2O = CHI_3 + CO_2 + 7HI.$$

Chloroform and **Bromoform** may be prepared by analogous reactions. In the case of chloroform, acetone is conveniently taken for the preparation. A steam-jacketed still is used provided with a set of revolving paddles consisting of carbon plates which serve as anode in the process. A 20 per cent. salt solution is placed in the still and acetone is admitted from the bottom. The acetone is converted into chloroform by the combined action of chlorine and sodium hydroxide, according to the following reactions:

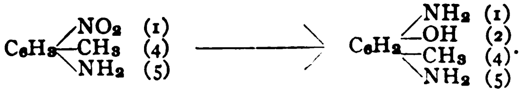
$$(CH_3)_2CO + 3Cl_2 = CH_3COCCl_3 + 3HCl.$$
$$CH_3COCCl_3 + NaOH = CH_3COONa + CHCl_3.$$

The chloroform distils off and sodium acetate remains in solution.

Chloral.—Aldehydes may be obtained by the electrolysis of alcohol or acids. However, from an industrial standpoint, it is cheaper to produce them indirectly, with a view to preparing chloral, by the oxidizing action of chlorine obtained from the electrolysis of chlorides. In a distilling vessel provided with a diaphragm and filled with a hot solution of potassium chloride are placed a copper cathode and a movable carbon anode which serves as a stirrer. Alcohol is gradually added to this fluid (kept at 100° C.) while electrolysis of the chloride is going on. The liberated chlorine oxidizes the alcohol to aldehyde, after which substitution takes place and hydrochloric acid gas is liberated. This is neutralized, however, in the cathodic apartment by the potassium hydroxide formed in the secondary reaction. The chloral formed is recovered by distillation. In the same manner chloral may be obtained from glucose, starch, or sugar.

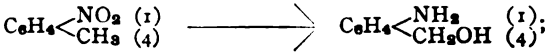
Nitro-Compounds.—Owing to the great technical importance of the aromatic nitro-compounds, the application of electrolysis to the reduction of these has received an unusual amount of attention. By means of oscillating electrodes, which generate nascent hydrogen, nitrobenzene may be reduced to aniline. By varying the conditions partial reduction products have been obtained, such as azoxybenzene, azobenzene, hydrazobenzene, and benzidine.

The electrolysis of aromatic nitro-compounds dissolved in sulphuric acid yields not only amido-hydrocarbons, but at the same time the hydrogen atom, which occupies the para position (to the amido group), is replaced by a hydroxyl residue. Thus, nitro-benzene yields para-amido-phenol. The homologous nitro-compounds react in like manner. Thus:



$$C_6H_3<\begin{matrix}NO_2\\CH_3\\NH_2\end{matrix}\begin{matrix}(1)\\(4)\\(5)\end{matrix}\longrightarrow C_6H_2<\begin{matrix}NH_2\\OH\\CH_3\\NH_2\end{matrix}\begin{matrix}(1)\\(2)\\(4)\\(5)\end{matrix}.$$

Under certain conditions oxidation of the para group may take place,—

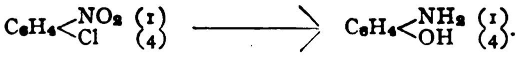


$$C_6H_4<\begin{matrix}NO_2\\CH_3\end{matrix}\begin{matrix}(1)\\(4)\end{matrix}\longrightarrow C_6H_4<\begin{matrix}NH_2\\CH_2OH\end{matrix}\begin{matrix}(1)\\(4)\end{matrix};$$

or the group in the para position is displaced,—

$$C_6H_4<\begin{matrix}NO_2\\COOH\end{matrix}\begin{Bmatrix}1\\4\end{Bmatrix}\longrightarrow C_6H_4<\begin{matrix}NH_2\\OH\end{matrix}\begin{Bmatrix}1\\4\end{Bmatrix};$$

likewise



$$C_6H_4<\begin{matrix}NO_2\\Cl\end{matrix}\begin{Bmatrix}1\\4\end{Bmatrix}\longrightarrow C_6H_4<\begin{matrix}NH_2\\OH\end{matrix}\begin{Bmatrix}1\\4\end{Bmatrix}.$$

Saccharine.—This important product may be made electrolytically direct from the sulphone-amides. Thus, ortho-toluene-sulphone-amide $\left(C_6H_4<\begin{matrix}CH_3\\SO_2NH_2\end{matrix}\begin{Bmatrix}1\\2\end{Bmatrix}\right)$ in alkaline solution separates at the anode as saccharine,—that is, anhydro-ortho-sulphamin-benzoic acid $\left(C_6H_4<\begin{matrix}CO\\OS_2\end{matrix}>NH\right)$. Derivatives and homologues of saccharine may be prepared in like manner.

Organic Colors.—On passing the electric current, using platinum or carbon electrodes, through an aqueous solution of an aniline salt a precipitate of aniline black $[(C_6H_5N)_x]$ is obtained; likewise, under similar conditions, solutions of toluidine, alkylaniline, diphenylamine, and para-phenylene-diamine yield red, violet, and blue colors. Substitutions may be carried out by means of the current. Thus, fuchsine can be methylated by electrolyzing its hydro-methyl-alcoholic solution in the presence of potassium iodide; likewise alizarin $\left(C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H_2<\begin{matrix}OH(1)\\OH(2)\end{matrix}\right)$ and purpurin $\left(C_6H_4<\begin{matrix}CO\\CO\end{matrix}>C_6H\equiv(OH)_3\ 1,\ 2,\ 4\right)$ are produced at the cathode by action of the current on a mixture of anthraquinone and fused potassium hydroxide.

Various tri-phenyl-methane color derivatives may be obtained by electrolyzing, in the presence of acids, such nitro-leuco bodies of the triphenyl-methane series as contain a nitro-group in the para position to the methane rest.* Para-rosaniline. $\left(\begin{matrix}H_2NC_6H_4\\H_2NC_6H_4\end{matrix}>C<\begin{matrix}C_6H_4NH_2\\OH\end{matrix}\right)$ may be

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* *Examples:* *p*-nitro-di-amido-ortho-di-tolyl-phenyl-methane.
p-nitro-di-benzyl-di-amido-o-ditolyl-phenyl-methane, etc.

obtained by the electrolytic reduction of *p*-nitro-di-amido-tri-phenyl-methane dissolved in concentrated sulphuric acid. Electrolytically, colors of the methylene-blue group may be obtained from *p*-amido-di-methyl-aniline and its homologues. Yellows are obtainable from the aromatic oxy-acids, as gallic acid, tannin, di-oxybenzoic, gallanilid, etc. The yellow alkaline reduction products of *p*-nitro-toluene-sulphonic acid (azoxy-azo-di-nitro-stilbene-di-sulphonic acid derivatives) yield orange colors through electrolysis.

Among the natural colors, the extraction of the glucoside hæmateïn ($C_{16}H_{12}O_6$) can be much facilitated by electrolyzing an aqueous extract of logwood for one-half hour with a current of 12 amperes and 60 volts. This product is then concentrated *in vacuo* and crystallized. Brasileïn ($C_{16}H_{12}O_5$) may be obtained from Brazil-wood in like manner. Piperidine ($C_5H_{11}N$) results from the electrolytic reduction of pyridine. By this same reaction quinoline bases may be converted into their hydrocarbons. Of late years the current has demonstrated its value in the ferment industry; while it assists in the culture of some organisms, it destroys others. Thus, the yeast-cells present in a mash may be protected from degeneration, while other undesirable fermentative growths may be destroyed by a careful regulation of the current.

APPENDIX.

For Table of Atomic Weights, according to the United States Pharmacopoeia, Ninth Revision, on the basis of O = 16, and atomic weights on the basis of H = 1, see inside back cover.

COMPARATIVE TABLE OF UNITS OF MEASURE.

LENGTHS.

UNIT.	Linear Inches.	Linear Feet.	Linear Millimeters.	Linear Centimeters	Linear Meters.
Linear Inch......	1.	0.0833	25.40	2.540	0.0254
Linear Foot......	12.	1.	304.8	30.48	0.3048
Linear Millimeter .	0.03937	0.003281	1.	0.1	0.001
Linear Centimeter	0.3937	0.03281	10.	1.	0.01
Linear Meter.....	39.37	3.281	1000.	100.	1.

AREAS.

UNIT.	Square Inches.	Square Feet.	Square Millimeters.	Square Centimeters.	Square Meters.
Square Inch.....	1.	.00694	645.1	6.4511	.000645
Square Foot.....	144.	1.	92900.	929.	.0929
Square Millimeter	0.00155	0.00001075	1.	.01	.000001
Square Centimeter	0.155	0.001075	100.	1.	.0001
Square Meter....	1550.	10.75	1000000.	10000.	1.

VOLUMES.

UNIT.	Cubic Inches.	Cubic Feet.	Cubic Centimeters.	Cubic Decimeters.
Cubic Inch..................	1.	0.000578	16.39	.01639
Cubic Foot..................	1728.	1.	28310.	28.31
Cubic Centimeter............	0.06102	0.00003532	1.	.001
Cubic Decimeter.............	61.02	0.03532	1000.	1.

N.B.— 1000 C.c. = 1 Liter = .2642 U. S. Gal.
29.57 " = 1 Fluid Ounce.
3785. " = 128 " Ounces = 1 Gallon.
1. " Distilled Water at 4° = 1 Gram.

COMPARATIVE TABLE OF ENGLISH AND METRIC WEIGHTS.

UNIT.	Apothecary's Grains.	Apothecary's Scruples.	Apothecary's Drams.	Apothecary's Ounces.	Apothecary's Pounds.	Avoirdupois Ounces.	Avoirdupois Pounds.	Grams.	Kilograms.
1 Apothecary's Grain........	1.	.05	.01667	.002083	.0001736	.002286	.0001429	.0648	.0000648
1 Apothecary's Scruple......	20.	1.	.3333	.04167	.003471	.0457	.002859	1.296	001296
1 Apothecary's Dram........	60.	3.	1.	.1250	.01042	.1371	.00857	3.888	.003888
1 Apothecary's Ounce.......	480.	24.	8.	1.	.08333	1.097	0686	31.10	.0311
1 Apothecary's Pound.......	5760.	288.	96.	12.	1.	.0514	.823	373.2	.3732
1 Avoirdupois Ounce........	437.5	21.88	7.292	.9115	.07596	1.	.0625	28 35	.02835
1 Avoirdupois Pound........	7000.	350.	116.7	14.58	1.215	16.	1.	453 6	.4536
1 Gram....................	15.43	.7715	.257	.03215	.00268	.03527	.002205	1	.001
1 Kilogram	15432.	771.5	257.2	32.15	2.68	35.274	2.205	1000	1.

Equivalents of Weights and Measures

Metric, Avoirdupois, and Apothecaries

Note.—The values given for the relation of weight to measure are for Water at the temperature of 4° C. (39.2° F.) *in vacuo*. For ordinary, practical purposes, these values may be used, without correction.

Weights.							Metric Weight and Measure.	Measures.		
Grains.	Apothecaries		Avoirdupois					Fluid		Fluidounces and fractions.
	oz.	grains.	lbs.	oz.	grains.		Gm. or Cc.	ounces.	minims.	
15432.4	32	72.4	2	3	119.9		**1000**	33	390.6	33.814
15360.0	**32**	....	2	3	47.5		995.311	33	314.5	33.655
15060.9	31	180.9	2	2	185.9		975.932	**33**	....	**33**
15046.6	31	166.6	2	2	171.6		**975**	32	464.9	32.968
14880.0	**31**	....	2	2	5.0		964.208	32	289.7	32.604
14660.8	30	260.8	2	1	223.3		**950**	32	59.1	32.123
14604.5	30	204.5	2	1	167.0		946.358	**32**	....	**32**
14400.0	**30**	....	2	..	400.0		933.104	31	264.9	31.552
14275.0	29	355.0	2	..	275.0		**925**	31	133.3	31.278
14148.2	29	228.2	2	..	148.2		916.785	**31**	....	**31**
14000.0	29	80.0	**2**	..	....		907.185	30	324.2	30.675
13920.0	**29**	....	1	15	357.5		902.001	30	240.0	30.500
13889.2	28	449.2	1	15	326.7		**900**	30	207.6	30.432
13691.8	28	251.8	1	15	129.3		887.211	**30**	....	**30**
13562.5	28	122.5	**1**	**15**	....		878.835	29	344.1	29.717
13503.4	28	63.4	1	14	378.4		**875**	29	281.8	29.587
13440.0	**28**	....	1	14	315.0		870.897	29	215.2	29.448
13235.4	27	275.4	1	14	110.4		857.637	**29**	....	**29**
13125.0	27	165.0	**1**	**14**	....		850.486	28	363.9	28.758
13117.5	27	157.5	1	13	430.0		**850**	28	356.0	28.742
12960.0	**27**	....	1	13	272.5		839.794	28	190.4	28.397
12779.0	26	299.0	1	13	91.5		828.064	**28**	....	**28**
12731.7	26	251.7	1	13	44.2		**825**	27	430.3	27.896
12687.5	26	207.5	**1**	**13**	....		822.136	27	383.8	27.800
12480.0	**26**	....	1	12	230.0		808.690	27	165.6	27.345
12345.9	25	345.9	1	12	95.9		**800**	27	24.5	27.051
12322.6	25	322.6	1	12	72.6		798.490	**27**	....	**27**
12250.0	25	250.0	**1**	**12**	....		793.787	26	403.7	26.841
12000.0	**25**	....	1	11	187.5		777.587	26	140.7	26.293
11960.1	24	440.1	1	11	147.6		**775**	26	98.7	26.206
11866.2	24	346.2	1	11	53.7		768.916	**26**	....	**26**
11812.5	24	292.5	**1**	**11**	....		765.437	25	423.5	25.882
11574.3	24	54.3	1	10	199.3		**750**	25	173.0	25.360
11520.0	**24**	....	1	10	145.0		746.483	25	115.9	25.241
11409.8	23	369.8	1	10	34.8		739.343	**25**	....	**25**
11375.0	23	335.0	**1**	**10**	....		737.088	24	443.4	24.924
11188.5	23	148.5	1	9	251.0		**725**	24	247.2	24.515
11040.0	**23**	....	1	9	102.5		715.380	24	91.1	24.190
10953.4	22	393.4	1	9	15.9		709.769	**24**	....	**24**
10937.5	22	377.5	**1**	**9**	....		708.738	23	463.3	23.965

Equivalents of Weights and Measures—*Continued*

Weights.						Metric Weight and Measure.	Measures.		
Grains.	Apothecaries		Avoirdupois				Fluid		Fluidounces and fractions.
	oz.	grains.	lbs.	oz.	grains.	Gm. or Cc.	ounces.	minims.	
10802.6	22	242.6	1	8	302.6	**700**	23	321.4	23.670
10560.0	**22**	....	1	8	60.0	684.276	23	66.2	23.138
10500.0	21	420.0	**1**	**8**	....	680.389	23	3.1	23.007
10497.0	21	417.0	1	7	434.5	680.195	**23**	....	**23**
10416.9	21	336.9	1	7	354.4	**675**	22	395.7	22.824
10080.0	**21**	....	1	7	17.5	653.173	22	41.4	22.086
10062.5	20	462.5	**1**	**7**	....	652.639	22	23.0	22.048
10040.6	20	440.6	1	6	415.6	650.621	**22**	....	**22**
10031.1	20	431.1	1	6	406.1	**650**	21	469.9	21.979
9645.3	20	45.3	1	6	20.3	**625**	21	64.1	21.134
9625.0	20	25.0	**1**	**6**	....	623.690	21	42.9	21.089
9600.0	**20**	....	1	5	412.5	622.069	21	16.6	21 035
9584.2	19	464.2	1	5	396.7	621.048	**21**	....	**21**
9259.4	19	139.4	1	5	71.9	**600**	20	138.4	20.288
9187.5	19	67.5	**1**	**5**	....	595.340	20	62.7	20.131
9127.8	19	7.8	1	4	377.8	591.474	**20**	....	**20**
9120.0	**19**	....	1	4	370.0	590.966	19	471.8	19.983
8873.6	18	233.6	1	4	123.6	**575**	19	212.6	19.443
8750.0	18	110.0	**1**	**4**	....	566.991	19	82.6	19.172
8671.4	18	31.4	1	3	358.9	561.900	**19**	....	**19**
8640.0	**18**	....	1	3	327.5	559.862	18	446.9	18.931
8487.8	17	327.8	1	3	175.3	**550**	18	286.8	18.598
8312.5	17	152.5	**1**	**3**	....	538.641	18	102.5	18.214
8215.1	17	55.1	1	2	340.1	532.327	**18**	....	**18**
8160.0	**17**	....	1	2	285.0	528.759	17	422.1	17.879
8102.0	16	422.0	1	2	227.0	**525**	17	361.1	17.752
7875.0	16	195.0	**1**	**2**	....	510.291	17	122.4	17.255
7758.7	16	78.7	1	1	321.2	502.753	**17**	....	**17**
7716.2	16	36.2	1	1	278.7	**500**	16	435.3	16.907
7680.0	**16**	....	1	1	242.5	497.656	16	397.3	16.828
7437.5	15	237.5	**1**	**1**	....	481.942	16	142.2	16.296
7330.4	15	130.4	1	..	330.4	**475**	16	29.6	16.062
7302.3	15	102.3	1	..	302.3	473.179	**16**	....	**16**
7200.0	**15**	....	1	..	200.0	466.552	15	372.4	15.776
7000.0	14	280.0	**1**	..	....	453.592	15	162.1	15.338
6944.6	14	224.6	..	15	382.1	**450**	15	103.8	15.216
6845.9	14	125.9	..	15	283.4	443.606	**15**	....	**15**
6720.0	**14**	....	..	15	157.5	435.449	14	347.6	14.724
6562.5	13	322.5	..	**15**	....	425.243	14	182.0	14.379
6558.8	13	318.8	..	14	433.8	**425**	14	178.0	14.371
6389.5	13	149.5	..	14	264.5	414.032	**14**	....	**14**
6240.0	**13**	....	..	14	115.0	404.345	13	322.8	13.672

Equivalents of Weights and Measures—*Continued*

Weights.						Metric Weight and Measure.	Measures.		
Grains.	Apothecaries		Avoirdupois				Fluid		Fluidounces and fractions.
	oz.	grains.	lbs.	oz.	grains.	Gm. or Cc.	ounces.	minims.	
6173.0	12	413.0	..	14	48.0	**400**	13	252.3	13.526
6125.0	12	365.0	..	**14**	....	396.893	13	201.8	13.420
5933.1	12	173.1	..	13	245.6	384.458	**13**	....	**13**
5787.2	12	27.2	..	13	99.7	**375**	12	326.5	12.680
5760.0	**12**	....	..	13	72.5	373.242	12	298.0	12.621
5687.5	11	407.5	..	**13**	....	368.544	12	221.7	12.462
5476.7	11	196.7	..	12	226.7	354.884	**12**	....	**12**
5401.3	11	121.3	..	12	151.3	**350**	11	400.7	11.835
5280.0	**11**	....	..	12	30.0	342.138	11	273.1	11.569
5250.0	10	450.0	..	**12**	....	340.194	11	241.6	11.503
5020.3	10	220.3	..	11	207.8	325.311	**11**	....	**11**
5015.5	10	215.5	..	11	203.0	**325**	10	475.0	10.989
4812.5	10	12.5	..	**11**	....	311.845	10	261.4	10.545
4800.0	**10**	....	..	10	425.0	311.035	10	248.3	10.517
4629.7	9	309.7	..	10	254.7	**300**	10	69.2	10.144
4563.9	9	243.9	..	10	188.9	295.737	**10**	....	**10**
4375.0	9	55.0	..	**10**	....	283.495	9	281.3	9.586
4320.0	**9**	....	..	9	382.5	279.931	9	223.5	9.466
4244.0	8	404.0	..	9	306.5	**275**	9	143.4	9.299
4107.5	8	267.5	..	9	170.0	266.163	**9**	....	**9**
3937.5	8	97.5	..	**9**	....	255.146	8	301.2	8.627
3858.1	8	18.1	..	8	358.1	**250**	8	217.7	8.453
3840.0	**8**	....	..	8	340.0	248.828	8	198.6	8.414
3651.1	7	291.1	..	8	151.1	236.590	**8**	....	**8**
3500.0	7	140.0	..	**8**	....	226.796	7	321.0	7.669
3472.3	7	112.3	..	7	409.8	**225**	7	291.9	7.608
3360.0	**7**	....	..	7	297.5	217.724	7	173.8	7.362
3194.7	6	314.7	..	7	132.2	207.016	**7**	....	**7**
3086.5	6	206.5	..	7	24.0	**200**	6	366.1	6.763
3062.5	6	182.5	..	**7**	....	198.447	6	340.9	6.710
2880.0	**6**	....	..	6	255.0	186.621	6	149.0	6.310
2738.4	5	338.4	..	6	113.4	177.442	**6**	....	**6**
2700.7	5	300.7	..	6	75.7	**175**	5	440.4	5.917
2625.0	5	225.0	..	**6**	....	170.097	5	360.8	5.752
2400.0	**5**	....	..	5	212.5	155.517	5	124.1	5.259
2314.9	4	394.9	..	5	127.4	**150**	5	34.6	5.072
2282.0	4	362.0	..	5	94.5	147.869	**5**	....	**5**
2187.5	4	267.5	..	**5**	....	141.748	4	380.7	4.793
1929.1	4	9.1	..	4	179.1	**125**	4	108.8	4.227
1920.0	**4**	....	..	4	170.0	124.414	4	99.3	4.207
1825.6	3	385.6	..	4	75.6	118.295	**4**	....	**4**
1750.0	3	310.0	..	**4**	....	113.398	3	400.5	3.834

Equivalents of Weights and Measures—*Continued*

Weights.						Metric Weight and Measure.	Measures.		
Grains.	Apothecaries		Avoirdupois				Fluid		Fluidounces and fractions.
	oz.	grains.	lbs.	oz.	grains.	Gm. or Cc.	ounces.	minims.	
1543.2	3	103.2	..	3	230.7	**100**	3	183.1	3.382
1440.0	**3**	....	..	3	127.5	93.310	3	74.5	3.155
1388.9	2	428.9	..	3	76.4	**90**	3	20.8	3.043
1369.2	2	409.2	..	3	56.7	88.721	**3**	....	**3**
1312.5	2	352.5	..	**3**	....	85.049	2	420.4	2.876
1234.6	2	274.6	..	2	359.6	**80**	2	338.5	2.705
1157.4	2	197.4	..	2	282.4	**75**	2	257.3	2.536
1080.3	2	120.3	..	2	205.3	**70**	2	176.1	2.367
960.0	**2**	....	..	2	85.0	62.207	2	49.7	2.103
925.9	1	445.9	..	2	50.9	**60**	2	13.8	2.029
912.8	1	432.8	..	2	37.8	59.147	**2**	....	**2**
875.0	1	395.0	..	**2**	....	56.699	1	440.3	1.917
771.6	1	291.6	..	1	334.1	**50**	1	331.5	1.691
617.3	1	137.3	..	1	179.8	**40**	1	169.2	1.353
480.0	**1**	....	..	1	42.5	31.1035	1	24.8	1.052
463.0	..	....	..	1	25.5	**30**	1	6.9	1.014
456.392	..	....	..	1	18.89	29.5737	**1**	....	**1**
437.5	..	....	..	**1**	....	28.350	..	460.1308	0.959
385.8	..	....	..	..	....	**25**	..	405.77	0.845
308.6	..	....	..	..	....	**20**	..	324.61	0.676
154.3	..	....	..	..	....	**10**	..	162.31	0.338
15.4324	..	....	..	..	....	**1**	..	16.23	0.0338
1	..	....	..	..	....	0.06479	..	1.0517	0.0022
0.9508	..	....	..	..	....	0.06161	..	**1**	0.0021

Equivalents of Weights and Measures—*Continued*

From 480 Grains down

Grains.	Metric Weight and Measure. Gm. or Cc.	Minims (of Water at 4° C.).	Grains.	Metric Weight and Measure. Gm. or Cc.	Minims (of Water at 4° C.).
480 [1 ℥	31.103	504.8	**240** [4 ʒ	15.552	252.4
478.4	**31**	503.1	231.5	**15**	243.5
475.4	30.805	**500**	228.2	14.786	**240**
463.0	**30**	486.9	**218.75** [½ av. oz.	14.175	230.1
456.4	29.573	**480** [1 f℥	216.1	**14**	227.2
450	29.160	473.3	**210**	13.608	220.9
447.5	**29**	470.7	200.6	**13**	211.0
437.5 [1 av. oz.	28.350	460.1	199.7	12.938	**210**
432.1	**28**	454.5	185.2	**12**	194.8
427.9	27.725	**450**			
420 [7 ʒ	27.216	441.7	**180** [3 ʒ	11.664	189.3
416.7	**27**	438.2	171.1	11.090	**180**
401.2	**26**	422.0	169.8	**11**	178.5
399 3	25.876	**420**	154.3	**10**	162.3
390	25.272	410.2	**150**	9.720	157.8
385.8	**25**	405.8	142.6	9.242	**150**
380.3	24.644	**400**	138.9	**9**	146.1
370.8	24.028	**390**	123.5	**8**	129.8
370.4	**24**	389.5			
360 [6 ʒ	23.328	378.6	**120** [2 ʒ	7.776	126.2
354.9	**23**	373.3	114.1	7.393	**120**
342.3	22.180	**360**	**109.37** [¼ av. oz.	7.087	115.0
339.5	**22**	357.1	108.0	**7**	113.6
330	21.384	347.1	**100**	6.480	105.2
324.1	**21**	340.8	95.1	6.161	**100**
313.8	20.331	**330**	92.6	**6**	97.4
308.6	**20**	324.6	**80**	5.184	84.1
			77.2	**5**	81.2
			76.1	4.929	**80**
			61.7	**4**	64.9
300 (5 ʒ	19.440	315.5	**60** [1 ʒ	3.888	63.1
293.2	**19**	308.4	57.0	3.697	**60**
285.2	18.483	**300**	**54.69** [⅛ av. oz.	3.544	57.5
277.8	**18**	292.2	47.5	3.081	**50**
270	17.496	284.0	**50**	3.240	52.6
262.4	**17**	275.9	46.3	**3**	48.7
256.7	16.635	**270**	42.8	2.772	**45**
246.9	**16**	259.7	**40**	2.592	42.1
			38.0	2.464	**40**
			33.3	2.156	**35**
			30.9	**2**	32.5

Equivalents of Weights and Measures—*Continued*

From 30 Grains down.

Grains.	Metric Weight and Measure. Gm. or Cc.	Minims (of Water at 4° C.).
30 [½ ʒ	1.944	31.55
28.52	1.848	**30**
23.77	1.540	**25**
20	1.296	21.00
19.02	1.232	**20**
15.4324	**1**	16.23
15	0.972	15.78
14.26	0.924	**15**
14	0.907	14.72
13.31	0.863	**14**
13	0.842	13.67
12.36	0.801	**13**
12	0.778	12.62
11.41	0.739	**12**
11	0.713	11.57
10.46	0.678	**11**
10	0.648	10.52
9.51	0.616	**10**
9	0.583	9.47
8.56	0.554	**9**
8	0.518	8.41
7.71	**0.5**	8.12
7.61	0.493	**8**
7	0.454	7.36
6.66	0.431	**7**
6	0.389	6.31
5.70	0.370	**6**
5	0.324	5.26
4.75	0.308	**5**
4	0.259	4.21
3.80	0.246	**4**
3	0.194	3.16
2.85	0.185	**3**
2	0.130	2.10
1.90	0.123	**2**
1	0.06480	1.0517
0.9508	0.06161	**1**

Weights from 5 Grains down.

Grammes.	Grains in decimal fractions.	Grains in common fractions (approximate).
0.324	**5**	**5**
0.291	4.5	**4½**
0.259	**4**	**4**
0.227	3.5	**3½**
0.194	**3**	**3**
0.162	2.5	**2½**
0.130	**2**	**2**
0.097	1.5	**1½**
0.065	**1**	**1**
0.0609	0.94	**15/16**
0.0583	0.90	**9/10**
0.0570	0.88	**7/8**
0.0531	0.82	**13/16**
0.0518	0.80	**4/5**
0.0486	0.75	**3/4**
0.0447	0.69	**11/16**
0.0408	0.63	**5/8**
0.0363	0.56	**9/16**
0.0324	**0.5**	**1/2**
0.0285	0.44	**7/16**
0.0259	0.40	**2/5**
0.0246	0.38	**3/8**
0.0201	0.31	**5/16**
0.0162	0.25	**1/4**
0.0123	0.19	**3/16**
0.0084	0.13	**1/8**
0.0039	0.06	**1/16**
0.0032	0.05	**1/20**
0.0026	0.04	**1/25**
0.0022	0.033	**1/30**
0.0018	0.028	**1/35**
0.0016	0.025	**1/40**
0.0013	0.02	**1/50**
0.0011	0.017	**1/60**
0.0010	0.015	**1/64**
0.0006	0.01	**1/100**
0.0005	0.008	**1/128**
0.0004	0.0065	**1/150**
0.0003	0.005	**1/200**
0.0002	0.003	**1/320**
0.0001	0.0015	**1/640**

TABLE OF WEIGHT AND VOLUME RELATIONS

Specific gravity apparent $\frac{25^\circ\text{C.}}{25^\circ\text{C.}}$	Specific volume (volume of 1 kilogram in liters).*	Weight of 1 U. S. gallon in pounds avoirdupois.†	Weight of 100 fluidounces in ounces avoirdupois.	Weight of 1 fluidounce in grains.	Volume in U. S. gallons of 100 pounds avoirdupois.‡	Volume in fluidounces of 100 ounces avoirdupois.	Volume in fluidounces of 1000 grains.
0.700	1.4286	5.819	72.74	318.2	17.185	137.48	3.143
0.710	1.4085	5.902	73.78	322.8	16.943	135.54	3.099
0.720	1.3889	5.985	74.82	327.3	16.707	133.66	3.056
0.730	1.3699	6.068	75.85	331.9	16.479	131.83	3.014
0.740	1.3514	6.151	76.89	336.4	16.256	130.05	2.973
0.750	1.3333	6.235	77.93	341.0	16.039	128.31	2.933
0.760	1.3158	6.318	78.97	345.5	15.828	126.62	2.894
0.770	1.2987	6.401	80.01	350.0	15.623	124.98	2.857
0.780	1.2821	6.484	81.05	354.6	15.422	123.38	2.820
0.790	1.2658	6.567	82.09	359.1	15.227	121.82	2.784
0.800	1.2500	6.650	83.13	363.7	15.037	120.30	2.750
0.810	1.2346	6.733	84.17	368.2	14.851	118.81	2.716
0.820	1.2195	6.817	85.21	372.8	14.670	117.36	2.683
0.830	1.2049	6.900	86.25	377.3	14.494	115.95	2.651
0.840	1.1905	6.983	87.28	381.9	14.321	114.57	2.619
0.850	1.1765	7.066	88.32	386.4	14.152	113.22	2.588
0.860	1.1628	7.149	89.36	391.0	13.988	111.90	2.558
0.870	1.1494	7.232	90.40	395.5	13.827	110.62	2.528
0.880	1.1364	7.315	91.44	400.1	13.670	109.36	2.500
0.890	1.1236	7.398	92.48	404.6	13.516	108.13	2.472
0.900	1.1111	7.481	93.52	409.1	13.366	106.93	2.444
0.910	1.0989	7.565	94.56	413.7	13.219	105.75	2.417
0.920	1.0870	7.648	95.60	418.2	13.075	104.60	2.391
0.930	1.0753	7.731	96.64	422.8	12.935	103.48	2.365
0.940	1.0638	7.814	97.68	427.3	12.797	102.38	2.340
0.950	1.0526	7.897	98.71	431.9	12.663	101.30	2.315
0.960	1.0417	7.980	99.75	436.4	12.531	100.25	2.291
0.970	1.0309	8.063	100.79	441.0	12.401	99.21	2.268
0.980	1.0204	8.147	101.83	445.5	12.275	98.20	2.245
0.990	1.0101	8.230	102.87	450.1	12.151	97.21	2.222
1.00	1.0000	8.313	103.91	454.6	12.029	96.23	2.200
1.02	0.9804	8.479	105.99	463.7	11.794	94.35	2.157
1.04	0.9615	8.645	108.07	472.8	11.567	92.54	2.115
1.06	0.9434	8.812	110.15	481.9	11.348	90.78	2.075
1.08	0.9259	8.978	112.22	491.0	11.138	89.10	2.037
1.10	0.9091	9.144	114.30	500.1	10.936	87.49	2.000
1.12	0.8929	9.310	116.38	509.2	10.741	85.93	1.964
1.14	0.8772	9.477	118.46	518.3	10.552	84.42	1.930
1.16	0.8621	9.643	120.54	527.4	10.370	82.96	1.897
1.18	0.8475	9.809	122.61	536.4	10.194	81.55	1.865

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* Or of one gram in cubic centimeters; strictly true only at 0° C. in vacuo.

† Multiply these figures by 2 for weight of one U. S. pint in ounces avoirdupois

‡ Divide these figures by 2 for volume in pints of 100 ounces avoirdupois.

TABLE OF WEIGHT AND VOLUME RELATIONS—*Continued.*

Specific gravity apparent 25° C./25° C.	Specific volume (volume of 1 kilogram in liters).	Weight of 1 U. S. gallon in pounds avoirdupois.	Weight of 100 fluidounces in ounces avoirdupois.	Weight of 1 fluidounce in grains.	Volume in U. S. gallons of 100 pounds avoirdupois.	Volume in fluidounces of 100 ounces avoirdupois.	Volume in fluidounces of 1000 grains.
1.20	0.8333	9.975	124.69	545.5	10.025	80.20	1.833
1.22	0.8197	10.142	126.77	554.6	9.860	78.88	1.803
1.24	0.8065	10.308	128.85	563.7	9.701	77.61	1.774
1.26	0.7937	10.474	130.93	572.8	9.547	76.38	1.746
1.28	0.7813	10.640	133.01	581.9	9.398	75.18	1.719
1.30	0.7692	10.807	135.08	591.0	9.253	74.02	1.692
1.32	0.7576	10.973	137.16	600.1	9.113	72.90	1.667
1.34	0.7463	11.139	139.24	609.2	8.977	71.82	1.642
1.36	0.7353	11.305	141.32	618.3	8.845	70.76	1.618
1.38	0.7246	11.472	143.40	627.4	8.717	69.74	1.594
1.40	0.7143	11.638	145.47	636.4	8.592	68.74	1.571
1.42	0.7042	11.804	147.55	645.5	8.471	67.77	1.549
1.44	0.6944	11.970	149.63	654.6	8.354	66.83	1.528
1.46	0.6849	12.137	151.71	663.7	8.239	65.91	1.507
1.48	0.6757	12.303	153.79	672.8	8.128	65.02	1.486
1.50	0.6667	12.469	155.87	681.9	8.020	64.16	1.466
1.52	0.6579	12.635	157.94	691.0	7.914	63.31	1.447
1.54	0.6494	12.802	160.02	700.1	7.811	62.49	1.428
1.56	0.6410	12.968	162.10	709.2	7.711	61.69	1.410
1.58	0.6329	13.134	164.18	718.3	7.614	60.91	1.392
1.60	0.6250	13.300	166.26	727.4	7.519	60.14	1.375
1.62	0.6173	13.467	168.33	736.5	7.426	59.41	1.358
1.64	0.6098	13.633	170.41	745.6	7.335	58.69	1.341
1.66	0.6025	13.799	172.49	754.6	7.247	57.98	1.325
1.68	0.5952	13.966	174.57	763.7	7.160	57.28	1.309
1.70	0.5882	14.132	176.65	772.8	7.076	56.61	1.294
1.72	0.5814	14.298	178.73	781.9	6.994	55.95	1.279
1.74	0.5747	14.464	180.80	791.0	6.913	55.31	1.264
1.76	0.5682	14.631	182.88	800.1	6.835	54.68	1.250
1.78	0.5618	14.797	184.96	809.2	6.758	54.06	1.236
1.80	0.5556	14.963	187.04	818.3	6.683	53.46	1.222
1.82	0.5495	15.129	189.12	827.4	6.610	52.88	1.209
1.84	0.5435	15.296	191.19	836.5	6.538	52.31	1.196
1.86	0.5376	15.462	193.27	845.6	6.467	51.74	1.183
1.88	0.5319	15.628	195.35	854.7	6.399	51.19	1.170
1.90	0.5263	15.794	197.43	863.8	6.331	50.65	1.158
1.92	0.5208	15.961	199.51	872.8	6.265	50.12	1.146
1.94	0.5155	16.127	201.59	881.9	6.201	49.61	1.134
1.96	0.5102	16.293	203.66	891.0	6.137	49.10	1.122
1.98	0.5051	16.459	205.74	900.1	6.075	48.60	1.111
2.00	0.5000	16.626	207.82	909.2	6.015	48.12	1.100

THERMOMETRIC EQUIVALENTS.

(*According to the Centigrade and Fahrenheit Scales.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
—39.4	—39	—20.5	—5	—1.1	30	18	64.4	37.2	99
—39	—38.2	—20	—4	—1	30.2	18.3	65	37.7	100
—38.8	—38	—19.4	—3	—0.5	31	18.8	66	38	100.4
—38.3	—37	—19	—2.2	0	32	19	66.2	38.3	101
—38	—36.4	—18.8	—2	0.5	33	19.4	67	38.8	102
—37.7	—36	—18.3	—1	1	33.8	20	68	39	102.2
—37.2	—35	—18	—0.4	1.1	34	20.5	69	39.4	103
—37	—34.6	—17.7	0	1.6	35	21	69.8	40	104
—36.6	—34	—17.2	1	2	35.6	21.1	70	40.5	105
—36.1	—33	—17	1.4	2.2	36	21.6	71	41	105.8
—36	—32.8	—16.6	2	2.7	37	22	71.6	41.1	106
—35.5	—32	—16.1	3	3	37.4	22.2	72	41.6	107
—35	—31	—16	3.2	3.3	38	22.7	73	42	107.6
—34.4	—30	—15.5	4	3.8	39	23	73.4	42.2	108
—34	—29.2	—15	5	4	39.2	23.3	74	42.7	109
—33.8	—29	—14.4	6	4.4	40	23.8	75	43	109.4
—33.3	—28	—14	6.8	5	41	24	75.2	43.3	110
—33	—27.4	—13.8	7	5.5	42	24.4	76	43.8	111
—32.7	—27	—13.3	8	6	42.8	25	77	44	111.2
—32.2	—26	—13	8.6	6.1	43	25.5	78	44.4	112
—32	—25.6	—12.7	9	6.6	44	26	78.8	45	113
—31.6	—25	—12.2	10	7	44.6	26.1	79	45.5	114
—31.1	—24	—12	10.4	7.2	45	26.6	80	46	114.8
—31	—23.8	—11.6	11	7.7	46	27	80.6	46.1	115
—30.5	—23	—11.1	12	8	46.4	27.2	81	46.6	116
—30	—22	—11	12.2	8.3	47	27.7	82	47	116.6
—29.4	—21	—10.5	13	8.8	48	28	82.4	47.2	117
—29	—20.2	—10	14	9	48.2	28.3	83	47.7	118
—28.8	—20	—9.4	15	9.4	49	28.8	84	48	118.4
—28.3	—19	—9	15.8	10	50	29	84.2	48.3	119
—28	—18.4	—8.8	16	10.5	51	29.4	85	48.8	120
—27.7	—18	—8.3	17	11	51.8	30	86	49	120.2
—27.2	—17	—8	17.6	11.1	52	30.5	87	49.4	121
—27	—16.6	—7.7	18	11.6	53	31	87.8	50	122
—26.6	—16	—7.2	19	12	53.6	31.1	88	50.5	123
—26.1	—15	—7	19.4	12.2	54	31.6	89	51	123.8
—26	—14.8	—6.6	20	12.7	55	32	89.6	51.1	124
—25.5	—14	—6.1	21	13	55.4	32.2	90	51.6	125
—25	—13	—6	21.2	13.3	56	32.7	91	52	125.6
—24.4	—12	—5.5	22	13.8	57	33	91.4	52.2	126
—24	—11.2	—5	23	14	57.2	33.3	92	52.7	127
—23.8	—11	—4.4	24	14.4	58	33.8	93	53	127.4
—23.3	—10	—4	24.8	15	59	34	93.2	53.3	128
—23	—9.4	—3.8	25	15.5	60	34.4	94	53.8	129
—22.7	—9	—3.3	26	16	60.8	35	95	54	129.2
—22.2	—8	—3	26.6	16.1	61	35.5	96	54.4	130
—22	—7.6	—2.7	27	16.6	62	36	96.8	55	131
—21.6	—7	—2.2	28	17	62.6	36.1	97	55.5	132
—21.1	—6	—2	28.4	17.2	63	36.6	98	56	132.8
—21	—5 8	—1.6	29	17.7	64	37	98.6	56.1	133

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
56.6	134	77.2	171	98	208.4	118.8	246	139.4	283
57	134.6	77.7	172	98.3	209	119	246.2	140	284
57.2	135	78	172.4	98.8	210	119.4	247	140.5	285
57.7	136	78.3	173	99	210.2	120	248	141	285.8
58	136.4	78.8	174	99.4	211	120.5	249	141.1	286
58.3	137	79	174.2	100	212	121	249.8	141.6	287
58.8	138	79.4	175	100.5	213	121.1	250	142	287.6
59	138.2	80	176	101	213.8	121.6	251	142.2	288
59.4	139	80.5	177	101.1	214	122	251.6	142.7	289
60	140	81	177.8	101.6	215	122.2	252	143	289.4
60.5	141	81.1	178	102	215.6	122.7	253	143.3	290
61	141.8	81.6	179	102.2	216	123	253.4	143.8	291
61.1	142	82	179.6	102.7	217	123.3	254	144	291.2
61.6	143	82.2	180	103	217.4	123.8	255	144.4	292
62	143.6	82.7	181	103.3	218	124	255.2	145	293
62.2	144	83	181.4	103.8	219	124.4	256	145.5	294
62.7	145	83.3	182	104	219.2	125	257	146	294.8
63	145.4	83.8	183	104.4	220	125.5	258	146.1	295
63.3	146	84	183.2	105	221	126	258.8	146.6	296
63.8	147	84.4	184	105.5	222	126.1	259	147	296.6
64	147.2	85	185	106	222.8	126.6	260	147.2	297
64.4	148	85.5	186	106.1	223	127	260.6	147.7	298
65	149	86	186.8	106.6	224	127.2	261	148	298.4
65.5	150	86.1	187	107	224.6	127.7	262	148.3	299
66	150.8	86.6	188	107.2	225	128	262.4	148.8	300
66.1	151	87	188.6	107.7	226	128.3	263	149	300.2
66.6	152	87.2	189	108	226.4	128.8	264	149.4	301
67	152.6	87.7	190	108.3	227	129	264.2	150	302
67.2	153	88	190.4	108.8	228	129.4	265	150.5	303
67.7	154	88.3	191	109	228.2	130	266	151	303.8
68	154.4	88.8	192	109.4	229	130.5	267	151.1	304
68.3	155	89	192.2	110	230	131	267.8	151.6	305
68.8	156	89.4	193	110.5	231	131.1	268	152	305.6
69	156.2	90	194	111	231.8	131.6	269	152.2	306
69.4	157	90.5	195	111.1	232	132	269.6	152.7	307
70	158	91	195.8	111.6	233	132.2	270	153	307.4
70.5	159	91.1	196	112	233.6	132.7	271	153.3	308
71	159.8	91.6	197	112.2	234	133	271.4	153.8	309
71.1	160	92	197.6	112.7	235	133.3	272	154	309.2
71.6	161	92.2	198	113	235.4	133.8	273	154.4	310
72	161.6	92.7	199	113.3	236	134	273.2	155	311
72.2	162	93	199.4	113.8	237	134.4	274	155.5	312
72.7	163	93.3	200	114	237.2	135	275	156	312.8
73	163.4	93.8	201	114.4	238	135.5	276	156.1	313
73.3	164	94	201.2	115	239	136	276.8	156.6	314
73.8	165	94.4	202	115.5	240	136.1	277	157	314.6
74	165.2	95	203	116	240.8	136.6	278	157.2	315
74.4	166	95.5	204	116.1	241	137	278.6	157.7	316
75	167	96	204.8	116.6	242	137.2	279	158	316.4
75.5	168	96.1	205	117	242.6	137.7	280	158.3	317
76	168.8	96.6	206	117.2	243	138	280.4	158.8	318
76.1	169	97	206.6	117.7	244	138.3	281	159	318.2
76.6	170	97.2	207	118	244.4	138.8	282	159.4	319
77	170.6	97.7	208	118.3	245	139	282.2	160	320

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
160.5	321	181.1	358	202	395.6	222.7	433	243.3	470
161	321.8	181.6	359	202.2	396	223	433.4	243.8	471
161.1	322	182	359.6	202.7	397	223.3	434	244	471.2
161.6	323	182.2	360	203	397.4	223.8	435	244.4	472
162	323.6	182.7	361	203.3	398	224	435.2	245	473
162.2	324	183	361.4	203.8	399	224.4	436	245.5	474
162.7	325	183.3	362	204	399.2	225	437	246	474.8
163	325.4	183.8	363	204.4	400	225.5	438	246.1	475
163.3	326	184	363.2	205	401	226	438.8	246.6	476
163.8	327	184.4	364	205.5	402	226.1	439	247	476.6
164	327.2	185	365	206	402.8	226.6	440	247.2	477
164.4	328	185.5	366	206.1	403	227	440.6	247.7	478
165	329	186	366.8	206.6	404	227.2	441	248	478.4
165.5	330	186.1	367	207	404.6	227.7	442	248.3	479
166	330.8	186.6	368	207.2	405	228	442.4	248.8	480
166.1	331	187	368.6	207.7	406	228.3	443	249	480.2
166.6	332	187.2	369	208	406.4	228.8	444	249.4	481
167	332.6	187.7	370	208.3	407	229	444.2	250	482
167.2	333	188	370.4	208.8	408	229.4	445	250.5	483
167.7	334	188.3	371	209	408.2	230	446	251	483.8
168	334.4	188.8	372	209.4	409	230.5	447	251.1	484
168.3	335	189	372.2	210	410	231	447.8	251.6	485
168.8	336	189.4	373	210.5	411	231.1	448	252	485.6
169	336.2	190	374	211	411.8	231.6	449	252.2	486
169.4	337	190.5	375	211.1	412	232	449.6	252.7	487
170	338	191	375.8	211.6	413	232.2	450	253	487.4
170.5	339	191.1	376	212	413.6	232.7	451	253.3	488
171	339.8	191.6	377	212.2	414	233	451.4	253.8	489
171.1	340	192	377.6	212.7	415	233.3	452	254	489.2
171.6	341	192.2	378	213	415.4	233.8	453	254.4	490
172	341.6	192.7	379	213.3	416	234	453.2	255	491
172.2	342	193	379.4	213.8	417	234.4	454	255.5	492
172.7	343	193.3	380	214	417.2	235	455	256	492.8
173	343.4	193.8	381	214.4	418	235.5	456	256.1	493
173.3	344	194	381.2	215	419	236	456.8	256.6	494
173.8	345	194.4	382	215.5	420	236.1	457	257	494.6
174	345.2	195	383	216	420.8	236.6	458	257.2	495
174.4	346	195.5	384	216.1	421	237	458.6	257.7	496
175	347	196	384.8	216.6	422	237.2	459	258	496.4
175.5	348	196.1	385	217	422.6	237.7	460	258.3	497
176	348.8	196.6	386	217.2	423	238	460.4	258.8	498
176.1	349	197	386.6	217.7	424	238.3	461	259	498.2
176.6	350	197.2	387	218	424.4	238.8	462	259.4	499
177	350.6	197.7	388	218.3	425	239	462.2	260	500
177.2	351	198	388.4	218.8	426	239.4	463	260.5	501
177.7	352	198.3	389	219	426.2	240	464	261	501.8
178	352.4	198.8	390	219.4	427	240.5	465	261.1	502
178.3	353	199	390.2	220	428	241	465.8	261.6	503
178.8	354	199.4	391	220.5	429	241.1	466	262	503.6
179	354.2	200	392	221	429.8	241.6	467	262.2	504
179.4	355	200.5	393	221.1	430	242	467.6	262.7	505
180	356	201	393.8	221.6	431	242.2	468	263	505.4
180.5	357	201.1	394	222	431.6	242.7	469	263.3	506
181	357.8	201.6	395	222.2	432	243	469.4	263.8	507

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
56.6	134	77.2	171	98	208.4	118.8	246	139.4	283
57	134.6	77.7	172	98.3	209	119	246.2	140	284
57.2	135	78	172.4	98.8	210	119.4	247	140.5	285
57.7	136	78.3	173	99	210.2	120	248	141	285.8
58	136.4	78.8	174	99.4	211	120.5	249	141.1	286
58.3	137	79	174.2	100	212	121	249.8	141.6	287
58.8	138	79.4	175	100.5	213	121.1	250	142	287.6
59	138.2	80	176	101	213.8	121.6	251	142.2	288
59.4	139	80.5	177	101.1	214	122	251.6	142.7	289
60	140	81	177.8	101.6	215	122.2	252	143	289.4
60.5	141	81.1	178	102	215.6	122.7	253	143.3	290
61	141.8	81.6	179	102.2	216	123	253.4	143.8	291
61.1	142	82	179.6	102.7	217	123.3	254	144	291.2
61.6	143	82.2	180	103	217.4	123.8	255	144.4	292
62	143.6	82.7	181	103.3	218	124	255.2	145	293
62.2	144	83	181.4	103.8	219	124.4	256	145.5	294
62.7	145	83.3	182	104	219.2	125	257	146	294.8
63	145.4	83.8	183	104.4	220	125.5	258	146.1	295
63.3	146	84	183.2	105	221	126	258.8	146.6	296
63.8	147	84.4	184	105.5	222	126.1	259	147	296.6
64	147.2	85	185	106	222.8	126.6	260	147.2	297
64.4	148	85.5	186	106.1	223	127	260.6	147.7	298
65	149	86	186.8	106.6	224	127.2	261	148	298.4
65.5	150	86.1	187	107	224.6	127.7	262	148.3	299
66	150.8	86.6	188	107.2	225	128	262.4	148.8	300
66.1	151	87	188.6	107.7	226	128.3	263	149	300.2
66.6	152	87.2	189	108	226.4	128.8	264	149.4	301
67	152.6	87.7	190	108.3	227	129	264.2	150	302
67.2	153	88	190.4	108.8	228	129.4	265	150.5	303
67.7	154	88.3	191	109	228.2	130	266	151	303.8
68	154.4	88.8	192	109.4	229	130.5	267	151.1	304
68.3	155	89	192.2	110	230	131	267.8	151.6	305
68.8	156	89.4	193	110.5	231	131.1	268	152	305.6
69	156.2	90	194	111	231.8	131.6	269	152.2	306
69.4	157	90.5	195	111.1	232	132	269.6	152.7	307
70	158	91	195.8	111.6	233	132.2	270	153	307.4
70.5	159	91.1	196	112	233.6	132.7	271	153.3	308
71	159.8	91.6	197	112.2	234	133	271.4	153.8	309
71.1	160	92	197.6	112.7	235	133.3	272	154	309.2
71.6	161	92.2	198	113	235.4	133.8	273	154.4	310
72	161.6	92.7	199	113.3	236	134	273.2	155	311
72.2	162	93	199.4	113.8	237	134.4	274	155.5	312
72.7	163	93.3	200	114	237.2	135	275	156	312.8
73	163.4	93.8	201	114.4	238	135.5	276	156.1	313
73.3	164	94	201.2	115	239	136	276.8	156.6	314
73.8	165	94.4	202	115.5	240	136.1	277	157	314.6
74	165.2	95	203	116	240.8	136.6	278	157.2	315
74.4	166	95.5	204	116.1	241	137	278.6	157.7	316
75	167	96	204.8	116.6	242	137.2	279	158	316.4
75.5	168	96.1	205	117	242.6	137.7	280	158.3	317
76	168.8	96.6	206	117.2	243	138	280.4	158.8	318
76.1	169	97	206.6	117.7	244	138.3	281	159	318.2
76.6	170	97.2	207	118	244.4	138.8	282	159.4	319
77	170.6	97.7	208	118.3	245	139	282.2	160	320

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
160.5	321	181.1	358	202	395.6	222.7	433	243.3	470
161	321.8	181.6	359	202.2	396	223	433.4	243.8	471
161.1	322	182	359.6	202.7	397	223.3	434	244	471.2
161.6	323	182.2	360	203	397.4	223.8	435	244.4	472
162	323.6	182.7	361	203.3	398	224	435.2	245	473
162.2	324	183	361.4	203.8	399	224.4	436	245.5	474
162.7	325	183.3	362	204	399.2	225	437	246	474.8
163	325.4	183.8	363	204.4	400	225.5	438	246.1	475
163.3	326	184	363.2	205	401	226	438.8	246.6	476
163.8	327	184.4	364	205.5	402	226.1	439	247	476.6
164	327.2	185	365	206	402.8	226.6	440	247.2	477
164.4	328	185.5	366	206.1	403	227	440.6	247.7	478
165	329	186	366.8	206.6	404	227.2	441	248	478.4
165.5	330	186.1	367	207	404.6	227.7	442	248.3	479
166	330.8	186.6	368	207.2	405	228	442.4	248.8	480
166.1	331	187	368.6	207.7	406	228.3	443	249	480.2
166.6	332	187.2	369	208	406.4	228.8	444	249.4	481
167	332.6	187.7	370	208.3	407	229	444.2	250	482
167.2	333	188	370.4	208.8	408	229.4	445	250.5	483
167.7	334	188.3	371	209	408.2	230	446	251	483.8
168	334.4	188.8	372	209.4	409	230.5	447	251.1	484
168.3	335	189	372.2	210	410	231	447.8	251.6	485
168.8	336	189.4	373	210.5	411	231.1	448	252	485.6
169	336.2	190	374	211	411.8	231.6	449	252.2	486
169.4	337	190.5	375	211.1	412	232	449.6	252.7	487
170	338	191	375.8	211.6	413	232.2	450	253	487.4
170.5	339	191.1	376	212	413.6	232.7	451	253.3	488
171	339.8	191.6	377	212.2	414	233	451.4	253.8	489
171.1	340	192	377.6	212.7	415	233.3	452	254	489.2
171.6	341	192.2	378	213	415.4	233.8	453	254.4	490
172	341.6	192.7	379	213.3	416	234	453.2	255	491
172.2	342	193	379.4	213.8	417	234.4	454	255.5	492
172.7	343	193.3	380	214	417.2	235	455	256	492.8
173	343.4	193.8	381	214.4	418	235.5	456	256.1	493
173.3	344	194	381.2	215	419	236	456.8	256.6	494
173.8	345	194.4	382	215.5	420	236.1	457	257	494.6
174	345.2	195	383	216	420.8	236.6	458	257.2	495
174.4	346	195.5	384	216.1	421	237	458.6	257.7	496
175	347	196	384.8	216.6	422	237.2	459	258	496.4
175.5	348	196.1	385	217	422.6	237.7	460	258.3	497
176	348.8	196.6	386	217.2	423	238	460.4	258.8	498
176.1	349	197	386.6	217.7	424	238.3	461	259	498.2
176.6	350	197.2	387	218	424.4	238.8	462	259.4	499
177	350.6	197.7	388	218.3	425	239	462.2	260	500
177.2	351	198	388.4	218.8	426	239.4	463	260.5	501
177.7	352	198.3	389	219	426.2	240	464	261	501.8
178	352.4	198.8	390	219.4	427	240.5	465	261.1	502
178.3	353	199	390.2	220	428	241	465.8	261.6	503
178.8	354	199.4	391	220.5	429	241.1	466	262	503.6
179	354.2	200	392	221	429.8	241.6	467	262.2	504
179.4	355	200.5	393	221.1	430	242	467.6	262.7	505
180	356	201	393.8	221.6	431	242.2	468	263	505.4
180.5	357	201.1	394	222	431.6	242.7	469	263.3	506
181	357.8	201.6	395	222.2	432	243	469.4	263.8	507

THERMOMETRIC EQUIVALENTS.—(*Continued.*)

C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°	C.°	F.°
264	507.2	271.6	521	278.8	534	286.1	547	293.3	560
264.4	508	272	521.6	279	534.2	286.6	548	293.8	561
265	509	272.2	522	279.4	535	287	548.6	294	561.2
265.5	510	272.7	523	280	536	287.2	549	294.4	562
266	510.8	273	523.4	280.5	537	287.7	550	295	563
266.1	511	273.3	524	281	537.8	288	550.4	295.5	564
266.6	512	273.8	525	281.1	538	288.3	551	296	564.8
267	512.6	274	525.2	281.6	539	288.8	552	296.1	565
267.2	513	274.4	526	282	539.6	289	552.2	296.6	566
267.7	514	275	527	282.2	540	289.4	553	297	566.6
268	514.4	275.5	528	282.7	541	290	554	297.2	567
268.3	515	276	528.8	283	541.4	290.5	555	297.7	568
268.8	516	276.1	529	283.3	542	291	555.8	298	568.4
269	516.2	276.6	530	283.8	543	291.1	556	298.3	569
269.4	517	277	530.6	284	543.2	291.6	557	298.8	570
270	518	277.2	531	284.4	544	292	557.6	299	570.2
270.5	519	277.7	532	285	545	292.2	558	299.4	571
271	519.8	278	532.4	285.5	546	292.7	559	300	572
271.1	520	278.3	533	286	546.8	293	559.1		

BAUMÉ'S SCALE FOR LIQUIDS HEAVIER THAN WATER.

Degrees.	Baumé, 17.5° C.	Rational Baumé Scale, 12.5° C.	Degrees.	Baumé, 17.5° C.	Rational Baumé Scale, 12.5° C.
	Sp. gr.	Sp. gr.		Sp. gr.	Sp. gr.
0	1.0000	1.0000	37	1.3370	1.3447
1	1.0068	1.0069	38	1.3494	1.3574
2	1.0138	1.0140	39	1.3619	1.3703
3	1.0208	1.0212	40	1.3746	1.3834
4	.0280	1.0285	41	1.3876	1.3968
5	1.0353	1.0358	42	1.4009	1.4105
6	1.0426	1.0434	43	1.4143	1.4244
7	1.0501	1.0509	44	1.4281	1.4386
8	1.0576	1.0587	45	1.4421	1.4531
9	1.0653	1.0665	46	1.4564	1.4678
10	1.0731	1.0745	47	1.4710	1.4828
11	1.0810	1.0825	48	1.4860	1.4984
12	1.0890	1.0907	49	1.5012	1.5141
13	1.0972	1.0990	50	1.5167	1.5301
14	1.1054	1.1074	51	1.5325	1.5466
15	1.1138	1.1160	52	1.5487	1.5633
16	1.1224	1.1247	53	1.5652	1.5804
17	1.1310	1.1335	54	1.5820	1.5978
18	1.1398	1.1425	55	1.5993	1.6158
19	1.1487	1.1516	56	1.6169	1.6342
20	1.1578	1.1608	57	1.6349	1.6529
21	1.1670	1.1702	58	1.6533	1.6720
22	1.1763	1.1798	59	1.6721	1.6916
23	1.1858	1.1896	60	1.6914	1.7116
24	1.1955	1.1994	61	1.7111	1.7322
25	1.2053	1.2095	62	1.7313	1.7532
26	1.2153	1.2198	63	1.7520	1.7748
27	1.2254	1.2301	64	1.7731	1.7960
28	1.2357	1.2407	65	1.7948	1.8195
29	1.2462	1.2515	66	1.8171	1.8428
30	1.2569	1.2624	67	1.8398	1.839
31	1.2677	1.2736	68	1.8632	1.864
32	1.2788	1.2849	69	1.8871	1.885
33	1.2901	1.2965	70	1.9117	1.909
34	1.3015	1.3082	71	1.9370	1.935
35	1.3131	1.3202	72	1.9629	1.960
36	1.3250	1.3324			

What is known as the "Rational" Baumé scale is calculated by taking water at the temperature chosen at 0° B. and sulphuric acid of 1.842 specific gravity at 66° B. and using the formula $\frac{144.3}{144.3 - n^\circ} = d$. (See Lunge's "Sulphuric Acid and Alkali," Vol. I. p. 20.)

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