INTRODUCTION TO
MODERN CHEMISTRY

AN INTRODUCTION TO

MODERN SCIENTIFIC CHEMISTRY

IN THE FORM OF POPULAR
LECTURES SUITED FOR UNIVERSITY
EXTENSION STUDENTS AND GENERAL READERS

BY

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AUTHOR'S PREFACE.

IN this INTRODUCTION TO MODERN SCIENTIFIC CHEMISTRY an attempt is made to give a succinct and accurate presentation of chemistry on strictly scientific lines, and at the same time in as popular a form as is compatible with the matter and the vast range of the subject. The book can be followed easily by anyone who takes a serious interest in natural science, and will not, I hope, be unwelcome to the younger chemists who are still pursuing their studies. A teacher of chemistry who may not have paid special attention to the methods of presenting his subject will perhaps find in the book something useful to himself and helpful to his hearers.

The form followed in lectures is used as far as possible; for, by pursuing the subject in this way, the reader seems to find for himself the results that chemistry has gained; and experience has shown that this form is the most interesting and the most easily understood.

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AN INTRODUCTION

TO

MODERN SCIENTIFIC CHEMISTRY.

BEFORE entering on the serious study of Chemistry it is necessary to have some clear notion concerning the range and scope of this department of natural science. For the name *Chemistry*, unlike the names of many parts of scientific study, does not tell what is the sphere of the science. Everyone knows, for example, that Botany is concerned with plants, Mineralogy with rocks, Zoology with animals. No one will confuse Chemistry with these departments of science, inasmuch as the field of activity of each is circumscribed by its name. But such confusion often arises with Physics, because the circumstances here are just the same as with Chemistry. No details regarding the questions with the solution whereof Physics is concerned are to be learnt from the name only. It is not difficult, however, to establish the difference between the problems of these two parts of natural science, which are often confounded. In doing this we shall also get to know the scope and range of Chemistry.

Briefly stated, the relations between these two sciences are as follows. Chemistry is concerned with the investigation of processes wherein substances are changed into other substances; Physics, on the other hand, examines processes wherein no changes occur in the substances which exhibit the phenomena that are studied.

Let us, for example, seize a bell and ring it (figs. 1 and 2 are given as helps to the memory only). We all hear the sound; but however long the bell is rung, the substance of it remains unchanged. Hence the study of sound belongs to Physics; and the questions to which that study has to find answers are such as these:—How is sound generally produced? In what way, and with what velocity, is it propagated?

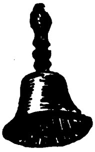

Fig. 1.

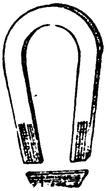

Fig. 2.

Now let us take a magnet and bring it near a piece of iron (fig. 2). When the magnet exerts its mysterious attractive force, which looks almost like the purpose of a living thing, and seizes the iron, the magnet itself remains unchanged. If we remove the piece of iron that has adhered to the magnet, the latter is found to be just the same as before, and its substance to be unaltered. Hence the investigation of magnetic phenomena also is a problem of Physics.

But if we now set fire to a piece of paper held in small pincers, we have to deal with a very different kind of phenomenon. The paper burns, and at the same time it seems to vanish altogether. We must, of course, say *seems*, for everyone nowadays has received so much schooling that he knows that matter cannot be destroyed, but can only be changed into other forms. And so what was a piece of paper now hovers around us in the form of various kinds of gases, which were produced from the paper while it was burning, and are now mixed with the air of the room wherein we are. We cannot at present comprehend what kinds of gases are produced, because we have not yet any chemical knowledge; but this ignorance will not last very long, and we shall be able clearly to understand what exactly has been produced from this piece of paper. Nevertheless, this much is certain—that the paper must now be something quite different from what it was before the burning, and that its substance has been wholly altered. In processes of burning, then, we have to do with changes of substances; and, consequently, the explanation of combustion-processes belongs to the province of Chemistry.

The marshalling of occurrences as belonging to Chemistry or to Physics is not always so easy as in the cases that have been chosen. For example, when water is frozen it is certainly different from liquid water; and water that is evaporated and made to take the form of water-vapour is also different from liquid water. But there can be no talk here of a change of the substance of water, like the change that occurred when a piece of paper was converted into gaseous substances. We can easily bring any water back into the state wherein it is most familiar to us—the liquid state—either by warming ice or cooling water-vapour. Taking into consideration such changes of substances as those of water, we must slightly widen the import of the definition that has been given of the business of chemistry. The definition must run thus:—*Chemistry is concerned with the investigation of processes wherewith changes in the forms of substances, and also essential changes in the composition of substances, are connected.*

We spoke a moment ago of changing water-vapour into water by cooling it. Such a process is very often carried out by chemists, not only with water-vapour, but also with vapours of many kinds. They intentionally change liquids into vapours, and by cooling the vapours again they obtain "*the distillates*" of the liquids. As we shall be using distilled water very often, for a reason that will be apparent immediately, it is advisable, at this stage, to perform a process of distillation, and especially the distillation of water. For this purpose we shall use (as we shall always use) the simplest possible apparatus, lest complications in the apparatus should put difficulties in the way of recognising what the experiment is intended to demonstrate and display. In order to distil water, we boil it in a glass flask. It is customary not to put such a glass vessel directly over a flame, but to place it on brass or iron wire-gauze, which helps to spread the heat over the bottom of the vessel, and so prevents the breaking of it (see fig. 3).

The glass vessels wherein liquids are boiled in chemical laboratories are exceedingly thin-walled—not much thicker than paper.

Consequently, when these vessels are heated, the heat spreads itself throughout their material almost instantly; their walls, being equally heated, expand equally, and cracking is avoided. If thick glass is heated, strains are soon developed which lead to the breaking to pieces of the glass, because glass is a very bad conductor of heat. If a glass drinking-vessel is placed over a flame, the outer surface is quickly heated and expands, while the interior parts remain cold, because of the small thermal conductivity of the glass, and do not expand at all. The great strains that are thus set up in the walls of such a thick vessel cause the glass to crack and break to pieces.

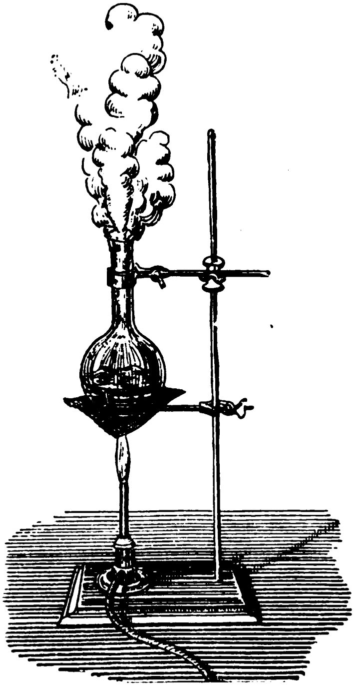

Fig. 3.—Boiling water; water-vapour.

As soon as the water boils we see what we take to be water-vapour issuing from the mouth of the flask (see fig. 3). What we see is not really water-vapour, for the vapour of water is colourless; and of this we may convince ourselves by observing that no vapour is visible inside the flask, and that only at the mouth of the flask does a cloud begin to be seen. There the vapour, which is at the temperature of 100° C. [212° F.]—for water does not boil until that temperature is reached—comes into contact with the air of the room, which is colder than the vapour; and, in consequence of the sudden cooling, the vapour is condensed to exceedingly fine droplets of water, which we see floating in the air and we call water-vapour.

If we place a cork, through a hole wherein is passed a long glass tube (bent as shown in fig. 4), in the mouth of the flask, the vapour coming from the boiling water must pass through this long tube. The water-vapour will then be much cooled, for the tube will communicate to the comparatively cold air wherewith it is surrounded the heat which the vapour brings with it. The result of this cooling process is that the water-vapour becomes liquid water. We see this liquid

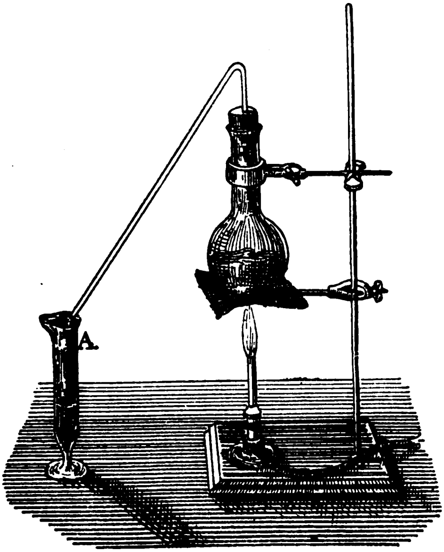

Fig. 4.—Distillation of water.

water dropping into the vessel A (fig. 4), placed under the outer end of the glass tube. The water which collects in the vessel A is, then, distilled water.

The apparatus that has been used for the distillation of water is the most simple that can be thought of for this purpose. That apparatus suffices for quite a few purposes only; for the glass tube which acts as a cooler soon becomes so hot that a large portion of the vapour passes through it without being liquefied, and so simply escapes into the air, and is lost for our purposes. A more effective cooling apparatus is therefore employed in laboratories. In this apparatus (see fig. 5) the tube A,

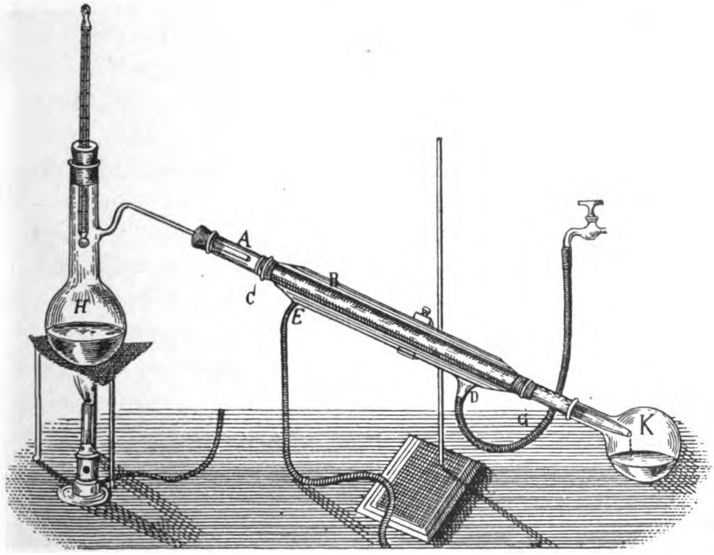

Fig. 5.—Distillation-apparatus as generally used in laboratories.

through which pass the vapours to be cooled, is surrounded by a wider tube (B), which is connected with A by the corks C. The side-piece D (of the tube B) is connected by caoutchouc tubing with the water supply: water flows between the tubes B and A, entering at D and flowing away by the side-piece E. The greater part of the cooling-tube A is thus surrounded by cold water, and, being kept cold, that tube is able to condense to liquid all the vapour that comes from the boiling-flask H. This flask (H) carries a thermometer, on which is read off the temperature of the vapour that passes over; for, as has been said already, liquids of diverse kinds and with very different boiling points are distilled in the laboratory. It is customary not to allow the distillate to drop into an open vessel, as was done in the simpler apparatus shown in fig. 4, but to collect it in a flask (K in the figure), into which the end of the cooling-tube passes.

The difference between the water which we have subjected to the process of distillation and the distillate obtained therefrom (that is, the distilled water) is as follows. All kinds of water in common use have been in contact with the soil; and every soil contains substances which are more or less soluble in water. If we recollect how easily sugar dissolves in water, we shall realise how many substances may be kept in solution in a natural water. All ordinary waters hold in solution very diverse substances which they have taken up from the soil—for example, small quantities of carbonate of lime, gypsum, and common salt, three substances whose names do not sound very unfamiliar, and which, for that reason, will be the only substances we shall mention at present.

Such dissolved substances as those just named are not volatile, and therefore they do not pass over with the vapour of water in the process of distillation, but remain behind in the flask. The vapour in the cooling-tube is free from these substances, and therefore the water that is formed by cooling this vapour, and flows from the cooling-tube, is free from those substances which natural waters take up from the soils: it is pure water.

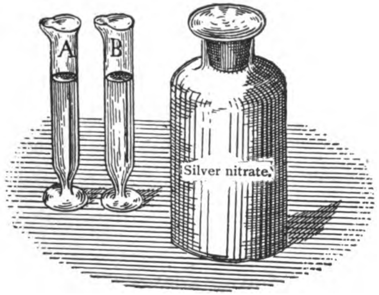

Fig. 6.—Behaviour of distilled and undistilled water with silver nitrate solution.

In order to make visible the difference between natural and distilled water, let us put some water that has not been distilled into the glass A (fig. 6), and some distilled water into the glass B, and let us add to each a few drops of a solution in water of nitrate of silver. Silver nitrate is a salt which is very soluble in water. We shall learn what this salt really is when we come to the consideration of nitric acid;* at present a solution of it is used by us only as a means to an end. We notice that the distilled water in B is not changed by the addition of the silver

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* References to later parts of the book should be located by the index.

nitrate solution, but that the natural water in A is immediately made turbid and appears like milk. The reason for this is as follows. The distilled water, which is nothing but water, only dilutes the solution of silver nitrate—that is, only adds more water to what is already there; the ingredients of the ordinary water, on the other hand, react with the nitrate of silver that is present in the solution which was added. Carbonate of silver, which is not soluble in water, and other insoluble compounds of silver, have been formed in the water in A, and we see these solid substances floating in the water and causing it to be turbid and like milk. Ordinary water cannot be used as a solvent or a diluent in accurate chemical experiments, because the substances that are dissolved in ordinary waters act on solutions of various bodies in different ways—we have just had a special example of such actions—and the substances that are produced interfere with the reactions which it is desired to study. Water must be distilled before it is used in the laboratory, in order to remove those substances which, if present, would exert disturbing actions. Thus we see why chemists almost always use distilled water.

Now that we know what distillation is and what purpose it serves, we shall return to chemical experiments; and we shall begin by allowing sulphur to react with iron. Sulphur has nothing mysterious about it, although many people may think it is a strange substance, because they are not accustomed to have to do with it. Quantities of sulphur are found in the soil, for instance, in Sicily: it is only necessary to separate the sulphur from the rocks wherewith it may be mixed in order to fit it for use. But it is otherwise with iron. Except in some meteorites, iron itself is not found in the earth; it must be produced, by very complicated processes, which we shall become acquainted with later, from the compounds of it which are found in the earth's crust. Although iron is much more difficult to prepare than sulphur, yet, considering that it is a substance in daily use, it does not seem to be especially worth a close examination. At present we require both sulphur and iron as finely powdered as we can get them.

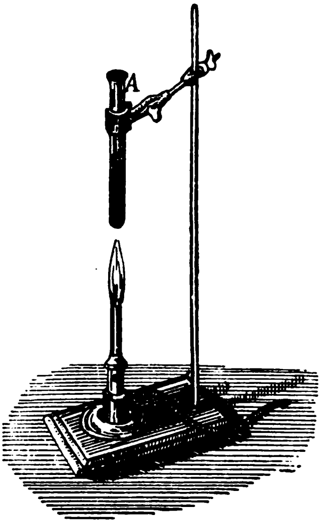

Fig. 7.—Preparation of iron sulphide.

We now mix the powdered iron with the powdered sulphur. They do not react on one another without further treatment. If, for instance, we move our magnet in the mixture, the iron is drawn out by the magnet; and in this way the two substances can be separated from one another. Let us now pour the mixture into a test-tube. A test-tube is a tube of glass closed at one end by melting the glass and letting it flow together; these tubes are very much used in making experiments. We place the test-tube A, half filled with the mixture, in a clamp, and heat it by a flame (see fig. 7). We see the contents of the tube suddenly begin to glow at one point; and although we at once remove the flame and thereby cease to add heat, the glowing continues and spreads throughout the whole mass.

When the mass has become cold and we examine it to see what has happened, instead of the yellow sulphur and the grey iron, we find a brownish black body, which has been melted, and is neither the one nor the other of the two materials wherewith we started. The magnet has no effect on the new substance, and the most powerful microscope fails to reveal particles either of iron or sulphur in it. We have to do here with an occurrence that belongs to the domain of chemistry. A compound of the two bodies has been produced, and this compound exhibits neither the properties of sulphur nor those of iron: a transformation has been effected of the two substances into a third—new—substance.

Experiments conducted like that just described, whereby we gain new bodies, are called synthetical experiments. We have carried out the synthesis of sulphide of iron. But, of course, we can reverse our method of working. We can try to answer the questions:—Of what substances are the various bodies formed which are around us? Are we in a position to separate them into simpler substances? This method of working, which is opposed to the synthetical method, is called analysis.

Now that we have become acquainted with a synthesis, we shall perform an analysis. That which is nearest our hand is to decompose the sulphide of iron we have made into its constituents—to obtain from it sulphur and iron. But that analysis would be too difficult to make clear at this stage of our progress, when we have hardly any chemical knowledge.

Just as we used iron and sulphur for conducting a synthesis, because these substances seemed especially suitable for our method of introducing the reader to a knowledge of chemistry, so we must select some substance especially suited for carrying out an analytical process.

Oxide of mercury will serve us well for this purpose. It is a red powder, found in commerce: we shall learn how to prepare it at a later time. The word *oxide,* which is so often heard, is derived from the name oxygen. As sulphide of iron is composed of sulphur and iron, so oxide of mercury (or mercury oxide) is a compound of oxygen and mercury. If we carry out the analysis of mercury oxide, the substance will thereby be decomposed into mercury and oxygen. The solution of this analytical problem is not difficult, because heating the compound causes its decomposition; hence, if we bring our red powder to a sufficiently high temperature, in a properly arranged apparatus, we shall obtain mercury and oxygen gas. In this experiment we obtain a gas, besides a metal; hence, before conducting the analysis we must learn something about general methods of manipulating and working with gases. To do that is not particularly difficult—at least, not so far as we need go into the matter. But as gaseous bodies must play an important part in an introduction to chemistry, we shall examine this subject somewhat in detail.

For working with gases a basin containing water is required; this basin, which may be round or with corners, is called a *pneumatic trough* (A, figs. 8 and 9). A vessel is needed for collecting the gas to be examined ; this vessel is made of glass, and is generally cylindrical in form. A strip of metal, pierced with holes, and called a *shelf*, hangs in the water in the trough (B, figs 8 and 9). This is all the apparatus required. If a glass cylinder with a foot is laid in the water in the trough so that it is entirely filled with water (see fig. 8), and it is then raised (with the foot upwards) without removing the open end from under the water (see fig. 9), the water in the cylinder will,

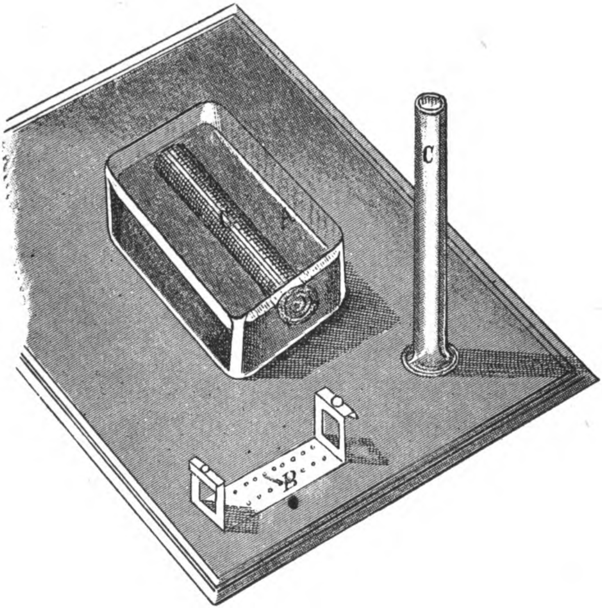

Fig. 8.—Apparatus for working with gases : pneumatic trough, shelf, and cylinder ; also method of filling a cylinder with water.

of course, be prevented from flowing out by the pressure of the air outside the cylinder. We are taught by physics that the atmospheric pressure will balance the pressure of a column of water about ten metres in height; our cylinder might, therefore, be ten metres long without there being any fear of the water flowing out when it was set up on end in the manner just described. When the cylinder C has been filled with water, and set upright with its open end under the water, it is pushed on to the shelf B, of course without removing it from the water in the trough. We have now what we wanted—namely, a space wherein we can collect a gas. If we allow a gas to enter the cylinder through one of the holes in the shelf (placed under the cylinder), as is shown in fig. 10, the light gas will rise through the water in the form of bubbles, and will collect above the water, which it will drive out of the cylinder.

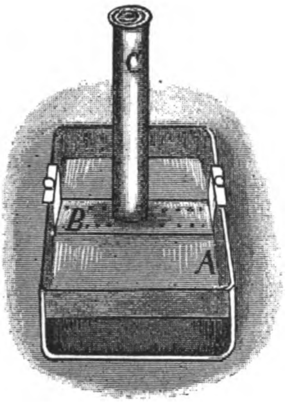

Fig. 9.—Cylinder filled with water, and inverted in water in pneumatic trough.

If a gas must not be collected over water, some other liquid—mercury, for instance—may be used in the place of water. The method of collecting gases over mercury differs in no respects from that which we have been using with water as the liquid. Fig. 43 represents an example of the use of mercury.

The analysis of mercury oxide is carried out in the following way. The red powder is shaken into the retort A (fig. 10). The receiver V is joined, air-tight, to the retort. The suitably bent glass tube E passes through a cork, which fits tightly into the opening D of the receiver V; the lower end of the glass tube passes under the water in the trough; this tube will serve to lead the oxygen gas under the shelf B, so that it may

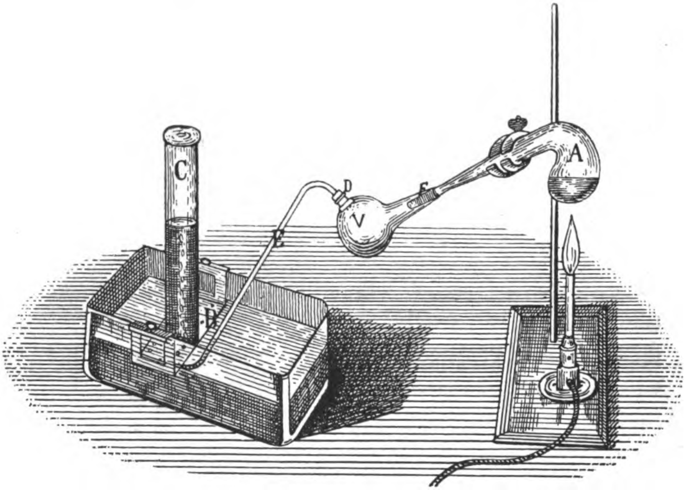

Fig. 10.—Decomposition of oxide of mercury into mercury and oxygen, and collection of the oxygen.

reach the cylinder C and collect therein. At the beginning of the experiment the open end of the gas-conducting tube should be under the water, but not yet under the shelf. If we now heat the mercury oxide in the retort, by placing a lamp beneath it, we at once see gas-bubbles escaping from the open end of the gas-conducting tube, rising in the water of the trough and issuing into the air. The bubbles which appear at the beginning of the experiment are nothing but air, which is expanded by the heat in the retort, and, not finding room enough in the apparatus, issues from the end of the glass tube that opens under the water. Soon, however, gas-bubbles begin to rise more regularly and in greater abundance. These, which partly consist of oxygen, are allowed to escape for a time, in order that they may carry with them the air from the retort and the other parts of the apparatus. After about two minutes this has been accomplished; and now, as pure oxygen is coming off, we move the end of the gas-conducting tube under the shelf, so that the gas may rise into the cylinder and collect therein, as shown in fig. 10.

In order to prove that the gas which has been gradually filling the cylinder is oxygen, we make use of the property of this gas to maintain combustion in the most vigorous way, and to act on burning or glowing bodies much more energetically than air, so that a slip of wood which just glows, and is therefore about to expire, in the air, bursts into flame immediately it is brought into this gas. For this purpose we slip the cylinder off the shelf into the open water, and place a glass plate on its open end under the water. Then we raise the cylinder from the trough, reverse it, and place it on the table in its ordinary position, with the open end upwards. At the moment when we remove the glass plate which has been closing the mouth of the cylinder we plunge a glowing slip of wood into the vessel. At once we see the slip of wood burning brightly within the cylinder (that is, in the gas contained therein), whereby the presence of oxygen gas is demonstrated.

It should be noted that the end of the gas-conducting tube which is in the trough should always be removed from the water before a process wherein gas is produced is discontinued—before, for instance, the flame is removed from under the vessel wherein the gas is produced.

If this is not done, water will be driven back into the apparatus by the pressure of the air, because the gas in the apparatus will contract as it cools. If the apparatus is hot, the cold water driven into it will probably cause it to break; in any case, the water will make the contents of the apparatus wet. If the open end of the glass tube is in the air, in place of in water, air will enter the apparatus: but this does no harm, for when the apparatus is thoroughly cold it is in the same condition as it was before the experiment began; it contains air, as it did then.

If we now look more closely at the receiver v connected with the retort, we notice that some mercury has collected therein. Mercury is volatilised—that is, it distils just as we saw water distil—at the high temperature needed for the decomposition of mercury oxide into its two constituents. The vapour of the mercury is condensed to liquid mercury by cooling in the receiver.

Our analysis is now finished. We have done what we proposed to do; we have separated mercury oxide into the two substances whereof it is composed—mercury and oxygen gas.*

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* Concerning the use of the words *gas* and *vapour*, it should be noticed that it is customary to speak of *gases* as those kinds of airs (including common air itself) which are not changed to liquids at the ordinary temperature, and of *vapours* as those kinds of airs which become liquids at the ordinary temperature.

The most appropriate thing to do now would certainly be to endeavour to analyse, more completely to decompose, the mercury and the oxygen which we have just obtained. Were we to make that attempt, we should find that all our labour was in vain. Both of the substances obtained from mercury oxide turn out to be undecomposable. Undecomposable substances, such as the two we have just recognised—substances that resist all analysis and must therefore be looked on as not composed of more than one thing—are called Elements in chemistry.

Our very simple analysis has brought us at once to the elements. During the hundreds of years chemists have been examining all our material surroundings everything has been analysed, in order to find out the elements—the constituents of bodies which cannot themselves be further decomposed, and by whose union these bodies are formed. Nothing has been forgotten, whether we think of the colouring materials wherewith the ceilings of our rooms are covered, or the bricks wherewith our houses are built, or the hair of our heads, or the coal-gas by whose burning our rooms are lighted in the evening. And these analyses of the numberless things we see on the earth have brought to light the remarkable fact that nature produces all these things with the help of an astonishingly small number of elements. About seventy-five elements are knwon to-day : this number cannot be said to be very large.

Now it also happens that most of the elements are so rare that they need not be taken into account by those who are not chemists, since they have no influence on the composition of the common things around us. To take an example: the element germanium, discovered in 1886, was obtained from a mineral, unknown before that time, which was found in a very deep working in a mine at Freiberg, in Saxony. This mineral, of which very small quantities are found in the workings referred to, is the source of germanium, although traces of that element have also been found in certain other very rare materials; hence we can understand that to obtain germanium in considerable quantities—if, indeed, that could be done at all—would be more difficult than to get quantities of, say, diamonds, which can be had by the bushel if only one will pay for them.

When, by their analyses, chemists determine the elements whereof the substances they examine are composed, they find that, speaking broadly and leaving out of account the rarer minerals, about twenty-five elements enter into the compositions of these substances. As the elements found in this or that substance could not be carried in the memory, it was necessary to note down the results of analyses—that is to say, the names of the elements. Of course, chemists would not write these few names in full every time, but from constant use they would learn to recognise what element was meant when only one or two letters of the name were noted. The custom of chemists of designating the elements by the initial letters of their names had its origin somewhat in this way. A similar device of shortening names is used in many cases in ordinary affairs; for instance, there is the custom of not writing the names of well-known people in full, because we know the signification of the contractions in common use. To take an example: everyone who read in *Punch's Essence of Parliament* of Mr. G. knew that contraction to refer to the Right Honourable W. E. Gladstone.* For phosphorus chemists write P, for bromine Br, for aluminium Al; and we can understand these contractions without any trouble when we find them in books which deal with chemistry. It is to be remarked here that, as learned people used the Latin language in the old days, the contracted form of the names of many elements which have been long known are derived from the Latin names of these elements; for instance, for iron one writes Fe (from the Latin *ferrum*), and for gold Au (from the Latin *aurum*). Every chemist, to whatever country he may belong, uses the same contractions; hence these contracted forms are equally well understood by all. It is scarcely necessary to say that no sort of mystery is to be attached to these abbreviations.

We shall now give an alphabetical list of the names of the elements at present known, and opposite each name we shall place the abbreviated symbol of the element that is employed everywhere.

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* The example given in the text is Just. v. Liebig, which every German knows to stand for Justus von Liebig.

LIST OF THE ELEMENTS,

AND THE ABBREVIATED METHOD OF WRITING THEIR NAMES.

Name of Element.	Shortened form of Name.	Name of Element.	Shortened form of Name.
Aluminium . .	Al	Molybdenum . .	Mo
Antimony (*stibium*).	Sb	Neodymium . .	Nd
Argon . . .	A	Neon . . .	Ne
Arsenic . . .	As	Nickel . . .	Ni
Barium . . .	Ba	Niobium. . .	Nb
Beryllium . .	Be	Nitrogen. . .	N
Bismuth. . .	Bi	Osmium. . .	Os
Boron . . .	B	Oxygen . . .	O
Bromine. . .	Br	Palladium . .	Pd
Cadmium . .	Cd	Phosphorus . .	P
Caesium . .	Cs	Platinum . .	Pt
Calcium . . .	Ca	Potassium (*kalium*)	K
Carbon . . .	C	Praseodymium .	Pr
Cerium . . .	Ce	Rhodium . .	Rh
Chlorine . .	Cl	Rubidium . .	Rb
Chromium . .	Cr	Ruthenium . .	Ru
Cobalt . . .	Co	Samarium . .	Sa
Copper (*cuprum*) .	Cu	Scandium . .	Sc
Erbium . . .	Er	Selenion . .	Se
Fluorine. . .	F	Silicon . . .	Si
Gallium . . .	Ga	Silver (*argentum*) .	Ag
Germanium . .	Ge	Sodium (*natrium*) .	Na
Gold (*aurum*). .	Au	Strontium . .	Sr
Helium . . .	He	Sulphur . . .	S
Hydrogen . .	H	Tantalum . .	Ta
Indium . . .	In	Tellurium . .	Te
Iodine . . .	I	Thallium . .	Tl
Iridium . . .	Ir	Thorium. . .	Th
Iron (*ferrum*) .	Fe	Tin (*stannum*) .	Sn
Krypton . . .	Kr	Titanium . .	Ti
Lanthanum . .	La	Tungsten (*wolfram*)	W
Lead (*plumbum*) .	Pb	Uranium . .	U
Lithium . . .	Li	Vanadium . .	V
Magnesium . .	Mg	Xeon . . .	Xe
Manganese . .	Mn	Ytterbium . .	Yb
Mercury (*hydrargyrum*) . .	Hg	Yttrium . . .	Y
		Zinc . . .	Zn
Metargon . .	Mt	Zirconium . .	Zr

With the help of these contracted forms, let us now write the two chemical compounds wherewith we are fairly familiar—namely, iron sulphide and mercury oxide. The process is very simple. The table shows that the abbreviation for sulphur is S, and for iron Fe, hence the letters SFe mean iron sulphide to the chemist; and as the contractions for mercury and oxygen respectively are Hg and O, he writes mercury oxide HgO. Such shortened forms of writing are called the *formulæ* of the compounds; SFe is the chemical formula of iron sulphide, and HgO is the chemical formula of mercury oxide.

To go a step farther. Not only can the chemical compounds be indicated by using the abbreviated forms of the names of the elements, but the chemical processes also whereby these compounds are formed can be expressed in a very simple way. Such expressions are called *chemical equations.*

For this purpose the sign + is placed between the formulæ of the substances which interact, and the formula of the substance formed is placed after the sign of equality. The formation of iron sulphide is expressed as follows :—

> Sulphur and iron produce iron sulphide; or, using the abbreviations, $S + Fe = SFe$.

Such *chemical equations* make it possible to express the results of the chemical reactions of substances in a very clear, brief, and precise way.

However pleasing and satisfactory may be this clear method of expressing chemical reactions by means of the shortened designations of the elements, it is not to be denied that, so far as our experience of the use of these contractions has gone, one might doubt whether much is to be gained from what may be called a special way of writing the expression of thoughts. To write the names of the elements in full would serve the purpose in view, and would save one the trouble of learning to understand this special method, which, it must be confessed, savours somewhat of stenography. But in a later part of this book, when we shall have more chemical knowledge, we shall learn the full meanings of these shortened expressions, which stand for much more than merely the names of the elements, and, understanding them, we shall be able to estimate their value. We shall perceive why these abbreviated expressions are indispensable to chemists, and why, considering the matter from the position whereat chemistry has now arrived, it is impossible even to think of giving them up.

If we now turn over in our minds what will be the best method of proceeding in order to advance from the desultory information we have acquired to *connected chemical knowledge*, we shall be convinced that without doubt the most suitable method would be to bring one element after another, and the compounds of one element after those of another, within the range of our consideration. By following this plan we should certainly overlook nothing; for, as all things are composed of the small number of elements given in the table on p. 22, this method would involve the consideration of all material substances that exist. The complete carrying out of this principle would, of course, demand unlimited time; nevertheless, the idea whereon the plan is based is certainly sound. We must limit ourselves to this extent only: we must confine our attention to certain selected elements and their compounds. By reviewing these bodies we shall gain what we are chiefly concerned to gain in this introduction to chemistry—some knowledge of those chemical occurrences which are especially important; and we shall be able to draw conclusions of general applicability and general interest, some of which extend far beyond the special domain of chemistry.

With which element, then, shall we begin?

The elements may be solid, liquid, or gaseous. Iron, for instance, is a solid, bromine a liquid, and hydrogen a gas. The elements are divided into two main classes—the metals and the non-metals. What kind of elements the metals are follows from the ideas we connect with the word *metal* in ordinary life. The non-metals are those elements which have not metallic properties. We shall begin with an element belonging to the class of non-metals—namely, *hydrogen*, which is the specifically lightest body that is known to us.

At this point it may be allowed to elucidate the notion of *specific gravity*—a notion we shall frequently use, and one which, perhaps, is not familiar to every reader. Suppose that a glass flask whose capacity, to a mark on the neck, is exactly one litre (see fig. 11) is filled with hydrogen; then, if the flask is weighed on a balance, the weight of it is less than would be the weight of the same flask filled with any other substance.

We should find that a litre of hydrogen weighs only ·0896 gram, whereas a litre of air, for example, weighs 1·295 grams. By dividing one of these numbers by the other we see that hydrogen is 14·4 times lighter than air. The density of hydrogen is one 14·4th part of that of air. We should, of course, have arrived at the same result had we compared the weights of any equal volumes of hydrogen and air; it is not necessary that one litre of each should be chosen. *Specific gravity* expresses, in a completely general way, the relation between the weights of those quantities of two substances which occupy equal volumes.

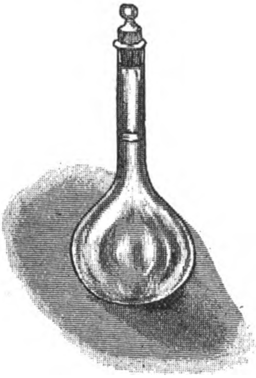

Fig. 11.—Litre flask.

While the specific gravities of gases are referred to hydrogen as the unit—or, as is often said, to hydrogen taken as unity—the specific gravities of all liquid and solid bodies are referred to water as unity, because if these also were referred to hydrogen the numbers expressing the specific gravities of solids and liquids would be inconveniently large. For instance, the specific gravity of iron is 7·78; this tells us that, as one cubic metre of water weighs 1000 kilograms, one cubic metre of iron weighs 7780 kilograms. Let us calculate how much lighter hydrogen is than water. A litre of hydrogen weighs ·0896 gram; a litre of water weighs 1000 grams: by dividing 1000 by ·0896 we obtain the desired number—namely, 11,160.

Hydrogen, then, is 11,160 times lighter than water; in other words, 11,160 litres of hydrogen weigh one kilogram.

It may not be without interest to learn what is the specifically heaviest metal, and thus to know what is the specifically heaviest substance found in nature. This substance is the metal *osmium*. The specific gravity of this metal is 22·48, referred to water as unity: hence a piece of osmium of the bulk of one litre weighs 22,480 grams—that is, 250,893 times as much as a litre of hydrogen; in other words, the specific gravity of osmium is 250,893 referred to hydrogen as unity.

HYDROGEN GAS.

THE name *hydrogen* [= water producer] indicates that this gas is an essential constituent of water. The chemical analysis of water shows that substance to consist of two gases. Because it occurs in water, one of these gases is called hydrogen; the other gas, which, by uniting with hydrogen, forms water, was obtained by us by analysing mercury oxide—it is oxygen.

After what we have already seen, we need not be at all astonished that two gases should unite to form a liquid. Mercury oxide, which we analysed, is a solid red body; when we decomposed it into its elements we found that it consists of mercury, which is a liquid, and oxygen, which is a gas. In that case we had to do with a solid body, which proved to be composed of a liquid and a gas; now we have to do with the liquid body water, which is composed of two gases. In short—and of this we shall have many examples as we proceed—the purely external characters of the elements are of no importance when we are considering the compounds which these elements form by uniting with one another.

If we could find anything for which oxygen has a greater affinity than it has for hydrogen—anything wherewith oxygen would unite in preference to uniting with hydrogen—we should be able to separate the two elements that are united in water. Oxygen will unite with any body by which it is more attracted than by hydrogen: when this occurs, the hydrogen of the water will be set free; and as hydrogen is a gas, it will escape from the water in bubbles. Now there are such substances — substances wherewith oxygen unites especially willingly. The metal sodium is one of these. This metal is a constituent of common salt, which consists of sodium and chlorine. We shall not stop here to examine the process whereby sodium is obtained by common salt; that will came later: at present we want this metal only as a means to an end.

Sodium has so great an affinity for oxygen that it soon unites with that element (which is a constituent of the atmosphere) if the metal is left exposed to the air. It must be kept, therefore, under some liquid which does not contain oxygen and will prevent the oxygen of the air getting at the sodium. Paraffin oil is usually employed for this purpose (see fig. 12).

To prepare hydrogen gas by the use of sodium, we wrap a small piece of the metal, taken from under paraffin oil, in wire-gauze, fasten this to the end of a rod (A, fig. 12), and bring it, in the manner shown in fig. 12, under a cylinder filled with water and standing on the shelf of a pneumatic trough. Gas-bubbles at once begin to rise in the cylinder, and after a short time the cylinder is quite filled with gas. This gas is hydrogen. We now slip a glass plate over the mouth of the cylinder under the water, and reverse the cylinder, just as we did when we filled a cylinder with oxygen (see p. 17); then we withdraw the glass plate, and *at once* bring a lighted taper to the mouth of the cylinder. The taper sets fire to the contents of the cylinder—that is, to the gas we have obtained from water — and we see the gas burning with a feebly luminous flame The metal sodium is, then, able to decompose cold water into its constituents, a fact which is certainly somewhat remarkable.

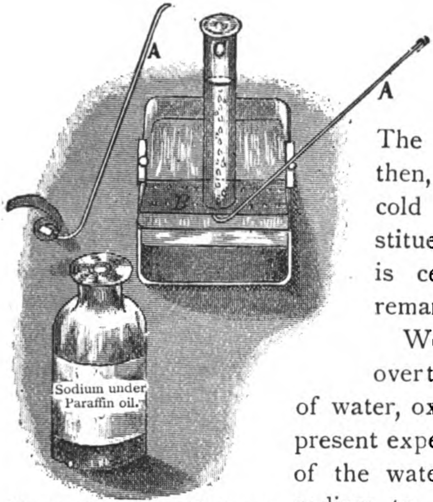

Fig. 12.—Production of hydrogen by reaction of sodium with water.

We must not pass over the other constituent of water, oxygen gas. In the present experiment the oxygen of the water unites with the sodium to form a compound which we know will be called sodium oxide. As that compound dissolves in the water, we have no direct visible proof of its production in this experiment. To obtain the compound it would only be necessary to evaporate the solution of it in water to dryness; but to do that is not our task at present.

The manipulation of sodium is not particularly convenient. Many metals that are known to us in ordinary life decompose hot water in the same way as we have seen sodium decompose cold water. Hydrogen was first obtained from water by passing water-vapour over red hot iron : under these conditions iron combines with the oxygen of the water to form iron oxide, and the hydrogen is set free. This experiment must be regarded as of fundamental importance; for the consideration of it teaches how greatly the way of looking at things of those who investigate nature, and indeed of the whole race, must have changed after the discovery, made in the last quarter of the eighteenth century by the aid of this experiment, that water—a substance thought of for a thousand years as something which could not be decomposed—was formed of two constituents.

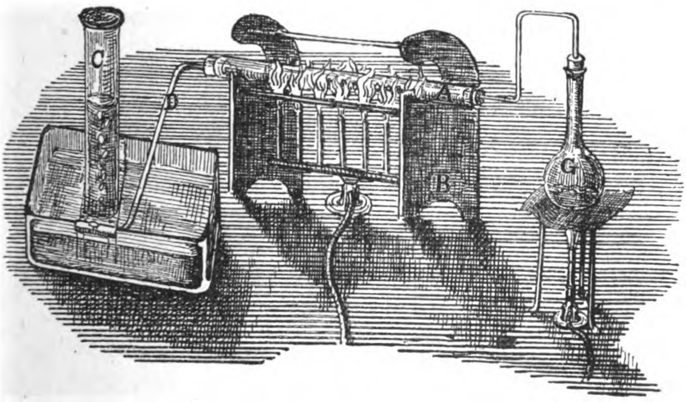

Fig. 13.—Preparation of hydrogen by passing water-vapour over red hot iron.

In conducting this experiment, which we shall do here because of its fundamental significance, we proceed as follows. We fill a porcelain tube (A, fig. 13) with little spirals of iron, formed by twisting thin iron wire, and we lay the tube in the furnace (B in the figure) in such a position that the corks in the ends of the tube are not burnt when the lamps of the furnace are lighted. Water is heated in the flask G; the water-vapour thus produced is allowed to pass through a glass tube into the porcelain tube A, wherein the gaseous water comes into contact with the red hot iron, which, being in the form of wire, exposes a large surface. Water heated above 100° C. [212° F.] is generally called water-vapour; from our experiments on the distillation of water we know that this vapour is a perfectly transparent air, and behaves in all respects as a gas. The glowing iron seizes the oxygen of the water-vapour, and, combining with it, forms an oxide of iron. The hydrogen gas, which is now set free, passes through the glass conducting-tube D, and issues under the inverted cylinder C (which is filled with water and stands in the pneumatic trough), wherein it collects. When the cylinder is filled with the gas, we convince ourselves, by the same means as before, that we have to do with a combustible gas, produced from the water; this gas, as we know, is called hydrogen.

Now that these two methods of preparing hydrogen have brought home to us the existence of this gas in water without giving us visible demonstration of the oxygen which forms a constituent of water, we are in a position to conduct the decomposition of water in such a way as to obtain the two gases. We shall do this with the help of electricity. The electric current is able to decompose compounds of various kinds, provided they conduct electricity, into their elements: it splits water into hydrogen and oxygen. The apparatus we require is very simple. The poles of a galvanic battery (A, fig. 14) are arranged in the water of a pneumatic trough so that they come beneath the cylinders H and O, which are filled with water. In this experiment the trough consists of a very short-stemmed funnel, stopped by a cork through which pass the conducting wires to the two poles. As soon as we cause the current to pass we notice bubbles of gas rising from the two poles. The hydrogen gas (H)

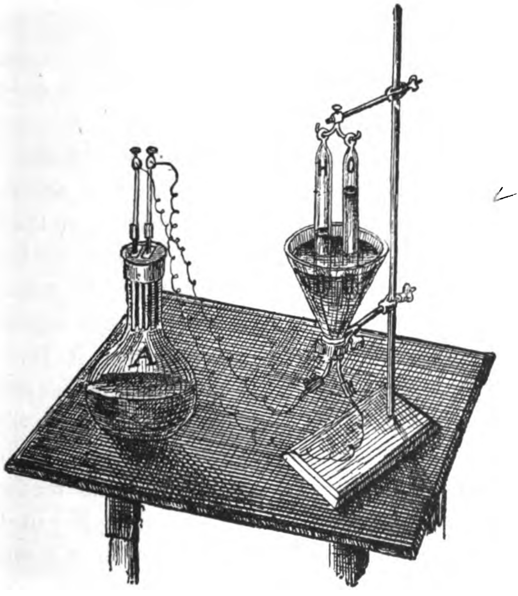

Fig. 14.—Electrolytic decomposition of water into hydrogen and oxygen.

collects at the negative pole, and the oxygen gas (o) at the positive pole; and we notice that the volume of the former is greater than that of the latter. Accurate investigations have shown that the volume of the hydrogen gas is double that of the oxygen gas.

There is another method for obtaining hydrogen gas, which is much more convenient than those we have used, and for that reason is generally employed in the laboratory. That method we shall now consider.

There are many metals which cause the production of hydrogen from a mixture of an acid with water when such a mixture is merely poured on them. In these reactions there is no need either to heat the metal or to use an electric battery. As we do not yet know what acids are, we must accept this method without going into details at present: it is for this reason that the process has been considered after the others. We shall soon, however, gain an insight into the chemical bearings of the reaction. To carry out the preparation of hydrogen by this method, we place the metal—zinc filings, for example—in a flask (A, fig. 15), and we close the flask with a cork bored with two holes, through one of which passes a long-stemmed funnel (B, fig. 15), and through the other a bent glass tube (D, fig. 15), which serves to lead the gas from the flask to a cylinder (C) in the pneumatic trough. As soon as the apparatus is arranged we pour diluted sulphuric acid through the funnel-tube B on to the zinc in the flask, and without more ado we obtain a stream of hydrogen gas. To prevent the gas escaping through the funnel-tube instead of streaming into the cylinder, we must, of course, pour so much diluted sulphuric acid into the flask that the lower end of the funnel-tube is under the surface of the liquid and is thereby closed.

By employing a large and suitable apparatus this method enables us to have always at hand a means of obtaining a stream of hydrogen. The stream will last, of course, only until the sulphuric acid or the zinc is used up, but that will be a considerable time. The apparatus generally employed for this purpose is that first proposed by Kipp. It consists of two parts—a funnel with a spherical widening (A, fig. 16), and a lower part into which the funnel is ground air-tight (at B, fig. 16). Fig. 16 shows the separate parts of the apparatus both when empty and when filled. The lower part consists of the bulb C, which is connected with the space D by the contraction V. The bulb C

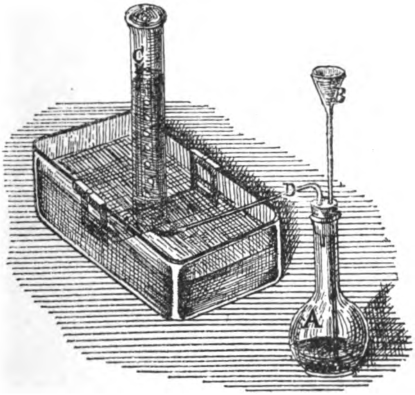

Fig. 15.—Collection of hydrogen gas over water.

has an opening (E)—such an opening is called a *tubulus* —closed by a cork through which passes a glass tube furnished with a stopcock (F). In using this apparatus for making hydrogen gas, the funnel A is set in the lower part, the bulb C is about half filled, through E, with pieces of zinc, which are prevented from falling into the lowest part D by the contraction V, and the tubulus is closed by pressing into it the cork with the stopcock F. Diluted sulphuric acid is then poured into the funnel A, through which it passes into the lower vessel D. As long as the stopcock F is kept closed the acid cannot either fill D or rise into C, and therefore cannot come into contact with the zinc, because it is prevented by the air in the lower vessel and in the bulb; but as soon as the stopcock F is opened the air escapes from C and D, driven out by the acid falling down from A, and the acid rises through V until it reaches the zinc. Immediately the acid and the zinc

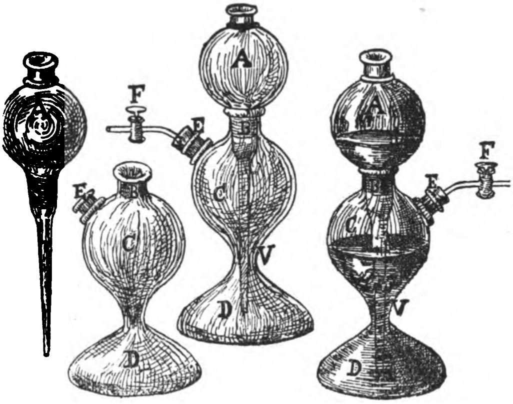

Fig 16.—Kipp's apparatus.

are in contact the evolution of hydrogen gas begins. When no more hydrogen is required the stopcock F is closed. As the acid and the zinc are still in contact, hydrogen continues to be produced; but as the gas cannot escape from C, it fills the bulb, and its pressure automatically drives the acid out of C and so removes it from the zinc. Part of the acid finds its way into the lower vessel D and part of it into the funnel A. The evolution of gas ceases, to begin again when the stopcock is opened and the acid is thereby allowed to reach the zinc. In a word, an apparatus of this kind is a convenient and portable hydrogen manufactory.

The extraordinary lightness of hydrogen gas may be demonstrated by the use of a small balloon made of collodion. Such a balloon is placed on the end of the glass tube leading from the Kipp's apparatus, the stopcock is opened, and so the balloon is filled with hydrogen. On removing the balloon from the apparatus, it rises like an "air-balloon" to the ceiling of the room; hence the balloon and its contents must be much lighter than the air which surrounds us.

Hydrogen is a colourless and odourless gas. When ignited it is burnt to water. The quickest way of proving this is to allow a hydrogen flame to burn within a large glass bell-jar, in the manner shown in fig. 17. In a very short space of time we see that the inside of the jar is moistened, and it is not long before drops of water trickle from the open end. This formation of water can be caused only by the flame which is burning in the jar; hence the hydrogen must be burning to water.

If hydrogen is mixed with air, we get a mixture which burns, when ignited, with a sharp explosion. To show this we fill a cylinder with water, invert it in the pneumatic trough, and allow hydrogen, from a Kipp's apparatus, to pass into it until it is half filled with that gas; we then raise the cylinder a little out of the water, so that the air enters and fills it. When a light is now brought to the mouth of the cylinder, the mixture of hydrogen and air ignites with a loud detonation.

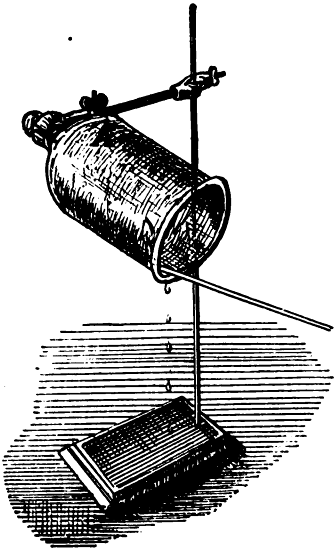

Fig. 17.—Formation of water by burning hydrogen.

If pure oxygen is used in place of air, we get a mixture which explodes with great violence when ignited: this mixture is known as *explosive gas.* It is, of course, the sudden combination of the whole of the gases in the cylinder to form water that causes the explosion. When a cylinder is filled with hydrogen and the gas is ignited, combination can take place only in so far as the outer air, which supplies the oxygen, is able to come into contact with the hydrogen.

We can scarcely say anything more about hydrogen at present, because of the other elements wherewith it forms compounds we know nothing except the names. In the course of this INTRODUCTION we shall, however, very often come back to hydrogen, because we shall have to speak of its compounds with other elements—compounds of the greatest importance—when we have learned something about these elements. The properties of hydrogen mark it off from the other elements, so that it stands in a somewhat isolated position.

We now proceed to a group of four elements which are very much alike; these are the elements chlorine, bromine, iodine, and fluorine.

CHLORINE, BROMINE, IODINE, FLUORINE,

AND THEIR COMPOUNDS WITH HYDROGEN.

CHLORINE, like hydrogen, is a gas. Just as we often omit the word *gas* when speaking of hydrogen or oxygen, so we do not always say chlorine gas, but only chlorine.

To prepare chlorine gas we use the reaction between *hydrochloric acid* and *pyrolusite*. These two substances are strange to us as yet. The first, hydrochloric acid, is a compound of hydrogen with chlorine, and we should therefore expect it to be called hydrogen chloride. We shall soon discover why it is spoken of as an acid. The second substance, pyrolusite, is a mineral, quantities of which are found in nature. Because of its chemical composition it is called *manganese peroxide*. Manganese is a metal resembling iron. As we may easily understand, the word *peroxide* implies that this compound is a body rich in oxygen. We already know that oxygen very readily combines with hydrogen to form water: the oxygen of manganese peroxide reacts with hydrochloric acid in such a way that it combines with the hydrogen of that compound to form water, while the chlorine is set free.

We shall become acquainted later with the equation—that is, the precise statement in chemical language—which expresses the reaction whereby chlorine gas is produced. That equation will also show us what becomes of the manganese in the reaction.

Chlorine was discovered in 1774. The name chlorine (from the Greek word χλωρός = yellow-green) was given to it because of its characteristic colour. The gas has a peculiar, choking smell; it acts on almost everything wherewith it comes into contact. The action of chlorine on the lungs, for instance, is very great; if it is breathed it soon causes blood-spitting; the gas must therefore be handled with the greatest care. Chlorine is fairly soluble in water, so that if we tried to collect it in a cylinder over water, as we collected hydrogen and oxygen, we should obtain scarcely any gas in the cylinder; for, as the gas is dissolved by water, it would not appear in the cylinder, but would be swallowed by the water. That gases should be dissolved by water can appear strange only for a moment; for why should not water, that dissolves so many things, such as salt, sugar, and the like, not dissolve gases also which are passed through it? A solution of chlorine in water is called *chlorine water.*

In order to prevent injury to health, experiments with chlorine should be conducted in a draught-chamber. A draught-chamber is an arrangement found in all laboratories; it is used to prevent accidents when working with poisonous gases or vapours. It is a cupboard with glass walls, the back whereof is the wall of the room (see fig. 18). A pipe leads through the wall to the open air in the manner of a chimney; this pipe should be carried above the roof of the building. If a flame is burnt in this pipe (every draught-chamber is furnished with a suitably arranged gas-jet; see A, fig. 18), all hurtful gases and vapours that may be

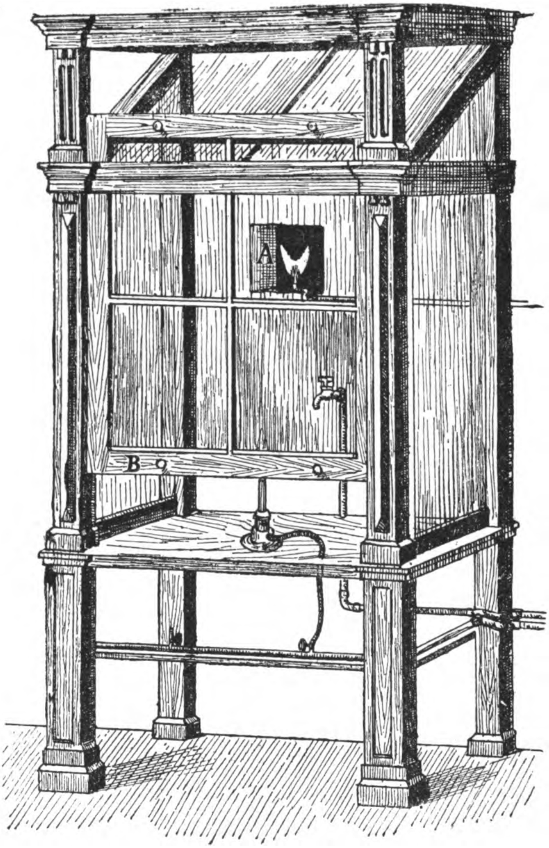

Fig. 18.—Draught-chamber for working with poisonous gases and badly smelling substances.

produced in the chamber are drawn up the pipe and are discharged into the open air above the roof of the building. If the front sash of the chamber (B, fig. 18) is kept slightly open, the draught will be so strong that no inconvenience will be experienced in the working-room when experiments with badly smelling gases are carried on in the chamber. A draught-chamber should always be furnished with gas and water taps, as is shown in the figure.

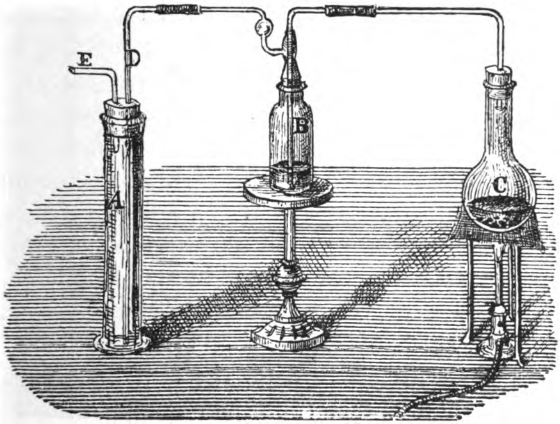

Fig. 19.—Collection of chlorine gas by making use of its high specific gravity.

The apparatus that is required for preparing chlorine is shown in fig. 19; this apparatus must be set up in the draught-chamber. Pyrolusite (manganese peroxide) is placed in the flask C; sufficient hydrochloric acid to cover the pyrolusite is added, and the flask is warmed. A yellowish gas very soon begins to come off from the mixture ; this gas gradually drives out the air and fills the whole apparatus. The method which is employed for filling vessels with hydrogen and most of the other gases, by using a pneumatic trough, cannot be applied in the case of chlorine. When we wish to fill a vessel with chlorine we take advantage of the fact that this gas is much heavier than air. Chlorine gas is 2·45 times heavier than air. If, then, we lead chlorine gas to the bottom of a cylinder (A, fig. 19), the cylinder will be gradually filled with the gas ; for the heavy chlorine, seeking to remain in the lower part of the cylinder, drives out the air. If the mouth of the cylinder were open, it would not be possible to prevent the admixture of some air with the chlorine in the upper part of the cylinder. In order to ensure the complete filling of the cylinder with chlorine, we place a cork, bored with two holes, in the mouth of the cylinder, and through one of these holes we pass a tube (D, fig. 19), which conducts the chlorine to the bottom of the cylinder, while through the other hole passes a short piece of glass tube (E in the figure), cut flush with the under surface of the cork, which allows the exit of the air from the cylinder. The air is thus gradually but completely driven out by the chlorine gas. When pure chlorine is issuing from the tube E we know that the cylinder is quite full of that gas.

Fig. 19 shows a flask (B), containing some liquid, placed before the cylinder which we wish to fill with chlorine. As the tube which conducts the chlorine passes under the surface of the liquid in the flask B, and nearly to the bottom of that flask, the stream of chlorine must bubble through the liquid in B. Such a flask, inserted in an apparatus for producing a gas, is called a *washing-flask* (sometimes a *wash-bottle*). In the present case the washing-flask contains water; this catches and retains any traces of hydrochloric acid that may be carried over from the vessel wherein the chlorine is produced.

Flasks of this kind can be used not only for washing, but also for drying, gases; for gases which are evolved from mixtures that contain water are moist, just as the air that surrounds us is moist because it is so often in contact with water. There are certain substances which have so strong an attraction for moisture that they take away, and retain, or hold fast, all the moisture from a gas passing through them. Sulphuric acid, which we shall examine in detail at a later time, is one of those substances which have a great attraction for water. Besides rendering this service, which is often of great importance, washing-flasks enable us to determine whether the evolution of a gas from the materials that produce it is proceeding too quickly or too slowly, and therefore whether it is necessary to slacken or to quicken the reaction: we have only to watch the rate whereat the bubbles of gas pass through the liquid in the washing-flask. For this reason, if for no other, almost every gas-evolving apparatus is furnished with a washing-flask.

We shall now use the cylinders we have filled with chlorine, in the way already described, for a series of experiments.

Into the first cylinder we shake some antimony.

Antimony is a metal-like element; it is so brittle that it can be powdered. Fig. 20 represents the antimony falling into the chlorine in a cylinder and burning therein. The two elements chlorine and antimony combine, and antimony chloride is produced. The striving to combine of the elements is so great that the act of combination is accompanied by the glowing of the materials and the phenomena of fire.

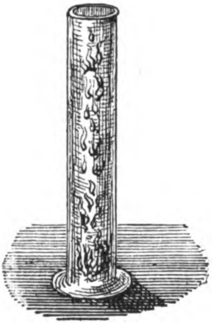

Fig. 20.—Antimony burning in chlorine.

Into the second cylinder we lower a small lighted candle fastened to the end of a wire (see fig. 21). At once the flame, which was white, becomes red, and, besides this, the cylinder gets filled with soot. This is due to the action of the chlorine on the compounds of the two elements carbon and hydrogen, called hydrocarbons, which are present in such a flame. The chlorine combines with the hydrogen of these compounds to form hydrochloric acid (we know that chlorine and hydrogen have a great tendency to combine with one another); hence the carbon must separate from the hydrocarbons. We see this carbon, in the form of soot, filling the cylinder.

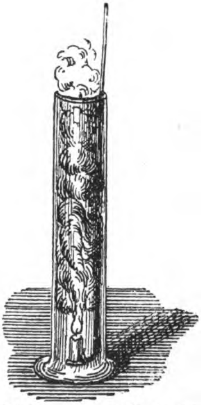

Fig. 21.—A candle burning in chlorine.

In these experiments we have two examples of the violent way wherein chlorine attacks various substances.

In one case chlorine combined with another element with the production of fire; in the other case it completely changed the character of a luminous flame.

The great striving to combine that there is between chlorine and hydrogen, which is the cause of the production of soot from a candle burning in chlorine, may be enforced directly. If a mixture of these two gases, prepared by filling a cylinder half with chlorine and half with hydrogen, is placed in ordinary daylight, the gases combine gradually to form hydrochloric acid; but if a direct ray of sunlight falls on the mixture, the gases combine instantaneously (of course, to form hydrochloric acid) and with a very violent explosion.

If some solution of indigo is poured into a third cylinder filled with chlorine, the indigo is at once decolourised. Pieces of coloured cloths fare no better; they are bleached in a very short time. Because of its chemical energy, chlorine rapidly destroys colours of many sorts. Very wide use is made of this property of chlorine; for instance, it is applied, as is well known, to bleaching clothes, material for making paper, and to many other industrial purposes. We have seen that it is not exactly agreeable to work with a substance so destructive of health as chlorine, even in a chemical laboratory. The use of chlorine in mills, paper factories, and the like would scarcely be possible. The difficulty has been got over in the following way. Chlorine is passed over slaked lime in specially constructed chemical factories. A substance called bleaching powder, which is known by everyone to have strong bleaching power, is thus produced. Bleaching powder can be bought for the purpose of any industry wherein bleaching is practised, so that it is not necessary for the manufacturer to concern himself with the preparation of chlorine.

Let us make some bleaching powder. To do this it is only necessary to arrange an apparatus as shown in fig. 22, and to allow chlorine, made from manganese peroxide and hydrochloric acid, and dried by passing through sulphuric acid in the washing-flask W, to pass over slaked lime placed in the long tube A. The large surface of lime exposed to the action of the chlorine hastens the saturation of the lime with that gas. After some time the lime is changed into bleaching powder.*

In the foregoing experiments the cork which closes the flask wherein the chlorine is generated is bored with two holes; through one of these passes the tube which leads the chlorine to the washing-flask W, and through the other a *safety funnel* is fitted. When hydrochloric acid is poured through this funnel a part of the liquid remains in the looped part of the funnel, as shown in the figure; hence gas cannot escape through the safety funnel, provided the production of gas in the flask is not so rapid that the whole of the gas cannot be carried off by the proper conducting tube (A in fig. 22). Should the rush of gas be too rapid, the increasing pressure in the flask wherein the reaction occurs will lift the liquid plug in the safety funnel, and gas will then be able to escape through that funnel. If there is no safety funnel, the apparatus may be separated into pieces, by the blowing of the cork out of the flask, or by something of that kind. Unskilled experimenters do well to place a safety funnel in every apparatus for making a gas.

The method of bleaching by means of bleaching

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* Bleaching powder is sometimes called *chloride of lime*. It must not be confused with another substance called chloride of calcium, which we shall become acquainted with later.

powder, which has made diverse industries independent of bleaching greens and sunshine, leaves nothing to be desired in the way of convenience. It has only one drawback: the chemical energy of the chloride of lime which destroys colours is not exhausted when the colours have disappeared. On the other hand, after it has bleached the colours—and it does this very quickly—the chloride of lime begins to act on and to destroy the fibres to which the colours adhere. It is therefore necessary, immediately the colours have vanished and the bleaching action has gone far enough, at once to stop the further action of the chloride of lime. This can be done very easily by adding one of several chemicals, all of which are classed together under the name "*antichlors*." These

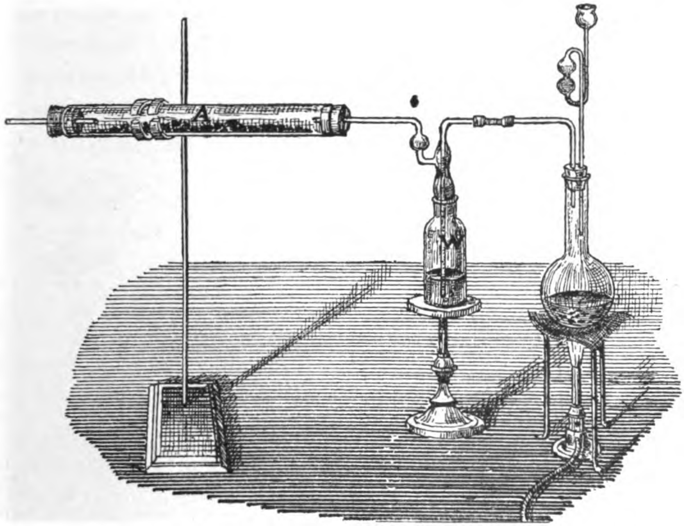

Fig. 22.—Preparation of chloride of lime (bleaching powder).

substances change chloride of lime into the perfectly harmless compound chloride of calcium—a compound related to, but very different from, chloride of lime—while the substances themselves are changed to others which have no harmful action on any kinds of fibres. Thiosulphate of sodium, commercially known as hyposulphite of soda, is the favourite antichlor: we shall learn something of this substance when we come to consider sulphur and its compounds. We shall also defer the consideration of the formula of chloride of lime, which is somewhat complicated, to a later part of the book.

Before leaving the subject of chlorine we shall make silver chloride, because the formation of this compound, which is quite insoluble in water, is used by chemists as a means of recognising the presence of chlorine, and the compound is therefore of especial interest. If a solution of nitrate of silver is added to any liquid containing chlorine, chloride of silver, being insoluble, separates from the liquid. In this way it is easy to make certain of the presence of chlorine in a solution. To observe this reaction, all we have to do is to add a solution of silver to, say, a solution of common salt—that is, sodium chloride. Chloride of silver at once falls down as a white, thick, and (as it is called) curdy precipitate; while nitrate of sodium, which is formed by the reaction of the two substances with one another, remains in the solution. The chemical change may be expressed thus:—

Sodium chloride + silver nitrate = silver chloride + sodium nitrate.
(soluble in water) (soluble in water) (insoluble in water and so precipitates) (soluble in water)

BROMINE.

The element bromine is a liquid with a dark red colour and a most unpleasant smell. Its specific gravity is 3·18 referred to water as unity. The Greek word βρῶμος means a bad smell, and the discoverer of the element derived the name from that word. Bromine is exceedingly like chlorine in its chemical behaviour. We can prepare bromine by a method very similar to that whereby we prepared chlorine. The heating of manganese peroxide with hydrochloric acid gave us chlorine; the heating of manganese peroxide with hydrobromic acid gives us bromine. As in the former case the oxygen of the peroxide seizes the hydrogen of the hydrochloric acid, so in the latter reaction the oxygen seizes the hydrogen of the hydrobromic acid and bromine is set free. But whereas chlorine is a gas, bromine is a liquid: therefore, in order to obtain bromine, we require, not an apparatus for producing a gas, but a retort and a receiver. We put the mixture of hydrobromic acid and manganese peroxide into a retort (A, fig. 23), heat the retort, and collect the bromine that is set free and distils over in a receiver (B, fig. 23). To guard ourselves from the

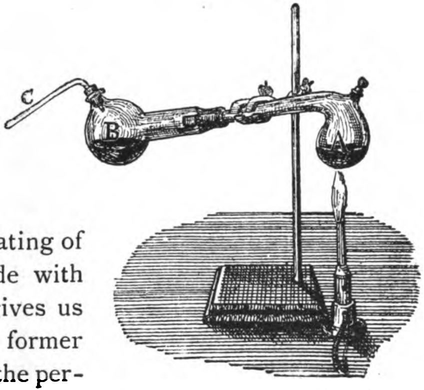

Fig. 23.—Preparation of bromine.

almost unbearable smell of bromine, we lead away any bromine which does not condense in the receiver by the glass tube c to the draught-chamber.

Bromine was discovered in the twenties of the nineteenth century in the mother-liquors of the sea-salts obtained in the south of France. The word *mother-liquor* should be explained before we proceed farther. The explanation may run somewhat as follows:—It seems to us self-evident, but only because we have heard nothing to the contrary, that a chemical compound should have the same composition wherever it may be found. No one doubts, for instance, that distilled water will always be the same substance, whether it be prepared by distilling the water of the Thames, the Orinoco, or the Ganges, or whether it be obtained from sea-water on board a ship in any part of the ocean. In the same way, it seems to us self-evident that common salt, which we know to consist of sodium and chlorine, must always have the same composition, in whatever part of the earth it may be found. A cogent proof of this identity is not, however, furnished save by further considerations. Nature might perfectly well have allowed slight differences in the compositions of chemical compounds in places far removed from one another—American oak, for instance, differs from European oak. But we shall see that, according to the atomic theory, with which we shall soon become acquainted—that is, according to the view that the elements are composed of atoms, a view which sets forth all the phenomena in the domain of chemistry, without exception, in a very wonderful way—*every chemical compound must always have exactly the same* *composition.* The constituents of complicated mixtures of chemical compounds of all kinds, such as that which in its totality represents the thing we call wood, may, of course, be put together in the most different proportions. But every single chemical compound which is found in wood—cellulose, for example—from whatever kind of wood it may be prepared, is always composed of the same elements united in the same proportionate quantities.

It is much less generally known that, besides giving to every chemical compound a composition which is unchangeable for all time, nature has bestowed a determinate form on every compound that appears as a solid. Everyone knows that formless water changes into six-sided star-like shapes at the moment when it becomes snow. This configuration of water which remains for ever the same is also to be recognised in ice. This shape is designated the crystalline form of the compound. Mixtures of any kind—wood, for instance—have no crystalline forms. In this respect there is an essential difference between mixtures and chemical compounds. That solid compounds may assume their proper crystalline form—and this is a point of special importance—nature has impressed on crystals, while they are forming, a tendency to crystallise from their solutions in as pure a state as possible. Hence it is that *crystallising out* is a method of purification constantly used, both by the chemist in his laboratory and by the manufacturer in his chemical industry; in numberless cases, indeed, this is the only method whereby the wished-for result can be gained.

The following experiment will make clear to us the mode and manner of applying this process to the purification of chemical compounds—that is, to the freeing of them from all impurities that are mixed with them. In carrying out a process of crystallisation we shall select a substance which will crystallise so quickly that we shall be able to realise the result of our work in the shortest time possible. Benzoic acid is very suitable for our purpose; we shall therefore choose that substance. Benzoic acid appears in commerce as a white glistening powder; we shall first of all intentionally make some of this powder impure, and then separate it from these impurities by crystallisation. For this purpose we mix some benzoic acid with sand and a little common salt; then we throw our mixture into water which is boiling in a beaker (A, fig. 24). The benzoic acid and the common salt dissolve in the hot water; the sand, of course, does not dissolve. To get rid

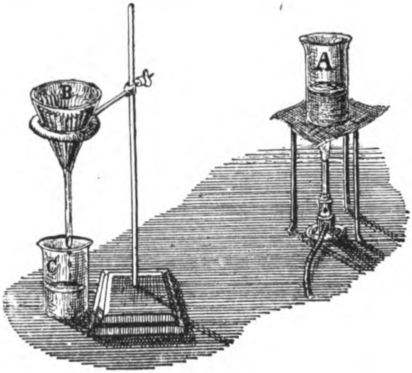

Fig. 24.—Filtration of a boiling liquid from which a solid is to be crystallised.

of the sand we run the liquor through a filter made of paper, placed in the funnel B (fig. 24). The sand cannot pass through the filter; it remains on the paper. In this way we have separated the sand from the benzoic acid which is found in the filtrate. As the warm and perfectly clear filtrate, which runs through the filter and collects in the beaker C (fig. 24), cools, it becomes filled with glistening crystals. These are crystals of benzoic acid: this compound is scarcely soluble in cold water, although it dissolves readily enough in hot water; hence, as the solution cools, the acid crystallises out in that special crystalline form which has been impressed on it by nature. The small quantity of common salt that we mixed with the benzoic acid remains dissolved in the cold liquid, so that the benzoic acid which has crystallised out is free from that impurity. The liquid which is above the crystals of benzoic acid is the mother-liquor from these crystals. *The name mother-liquor is applied to any liquid from which something has crystallised out.* In the olden days such a liquid was thought of as the mother of the crystals that separated from it; the name derived from this conception has remained until now. If we throw the mother-liquor and the crystals of benzoic acid therein on to a filter, the benzoic acid remains on the filter, and the filtrate—that is, the mother-liquor—which contains the common salt, runs through. Should we be afraid that the benzoic acid on the filter may have a little salt adhering to it, we may, of course, repeat the whole process: we dissolve the solid in a fresh quantity of hot water and proceed as before, and in this way we purify our benzoic acid by *re-crystallisation*, as this process is called. The traces of salt which may have adhered to the once-crystallised benzoic acid are certain to remain in the mother-liquor after the second crystallisation, and the benzoic acid obtained by this repetition of the process of crystallising is undoubtedly free from common salt. It is only necessary to throw the crystals on to a filter, to allow the mother-liquor to drain away, and to dry the solid that remains, in order to obtain pure benzoic acid. In difficult cases one may have to crystallise thirty times, or even more, in order to free a substance from all impurities wherewith it may be mixed. These impurities remain at last in the mother-liquors.

The method we have illustrated by our experiment with benzoic acid is employed, not only in laboratories, but also in manufactures. To take an example. There are large districts in Chili where soda saltpetre—or Chili saltpetre, as it is often called—is found. When we come to speak of artificial manures we shall meet this substance again ; at present we are using it only as an illustration. Chili saltpetre is very soluble in hot water ; if, therefore, some of the soil wherein this compound is found is boiled with water, the saltpetre is dissolved in the water. If the hot solution is then separated from the undissolved soil, in the manner whereby we separated the sand intentionally added to benzoic acid from the benzoic acid, the saltpetre will crystallise out from the filtrate as that cools. The crystallisation will proceed in this case much more slowly than in the case of benzoic acid, and some days may elapse before the process is completed. We shall very soon have to concern ourselves with the liquid from which Chili saltpetre crystallises—that is, with the mother-liquor of that substance—because that liquid contains iodine; and this is another reason why this especial case has been chosen as an example of the use of crystallisation in chemical industries.

As has been said already, bromine was discovered in the mother-liquor of certain sea-salts. In some parts of the countries around the Mediterranean the sea-water is allowed to flow, in the summer months, into shallow basins, called salt-gardens, which are separated from the sea after they have been filled with sea-water. The water in these basins soon evaporates, because of the high summer temperature of these parts; hence the sea-water becomes so concentrated that the common salt, which is present to the extent of about 2·7 per cent. in all sea-water, can no longer remain in solution, but must crystallise out. This salt is sent into the market. The liquid that remains above the salt, which is called the mother-liquor of sea-salts, is found by analysis to contain fair quantities of bromine. It was from this source that bromine was first obtained in the year 1826.

The sea long remained the provider of bromine; but eventually the process of manufacturing bromine passed to inland countries, especially to Stassfurt, in the neighbourhood of Magdeburg. This mining centre is the only place at present known to have a practically inexhaustible supply of potash salts. As these salts*

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* We shall deal with these compounds in some detail when we come to the metal potassium.

are most important artificial manures, the Stassfurt industries supply all parts of the world with this indispensable aid to rational agriculture. The Stassfurt mines have been used as a source of potash salts since the sixties of the nineteenth century. Before that time, potashes—that is potassium carbonate—was the chief source of the potash salts required for various purposes. But potassium carbonate is much too expensive to-day to be used for making artificial manure.

The accumulation of vast deposits of potash salts in the neighbourhood of Stassfurt is explained if we suppose that once there was there a deep arm of the sea connected with the main ocean only by a shallow canal, that as the water in the basin evaporated its place was supplied by water flowing in from the sea, and that at some time the basin was cut off from the main ocean by the silting up of the canal or by some upheaval of the earth. As the water of what was now an inland sea became more and more concentrated by evaporation, the common salt must have crystallised out gradually. This substance is found in largest quantity in the lowest parts of the Stassfurt deposits. But, as time passed, the mother-liquor above the separated salt must have become constantly more concentrated, until at last it dried up, and so left behind the potash salts it contained in the form of solid masses. Sea-water contains small quantities of potash salts besides larger quantities of sodium chloride (common salt). Because of the small quantity of them, these potash salts remain in the mother-liquor when sea-salts are separated from sea-water in the way already described, and they do not crystallise out until that mother-liquor is concentrated again. The proportion of common salt to potash salts in the Stassfurt deposits shows that something has occurred there similar to what we caused to take place when we separated benzoic acid by crystallisation from a little salt wherewith we had mixed it. In that process one of the substances crystallised out while the other remained in the mother-liquor.

But if the Stassfurt potash salts are derived from the sea, if they have been separated in a huge natural sea-salt factory, they must contain compounds of bromine, judging from what we know of the composition of artificially prepared sea-salts. And they do contain bromine compounds.

The crude potash salts found at Stassfurt must be purified for the purposes of agriculture : this is done by crystallising from hot water. The mother-liquors left after crystallising out the potash salts contain the bromine compounds from which the element bromine is obtained. So great is the demand for potash salts that there are sufficient quantities of these mother-liquors at Stassfurt to furnish more bromine than is required by the whole of Europe. Besides the chief factory, there are a few salt-works in North America from the mother-liquors of which bromine is obtained.

The chemical behaviour of bromine towards other bodies is exceedingly like that of chlorine, only everything is slightly weakened, so to speak. Chlorine is a yellow-green gas; bromine is a dark red liquid, which can be gasified very easily, as it boils at 58° C. [136° F.]. Chlorine reacts with almost everything; bromine reacts similarly, but more slowly. Bromine is only slightly less dangerous than chlorine in its action on the lungs; and so on.

Bromine finds its chief application in photography. Bromine can be united with potassium to form potassium bromide. It has been remarked already that such compounds as this are called *salts*. This word has a very comprehensive meaning: we shall learn more about what it means as we proceed. Potassium bromide dissolves in water: if a solution of silver nitrate is added to this solution, silver bromide separates at once, because that compound is quite insoluble in water, while potassium nitrate remains in solution (see p. 50).

Potassium bromide + silver nitrate = silver bromide + potassium nitrate.
(Soluble in water) (soluble in water) (insoluble in water) (soluble in water)

Silver bromide for photographic purposes is, of course, prepared in the dark. The two solutions are mixed in a room into which light is not admitted.

Potassium bromide, and also the two very similar salts sodium bromide and ammonium bromide, are used as drugs. Small quantities of these salts are sometimes added to Seltzer water to give the liquid a soothing action on the nerves. Bromine is also made use of in the aniline-colours industry; but the reactions are too complicated to be considered here.

The total consumption of bromine is not very great; about 750,000 kilos. [approximately 730 tons] are used annually for all purposes.

IODINE.

Iodine, like bromine, is found in sea-water; but the quantity of iodine is so small that the direct preparation of this element from sea-water, or even from the mother-liquors thereof, is impracticable. The preparation from sea-water is made possible, however, by the following facts. Certain sea-plants, as they grow, withdraw iodine compounds from sea-water. These plants are collected, dried, and burnt, in order to obtain their ashes; and these ashes contain not inconsiderable quantities of iodine compounds. It was from the ashes of sea-plants that iodine was first prepared in 1811.

The ashes of sea-plants were the sole source of iodine until the middle of the seventies of the nineteenth century, when a new and more abundant source was made available. We have already learnt something about Chili saltpetre, and we know that it crystallises from a liquid which yields a mother-liquor after the removal of the saltpetre. That mother-liquor, as has been mentioned before, contains a little iodine, the extraction of which has been conducted since the time mentioned. The large quantity of these mother-liquors which is available makes it possible for Chili to supply more iodine than is demanded by the whole world, so that, as in the case of bromine, the whole of the mother-liquors existing at any time are not worked up. When we are dealing with manganese we shall learn the methods whereby the mother-liquors are manipulated.

In order to prepare iodine we shall proceed just as we did in preparing bromine, and we shall use an apparatus similar to that we used then.

This time hydriodic acid is heated with manganese peroxide in the retort A (fig. 25). As in the case of hydrochloric and hydrobromic acids, so here the oxygen of the peroxide seizes the hydrogen of the hydriodic acid in order to form water, with the result that the iodine is set free. Now, iodine is a solid body which does not melt when it is heated, but passes directly into the state of gas: in this respect it differs from most ordinary solid bodies that are capable of being volatilised. When such bodies are heated they generally melt before they become gases; as examples we recall ice, water, and water-vapour. Moreover, when iodine vapour is cooled it passes from the state of gas to that of a solid: there seems to be no intermediate liquid condition for this substance. Crystals of iodine, therefore, separate on the colder parts of the apparatus wherein the preparation is conducted—in our figure (25) in the receiver B. One does not say of bodies that behave like iodine "they distil," but "they sublime." Iodine belongs to the sublimable bodies. To get it perfectly pure it is sublimed repeatedly.

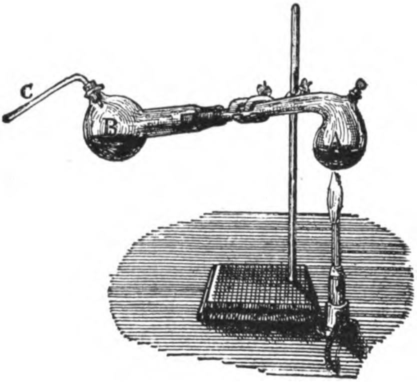

Fig. 25.—Preparation of iodine.

Iodine is a greyish black body, having the specific gravity 4·95. It forms a violet vapour when heated: we have noticed vapours of this colour filling the retort wherein we conducted our preparation of iodine. The Greek word ἵωδης signifies violet-blue, and the name *iodine* given to the element has reference to the colour of its vapour, or, to put it more correctly, to the appearance of the body in the state of gas. Iodine is slightly soluble in water, but it dissolves easily in alcohol, and such a solution forms the *iodine tincture* of the Pharmacopeia which is applied externally for several purposes.

Iodine is one of those bodies which can be recognised in very minute quantities; even an exceedingly dilute solution of it gives a deep blue colour with starch paste. The fact has been established quite recently that iodine is a normal constituent of the human body. It is found, in what chemists call small traces, in the thyroid gland, which is one of the glands of the neck. The enlargement of this gland produces goitre. Since iodine has been found in the thyroid gland the well-known beneficial action of iodine in goitre has become explicable.

A solution of iodine is much too corrosive in its action to allow of its being employed internally. When, therefore, it is to be administered internally, it is given in the form of one of its salts, and most commonly in the form of potassium iodide, which is easily dissolved by water. This salt has absolutely no corrosive action—a fact which cannot be at all strange to us, for the circumstances are quite the same with common salt (sodium chloride), for example. We know already that it would be quite impossible to introduce chlorine regularly into the human system; while, on the other hand, this element combined with sodium—that is to say, common salt—is altogether indispensable.

We have prepared iodine by a method which is exactly comparable with those whereby chlorine and bromine are produced. If we add a solution of silver nitrate to a solution of potassium iodide, we obtain insoluble silver iodide along with potassium nitrate. This reaction is similar to those that occur with chlorine and bromine compounds. To sum up, a detailed examination, carried out in diverse directions, shows that iodine is similar in every respect to chlorine and bromine. It is also used for purposes like those for which these elements are employed. The yearly consumption of iodine throughout the world amounts to about 600,000 kilograms [approximately 600 tons].

FLUORINE.

The existence of fluorine as an element has long been established. Compounds of it have been known since olden days: fluorspar, for instance, which is calcium fluoride, occurs abundantly in nature. The preparation of fluorine in the free state—that is, uncombined with any other element—dates, however, only from 1886. Fluorine is not only the most active member of the group of four elements we are now considering—which four elements are called the group of *the halogens*—but it is the most active of all the elements. An explanation of the word *halogen* cannot be given until we reach a later part of this book. Because of its extraordinary readiness to combine with other substances, fluorine attacked all the vessels wherein attempts were made to prepare it—and these attempts were numberless; hence it could not be obtained uncombined with other elements. Methods which ought to give fluorine, arguing from its similarity to chlorine, bromine, and iodine—the action of hydrofluoric acid on manganese peroxide, for instance—did not enable the element to be obtained. Instead of free fluorine, a compound of it with some constituent of the material of the vessel—with a constituent of glass, for instance—was always obtained. At last, however, the element was secured by passing an electric current through its hydrogen compound (hydrofluoric acid) contained in a vessel made mainly of platinum, at a low temperature, which exerts a moderating influence on all reactions, and therefore diminishes the energy of fluorine. We have already learned, from our experiment with water (p. 33), that the electric current is able to decompose chemical compounds into their elements. In this case also, when the conditions were suitable, the current retained its power, and it became possible to separate hydrofluoric acid into its two constituents, hydrogen gas and the long-sought-for fluorine.

Fluorine is a pale yellow-green gas, resembling chlorine, but much more energetic in its actions than that element. For example, it combines energetically with hydrogen, even in the dark, when it is mixed with that gas. Chlorine does this only in sunlight.

THE HYDROGEN COMPOUNDS OF CHLORINE, BROMINE, IODINE, AND FLUORINE.

Now that we have learned something of the four elements of the halogen group, considered by themselves, the best way of proceeding to increase our chemical knowledge is to consider the compounds of these elements with hydrogen, wherewith we have a more intimate acquaintance. Each of the four elements forms only one compound with hydrogen. This fact should be noted carefully, as we shall find it to be of striking importance in considering the whole theoretical foundation of chemistry. These four compounds—hydrogen chloride, hydrogen bromide, hydrogen iodide, and hydrogen fluoride—are all gaseous bodies, although bromine is a liquid and iodine is a solid.

Hydrochloric Acid Gas.

Hydrogen chloride is one of those gases which are very soluble in water. An aqueous solution of this compound is called hydrochloric acid (sometimes muriatic acid); in other words, commercial hydrochloric acid is water wherein hydrogen chloride gas is dissolved.

The gas is obtained by warming common salt with sulphuric acid. If we give the name sodium hydrochloride to common salt, which is a compound of sodium and chlorine, we shall perhaps better follow the preparation of hydrochloric acid gas. Sulphuric acid, which is said by chemists to be a stronger acid than hydrochloric acid, drives the latter acid out of the sodium hydrochloride, and, taking the place of the hydrochloric acid, forms a compound with the sodium.

Sodium hydrochloride + sulphuric acid = hydrochloric acid gas + sodium sulphate.

We shall employ the apparatus shown in fig. 26 for preparing hydrochloric acid gas and a solution of that gas in water. The apparatus resembles that employed in the manufacture of the acid. Common salt and sulphuric acid are placed in the flask A; as soon as this mixture is warmed, a regular evolution of gas begins, and is made evident by the bubbles which we see passing through the washing-flasks D and E. As the apparatus remains quite transparent and we cannot see the gas therein, we conclude that hydrochloric acid, in contradistinction to the yellow-green chlorine, is a colourless gas. If we open the stopcock B, so that the gas streams into the air at C, we notice that white clouds form immediately at the place where the gas comes into contact with the air. These clouds indicate that the hydrochloric acid gas at once draws to itself the moisture of the air, and dissolves therein to form a solution of hydrochloric acid, the minute globules whereof are visible as a cloud. This teaches us that hydrochloric acid gas is very eager to draw water to itself and to dissolve therein. If we now close the stopcock, we notice that, as soon as all the air is driven out of the apparatus by the stream of gas, the gas coming from the flask wherein the reaction is proceeding is completely absorbed by the water in the first washing-flask D. A considerable time is required for the complete saturation of the small quantity of water in D by the hydrochloric acid gas, for the gas is very soluble in water. When the water in D is saturated, the gas passes through that washing-flask and is absorbed in E.

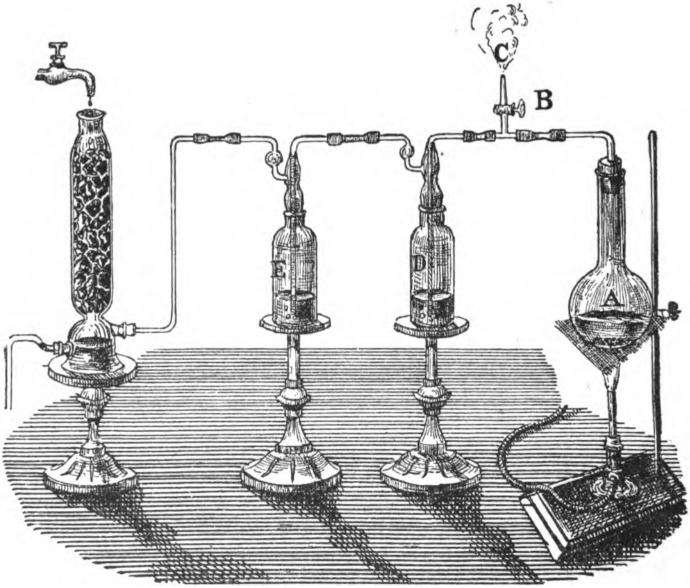

Fig. 26.—Preparation of hydrochloric acid.

In order to prevent the escape of any hydrochloric acid gas into the room—for the horribly penetrating smell of the gas would soon make it impossible to remain in the room—we have placed a *tower* after the washing-flasks. This glass apparatus represents the very large towers, built of brick or stone, that are used in chemical works where hydrochloric acid is made. In such works, where perhaps 100 kilos. [say 200 lb.] of common salt are decomposed by sulphuric acid, in a properly constructed apparatus, about thirty-six earthenware pots, containing water, are placed one after the other, for the purpose of absorbing the acid gas (these are represented in our apparatus by the two washing-flasks); and the final absorbing tower is more than twenty metres [say sixty-five feet] high.

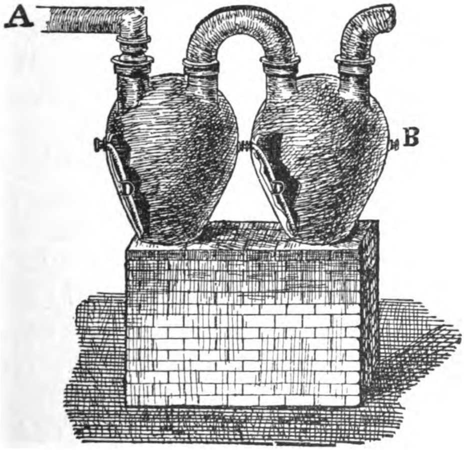

Fig. 27.—Earthenware jars used in the manufacture of hydrochloric acid.

Fig. 27 represents two of these earthenware pots, sometimes called *touries*. The hydrochloric acid gas enters at A, and passes through the water in the pot into another pot, and so on to the tower. A stream of water is kept constantly flowing through the pots in the opposite direction to that wherein the gas passes, for the purpose of absorbing the gas. As the solution of hydrochloric acid that is produced is heavier than water, the constantly flowing stream of water will drive the liquid laden with hydrochloric acid from the lower part of one pot into the pot next nearer the furnace. The illustration shows a pipe (D) passing from a tubulus in the side of each pot to the bottom of the next pot. The overflow from one pot to the next must pass through this pipe. A completely saturated aqueous solution of hydrochloric acid flows from the last pot: this solution is sold as hydrochloric (or muriatic) acid. The first tower contains coke which is besprinkled with water, as was done on the small scale in the glass tower of our apparatus, into which water dropped from the tap (see fig. 26). The very large water-surface which is exposed by the wet coke insures that the last traces of the hydrochloric acid gas are given every opportunity to dissolve in water, and so prevents the escape into the air of any of the acid gas. This method, employed in factories for the complete absorption of the hydrochloric acid gas, is practised also in our small apparatus, from which no acid vapours escape into the room, as is made evident by the fact that we do not see any formation of clouds round the upper opening of the tower.

The hydrochloric acid which we obtain in our washing-flasks is colourless, while the commercial acid, wherewith our acid should be identical unless especial means are taken to make it very pure, is yellowish as it flows from the pots. The reason for this difference in the appearances of the laboratory-product and the acid made on the large scale is that the commercial acid has a little iron dissolved in it, which iron comes from some of the many pieces of apparatus made of iron or containing iron that are used in the chemical works. As our apparatus is made wholly of glass, the presence of iron in our acid is, of course, avoided. If we put a few rusty nails into the colourless acid we have made, that acid will soon show the same yellow colour as the commercial product.

Liquid hydrochloric acid—that is, a solution of hydrochloric acid gas in water—fumes in the air just as the gas does; in other words, if we open a bottle containing the liquid acid, we see fumes rising from the mouth of the bottle. The reason of this is that some hydrochloric acid gas escapes from the solution and forms clouds in the air, in the way explained already. It is, of course, only the very concentrated acid that fumes in the air—the acid, that is, which is so concentrated that the water can scarcely retain in solution all the acid gas that has been dissolved in it. The acid which is produced by the manufacturer is generally made as concentrated as possible, in order to bring the cost of transport to a minimum. If the "*fuming acid*" is diluted with water, it loses the property of fuming in the air, for there is now enough water to keep the whole of the hydrochloric acid gas in solution easily, so that none escapes from the liquid. Strong—that is, concentrated—hydrochloric acid contains rather more than 40 per cent. of hydrochloric acid gas—that is, more than 400 grams per litre [about 28,000 grains per gallon].

Aqueous hydrochloric acid has already been used by us in the preparation of chlorine; we oxidised the hydrogen of the acid to water, and the chlorine was set free. We have made especial use of manganese peroxide as a means of effecting oxidations. This compound is, of course, not the only substance available for the purpose, for almost any compound which is very rich in oxygen will enable us to get chlorine from hydrochloric acid. Manganese peroxide is, however, the cheapest material that can be used for the purpose. As we know that hydrochloric acid is obtained from common salt by a very simple process, we can easily see that the chlorine which is got from the acid—and hence such other chlorine preparations as chloride of lime (bleaching powder)—ought not to be very expensive.

ACIDS, BASES, AND SALTS.

Although we have only now prepared one acid—namely, hydrochloric acid—we could not avoid the use of the term *acid* in the earlier parts of this book. The word acid originally designated substances which have a sour taste or a sour smell, such as vinegar, hydrochloric acid, and sulphuric acid. It is evident that chemistry could not remain satisfied with a reference to this purely external property, especially as when acids are very greatly diluted by the addition of much water the taste and the smell must generally vanish, although the liquids still contain acids in the chemical meaning of the word. Now it was found, a long time ago, that acids change the colours of many vegetable colouring matters even when the acids are greatly diluted. The blue colouring matter called *litmus*, which is found in many species of lichens and is a substance easily obtained, is one of those bodies which are readily changed by acids. This substance is very soluble in water: its blue aqueous solution is turned red by the smallest trace of any acid. This very convenient means of detecting acids is far superior to the tests of taste and smell; but as this also is purely an external and accidental means, it cannot be regarded as sufficient in scientific work. There are liquids which cause litmus solution that has been reddened by acids to turn blue again. These liquids behave towards such a vegetable colouring matter as litmus in a way directly the opposite of that of acids; they annul, or, it may be said, they neutralise, the effects produced by acids. One says of such liquids which turn reddened litmus blue that they have a basic, or alkaline, reaction. These two expressions, *base* and *alkali*, are used to-day as synonymous;* we shall employ them both without any difference of meaning. The word base is derived from the Latin *basis*; the word alkali is of Arabic origin. Basic, or alkaline, liquids do not taste sour, but rather saline. They are not less corrosive than the acids; the expression *caustic ley*, for instance, implies the possession of corrosive power. (We shall soon consider this

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* In English books on chemistry the term *base* is generally used with a wider signification than the word *alkali*. [TR.]

substance more fully.) If the reactions that occur when bases are neutralised by acids are followed more narrowly, we find that the acids combine with the bases to form a special class of compounds, and that the opposing functions both of the acids and the bases are balanced, so that the products of these actions have, generally, no action on the colour of litmus.

That which is formed by the reaction of an acid with a base is called a salt. A great number of acids and bases is known; hence a great number of salts is produced by the reactions of these acids and bases. In ordinary language the word salt is applied to one substance only—common salt. No mention has been made in the foregoing statements of the external characteristics of acids, bases, and salts. It is not at all necessary that acids and bases should be liquids, as one might be apt to suppose when beginning the study of these bodies, nor that all of them should act on vegetable colours; the essential point is this—*what combines with an acid to form a [illegible] is a base, or, conversely, what combines with a base to form a salt is an acid.*

Hydrochloric acid is not a liquid, but a solution of a gas in water; on the other hand, sulphuric acid and acetic acid (the acid of vinegar) are liquids. The acids hitherto spoken of, which are such good representatives of the general type of acid, colour litmus red; but sand does not do so. Nevertheless, sand is an acid (chemists call it *silicic acid*); it combines with bases—with potash, for instance, it forms a salt called potassium silicate.

The bases, or alkalis, also may be solid, liquid, or gaseous bodies. The bases caustic potash and caustic soda are solids. Aniline is a liquid base: although it does not colour reddened litmus blue, it is manifestly a base, for it combines with sulphuric acid to form a salt—aniline sulphate—and with hydrochloric acid to form a salt—aniline hydrochloride. Ammonia is a gaseous base, which we shall consider hereafter pretty fully, as it is of great general interest. It is true that common salt is soluble in water; but solubility or insolubility in water has no importance in the chemical conception of *salt*: as a matter of fact, a great many salts are insoluble in water—for instance, lead carbonate and calcium silicate. But a further treatment of the conception of *salt* must be deferred until a later period of this book.

Which are the elements compounds whereof are acids, and of what elements are bases composed? The following is a broad and general answer to this question. When we come to deal with individual elements we shall have many illustrations of what is said here.

The oxides of the non-metallic elements react with water to produce acids—we speak of sulphuric acid, phosphoric acid, and so on. The oxides of the metals give the bases—as lead oxide, copper oxide, and the like. A complete exception to this statement, which holds good only broadly and generally, is furnished by the group of elements chlorine, bromine, iodine, and fluorine, for the compounds of these with hydrogen alone are acids.

HYDROBROMIC, HYDRIODIC, AND HYDROFLUORIC ACID.

Now that we know something of acids, bases, and salts, and have considered hydrochloric acid in some detail, we must review the three acids hydrobromic, hydriodic, and hydrofluoric.

Hydrobromic and hydriodic acids resemble hydrochloric acid in every way. They are colourless gases, very soluble in water; hence, like hydrochloric acid, they are kept in aqueous solutions, that being the most convenient way of storing them. With regard to hydrofluoric acid, which is a solution in water of hydrofluoric acid gas, it is especially to be noted that, in contradistinction to the other three acids, it must *not* be kept in glass vessels, because, like fluorine itself, it attacks glass. The preparation of this acid is chemically similar to that of hydrochloric acid; but leaden vessels must be used, because these are not acted on by the acid, although they are corroded by fluorine. This acid is kept in flasks made of caoutchouc, which are much lighter than leaden vessels, because experiments have shown that the acid does not act on this material. The acid is known commercially as *fluoric acid*, because for the last two hundred years it has been prepared from fluorspar (calcium fluoride), for the purpose of etching glass, by heating that substance with sulphuric acid. In making hydrochloric acid we started with sodium chloride, a substance found native in abundance. Sodium fluoride is not found in nature, but calcium fluoride is a mineral; in this case, therefore, we use calcium fluoride:—

Calcium fluoride + sulphuric acid = hydrofluoric acid + calcium sulphate.

Hydrofluoric acid is chiefly used for etching glass—that is, for fixing lines or writing on glass. The glass is covered with wax or paraffin by allowing one of these substances to melt on the warm glass and then running it over the surface; after cooling, the desired outline is cut through the covering material, and hydrofluoric acid is poured on. The exposed parts of the glass are etched in a few minutes. The acid is then washed away, and the covering is removed by melting it, whereupon the etching is visible. The applicability of wax or paraffin as a material for use in etching with hydrofluoric acid has been established by purely practical trials, just as caoutchouc flasks have been found to be suitable for storing the acid.

ATOMS AND THEIR WEIGHTS.

THE method we have used in advancing our knowledge of chemistry cannot be called unscientific. Nevertheless, we have proceeded hitherto rather after the manner of the descriptive sciences, such as botany or mineralogy; but chemistry is an abstract and theoretical* natural science. We have contented ourselves, on the whole, with discovering the external properties of the bodies we have been considering, and how their actions on one another manifest themselves. Hitherto we have paid no attention to the quantities of the substances required in the different experiments. But as long as one does not take into account the relations between the weights of the substances used in chemical investigations, it is impossible to speak of making any genuine scientific advance in chemistry. The serious use of the balance in chemistry dates from the second half of the eighteenth century. Before that time, speaking broadly, no advance was made beyond alchemy, which we name to-day with a shrug of the shoulders.

The full consideration of weight-relations in investi-

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* The expression in the original is *eine spekulative Naturwissenschaft.* [TR.]

gations in the domain of chemistry has gradually led to those great results which have insured for chemistry so prominent a place among the special branches of the whole body of natural science. We must, therefore, as we proceed, always take these relations into account.

In our experiments we obtained regular streams of chlorine, hydrochloric acid, and the like with the greatest ease. But if anyone were to try to prepare such chemical compounds with no more knowledge of the reactions than he may have acquired from what has been said hitherto in this book, he would find in most cases, little to his delight, that matters are not so simple as he thought. Either he would obtain, in all probability, such violent streams of gas that he would hardly know how to guard himself against them, or the opposite would happen, and the production of gas would take place in such a feeble way that he would not be able to do anything with it.

Why is it, then, that the man who has had experience in these matters is able to regulate such processes with ease and have them completely under his control? The reason has been alluded to already; it is that in the examinations we have made hitherto of reactions between substances, wherever it was necessary, the proper relative weights of the reacting bodies have been used. The substances have not been mixed in indefinite quantities. But how is it possible to determine beforehand what are the proper quantities by weight of any two chemical compounds which should be used in a reaction between these bodies? What are the connections between two such different substances as common salt and sulphuric acid, from which we produced hydrochloric acid gas, which enable us to calculate the proportions by weight wherein they must be mixed? We shall try to express ourselves clearly on this point. There is no special difficulty. But these fundamental conceptions, whereon the whole structure of scientific chemistry rests, cannot be mastered in a hurry; they must be thought about quietly.

We have already become acquainted with hydrochloric acid gas, and we know that it consists of hydrogen gas and chlorine gas. We also know that hydrobromic acid gas and hydriodic acid gas consist of bromine and hydrogen, and iodine and hydrogen, respectively. We need not take hydrofluoric acid gas into consideration, as the three gases we have mentioned will suffice for our purpose.

If we determine, by the help of a balance (and the determinations are not overpoweringly difficult), how much chlorine, how much bromine, and how much iodine is combined, in one or other of the three compounds, with *one part by weight* of hydrogen—that is, with one part by weight of the specifically lightest of all substances—we find that with unit weight of hydrogen there is combined 35·5 parts by weight of chlorine in hydrochloric acid, 80 parts by weight of bromine in hydrobromic acid, and 127 parts by weight of iodine in hydriodic acid. *These numbers, which express parts by weight of the three elements—namely,* 35·5 *for chlorine,* 80 *for bromine, and* 127 *for iodine—are* *maintained in a very remarkable way in the compounds of the three elements with other elements, for instance, with silver, sodium, etc.*

For example, we know that common salt is sodium chloride. If we determine, with the help of the balance, how many parts by weight of sodium are combined in this compound with 35·5 parts of chlorine—that is, with that quantity of chlorine which combines with one part by weight of hydrogen—we find that 23 parts by weight of sodium are so combined. If we now find how much bromine combines with 23 parts by weight of sodium to form sodium bromide, the result is 80 parts of bromine, which is the weight-number we have determined for bromine from the composition of hydrobromic acid gas. Moreover, we find that 23 parts by weight of sodium combine with 127 parts by weight of iodine to form sodium iodide; but 127 is the weight-number determined for iodine from the composition of hydriodic acid gas.

To go farther. If we throw 23 parts by weight of sodium into water, we discover that this quantity suffices to set free exactly one part by weight of hydrogen (see the experiment described on p. 29). To put the matter in a few words, 23 parts by weight of sodium combine with exactly the same quantities by weight of chlorine, bromine, and iodine as combine with one part by weight of hydrogen; and 23 parts by weight of sodium set free from water exactly one part by weight of hydrogen.

An examination of the quantities by weight wherein elements combine, such as that we have now conducted for five elements, can, of course, be carried out for all the elements. This has been done. The result is that all the elements combine with one another in fixed proportions by weight, which never change, or in moderately large simple multiples of these proportions, so that the weights of the elements which combine to form chemical compounds always bear the same proportion to one another. Taking chlorine, for example, we *always* find that 35·5 parts by weight, or a simple multiple of this quantity, of chlorine enters into combination, referred to one part by weight of hydrogen; in hydrochloric acid, 35·5 parts by weight of chlorine are combined with one part by weight of hydrogen; in compounds which contain other elements besides these two, we find 2 × 35·5, or 3 × 35·5, etc., parts by weight of chlorine. It may almost be said that a certain weight-number adheres to each element. What has been said is absolutely certain; there is nothing theoretical about it; it is not arrived at by speculative thinking, but all the weight-numbers are determined by the use of the balance, which eliminates all errors.

But we must now ask whether an explanation can be found of these facts, which have been established by applying the balance to determine the proportions by weight wherein the elements combine with one another. As the invariability, the perpetual constancy, of the proportions by weight wherein the elements enter into their compounds, and wherein we find them in their compounds, holds good for all elements, and as all the elements taken together represent the totality of matter, it follows immediately from these facts that what we have found to hold good must depend on some general property of matter.

To arrive at an explanation of this behaviour of matter, let us pursue the following train of thought. We hold a solid bar of metal—say a bar of steel—in our hand. Now, this bar will either altogether and completely fill the place—or, as we may equally well say, the space—wherein it is, or it will not absolutely fill that space. No other hypothesis is feasible. Evidently no chemical knowledge is required to arrive at this conclusion; it belongs to the domain of philosophy, and the ancient Greek philosophers busied themselves with conceptions about the filling of space by matter. The careful consideration of the supposition that matter entirely fills space soon leads to conclusions which no branch of natural science, and no inquiry that rests as much as possible on experiments and facts perceptible by our senses, can make anything of. (It is true that certain philosophers, of late years, have constructed a world on the foundation of the absolute filling of space by matter; but they do not consider it necessary to rest their conceptions on experimental evidence, and with words one may dispute most excellently.) On the other hand, everything that has been observed by investigators of nature can be presented clearly if we think of matter as *not* filling space entirely, but as consisting of exceedingly minute particles, which are very near one another, but not so near as to prevent the possibility of there being any interstices between them. These particles, which we may think of as spherical, are regarded as so small that they are not further divisible. A special term is applied to these smallest particles supposed by this view to exist—namely, the term *atom*, a word which was used by the ancient Greek philosophers. Translated literally, the word means not capable of being cut: we generally render it by indivisible. We must also assume that *the smallest particles of any particular element are equally large and of equal weights*—for instance, that all the atoms of hydrogen are of equal size and equal weight, all the atoms of chlorine are of equal size and equal weight, and so on.

To recapitulate. The elements are composed of atoms, the atoms of each element have all the same weight, and the weight of the atoms of one element differ from the weights of the atoms of the other elements. With the help of this simple conception it is easily possible to determine the weights of the atoms of the elements, by making use of those numbers which are determined by the balance and express the weights of the elements that mutually combine. It is, of course, impossible to make direct weighings of atoms; for they, the smallest parts of matter that we can conceive, are naturally so minute that no human eye can see them even when aided by the strongest microscope, no finest machinery can handle them, no most delicate balance can weigh them. But their weights relatively one to another —for instance, how many times an atom of chlorine is heavier than an atom of hydrogen—can be established without very much trouble in the following manner.

Notwithstanding many attempts to prepare other compounds, only one compound of chlorine with hydrogen, one of bromine with hydrogen, and one of iodine with hydrogen, is known. These three compounds are hydrochloric acid, hydrobromic acid, and hydriodic acid. As only one compound of each of these three elements with hydrogen has been prepared, despite the great trouble that has been taken to form others, one is really driven to adopt the hypothesis that, if the elements are formed of atoms, then a single atom of chlorine, a single atom of bromine, and a single atom of iodine is combined with a single atom of hydrogen in these three compounds, respectively. Whatever other hypothesis may be made, none is so simple as this, which suggests itself so readily and is not contradicted by any known facts. If this supposition is accepted—and it commends itself to our perceptions and satisfies our mode of thought more than any other—then we at once arrive at a knowledge of the weights of these atoms, by the following process. We know that 35·5 parts by weight of chlorine are combined with one part by weight of hydrogen in hydrochloric acid: according to our hypothesis, this compound is formed of one atom of hydrogen and one atom of chlorine; hence an atom of chlorine is 35·5 times heavier than an atom of hydrogen; for, as the total quantity of chlorine in hydrochloric acid is 35·5 times heavier than the total quantity of hydrogen, the ratio of the weight of the smallest quantity of chlorine to that of the smallest quantity of hydrogen in that compound is, of course, also as 35·5 to 1; and these smallest quantities are one atom of chlorine and one atom of hydrogen respectively. If we carry over this way of considering the facts to hydrobromic and hydriodic acids, we arrive at the conclusion that an atom of bromine is 80 times heavier, and an atom of iodine is 127 times heavier, than an atom of hydrogen. Nothing is left out of account in this determination of atomic weights; the weights of the atoms of these elements are determined completely.

But it may be asked why we are entitled to take the atomic weight of hydrogen as unity. We do that without hesitation; for all weights must be finally referred to a unit weight, which must be accepted once for all. This is done in the ordinary system of weights wherein quantities are reckoned in grams. For instance, when we say that a certain vessel, with its contents, weighs 735 grams, what we assert is that the weight of the thing is 735 times greater than one gram. It has been agreed, once for all, that the weight of one cubic centimetre of water shall be called a gram, and shall be the unit of our system of weights wherewith all other weights shall be compared.* Exactly in the same way, in chemistry it is agreed that the weight

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* In our preposterous English weights and measures there is no such simple relation between the units of weight and volume as exists in the metric system. The very simple relations between the units of weight, volume, and length of the metric system constitute the great advantage of that system over all others. [Tr.]

of an atom of hydrogen is to be taken as the unit in terms whereof the weights of all other atoms shall be stated.

The foregoing explanation will enable us easily to understand the proper significations of the abbreviated forms of the names of the elements, and the chemical formulæ which are constructed by using these symbols. The abbreviations denote the elements themselves, as we know already; but they also signify much more: each signifies one atom of the element in question. Cl is not only the symbol for chlorine, but *Cl signifies one atom of chlorine, Fe signifies one atom of iron,* and so on. As the atoms represent definite weights, so do these abbreviations indicate that such or such a quantity by weight of this or that element is present in the compound under consideration. The formula HCl signifies not only hydrochloric acid, but it tells us that hydrochloric acid is formed by the union of one atom of hydrogen with one atom of chlorine, and also that this compound is composed of one part by weight of hydrogen and 35·5 parts by weight of chlorine.

Before proceeding to make use of the knowledge we have now gained, we shall repeat the table of the elements (given on p. 22), adding, after the abbreviated form of the name of each element, the weight of the atom of that element. To repeat once more: these weight-numbers tell us how many times heavier an atom of each element is than an atom of hydrogen.

LIST OF THE ELEMENTS,

AND THE ABBREVIATED METHOD OF WRITING THEIR NAMES.

Name of Element.	Shortened form of Name.	Atomic weight.
Aluminium	Al	27·1
Antimony (*stibium*)	Sb	120
Argon	A	40
Arsenic	As	75
Barium	Ba	137·4
Beryllium	Be	9·1
Bismuth	Bi	208·5
Boron	B	11
Bromine	Br	79·9
Cadmium	Cd	112
Caesium	Cs	133
Calcium	Ca	40
Carbon	C	12
Cerium	Ce	140
Chlorine	Cl	35·5
Chromium	Cr	52·1
Cobalt	Co	59
Copper (*cuprum*)	Cu	63·6
Erbium	Er	166
Fluorine	F	19
Gallium	Ga	70
Germanium	Ge	72
Gold (*aurum*)	Au	197·2
Helium	He	4
Hydrogen	H	1
Indium	In	114
Iodine	I	126·8
Iridium	Ir	193
Iron (*ferrum*)	Fe	56
Krypton	Kr	—
Lanthanum	La	138
Lead (*plumbum*)	Pb	206·9
Lithium	Li	7
Magnesium	Mg	24·4
Manganese	Mn	55
Mercury (*hydrargyrum*)	Hg	200·3
Metargon	Mt	—
Molybdenum	Mo	96
Neodymium	Nd	144
Neon	Ne	—
Nickel	Ni	58·7
Niobium	Nb	94
Nitrogen	N	14
Osmium	Os	191
Oxygen	O	16
Palladium	Pd	106
Phosphorus	P	31
Platinum	Pt	194·8
Potassium (*kalium*)	K	39·1
Praseodymium	Pr	140
Rhodium	Rh	103
Rubidium	Rb	85·4
Ruthenium	Ru	101·7
Samarium	Sa	150
Scandium	Sc	44·1
Selenion	Se	79·1
Silicon	Si	28·4
Silver (*argentum*)	Ag	107·9
Sodium (*natrium*)	Na	23
Strontium	Sr	87·6
Sulphur	S	32
Tantalum	Ta	183
Tellurium	Te	127
Thallium	Tl	204·1
Thorium	Th	232
Tin (*stannum*)	Sn	118·5
Titanium	T	48·1
Tungsten (*wolfram*)	W	184
Uranium	U	239·5
Vanadium	V	51·2
Xeon	Xe	—
Ytterbium	Yb	173
Yttrium	Y	89
Zinc	Zn	65·4
Zirconium	Zr	90·6

The formula of a chemical compound, then, tells us not only of what elements the compound consists—as these elements are all enumerated in the formula—but also how much of each element is contained in the compound. We are now able to see of what great importance these formulæ are in all chemical inquiries.

The simple calculations which we shall have to make will quickly convince us that scientific chemistry, and therewith the only way of studying chemistry which can be successful, could not be advanced nowadays without employing these formulæ, which are based on a knowledge of the atomic weights of the elements. It is to be expressly remarked that all such calculations, in so far as we shall consider them, will take a very simple form. Indeed, it will not be necessary to employ anywhere in this book any calculation which demands greater arithmetical knowledge than is possessed by everyone who has attended a board school.

The first formula we wrote down was that of iron sulphide, FeS. At that time the formula merely informed us that the substance consists of iron and sulphur. We now know that the formula tells much more than that; we know that the compound is not composed of any indefinite quantities of iron and sulphur, but that one atom of iron is combined therein with one atom of sulphur. Moreover, the formula tells that 56 parts by weight of iron are combined with 32 parts by weight of sulphur in iron sulphide—the table informs us that the atomic weights of iron and sulphur are 56 and 32 respectively. As we are accustomed to reckon in grams, the ratio of the weights will be expressed in the clearest way by using the gram as unit of weight, and saying that 32 grams of sulphur are united with 56 grams of iron in iron sulphide.* If we melt together 56 grams of iron and 32 grams of sulphur, the compound iron sulphide, FeS, is produced directly. But if, in place of using 56 grams of iron, we used only 50 grams, for 32 grams of sulphur, a corresponding quantity of sulphur would remain uncombined with iron; for some sulphur would lack iron wherewith to combine, and that sulphur would remain over. A simple proportion enables us to calculate what that quantity of sulphur must be; for, as 56 parts of iron require 32 parts of sulphur, we have merely to find the weight of sulphur, x, required by 50 parts of iron. Here is the calculation:—

$$56 : 32 = 50 : x;$$

$$\text{therefore } x = \frac{50 \times 32}{56} = 28{\cdot}6.$$

That is to say, 50 grams of iron combine with 28·6 grams of sulphur; hence it follows that 3·4 grams of sulphur (32—28·6) remain uncombined when 50 grams of iron are melted with 32 grams of sulphur.

Suppose we desire to know the quantities of chlorine and sodium which form common salt. The formula of common salt is $NaCl$; the atomic weights of chlorine and sodium are 35·5 and 23 respectively, and

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* Of course, we may say that 32 grains, or 32 lb., or 32 oz. of sulphur are combined with 56 grains, lb., or oz. of iron. [Tr.]

the sum of these numbers is 58·5; therefore 58·5 parts by weight—let us say 58·5 grams—of common salt contain 35·5 grams of chlorine. Now we are accustomed, for the sake of clearness, to calculate all such proportions to parts per hundred; we shall therefore state the quantity of chlorine in common salt as a percentage. The proportion sum is simple enough :—

$58·5 : 35·5 = 100 : x$ (for if 58·5 parts of salt contain 35·5 of chlorine, x parts of chlorine will be contained in 100 of salt);

$$\text{hence } x = \frac{35·5 \times 100}{58·5} = 60·7.$$

We find, then, from the formula of common salt, $NaCl$, that this compound contains 60·7 per cent. of chlorine. As a man consumes about 25 grams [about five-sixths of an ounce] of common salt daily, he takes something like 15 grams [say half an ounce] of chlorine.

By the method illustrated in the case of common salt we can, of course, calculate the percentage weight of each element contained in any compound when the formula of that compound is known.

As water is a substance of especial interest to everyone, let us deduce the percentage composition of that compound from its formula. The formula of water is H_2O. As the atomic weight of hydrogen is 1, and that of oxygen is 16, the sum of the atomic weights in this formula is 18; for H_2, which represents 2 atoms of hydrogen, weighs 2. In 18 parts by weight—let us say in 18 grams—of water are contained 2 parts by weight—let us say 2 grams—of hydrogen and

16 parts by weight—16 grams—of oxygen. Calculating to percentages, we have:—

$$\text{(i) } 18 : 2 = 100 : x\text{; hence } x = \frac{2 \times 100}{18} = 11{\cdot}11.$$

$$\text{(ii) } 18 : 16 = 100 : x'\text{; hence } x' = \frac{16 \times 100}{18} = 88{\cdot}89.$$

That is to say, water consists of 11·11 per cent. of hydrogen and 88·89 per cent. of oxygen.

It is not to be expected that a single atom of one element should always unite with a single atom of another element to form a compound. The formula which has just been given for water, H_2O, shows that two atoms of hydrogen unite with one atom of oxygen to produce this compound. The number of atoms of the individual elements that enter into compounds varies greatly.* Although it is evident, from what has been said about the atomic compositions of the elements, that these bodies must always combine in atomic proportions, nevertheless we must not omit to emphasise this fact in an especial way. In some compounds we find 1 atom of hydrogen, in others 20 atoms of hydrogen; we find, it may be, 5 atoms of

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* In the earlier part of this book, for the sake of simplicity and clearness, we used the abbreviated forms of the names of the elements only as abbreviations of the names—H, for instance, meant hydrogen, and O meant oxygen. Under these conditions it was not possible to write any formula wherein more than one atom of an element occurred. That FeS should signify iron sulphide was quite apparent; but why should one write H_2O, for instance, if H signifies hydrogen and O means oxygen? How should anyone understand this H_2 as long as he is unaware that the abbreviation H represents one atom of hydrogen and O one atom of oxygen? If the

chlorine, or 2 atoms of iron, and so on : but we never find $1\frac{1}{2}$ atoms of hydrogen, or $1\frac{1}{3}$ atoms of chlorine, or anything of that kind; for such a state of affairs is altogether at variance with the idea of the atom, which signifies indivisible. Once we have grasped the fact that the number of the atoms of the individual elements that enter into compounds may vary in a remarkable way, we are in a position to understand those formulæ which are much more complicated than any we have yet written down. To take, for instance, the formula of morphia, which is $C_{17}H_{19}NO_3$. The sum of the atomic weights is easily calculated. As the weight of an atom of carbon, C, is 12, C_{17} amounts to $17 \times 12 = 204$; the 19 atoms of hydrogen weigh 19 (because the atomic weight of hydrogen is 1); as the atomic weights of nitrogen and oxygen are 14 and 16 respectively, evidently $N = 14$, and $O_3 = 48$. The sum of these four numbers, $204 + 19 + 14 + 48$, is 285. Suppose we wish to know the percentage of nitrogen in morphia; we find it by the proportion sum :—

$$285 : 14 = 100 : x;\ x = \frac{14 \times 100}{285} = 4{\cdot}92.$$

The percentages of carbon, hydrogen, and oxygen in morphia are found by a similar method of calculation.

abbreviations had no other meaning than the names of the elements, the expression HO would suffice to represent water, as that compound consists of hydrogen and oxygen. It was necessary to use formulæ very sparingly in the former parts of this book, as we were in a position to employ only those compounds which consist of single atoms of their constituent elements, considering that the reader did not know that the abbreviations symbolised atoms of the various elements, and, therefore, could not understand the meaning of the small figures attached to some of these abbreviations.

CALCULATING FORMULÆ FROM THE RESULTS OF ANALYSES.

So far we have used our knowledge of atomic weights to calculate, from the formula of a compound, the quantity of each element contained in 100 parts of that compound. If we think over the matter a little, we shall see that we may begin from the other end, so to speak; for hitherto we have assumed such formulæ as those of water and morphia, as things given to us. Formulæ are not at all such things, however. It is very necessary to inquire how chemists arrive at these formulæ—how they are able to deduce the formulæ of compounds from the proportionate weights of the elements therein. For instance, how was the conclusion arrived at that morphia, after its preparation from opium and thorough purification by re-crystallisation (this was done in 1817), is composed of 17 atoms of carbon, 19 atoms of hydrogen, 1 atom of nitrogen, and 3 atoms of oxygen? The method is as follows.

Every chemical compound whose formula is to be established is, first of all, analysed qualitatively. From this we learn of what elements the substance is composed. Then one proceeds to a quantitative analysis—that is to say, a determination is made, by the use of the balance, of the quantity of each element in the compound. As the methods of quantitative analysis have been very fully developed, this is not generally a very difficult task. The results of the quantitative analysis are stated in percentages of each element, and the formula of the compound is arrived at by dividing the quantity of each element in 100 parts of the compound by the atomic weight of that element. The quotients thus obtained are proportional to the numbers of the atoms, and from these quotients the numbers of atoms are easily found. This statement sounds more complicated than the affair really is; a few examples will best elucidate the matter.

A quantitative analysis of water, made by a method which we shall very soon become acquainted with, shows that water is composed of 11·11 per cent. hydrogen and 88·89 per cent. oxygen. To get this length requires the balance, but not chemical formulæ. How does one pass from this result to the formula of water, H_2O? For this purpose the atomic weights of the elements are divided into the percentage quantities of these elements. As the atomic weight of hydrogen is 1, the number 11·11 remains unchanged. The quotient obtained by dividing 88·89 by 16 (which is the atomic weight of oxygen) is 5·55. *The ratio of the numbers of atoms of hydrogen to that of the atoms of oxygen is, therefore, as* 11·11 : 5·55, *or as* 2 : 1. In water, then, there are always present two atoms of hydrogen to one atom of oxygen; therefore we write the formula of water as H_2O.

As a second example we shall take the calculation of the formula of iron oxide, a substance so often seen on vessels made of iron. The quantitative analysis of this substance, made by using the balance, tells that it consists of 70 per cent. of iron and 30 per cent. of oxygen. Dividing these percentages by the atomic weights, 56 for iron and 16 for oxygen, we have these results :—

$$\frac{70}{56} = 1·25, \text{ and } \frac{30}{16} = 1·875.$$

Looking at the ratio 1·25 : 1·875, *we see that it is as* 2 : 3. For two atoms of iron, then, there are always three atoms of oxygen in this compound; hence the formula of this oxide of iron is Fe_2O_3.

Our third example shall be a more complicated one. We will bring morphia again under consideration. Here are the results of the quantitative analysis of this compound :—

Carbon .	71·58 per cent.	Atomic weight of	carbon (C)	= 12.
Oxygen .	16·84 ,,	,, ,,	oxygen (O)	= 16.
Hydrogen	6·66 ,,	,, ,,	hydrogen (H)	= 1.
Nitrogen .	4·92 ,,	,, ,,	nitrogen (N)	= 14.

Let us divide these percentage quantities by the atomic weights of the elements. The results are these :—

$$\frac{71·58}{12} = 5·97 \text{ for carbon; } \quad \frac{16·84}{16} = 1·05 \text{ for oxygen;}$$

$$\frac{6·66}{1} = 6·66 \text{ for hydrogen; } \quad \frac{4·92}{14} = ·35 \text{ for nitrogen.}$$

The numbers of the atoms of the four elements whereof morphia is composed are in the ratio 5·97 : 1·05 : 6·66 : ·35.

If we calculate these numbers to whole numbers, assuming that there is in the compound only one atom of that element which is present in the smallest quantity, we arrive at this result :—

(i) $\cdot 35 : 1 = 5\cdot 97 : x;\quad x = \frac{1 \times 5\cdot 97}{\cdot 35}$ = almost exactly* 17.

(ii) $\cdot 35 : 1 = 1\cdot 05 : y;\quad y = \frac{1 \times 1\cdot 05}{\cdot 35}$ = ,, ,, 3.

(iii) $\cdot 35 : 1 = 6\cdot 66 : z;\quad z = \frac{1 \times 6\cdot 66}{\cdot 35}$ = ,, ,, 19.

Hence morphia is composed of 17 atoms carbon, 3 atoms oxygen, 19 atoms hydrogen, and 1 atom nitrogen ; in other words, the formula of morphia is $C_{17}H_{19}NO_3$.

The calculation, and hence the determination, of the formula of a compound is scarcely rendered more difficult should there be more than a single atom of each of the elements that form the compound, and not, as in the case of morphia, only a single atom of one of these elements.

As an example of a case of this kind, let us take benzoic acid, the compound we used to illustrate the process of crystallisation. The quantitative analysis of this compound shows that it is composed of 68·85 per cent. carbon, 26·23 per cent. oxygen, and 4·92 per cent. hydrogen. Dividing these numbers by the atomic weights, we obtain for carbon $\frac{68\cdot 85}{12} = 5\cdot 74$, for oxygen $\frac{26\cdot 23}{16} = 1\cdot 64$, and for hydrogen $\frac{4\cdot 92}{1} = 4\cdot 92$. The

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* The reason for the slight divergences of the numbers from whole numbers is that we have used whole numbers as values for the atomic weights. The atomic weight of carbon is 11·97, not 12, and so on.

ratio of the numbers of atoms in this case is, then, 5·74 : 1·64 : 4·92. An examination of these figures shows that they are in the same ratio as 3½ : 1 : 3. But we cannot have half-atoms; therefore, to get whole numbers, we multiply all these figures by 2, and obtain the ratio 7 : 2 : 6 as that which the numbers of atoms bear to one another: in other words, we arrive at the formula $C_7O_2H_6$ for benzoic acid.

We have now examined sufficiently the method whereby the formulæ of compounds are deduced from the results of the quantitative analyses of these compounds (made by employing the balance) with the aid of the atomic weights of the elements. For even if the numbers of the atoms are in a more complex ratio than is shown in any of our examples, it is evidently always possible to state the ratio in whole numbers without much difficulty.

MOLECULES AND THEIR WEIGHTS.

THE conception that all bodies are composed of the smallest particles—that is, of atoms—has sufficed for philosophy for two thousand years. It has not sufficed for chemistry. The untenability of the hypothesis that the smallest particle of every substance around us is an atom is demonstrated very simply by the following considerations. We may certainly very well suppose that the smallest particle of an element—say of iron, lead, chlorine, or hydrogen—is an atom, in the sense wherein we have hitherto always used this word; but what about the smallest particle of a compound—for instance, of that compound which we have so often spoken about, hydrochloric acid? The smallest particle of that body always consists of two atoms of the elements whereof the body is composed: it consists of one atom of hydrogen and one atom of chlorine, it is a complex of two atoms, and it is therefore certain that this smallest particle is not indivisible—that it is *not* an atom. And as with this, so, of course, with other compounds. The smallest particle of a compound must always, and self-evidently, consist of atoms of the elements which compose that compound: it must always be a cluster of atoms. As the designation *atom* is impossible, indeed meaningless, if applied to the smallest particles of compound bodies, it is necessary to have a special name for these particles. They are called *molecules.* The smallest particle of hydrochloric acid is, then, a molecule of hydrochloric acid; the smallest particle of common salt—sodium chloride—is a molecule of sodium chloride. These two molecules both consist of two atoms. But molecules may be very large as compared with atoms. Think of morphia, for example. The formula $C_{17}H_{19}NO_3$ shows that the molecule, the smallest particle we can think about, of this compound consists of forty atoms.

We now know something of the signification of the expression *molecule.* We will proceed to a further consideration of molecules and their weights. If the reader has got a firm hold of the conception of the molecule from the statements which have been given, he will certainly be able to follow the later parts of this book without those more difficult deductions about the weights of molecules which we are about to consider. On that account let us recapitulate in a word. An atom is the smallest part of an element; a molecule is the smallest part of a compound body.

The word molecule is derived from the Latin: *molecula* means a small mass. The detailed statements concerning molecules will be a little more complicated than those concerning atoms and atomic weights. These statements form the chapter of this book which requires more attention than any other. All the later considerations are easily to be understood if the hypothesis of the existence of atoms and molecules is granted.

The few fundamental considerations which we have found it necessary to lay down in our development of the hypothesis of atoms and the weights of atoms were grounded, essentially, on the behaviour of hydrogen towards chlorine, bromine, and iodine. For this reason we have dwelt somewhat fully on the experimental examination of the compounds of these elements. For our treatment of the development of the atomic theory, the fact is of the utmost importance that only a single compound of hydrogen with each of these elements has been obtained—namely, hydrochloric acid (HCl), hydrobromic acid (HBr), and hydriodic acid (HI)—notwithstanding the many attempts that have been made to form more compounds than these.

In deducing atomic weights, we have made calculations concerning the quantities by weight of hydrogen, chlorine, bromine, and iodine contained in these gases as if we were dealing with solid bodies; we have paid no heed in our calculations to the fact that we have had to do with gases. Now, however, we shall make up for that neglect. Let us begin by using the balance and proceeding as we did in deducing atomic weights; let us keep away from every theory until we have established facts. The result of determining the specific gravity of chlorine is that this gas is 35·5 times heavier than an equal volume of hydrogen. By heating bromine we change that liquid element into a gas; then, determining the specific gravity of the gas, we find that it is 80 times heavier than hydrogen at the same temperature; in other words, the specific gravity of bromine gas is 80. Proceeding in a similar way, we find the specific gravity of iodine gas to be 127. Let us now place the values we found for the atomic weights of the four elements side by side with those we have just established for the specific gravities of the same elements in the state of gas. A very striking fact is apparent.

Name of Element.	Atomic weight of Element.	Specific gravity of Element in state of gas.
Hydrogen	1	1
Chlorine	35·5	35·5
Bromine	80	80
Iodine	127	127

The table shows that the numbers which express the atomic weights of these elements are the same as those which express the specific gravities of the elements in the gaseous state.

The remarkable and astonishing agreement between these two sets of numbers could not have been foreseen, and could not have been established except by using the balance. This agreement, which was known first in the early years of the nineteenth century, is in keeping with the general behaviour of all gases which have been examined by physicists during the last two hundred years—that is, long before chemists had developed their theory of atoms and molecules. Physicists established the fact that all gases, and all chemical compounds in the state of gas—water-gas, for instance—have certain properties which are common to all of them. For instance, they behave similarly towards temperature and pressure; that is to say, all gases or gasified compounds are equally compressed by equal pressures, expand equally by equal increments of temperature, and contract to the same extent by equal lowerings of temperature.

Inasmuch as this statement holds good for all gases, and for all chemical compounds when gasified—for chlorine gas and bromine gas as for water-gas and hydrochloric acid gas—it is evident that the chemical compositions of gaseous bodies have no influence on their behaviour towards pressure and temperature, which is always the same for all gases. A consideration of this uniform behaviour of all gases shows that, although gases may differ radically in chemical composition—what chemical likeness is there, for instance, between chlorine gas and water-gas?—yet they must all have something in common. This common something cannot have to do with the chemical relations of the gases.

Careful reflection at last led to the conclusion that the only way of making intelligible this behaviour, which is common to all gases, was by supposing that equal volumes—say one litre—of all gases contain equal numbers of smallest particles, whether these smallest particles be particles of, let us say, chlorine, or water-gas, or hydriodic acid gas. This conclusion seems forced, but no serious objection has been found against it; it has been arrived at, not only by chemists, but also by physicists, from a study of the behaviour of gases, for all the phenomena of gases which are studied in physics compel us to suppose that equal numbers of smallest particles are contained in equal volumes of all gases.

Suppose we assume, for instance, that there are a hundred million smallest particles in one litre of hydrogen gas, a hundred million smallest particles in one litre of chlorine gas, and a hundred million smallest particles in one litre of bromine gas; then we can readily understand that these three gases, although they are certainly, in a chemical sense, exceedingly unlike one another, for each is a particular element, nevertheless are equally compressed by equal pressures and expand equally for equal increments of temperature. But if we make the supposition that a litre of hydrogen contains, say, a hundred and ten million smallest particles, a litre of chlorine gas ninety million, and a litre of bromine gas eighty-five million, smallest particles, then there is an end to all possibility of conceiving how, under these circumstances, the three gases should behave in the same way towards pressure and temperature.

It is certainly not difficult to follow this argument, which is of a negative character it is true, for the existence of an equal number of smallest particles in equal volumes of all gases. But the facts we have now to consider seem to be in complete contradiction to our supposition that equal numbers of smallest particles are contained in equal volumes of all gases. The elucidation of this apparent impossibility—that is, the clear setting forth of the reasons for it—has caused endless trouble.

Let us make a practical application of our supposition. Let us cause one volume of hydrogen gas, containing, let us say, one thousand smallest particles, to unite with an equal volume of chlorine gas, which will also contain one thousand smallest particles.* We should expect to obtain *one* volume of hydrochloric acid gas, which must also contain one thousand smallest particles of hydrochloric acid; for equal numbers of smallest particles are contained, according to our supposition, in equal volumes of all gases. To make the quantities such as may be most conveniently thought of by us, let us suppose we take one litre of each gas; then one litre of hydrogen and one litre of chlorine should yield *one* litre of hydrochloric acid gas. Now, *if the experiment is actually conducted, we obtain, not one litre, but two litres, of hydrochloric acid gas.*

To sum up. This incontrovertible experimental result, which is always obtained when the experiment is repeated, seems to be in complete contradiction to our assumption of the equality of the numbers of smallest particles in equal volumes of all gases. The contradiction is, however, only apparent. It is we who are responsible for the contradiction; for we have confused things which have nothing to do with one another, although it is true that the matter is a difficult one; and it is this difficulty which accounts for the long time that was required to make it clear.

The smallest particle of hydrogen, H, is an atom; the smallest particle of chlorine, Cl, is also an atom;

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* As we have already learned (p. 47) that these gases combine in sunshine, we know how the experiment may be conducted.

but is the smallest particle of hydrochloric acid, HCl, also an atom? No, that particle is not an atom, for it consists of two atoms; as we know already, that particle is a molecule. Now the contradiction begins to be cleared up. We have been trying to compare with one another smallest particles which are not comparable; for there are two kinds of smallest particles, and these are quite different one from another.

But how will keeping definitely apart the conceptions of the atom and the molecule enable us to explain the apparent contradiction in the behaviour of the gases we have been examining? The following considerations will be helpful.

We must certainly ascribe to the atoms of every element a tendency to combine with atoms of many other elements. If this were not so, the elements would remain for ever as such, side by side, and no compounds would be formed between them. What becomes of this tendency of the atoms when the elements make their appearance as such? For instance, what becomes of this tendency when hydrogen gas or chlorine gas is prepared? We must suppose that in the cases of these elementary gases—or, to express it otherwise, in these gaseous elements—this tendency of the atoms to combine finds its outcome in binding together the atoms of these gaseous elements (since there are no atoms at hand of other elements wherewith the atoms in question might perhaps more willingly combine), so that in these gases two atoms are joined together to form a molecule.

The following is an argument which may be adduced in favour of what we have stated to be the behaviour of the atoms in the elementary gases. At the moment when they are set free, when they must be considered [by our supposition] to exist as atoms, the behaviours of the elementary gases differ from their behaviours when we see them as completely formed gases, when their atoms have had time to combine with one another and form molecules.

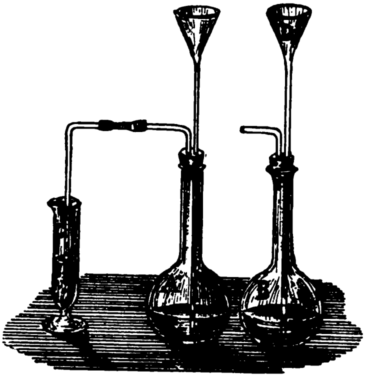

Fig. 28.—Experiments to illustrate reactions of nascent hydrogen.

The following demonstration, which is easily followed, will be especially serviceable. The reaction of zinc and diluted sulphuric acid produces hydrogen gas (p. 34). We shall make use of that reaction. We put the two substances into the flask A, and also into the flask B (fig. 28), and we pass the gas from A into a liquid called *nitrobenzene*, contained in the vessel C. Nitrobenzene is a compound of 6 atoms of carbon, 5 atoms of hydrogen, 1 atom of nitrogen, and 2 atoms of oxygen: its formula is $C_6H_5NO_2$. For however long a time we pass hydrogen gas through nitrobenzene, in the manner of this experiment, the nitrobenzene remains unchanged. But quite a different result is obtained if we pour some nitrobenzene (through the funnel D into the flask B, fig. 28) directly into a mixture of zinc and diluted sulphuric acid, although the substances employed—zinc, diluted sulphuric acid, and nitrobenzene—are the same as before. The inclination of hydrogen to form water by combining with oxygen now comes into play. The whole of the oxygen of the nitrobenzene combines with hydrogen, produced in the flask B, to form water, and is thus removed from the nitrobenzene. Two atoms of hydrogen—the source of which is, of course, the zinc and sulphuric acid—take the place of the oxygen. The body which is thus formed from nitrobenzene, and is found in the flask B in the place of the nitrobenzene, is *aniline*, the mother-substance of the aniline colours. The following equation expresses the change of nitrobenzene, $C_6H_5NO_2$, into aniline, $C_6H_5NH_2$:—

$$\begin{array}{ccccccc} C_6H_5NO_2 & + & 6H & = & C_6H_5NH_2 & + & 2H_2O. \\ \text{Nitrobenzene} & + & \text{hydrogen} & = & \text{aniline} & + & \text{water.} \end{array}$$

The foregoing experiment shows that hydrogen at the moment of its formation—*in the nascent state*, as the phrase is—reacts with nitrobenzene differently from the manner wherein it reacts when it is made and then passed into nitrobenzene. Many other bodies show reactions like this of nitrobenzene, under corresponding conditions. For the following reasons, these facts are explicable only in terms of the hypothesis we have made that molecules, not free atoms, are present in elementary gases when these exist as such. When zinc and diluted sulphuric acid are brought into contact with one another, hydrogen is formed, and in the first moment of its formation that gas must surely be produced atom by atom. If nitrobenzene is added to this mixture, the single atoms of hydrogen rush upon the oxygen of the nitrobenzene with all the tendency to combine which is naturally inherent in them, and, uniting therewith, form water. In the nascent state (or, one may say, at the moment of their birth) these atoms act successfully. But if the hydrogen gas is allowed to escape as such from the mixture, the two atoms of hydrogen combine together to form a molecule, each thereby satisfying part of the tendency to combine of the other, and so using up some of their energy of combination. Hence the energy remaining in such a molecule of hydrogen is not sufficient to drag away the oxygen from nitrobenzene when the hydrogen comes into contact with that compound; and so it is that hydrogen gas, in contradistinction to hydrogen in the nascent state, does not change nitrobenzene, as was shown in our experiment. As gaseous hydrogen is not able to perform actions which hydrogen in the nascent state can perform, there cannot be any single atoms present in hydrogen gas existing as such. Part of the energy of the atoms must have been satisfied by their mutual combination: they must have united to form molecules.

Hence *there are no single atoms in the elementary gases*—or, to express it otherwise, in the gaseous elements—*such as hydrogen gas or chlorine gas; but two atoms are always combined in these gases, to form a molecule of hydrogen,* H_2, *or a molecule of chlorine,* Cl_2.

Now, if in the elementary gases, such as hydrogen gas and chlorine gas, there are no free single atoms, but these are united in pairs, so forming molecules, we are in a position to explain the apparent contradiction (with which we are now dealing)—namely, that one volume of hydrogen gas and one volume of chlorine gas produce two volumes of hydrochloric acid gas. The explanation is this :—The thousand smallest particles contained in one volume of hydrogen are not, as we before assumed, a thousand atoms of hydrogen, H, but they are a thousand molecules, H_2; and an equal volume of chlorine gas contains, not a thousand atoms of chlorine, Cl, but a thousand molecules, Cl_2. When these two volumes combine, they produce, of course, two thousand smallest particles—that is, two thousand molecules—of hydrochloric acid.

$$1000H_2 + 1000Cl_2 = 2000HCl.$$

The theory of gases, which states that equal volumes of all gases contain equal numbers of smallest particles, shows that two thousand smallest particles—that is, two thousand molecules—of any gas occupy twice the volume of one thousand molecules of any other gas. Hence the two thousand molecules of hydrochloric acid, HCl, occupy twice the space occupied by a thousand molecules of hydrogen, H_2, or a thousand molecules of chlorine, Cl_2. We must, therefore, obtain two litres of hydrochloric acid gas from one litre of hydrogen gas and one litre of chlorine gas, as we found to be the case in that experiment which at first seemed to yield an impossible result. The explanation of that result is seen to be impossible so long as the conceptions of the atom and the molecule are not sharply differentiated.

The combination of a thousand molecules of hydrogen, H_2, with a thousand molecules of chlorine, Cl_2, to produce two thousand molecules of hydrochloric acid gas, HCl, may perhaps be made clearer to many by the following illustration. Imagine a thousand male twins and a thousand female twins — these would represent the molecules H_2 and Cl_2; let them all marry with one another; there will be two thousand married couples, corresponding with the two thousand molecules, HCl.

What we have demonstrated for hydrochloric acid gas holds good, of course, for all bodies in the gaseous state.

The weight of the molecule of a substance in the state of gas can be found from the specific gravity of that gas, because equal numbers of molecules are contained in equal volumes of all gases. Let us take water as an example. The specific gravity of water-gas (water above 100° C.) [212° F.] is 9, referred to hydrogen as unity. A litre of water-gas is nine times heavier than a litre of hydrogen at the same temperature. Now we must compare like with like; and as water-gas consists of molecules, we must compare it with the molecule of hydrogen, H_2. Hence the *molecular weight* is twice the specific gravity of the gas—that is, $2 \times 9 = 18$; and the formula H_2O (which represents the weight 18) corresponds with this result. The weight of the molecule of any gasifiable chemical compound may be determined in this way. Such determinations are of great importance in scientific work—for instance, when one has to deal with a newly discovered substance.

The main result of our considerations regarding atoms and molecules is, then, the following. Atoms are the smallest, indivisible particles of elements, molecules the smallest, divisible particles of compounds. It is possible, by using the balance, to determine the weights both of atoms and molecules, the weight of an atom of hydrogen being taken as unity.

We now proceed once more to the acquisition of purely chemical knowledge, which will gradually lead on to new general conclusions. We shall begin by turning our attention to oxygen.

OXYGEN.

ONE of our first experiments was to prepare oxygen gas by decomposing mercury oxide into its components. In connection with that method we explained what is meant by *analysis*. But the method is not a good one for preparing oxygen, because the quantity of oxygen, proportional to that of mercury, in mercury oxide is small. Let us calculate the quantity of oxygen in the compound. The formula of mercury oxide is HgO. The atomic weights of mercury and oxygen respectively are 200 and 16. Hence 216 parts by weight—let us say 216 grams—of mercury oxide contain 16 grams of oxygen; therefore (from the proportion $216 : 16 = 100 : x$) the percentage of oxygen is 7·4 only.

There is a salt known in commerce as chlorate of potash (it is more accurately called *potassium chlorate*), which is very rich in oxygen, and, like mercury oxide, yields the whole of its oxygen when it is heated. We shall learn how this salt is made at a later time; meanwhile, as it can be dealt with as conveniently as mercury oxide, we shall make use of it. The formula of potassium chlorate is $KClO_3$. As the atomic weight of potassium, K, is 39, that of chlorine, Cl, is 35·5, and that of oxygen, O, is 16, and as there are three atoms of oxygen in the compound, the molecular weight of the salt is 122·5.

$$\begin{array}{ccccccc} K & & Cl & & O_3 & & \\ 39 & + & 35{\cdot}5 & + & (3 \times 16) & = & 122{\cdot}5. \end{array}$$

In 122·5 grams of potassium chlorate there are 48 grams of oxygen; this is equal to 39·2 per cent. of oxygen, which is fully five times more than the percentage of oxygen in mercury oxide.

This time we shall collect our oxygen in a gasholder. The arrangement of such a gasholder as is commonly used in the laboratory is shown in fig. 29. This apparatus, which is evidently very different from the gasometers used in gas-works, consists of a lower vessel (A) holding about 15 litres [say, 4 gallons], connected with an upper vessel (B). The lower vessel is closed air-tight, and a tube (C) with a stopcock (K) passes from the upper vessel to the bottom of the lower one. There is also an opening (D) near the bottom of A; this opening can be closed by a screw-cap (E). The top of the lower vessel carries a second tube, provided with a stopcock (F) and connected with a tube drawn to a fine opening (H): L serves as a third support for the upper vessel B. If the reservoir B is filled with water, and the stopcocks K and F are opened, water will flow into A, and the air in that vessel will escape through H until, by using sufficient water, the lower vessel is filled with water. While this is being done, the opening D is, of course, closed by the screw-cap E. If both stopcocks are now closed, and D is set open (by unscrewing the cap E), the water in A will not flow out, for the same reason as that which prevented water from flowing out of the cylinders which we filled with water and inverted under water in the pneumatic trough. For, as the vessel A is closed completely at the top, air cannot get into that vessel, and therefore the water cannot flow out at the bottom. But if we now lead oxygen gas into A, by the opening D, the vessel A—that is to say, our gasholder—will get filled with oxygen, while water will flow out (at D) as the oxygen passes in.

Fig. 29.—Gasholder.

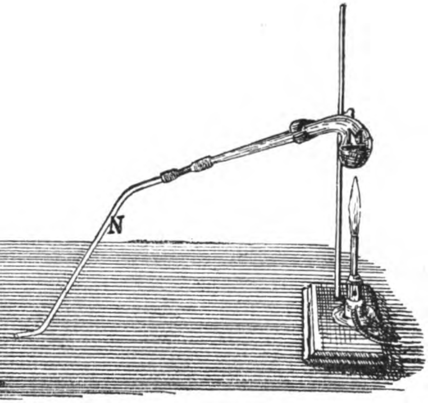

Fig. 30.—Filling a gasholder with oxygen gas.

To prepare oxygen, we place potassium chlorate in the retort M (fig. 30), and heat it; we then insert the tube N into the opening of the gasholder D; and when the vessel is filled with oxygen, we screw the cap E on to D. Were we now to open the stopcock K, water would, of course, tend to flow from the reservoir into the closed lower vessel; but as that vessel is closed completely, and is quite filled with oxygen gas, the water, not being able to enter the vessel, would exert a pressure on the gas contained therein. But if we now open the stopcock F, water will flow into A, and the gas will flow out at H in proportion to the inflow of water from B into A. As the entering water drives the gas before it, and causes the gas to leave the gasholder, we can lead the stream of gas to any place where we wish to have it by connecting a leading-tube to H by caoutchouc tubing; moreover, we can store the gas in the gasholder as long as we please.

Oxygen is an odourless and tasteless gas. It is exceedingly active—that is, very disposed to enter into combination. Compounds of oxygen are known with all elements except fluorine [argon, helium, and the companions of argon]. The compounds which are composed of oxygen and one other element are called *oxides*. As we already know (see p. 75), the bases are oxides, and most of the acids are formed from oxides. The oxygen compounds of the non-metals yield acids; those of the metals, with a few exceptions, are bases.

If we now burn some elements in pure oxygen gas, we see them combining therewith with great brillancy. For example, let us place a little phosphorus on a small spoon connected to a long wire which passes through a cork, ignite the phosphorus, and plunge it into a jar filled with oxygen. The phosphorus burns with a brilliancy that dazzles the eyes, and changes into white clouds (see fig. 31). If the white solid that is formed is analysed quantitatively, it is found to be composed of 43·66 per cent. phosphorus and 56·34 per cent. oxygen; from which result, using the atomic weights [of phosphorus (31) and oxygen (16)], it follows that the substance is formed of two atoms of phosphorus and five atoms of oxygen: hence the formula of the compound is P_2O_5. It is called *phosphorus pentoxide* (Greek πέντε = *five*). But this compound is also called *phosphoric anhydride.* The word anhydride, derived from the Greek ὕδωρ (= water), signifies without water. The second name is given because the oxide produces phosphoric acid as soon as it comes into contact with water: with one molecule of water the oxide produces a special acid called *metaphosphoric acid.* (We shall learn hereafter why this acid is not called simply phosphoric acid.) The oxide itself is not an acid; it is an acid anhydride. These two conceptions, acid and acid anhydride, must not be confused.

Fig. 31—Phosphorus burning in oxygen.

P_2O_5	+	H_2O	=	$2HPO_3$.
One molecule phosphorus pentoxide	+	one molecule water	=	two molecules metaphosphoric acid.

Metaphosphoric acid, having the composition HPO_3, is called anhydrous metaphosphoric acid, in distinction to phosphoric anhydride. This compound does not contain any water, in the sense that water itself is present in the compound; *but it is only* *when a molecule of water has combined chemically with the anhydride that the anhydride is changed to an acid.* If this acid, which has the composition expressed by the formula HPO_3, is dissolved in water, the liquid is called an aqueous solution of metaphosphoric acid; and by using less or more water, a concentrated or a dilute solution is obtained.

Exactly similar conditions hold good with sulphuric acid, for example. (We shall learn about the preparation of this acid when we come to consider sulphur.) The oxide of sulphur, SO_3, is called sulphur trioxide, or sulphuric anhydride, just as we speak of phosphorus pentoxide or phosphoric anhydride. Sulphuric acid, H_2SO_4, is formed by combining the oxide with one molecule of water.

$$\underset{\text{Sulphur trioxide}}{SO_3} + \underset{\text{water}}{H_2O} = \underset{\text{sulphuric acid.}}{H_2SO_4.}$$

The compound H_2SO_4 is sulphuric acid; but for the chemist it is anhydrous sulphuric acid, for the molecule of water added to SO_3 is an essential part of sulphuric acid. Sulphur trioxide itself is an oxide, not an acid. *The molecule of water has combined chemically with the sulphur trioxide*, SO_3; it has not dissolved the SO_3 after the manner of a solvent. It is only when more water is added than is shown in the foregoing equation that the ordinary sulphuric acid, containing water, is produced. Commercial sulphuric acid contains about 97 per cent. H_2SO_4—that is, 97 per cent. anhydrous sulphuric acid—and 3 per cent. water. It is so troublesome to remove this last 3 per cent. of water that it is allowed to remain in the commercial acid.

To recapitulate. Chemists distinguish between acid anhydrides, which are nothing but oxides, and anhydrous acids: the latter are composed of the oxides with one, two, three, or more molecules of water. As the anhydrides are not acids until they have combined with definite quantities of water, this water belongs to the *constitution* of the acids.

If we bring a glimmering piece of charcoal, C, into a flask containing oxygen, it glows brightly, and burns to CO_2 by combining with two atoms of oxygen. The compound CO_2 is a gas, commonly, but incorrectly, called carbonic acid. This gas is properly called *carbon dioxide*, or *carbonic anhydride*, in accordance with what was said concerning phosphoric anhydride and sulphuric anhydride. One or other of the two names just mentioned is always given to this compound in accurately scientific works.

Certain substances which we are not accustomed to see burning will burn in pure oxygen gas; for instance, glowing iron brought into this gas combines therewith and throws out a shower of sparks (see fig. 32). The iron burns, as we should expect, to an oxide—to an iron oxide, which has the formula Fe_3O_4. Similarly zinc burns to zinc oxide, ZnO. Such oxides, being oxides of metals, are bases (see p. 75), and they combine with acids to produce salts. Zinc oxide and sulphuric acid, for instance, form zinc sulphate.

Fig. 32.—Iron burning in oxygen.

The reaction of sulphuric acid with zinc oxide proceeds as shown in the following equation :—

$$H_2SO_4 + ZnO = ZnSO_4 + H_2O.$$

Sulphuric acid + zinc oxide = zinc sulphate + water.

Such a salt as zinc sulphate used to be called sulphate of oxide of zinc. If we look closely at the formula of the salt, we see that the metal—in this case zinc—has taken the place of both the atoms of hydrogen in the sulphuric acid. We have already found that hydrogen gas is given off when diluted sulphuric acid is poured upon zinc. Hitherto we have paid heed to this part of the reaction only. But if we examine the solution from which the hydrogen escapes, we find that it contains zinc sulphate in place of sulphuric acid. Hence the zinc has taken the place of the hydrogen which it has driven out of the sulphuric acid.

$$H_2SO_4 + Zn = ZnSO_4 + H_2.$$

Sulphuric acid + zinc = zinc sulphate + hydrogen gas.

As the formulæ of salts may be regarded as if the metals in them have replaced the hydrogen of acids, and as this view is accepted, the names of salts are not nowadays derived from the names of the metallic oxides, but from the names of the metals themselves. In modern chemistry one speaks of zinc sulphate, copper sulphate, lead acetate, sodium carbonate, and so on.

Oxygen is that constituent of the atmosphere which makes possible those combustions which we are familiar with in ordinary life. The following is the average composition of atmospheric air :—*

Nitrogen	77·41	per cent.
Oxygen	20·77	„
Moisture	0·85	„
Carbon dioxide ...	0·03	„
Argon	0·94	„
	100·00	

The minute traces of the gases metargon, krypton, neon, and xenon, which have been discovered recently in the air by extraordinarily delicate methods of examination, are included in the ·94 per cent. of argon in the foregoing statement.

Oxygen gas, then, forms about one-fifth of any volume of air ; it is diluted with about four-fifths of

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* The quantities of nitrogen and oxygen in air vary very slightly; the quantity of carbon dioxide varies more; and the quantity of moisture varies much. [TR.]

other gases. Hence processes of combustion proceed more moderately in air than we saw them proceeding in pure oxygen.

We are now in a position to follow what happened when we set fire to a piece of paper and allowed it to burn in the air, at the very beginning of our considerations, in order to obtain some notion of chemical processes. Paper is nearly pure *cellulose.* That compound is composed of 6 atoms of carbon, 10 atoms of hydrogen, and 5 atoms of oxygen; its formula is $C_6H_{10}O_5$. When it is burnt, the carbon is changed to carbon dioxide (CO_2), and the hydrogen to water (H_2O). To do this, 17 atoms of oxygen are required—namely, 12 atoms of oxygen to change $6C$ to $6CO_2$, and 5 atoms of oxygen to change $10H$ to $5H_2O$. The cellulose ($C_6H_{10}O_5$) already contains 5 atoms of oxygen; the remaining 12 atoms of oxygen must be obtained from the air. The equation which represents the changes that occur when the paper burns will be as follows:—

$$\begin{array}{ccccccc} C_6H_{10}O_5 & + & 12O & = & 6CO_2 & + & 5H_2O. \\ \text{Cellulose} & + & \text{oxygen} & = & \text{carbon dioxide} & + & \text{water.} \\ \text{(paper)} & & \text{(from the air)} & & & & \end{array}$$

We shall suppose that the piece of paper we burned weighed 2 grams; let us calculate—and this we can do easily—the weight of the products of burning this piece of paper. From the formula $C_6H_{10}O_5$, and the atomic weights $C = 12$, $H = 1$, $O = 16$, we find that—

$$\overset{C_6}{(12 \times 6)} + \overset{H_{10}}{10} + \overset{O_5}{(5 \times 16)} = 72 + 10 + 80 = 162.$$

And, treating the products of combustion in the same way, we see that—

$$6\,(\overset{\mathrm{C}}{12} + \overset{\mathrm{O_2}}{[2 \times 16]}) + 5\,(\overset{\mathrm{H_2}}{[1 \times 2]} + \overset{\mathrm{O}}{16})$$

$$= \overset{6\mathrm{CO_2}}{(6 \times 44)} + \overset{5\mathrm{H_2O}}{(5 \times 18)}$$

$$= 264 + 90 = 354.$$

As 162 parts by weight of cellulose yield 354 parts by weight of combustion-products, the proportion

$$162 : 354 = 2 : x; \quad \text{or, } x = \frac{354 \times 2}{162} = 4{\cdot}37$$

tells that 2 grams of paper yield 4·37 grams of combustion-products.

The products of combustion are heavier than the substance that was burnt. This is self-evident from the description that has been given of the process of burning, because the burning substance combines with oxygen, and the increase of weight must be equal to the weight of the oxygen wherewith it has combined.

The fact that the products of a combustion weigh more than the combustible substance may be demonstrated in the following way. A cylinder (A, fig. 33) is suspended from one end of the beam of a balance. A piece of wire-gauze is fixed in the cylinder, and pieces of caustic soda ($NaOH$) sufficient to fill the cylinder are placed on the gauze. A small candle is placed under the cylinder, and the balance is brought into equilibrium by placing another similar cylinder and candle on the other pan. When the candle under A is lighted, the caustic soda, which is a base, will combine with the carbonic anhydride, which is produced by the burning substance (and is drawn into the cylinder as into a chimney), and sodium carbonate will be produced. As caustic soda is one of those substances which absorb water (see p. 45), it will also retain the water that is formed by burning the hydrogen of the wax. These two substances, carbon dioxide and water, are the only products of burning wax, as that substance is composed of the elements carbon, hydrogen, and oxygen. The products of combustion, in this case, must weigh more than the candle, for the same reason as held good in the case of the paper; therefore we notice that the pan whereon the burning candle is placed sinks soon after the candle is lighted, and we thus see that this pan of the balance becomes heavier as the candle burns.

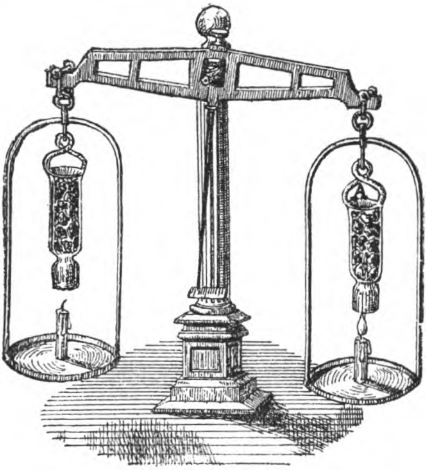

Fig. 33.—Experiment to show that the products of combustion of a candle weigh more than the candle.

The reason why the products of a combustion weigh more than the combustible substance is clear from the statements and descriptions which have been given. But the explanation of the phenomena of combustion, which we have been able to grasp so easily because of our knowledge of the reactions of oxygen, was formerly beset with many difficulties, and had to wait two thousand years before it was established. We are still accustomed to speak of the destruction of substances by fire, because the combustible materials generally disappear from sight during the process of burning. And in the olden times, when no clear conception had been formed of gases, because they could not be directly seen, the opinion prevailed that the ponderable matter was not only apparently, but really, destroyed by burning. There was supposed to be a fire substance which resolved the combustible body into non-existence.

About two hundred years ago people began to investigate special combustion-products, which they had gradually learnt to collect (for at that time men were not accustomed always to consult the balance in chemical investigations); but, still hampered by the very ancient view—which is met with in the Bible—they came to a conclusion which was diametrically opposed to the actual facts. They adopted the opinion that the products of burning were present in the combustible material *before* burning, and that the combustion-process consisted in setting free these products from the combustible substance. Thus regarded, a combustion process was a decomposition of the combustible material into the products of combustion; it was a process of division, whereas in fact it is a process of addition, and consists in the taking up of oxygen by the combustible material, with the appearance of fire.

In the seventeenth century it was supposed that the gas which is given off when charcoal burns (now called carbonic anhydride; see p. 119) pre-existed in the charcoal. (We know to-day that this gas, CO_2, is formed by the union of carbon, C, with oxygen, O, in the air.) Charcoal (carbon) was supposed to be composed of this gas and the principle of fire. In the same way it was thought that the brown substance which is formed by heating iron in the air already existed in the iron. (We know to-day that the substance is an oxide of iron—a compound of iron with the oxygen of the air.) Following this naïve way of looking at the matter, metallic iron would be regarded as composed of iron oxide and a principle of combustibility.

This combustible principle was supposed to be fixed in the metals, a view which certainly seems to us very odd. Stahl, who was a very able chemist in his day, at the beginning of the eighteenth century developed this view into a general theory, which was destined to rule the chemical world for nearly a hundred years. The theory declared that the phenomena of combustion, be the combustible bodies what they may, depend on the presence of a something which is common to all bodies that can be burnt: if this something is called fire-stuff, then the same fire-stuff is in all combustible substances. Stahl called this thing *phlogiston*, which means *burnt* (to-day it would be translated *combustible*). According to Stahl, the better a body burns, the richer it is in phlogiston; hence carbon and phosphorus contain very much phlogiston. It followed that combustion consists in the outrush of phlogiston from the burning body. It must be confessed that this theory, which seems to us so remarkable, explained most of the phenomena of combustion known at the time, as long as the aid of the balance was not invoked.

If phlogiston escapes during combustion, this loss must cause the product of combustion to be lighter than the unburnt material; but no one troubled about this at the time we are speaking of. We have already convinced ourselves of the accuracy of a conclusion just the opposite of that drawn by the phlogistic theory, both by calculating the weight of the combustion products of paper compared with that of the unburnt substance, and also by the ocular demonstration of the burning candle.

We have already seen that the combustion-products are heavier than the combustible material which yields them. It is to the immortal fame of Lavoisier that he, in the last quarter of the eighteenth century, conclusively proved the inconsistency of the phlogistic theory, after many of his contemporaries had striven to overthrow it, but in vain. Lavoisier's investigation, which gave the finishing stroke to the whole phlogistic theory, is markedly simple, like many another experiment of fundamental importance. He also was the first to render possible the building of modern chemistry; for it was by his investigations that a final explanation was given of the processes occurring in the burning fire, which are the most remarkable and striking phenomena connected with material changes (and therefore are purely chemical phenomena) that are met with without making intentional experiments. All chemistry antecedent to that explanation must remain piecework in the most disparaging sense of the term.

For the purpose of his investigation, Lavoisier placed metallic tin in a retort, and closed the end thereof by melting the glass (see fig. 34). Nothing could now enter the retort, nor could anything escape from it. Things being thus arranged, he weighed the retort and its contents. The retort was then heated for some days in one of the charcoal furnaces that were used in laboratories at that time (represented in fig. 34). During this heating the tin gradually changed to what we now call tin oxide—that is to say, it combined with the oxygen of the air in the retort. At that time, when oxygen was not yet known, this reaction of the metals was called calcination; the tin was said to be changed to calx of tin. A weighing of the retort and its calcined contents, after cooling, showed that the weight was the same as before heating; hence it

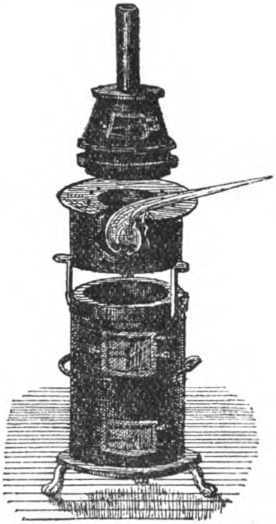

Fig. 34.—Heating tin in a closed retort in a furnace.

followed that, contrary to the requirement of the theory, no phlogiston had escaped from the retort during the calcination of the metal; for, had phlogiston escaped, the retort and its contents must have weighed less after the calcination of the tin than they weighed before. According to the upholders of the phlogistic theory, phlogiston was so light and thin a substance that it could pass through glass (somewhat after the manner of light); hence it must have escaped under the conditions of the experiment. This one process of weighing made by Lavoisier sufficed, indeed, to disprove completely the phlogistic theory.

Proceeding with his experiment, Lavoisier opened the retort, and noticed that, thereupon, air rushed into the vessel. On weighing once more, he found, of course, that the whole had become heavier. He then removed the calcined tin from the retort and weighed it. He found that the increase of weight, in relation to the quantity of tin used, amounted to as much as the retort and its contents had gained in weight after air had been allowed to rush in, by opening the retort, when the heating in the furnace was finished. The increase in the weight of the tin was just equal to the weight of the air which had rushed into the retort. Lavoisier was soon afterwards in a position to give the correct explanation of this remarkable fact.

At that time—1774—oxygen gas had just been discovered by Priestley, who was the first to obtain it by the method, familiar to us, of heating mercury oxide. Lavoisier, with the penetration of genius, very soon recognised this gas (which he had, meanwhile, himself prepared) to be the constituent of the air which brings about all processes of combustion, and that the metallic calces are nothing else than compounds of the metals with oxygen. Moreover, he perceived that, notwithstanding the long duration of the heating process, only a portion of the air in his retort had combined with the metal; and from this he drew the conclusion that the air must be composed of two constituents at least.

It is scarcely possible for us, to-day, to appreciate the revolution in scientific conceptions that was caused by Lavoisier's elucidation of the processes that occur during burning. Until the time of Lavoisier, but little heed was given to the quantitative prosecution of chemical experiments, the importance whereof has already been sufficiently brought home to us. It was supposed that heat was something ponderable, although no one had succeeded in establishing its weight. All results of weighing which did not fit in with the older views, and, consequently, not with the phlogistic theory, were attributed to changes in the weight of heat; and all those quantitative results which were in contradiction to the view that then prevailed were attributed to the same cause. But when Lavoisier's investigation had shown that, without doubt, heat played no part in combustions so far as changes of weight were concerned—in the oxidation of tin to tin oxide, for example—but that, on the contrary, heat was something imponderable, one was forced to acknowledge that all other changes of weight in combustion-processes were dependent on exchanges of material substances—that is, were purely chemical occurrences.

Lavoisier's investigation showed that the atmosphere is composed of at least two kinds of airs—one which supports burning, and one which cannot do this. It is not necessary, of course, that the latter should be homogeneous; it may be a mixture of different gases: we already know that the former is oxygen gas.

The following experiment, performed with a little piece of phosphorus, will convince us very quickly that oxygen forms only a small part of atmospheric air. As a preliminary, let us burn a little bit of phosphorus in the air. The burning proceeds, just as it does in pure oxygen, with the production of a great deal of white smoke (see A, fig. 35). Remembering this, we now place a little bit of phosphorus in a small basin, and attach this basin to a cork, which is floated on water, and can be covered by a bell-glass (see B, fig. 35). Then we ignite the phosphorus floating on the water; and now we place a bell-glass over the burning phosphorus (as shown in R, fig. 35), which continues to burn, briskly for a time, in the air that is cut off by the water from the surrounding

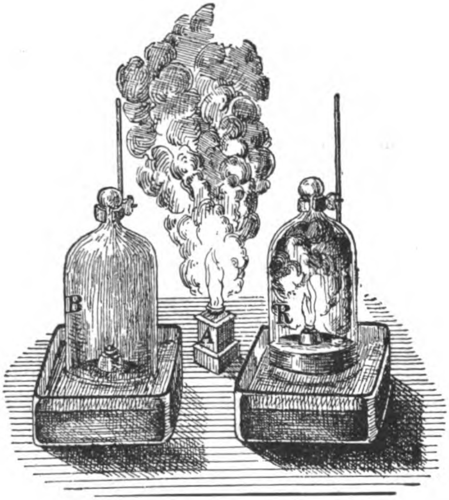

Fig. 35.—Burning phosphorus; and determination of the quantity of oxygen in the air.

atmosphere. We see white clouds of phosphoric anhydride, P_2O_5, forming in the bell-glass; but the brilliancy of the combustion is greatly less than that of phosphorus burning in pure oxygen. The phosphorus gradually ceases to burn, and goes out long before all the air in the bell-glass has disappeared. The rising of the water to take the place of the oxygen in the bell-glass (whose disappearance, or rather the combination whereof with the phosphorus to form solid phosphoric anhydride, has caused a vacuum inside the glass) shows us that about one-fifth of the air has vanished (for the water now fills about a fifth of the glass); hence this portion of the air must have combined with the phosphorus to form a solid body. This analysis of air shows that oxygen forms about one-fifth of the air that surrounds us.

The oxygen of the air is used up in all processes of burning; it combines with everything that burns. This occurs, not only when the burning is accompanied by the appearance of fire or flame, but also when the burning proceeds without that purely external adjunct; the rusting of iron, for instance, is nothing else than the union of iron with oxygen. Processes like that just mentioned can scarcely be described appropriately as burnings, for we are always accustomed to connect burning with the phenomena of fire and light. The word *oxidation* is used in such cases: chemists speak of the rusting of iron as an oxidation. Although oxidations may occur without the appearance of fire, yet they are always accompanied by the production of the heat which can be made available by the combination of the substance in question with oxygen. We are not conscious of the production of heat in such a process as the rusting of iron, because the process occupies so long a time—it may be spread over a period of a year or more—that we do not notice the heat that is evolved.

One kilo. of carbon produces the same quantity of heat when it is burned very rapidly to CO_2 (see p. 118) as when it is oxidised quite slowly to CO_2 without the appearance of fire or flame.

Our existence depends on the slow oxidation of carbon to which we have referred, in so far as the heat of our bodies is maintained by such a gradual oxidation of substances that contain carbon. All the food-stuffs we consume contain carbon. We notice that such substances become black when they are burned; the expression *to char*, which is in common use, is, therefore, quite correct. When the processes of digestion have acted on those constituents of food-stuffs that are needed for our nourishment in an appropriate way—that is to say, have made them soluble in water—these constituents reach the blood-stream, in forms very different from their original states, and are carried by the blood to those parts of the body where they are required. The blood passes through the lungs in the course of its circulation; and in these organs it reaches certain extremely fine veins, wherein it comes into contact with atmospheric oxygen that has diffused through the walls of these veins. The blood is thus constantly brought into contact with oxygen, and the oxygen exerts an oxidising action on those compounds of carbon that have been derived from the food-stuffs taken into the body. The blood also carries with it the carbonic anhydride, CO_2, which is formed in the tissues, and this gas is exchanged for oxygen in the lungs. Hence it follows that expired breath is very rich in carbonic anhydride.

The presence of carbonic anhydride in expired breath may be demonstrated in the following way. First of all we prepare some lime-water. We slake some burnt lime (lime has the composition CaO; it is the oxide of the metal calcium, Ca) by pouring water on to it. The lime combines with the water with the production of much heat :—

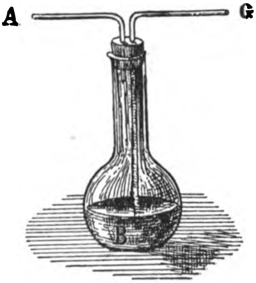

Fig. 36.—Detection of carbon dioxide in expired breath.

$$\underset{\text{Burnt lime}}{CaO} + \underset{\text{water}}{H_2O} = \underset{\text{slaked lime.}}{Ca(OH)_2}.$$

If much water is added to our slaked lime, a solution is produced which is called *lime-water.*

We now place some clear lime-water in a flask fitted with a cork and two tubes, as shown in fig. 36, and we draw a stream of air through the lime-water, by sucking at A. The lime-water remains practically unchanged by the air that passes through it. The quantity of carbon dioxide contained in ordinary air is so small (see the analysis of air, p. 120) that the stream of air would require to be continued for a long time to make the presence of the carbon dioxide apparent. But matters are very different when we send our expired breath through the lime-water, by blowing into the tube G (fig. 36). The lime-water becomes turbid in a very short time, through the formation in it of carbonate of lime, which is formed by the union of the lime with the carbonic acid in the breath; for this compound, being insoluble in water, soon separates as a solid, and we see it floating in the water in the form of a white powder.

The following equation expresses the formation of the carbonate of lime:—

$$CO_2 + Ca\,(OH)_2 = CaCO_3 + H_2O.$$

Carbonic anhydride + slaked lime = calcium carbonate + water.

We have used the name *calcium carbonate* in the equation because this is more correct than *carbonate of lime* if we desire to follow the usual notation of salts (see p. 120).

A litre of air weighs 1·293 grams; hence air is 773 times lighter than water; but it is 14·446 times heavier than hydrogen gas. As a column of mercury 760 millimetres [about 30 inches] long balances the weight of the air at the sea-level—such a column of mercury is used, under the name of a barometer, for measuring the pressure of the air and observing the oscillations of that pressure—we are able to calculate the weight of the atmosphere that surrounds the earth, in the following way. Taking the mean pressure of the air on the earth as equal to that of 750 millimetres of mercury (because of the many mountains), it follows that a spherical shell of mercury the size of the earth's surface and 750 millimetres thick would have the same weight as the sea of air which surrounds the earth. The result of this calculation is that the atmosphere weighs 5·2 trillion kilos. and contains 1·196 trillion kilos. of oxygen [about fifty thousand billion tons, containing about eleven thousand billion tons of oxygen].

The mass of oxygen in the atmosphere is so enormous that the quantities of this gas used for combustions, and for the breathing of men and animals, appear unimportant. Nevertheless, nature has taken care to make amends for what is used; for the plants breathe out oxygen, and so supply that gas to the atmosphere. Plants require carbon for their life-processes and growth. They take this carbon from the air, for their leaves are able to decompose the carbonic acid (CO_2) in the air. The plants retain the carbon they require, and return to the atmosphere part of the oxygen that was combined with carbon in the carbonic acid they absorbed. It is supposed that the leaves exert on the carbonic acid (CO_2) a *reducing action*—this expression here signifies adding hydrogen—and that the first product of this action is a compound called *formic aldehyde*, which has the composition COH_2. The formation of this compound from carbonic acid may be represented thus :—

$$\underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{hydrogen}}{H_2} = \underset{\text{formic aldehyde}}{COH_2} + \underset{\text{oxygen.}}{O.}$$

Formic aldehyde is extraordinarily ready to enter into chemical reactions; it is a body which yields numberless complicated compounds with great readiness. Hence the chemist easily comprehends that it may serve for the building up of the most various substances in living plants.

With regard to the presence of argon, metargon, krypton, neon, and xenon in the atmosphere, it is to be noted that these gases (which have been discovered recently) show absolutely no inclination to combine with other elements: not a single compound of any one of them is known. In this respect they are the complete opposite of all the elements which were known before their discovery, whose numberless compounds form our earth. One might almost say that these five elements belong to another sort of world than ours.

The air is not a chemical compound of certain gases; it is a mixture of these gases. The gases exist in the air side by side, the one uninfluenced by the others. That this is so is shown, in an inverse way, by the fact that if oxygen and nitrogen are prepared separately, and are mixed, a mixture is obtained wherein the two gases exhibit their properties unchanged, although that mixture behaves exactly like air, provided the proportion of the two gases is the same as in air. Moreover, when air is shaken with water, more oxygen dissolves than nitrogen, which would not be probable if the two gases were chemically combined.

We now pass to the most important compound of oxygen with hydrogen, which compound is water. We know that when a flame is brought to a mixture of oxygen gas and hydrogen gas these gases combine, with a loud explosion, to produce water (see p. 38). If we arrange matters so that the two gases are not allowed to mingle until the moment before the mixture is lighted, we obtain an exceedingly hot flame—the oxyhydrogen flame. We do this in the following way. Hydrogen gas is led through the tube B (fig. 37), and is ignited at A: we now have a hydrogen flame which must get its oxygen from the surrounding air. Oxygen is now led, by the tube C, into the midst of this hydrogen flame. In this arrangement the hydrogen and oxygen combine in the flame quite quietly and with complete safety. The oxy-hydrogen flame finds several technical applications—for instance, in manufacturing platinum, because that metal cannot be melted in any ordinary furnace. If this extremely hot flame is caused to impinge on an infusible substance—on lime, for instance—the substance (in this case the lime) is raised to a fervid heat, and, consequently, emits very white light. This arrangement is called the limelight: it has been used for many purposes—for example, in lighthouses; but since the electric arc-light has been made so easily accessible the limelight has lost its importance.

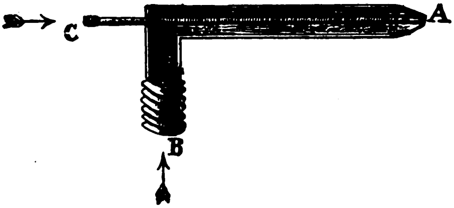

Fig. 37.—Burner for oxy-hydrogen flame.

In examining the methods of preparing hydrogen we found that water is decomposed by electrolysis into its two components, hydrogen and oxygen (see p. 33), and thereby we made a qualitative analysis of water.

We will now go a step forward, and effect a quantitative determination of the composition of water. We shall now find out exactly how the knowledge is gained that water consists of 11·11 per cent. of hydrogen and 88·89 per cent. of oxygen, with the help of which facts, taken as known, we have already calculated the formula H_2O (p. 91). Our method of procedure depends on the fact, already known to us, that hydrogen very readily combines with oxygen to form water. This is the reason why hydrogen reduces most oxides of metals, at a high temperature, to metals; that is to say, hydrogen removes oxygen from such oxides (combining therewith to produce water), so that the metals themselves remain. Copper oxide, CuO, is a metallic oxide; hence metallic copper and water are obtained when hydrogen gas is passed over red-hot copper oxide. The following method of analysing water quantitatively is made possible by carrying out this process with the helping hand of the balance:—

$$\underset{\text{Copper oxide}}{CuO} + \underset{\text{hydrogen gas}}{H_2} = \underset{\text{copper}}{Cu} + \underset{\text{water.}}{H_2O.}$$

Let us place, not any indefinite quantity, but an exactly weighed amount, of copper oxide—say, 1·5634 grams—in the bulb A of the apparatus represented in fig. 38, and let us pass dry hydrogen gas over this copper oxide. We obtain the hydrogen from a Kipp's apparatus (D, fig. 38; compare p. 35); but, to prevent the gas carrying any moisture with it, we dry it by leading it through the tube G before allowing it to pass over the copper oxide. The drying-tube G contains a salt, called calcium chloride, which is so hygroscopic—that is, eagerly attracts moisture—that gases are dried completely by passing over it. Of course, we might have dried our hydrogen by means of a washing-flask containing sulphuric acid, but we wish in this case to exemplify another method of drying.

A stream of dry hydrogen gas is now passing over the copper oxide in the bulb A of our apparatus. If we now heat the bulb and its contents, the copper oxide will be changed to copper gradually and completely. As the copper oxide is black, and it is changed to copper, which is red, we can easily follow the progress of the reaction. All the oxygen of the oxide will be combined with hydrogen at the end of the process, so forming water. The water that is thus produced is carried onwards by the stream of dry hydrogen that continues to flow from the Kipp's apparatus, and reaches the tube B (fig. 38), which also is filled with calcium chloride. This tube will hold fast all the water which is produced by the reduction of the copper oxide by hydrogen and is carried forwards, from the

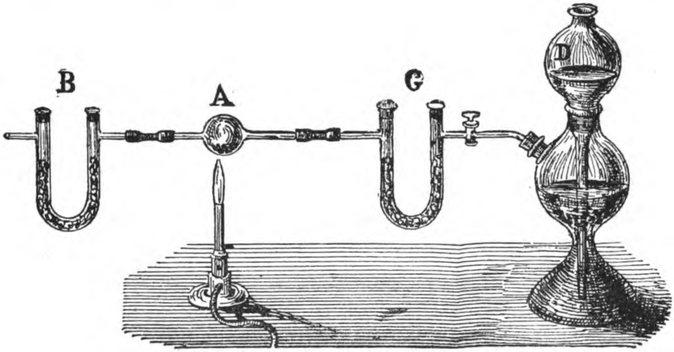

Fig. 38.—Quantitative synthesis of water.

bulb A, by the stream of dry hydrogen. The tube B must have been weighed before the experiment began, and must be weighed again when all the copper oxide has been changed to copper. The increase in the weight of this tube gives the weight of the water that has been produced in our experiment. We find this increase of weight to be 0·3535 gram.

If we also weigh the copper in the bulb A, we find that its weight is 1·2491 grams; the loss of weight suffered by the copper oxide is therefore 0·3143 gram [1·5634 − 1·2491]. This number, ·3143, is the weight of the oxygen which was combined with copper—forming copper oxide, CuO—and is now combined with hydrogen, forming the ·3535 gram of water which we have caught in the calcium chloride tube B.

These numbers tell us that ·3535 gram water contains ·3143 gram oxygen (because this is the quantity of oxygen that was contained in the 1·5634 grams copper oxide which was reduced to copper). If we deduct this number, ·3143, from the weight of water formed—that is, from ·3535—the difference must be the weight of hydrogen which has combined with the ·3143 gram of oxygen. The weight of hydrogen is [·3535 − ·3143] ·0392 gram; hence our quantitative experiment tells us that ·3535 gram water consists of ·3143 gram oxygen and ·0392 gram hydrogen. We have only to state these numbers in percentages in order to have the composition of water expressed in the form we are accustomed to employ. To do this we make use of the two proportions:—

(i) ·3535 gram water : ·0392 gram hydrogen $= 100 : x$;
(ii) ·3535 gram water : ·3143 gram oxygen $= 100 : y$;

whence we find that $x = 11{\cdot}11$ and $y = 88{\cdot}89$. The quantitative synthesis of water, then, shows that compound to be composed of 11·11 per cent. of hydrogen and 88·89 per cent. of oxygen.

Another compound of hydrogen and oxygen is known besides water; it is called *hydrogen peroxide.* That compound is richer in oxygen than water by one atom; $H_2O + O = H_2O_2$. It contains more oxygen than any other known compound. The molecular weight of the compound is 34 ($H_2 = 2 + O_2 = 32$); hence 34 parts by weight contain 32 parts by weight, corresponding to 94·1 per cent., of oxygen. We shall consider the preparation of hydrogen peroxide under sodium.

There is a modification of oxygen, called *ozone.* But we cannot properly understand how a substance which is an element (or, as one might say, a thing in itself)—and oxygen is an element—can exist in several forms, in several modifications (for that seems to be impossible), until we have grasped clearly the conception of the valency of atoms. But that conception cannot be elucidated until we have acquired more purely chemical knowledge than we possess at present. We shall therefore proceed to collect such knowledge.

WE know that fluorine, chlorine, bromine, and iodine form a group of four elements which are very much alike in their chemical relations. In like manner oxygen belongs to a group of four elements which are chemically very similar. These four elements are oxygen, sulphur, selenion, and tellurium.

SULPHUR.

Sulphur is found in abundance on the earth's surface. Sulphur itself—*native sulphur*, as it is called—occurs in volcanic districts; in Sicily, for example, which supplies the requirements of the whole of Europe. But much larger quantities of sulphur are found in combination with metals, in all parts of the world; and very considerable quantities of sulphur combined with oxygen and a metal are found in the form of *gypsum*, which is calcium sulphate.

Crude sulphur is worked in the Sicilian mines. It is purified by distillation, whereby the impurities (such as mineral *débris*) that adhere to it are left behind in the distilling vessel. If the distillation is conducted rapidly, the chambers, into which quantities of sulphur-vapour are poured, become so hot that the sulphur melts in these chambers; when it has cooled and has been removed from the chambers, this forms the *stick-sulphur* of commerce. If the distillation is allowed to proceed slowly, the sulphur-vapour falls down like rain in the form of a fine dust, and does not melt in the comparatively cold chambers. This dust is the commercial *flowers of sulphur*. The ease wherewith sulphur can be distilled permits the exhibition of the process in such an apparatus as is represented in fig. 39. The sulphur is heated in the retort A, and distils into the large glass balloon B, which represents the brick-built chambers of the factory.

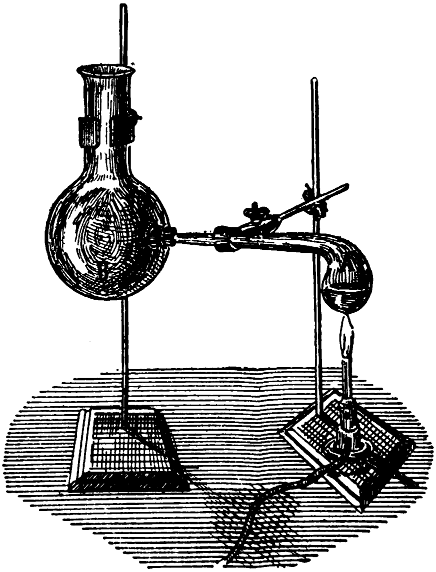

Fig. 39.—Purifying sulphur by distillation.

Sulphur combines with almost all other elements, just as oxygen does. The formation of iron sulphide, from iron and sulphur, was one of the first chemical experiments we performed. The first compound of sulphur we shall now consider is that with hydrogen. This compound is a gas, and is called *sulphuretted hydrogen.* Hydrogen is obtained when a acid—say hydrochloric acid—reacts with iron; if iron sulphide is substituted for iron, the gas which is formed is sulphuretted hydrogen. The following equations give a clear presentment of these reactions:—

(i) $2HCl + Fe = H_2 + FeCl_2$.
Hydrochloric acid + iron = hydrogen gas + iron chloride.

(ii) $2HCl + FeS = H_2S + FeCl_2$.
Hydrochloric acid + iron sulphide = hydrogen sulphide gas + iron chloride

Sulphuretted hydrogen is a colourless gas; it is at once recognised by its very disagreeable odour of rotten eggs. As one might suppose, it is more correct to say that rotten eggs smell of sulphuretted hydrogen: the albumin of eggs contains sulphur, and when the eggs decay the albumin is completely decomposed and sulphuretted hydrogen gas is given off. Sulphuretted hydrogen is very poisonous. The gas may be burnt; the products of its combustion are water and sulphur dioxide, for the hydrogen changes to water, and the sulphur combines with two atoms of oxygen, just as carbon does when it is burnt. As carbon gives carbon dioxide, so sulphur produces sulphur dioxide; and as carbon dioxide is also carbonic anhydride, so sulphur dioxide is also sulphurous anhydride.

$$H_2S + 3O = H_2O + SO_2.$$
Sulphuretted hydrogen + oxygen = water + sulphurous anhydride.
(from the air)

Sulphuretted hydrogen is only slightly soluble in water: it dissolves to the extent of about half a per cent.; that is to say, one litre of water [1000 grams] saturated with sulphuretted hydrogen, by passing the gas into the water until no more gas dissolves, contains about 5 grams of the compound. We found that one litre of water dissolves about 400 grams of hydrochloric acid gas (p. 72).

In spite of its smell, which is certainly not agreeable, sulphuretted hydrogen is much used in chemical laboratories; for it is practically indispensable for the detection of the metals, notwithstanding the many endeavours that have been made to find a less evil-smelling substitute.

We will endeavour to set forth shortly the reasons for the usefulness of sulphuretted hydrogen in analysis, and at the same time to give an approximate presentment of the methods generally followed in analysis. One cannot learn analysis properly by demonstrations, much less by descriptions; the only way is personal work in the laboratory.

Almost all analyses are made *in the wet way*; that is to say, the substance to be analysed is brought into solution. To do this presents no great difficulties in the case of metals, for most of these are dissolved by hydrochloric acid, nitric acid, or *aqua regia* (which we shall soon become acquainted with). Even such hard and solid bodies as granite and the like may be transformed into compounds suitable for analytical purposes, and soluble even in water, without very great difficulty. For this purpose the finely powdered rock is mixed with a strong alkali, and the mixture is fused in a crucible. The silicic acid of the rock becomes alkali silicate, which is soluble in water (see p. 74); when this has been dissolved in water, the residue consists for the most part of the bases—such as lime, magnesia, iron oxide, etc.—which were combined with silicic acid in the original substance, and these bases are soluble in various acids, in hydrochloric acid, for example.

When sulphuretted hydrogen is passed into a liquid wherein certain metals are dissolved, it precipitates the metals as sulphides; that is to say, the sulphuretted hydrogen converts the metals into sulphur compounds which are insoluble in water, and, therefore, must separate from the solution. We have once already made use of a solution of silver. (We shall become acquainted with the preparation of such a solution when we study nitric acid.) If we pass sulphuretted hydrogen into this solution, it becomes brownish black, for the silver is changed to silver sulphide, which has that colour.

The apparatus represented in fig. 40 may be used. The flask A contains iron sulphide and hydrochloric acid. The sulphuretted hydrogen which is formed by the interaction of these two substances is washed in B, and then passes into the silver solution in C. This apparatus must, of course, be placed in a draught-cupboard (see p. 41). The silver sulphide soon settles down, as a precipitate, in c; and it may be collected on a filter. To remove the silver sulphide from the liquid we proceed just as we did when we separated sand from a boiling solution of benzoic acid (see p. 54). The filtrate—that is, the liquid which runs through the filter—is now free from silver, and can be examined for any other substances which it may contain. In conducting such an examination heed must be given to the following facts˙ If solutions are made alkaline, by adding ammonia—for ammonia is an alkali (compare p. 75)—then *sulphuretted hydrogen precipitates all the heavy metals, as sulphides, from such alkaline solutions; but if the solutions are made acid, then sulphuretted hydrogen precipitates only some of these metals.*

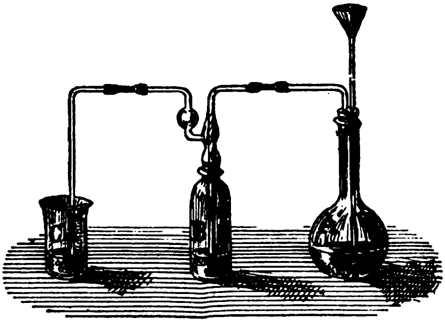

Fig. 40.—Leading washed sulphuretted hydrogen into a solution of a metal.

The metals in a solution may then be divided into two main classes, by the use of sulphuretted hydrogen, in the following manner. Some hydrochloric acid is added to the solution, and the gas is passed into this acid liquid. Certain sulphides are now precipitated—for example, copper sulphide, lead sulphide, and tin sulphide. The liquid is filtered, and the sulphides of the metals of the first class are obtained on the filter. The filtrate—which is now free from copper, lead, etc.—is made alkaline by the addition of ammonia, and sulphuretted hydrogen is passed into it. If a precipitate is produced, that precipitate consists of those metallic sulphides which are not precipitated from an acid solution, such as iron sulphide, zinc sulphide, etc. The second class of metallic sulphides may be collected on a filter.

Our method of procedure has shown us how the metals in any solution may be divided into two main classes by converting them into their sulphides. The further separation of the individual members of each class does not concern us here.

We must now regard the solution we have been examining as having been freed from all heavy metals by means of sulphuretted hydrogen. Of the better-known elements it can now contain, only perhaps calcium, magnesium, potassium, and sodium. The detection of these is proceeded with by methods similar to that we have already used; for instance, any calcium that may be present is precipitated as calcium carbonate, which may be removed by filtration; and the filtrate may be examined for magnesium, potassium, and sodium by appropriate methods, which are, broadly, like those we have employed.

Sulphur combines with chlorine, bromine, and iodine to form sulphur chloride, sulphur bromide, and sulphur iodide; but a survey of these compounds would not benefit us much. The compounds of sulphur with oxygen are as important as that compound with hydrogen we have been considering. These oxygen compounds form acids by reacting with water. Of those acids which are thus derived from sulphur we shall make the acquaintance of sulphurous acid, sulphuric acid, and thiosulphuric acid, passing over as unimportant to us the six other oxy-acids of sulphur. No other element furnishes so many acids of this kind [that is, acids containing oxygen] as sulphur.


Fig. 41.—Experiment to show that an acid is formed by burning sulphur.

We already know (p. 144) that the gaseous oxide SO_2—called sulphur dioxide or sulphurous anhydride—is formed when sulphur burns in air; the same oxide is formed when sulphur is burnt in oxygen. Sulphur, then, like carbon, disappears when it is burnt; the ordinary expression is that "fire destroys sulphur as it destroys carbon." In sulphurous acid gas (which is a third name for the compound also called sulphur dioxide and sulphurous anhydride) one atom of sulphur is combined with two atoms of oxygen. If we set fire to a little sulphur and allow it to burn in a flask containing some water, as shown in fig. 41, the sulphur dioxide which is produced will dissolve in the water, as it is a gas which is very soluble in water. If we now pour some litmus solution into the flask, the blue litmus will be turned red, a proof that the solution in water of the gas formed by burning sulphur contains an acid.

Sulphurous acid has the composition shown by the formula H_2SO_3 ($SO_2 + H_2O = H_2SO_3$). The acid, of course, forms salts. The sodium salt is Na_2SO_3 (compare p. 120). The most convenient way of preparing this salt is to *neutralise* the acid by caustic soda—that is, to add caustic soda to a solution of the acid containing a little litmus until the red colour of the litmus just begins to turn blue. (A similar method is generally the most convenient for preparing other sodium salts.) The chemical reaction is expressed thus in an equation:—

$$H_2SO_3 + 2NaOH = Na_2SO_3 + 2H_2O.$$

Sulphurous acid + caustic soda = sodium sulphite + water.

We have seen before, we see here, and we shall always see, that water is formed, besides a salt, whenever an acid and a base react. *The accurate description of acid and base is that they are compounds which by their interaction produce a salt and water* (compare p. 74).

Let us look at the reaction we have just been considering in the case of a hydracid of one of the halogens—say hydrochloric acid. When this acid is neutralised by caustic soda we obtain common salt and water:—

$$HCl + NaOH = NaCl + H_2O.$$

Hydrochloric acid + caustic soda = sodium chloride + water.

We might, therefore, very well call sodium chloride (NaCl) sodium hydrochloride. The metal sodium takes the place of the atom of hydrogen in the acid HCl (compare p. 67). In NaCl the element chlorine is directly joined to sodium, forming a salt. Similar relations hold good in the cases of the other three halogens, bromine, iodine, and fluorine. These four elements combine directly with metals to form salts; hence the name *halogens* (salt formers) given to them (from the Greek ἅλς = salt). These four elements are characterised by this reaction, that they form salts directly; whereas not the other elements themselves, but their oxides, are the bodies wherefrom salts are formed.

If sulphur is added to a solution in water of sodium sulphite—which we have spoken of a moment or two ago—and the liquid is boiled for a considerable time, the sulphur gradually dissolves, although sulphur is quite insoluble in water alone. As the solution cools, a new salt crystallises from it, in place of the sodium sulphite; this new salt is *sodium thiosulphate.* [Commercially it is known as *hyposulphite of soda*; and it is often referred to merely as *hypo.*]

$$Na_2SO_3 + S = Na_2S_2O_3.$$

Sodium sulphite + sulphur = sodium thiosulphate.

Sodium thiosulphate, $Na_2S_2O_3$, is used as an *antichlor* (see p. 49). As soon as this salt is added to a solution of bleaching powder the two salts interact, and new substances are formed which do not injure clothes as bleaching powder does. The interaction between these two compounds is very complicated; we shall not, therefore, write down the equation that expresses it, as the equation is not easy to follow.

Sodium thiosulphate is also much used in photography. In order to obtain a picture, plates whereon is spread a thin film of silver bromide (compare p. 60) are exposed in the camera. The rays of light which proceed from the object to be pictured decompose the silver bromide exactly in proportion to their strength. The picture which is formed on the plate, by a brief exposure thereof, and is not visible to the human eye, is strengthened until it attains the desired distinctness by means of a "developer," in the dim red light of the dark-room. Besides the picture, all the silver bromide which has not been affected by the light still remains on the plate. But this unchanged silver bromide must be removed; for if the plate were brought into the daylight, the unchanged silver bromide on it would be decomposed by the light, and the whole plate would be blackened. To remove the unchanged silver bromide the plate is laid in a solution of sodium thiosulphate after the development of the picture. Silver bromide is soluble in a solution of sodium thiosulphate, whereas silver bromide which has been changed by light—that is to say, the picture formed on the plate—is insoluble therein. The silver bromide which has been altered by light comes, therefore, unchanged from the sodium thiosulphate bath, while the excess of silver bromide—that is, the portion not used for forming the picture—is removed.

SULPHURIC ACID.

Sulphuric acid plays an incomparably more important part than either sulphurous or thiosulphuric acid. The formula of sulphuric acid is H_2SO_4; it contains, therefore, one atom of oxygen more than sulphurous acid.

$$H_2SO_3 \quad + \quad O \quad = \quad H_2SO_4.$$
Sulphurous acid + oxygen = sulphuric acid.

To change sulphurous to sulphuric acid it is only necessary to oxidise the first-named acid—that is, to add more oxygen to it. But in what way can this best be done? As sulphuric acid is used in enormous quantities in chemical manufactures, it is important that the oxygen should be obtained as cheaply as possible—that is to say, it should be obtained from the air. But this object has not been realised without some difficulty. We know already that sulphur burns in the air only to sulphurous anhydride, SO_2; or, to use another form of words, that by mere burning sulphur is oxidised only to sulphur dioxide. Sulphur does not form sulphuric anhydride, SO_3, by direct combination with oxygen; in other words, it does not burn directly to sulphur trioxide. The last-named oxide would certainly at once form sulphuric acid by reacting with water.

$$SO_2 \quad + \quad O \quad = \quad SO_3.$$
Sulphurous anhydride + oxygen = sulphuric anhydride.

$$SO_3 \quad + H_2O \quad = \quad H_2SO_4.$$
Sulphuric anhydride + water = sulphuric acid.

It is easy enough to represent these changes, on paper, in equations; but it is a different matter to realise them in practice.

In course of time methods have been found, somewhat roundabout it is true, for overcoming all the difficulties in the way of carrying out the desired oxidation. As sulphur could not be burnt directly to SO_3, an instrument was sought for, and has been found, which should carry over the oxygen of the air to the sulphurous anhydride, SO_2, which is produced by the direct burning of sulphur. This process serves to oxidise sulphur to the oxide SO_3, indirectly, by means of the oxygen of the air. Hence it attains the wished-for goal—namely, the preparation of sulphuric acid. The by-path which leads to this result is the calling in the help of nitric acid in the manufacture of sulphuric acid.

Nitric acid, with which we shall soon become acquainted in detail, is very rich in oxygen. It is an acid that contains nitrogen; its formula is HNO_3. The abundance of oxygen in this acid is the only thing about it which interests us at present. Let us calculate the quantity of oxygen. As the atomic weights of hydrogen, nitrogen, and oxygen are 1, 14, and 16 respectively, the molecular weight of nitric acid is—

$$\overset{H}{1} + \overset{N}{14} + \overset{O_3}{(3 \times 16)} = 63.$$

In 63 parts by weight of nitric acid are, therefore, contained 48 parts by weight of oxygen; hence, putting x as the percentage of oxygen, we have the proportion—

$$63 : 48 = 100 : x; \text{ or, } x = \frac{48 \times 100}{63} = 76{\cdot}2.$$

Nitric acid, then, contains 76·2 per cent. of oxygen. Hence we are not surprised that nitric acid should be a strong oxidising agent; or, to express the leading property of the acid without making use of this technical term, we are not surprised to find that nitric acid is very ready to give up oxygen to other bodies.

Sulphurous anhydride, SO_2, is one of those bodies whereto nitric acid readily gives up part of its oxygen. In conducting the manufacture of sulphuric acid matters are so arranged that the combustion product of sulphur—that is, gaseous sulphurous anhydride (SO_2)—is led, along with steam, into chambers made of leaden plates, wherein are placed pans containing nitric acid. "Lead chambers" are employed because these best resist the action of sulphuric acid. The nitric acid exerts an oxidising action on the sulphurous anhydride gas. As there is water in the chambers in the form of steam, the wished-for sulphuric acid is produced from the materials that are present, and collects as a liquid at the bottom of the chamber.

SO_2	+	H_2O	+	O	=	H_2SO_4.
Sulphurous anhydride gas	+	water	+	oxygen	=	sulphuric acid.
(obtained by direct burning of sulphur)		(in the form of steam)		(from the nitric acid)		

As the oxygen that is required for this process is obtained from nitric acid, that acid must be robbed of part of its oxygen. Hence one would suppose that the process would require very large quantities of nitric acid. *But the requirement is only apparent*, and that for the following reasons. The nitric acid certainly gives the oxygen that is needed for the formation of sulphuric acid in the chambers; but the compounds, poorer in oxygen than nitric acid, that are produced by this giving up of oxygen are again continuously oxidised to nitric acid by the oxygen of the air, which is intentionally allowed to flow into the chambers in large quantities, along with the sulphur dioxide gas and the steam. It is the oxygen of the air which keeps constantly going the further oxidation of the sulphurous anhydride, by insuring the constant presence of nitric acid. To put it shortly: *the nitric acid acts only as a carrier of the oxygen of the air in the manufacture of sulphuric acid.* A determinate quantity of nitric acid should suffice for the preparation of an unlimited amount of sulphuric acid; but unavoidable losses in the manufacture render it necessary to make very small, constant additions of nitric acid. Sulphur is not an expensive material; oxygen from the air is cheap enough; hence the low price of sulphuric acid.

The sulphurous anhydride gas required in the manufacture of sulphuric acid used to be made by burning sulphur, which had to be obtained from Sicily. But cheaper sources have been made use of for the last sixty years. Most of the sulphur used in Europe still comes from Sicily; but, as we have already remarked, there are large quantities of easily worked sulphur compounds—iron sulphide, for instance—in various other places. Native iron sulphide, called *pyrites* by mineralogists, has the composition FeS_2, and contains more than 50 per cent. of sulphur. Like sulphur, pyrites may be burnt in a kiln. From what we have learned before, we can see that the products of combustion will be sulphurous anhydride gas, SO_2, and iron oxide, Fe_2O_3; and, hence, that the change must be expressed by the following equation :—

$2FeS_2$	$+$	$11O$	$=$	Fe_2O_3	$+$	$4SO_2$
Pyrites	+	oxygen	=	iron oxide	+	sulphurous anhydride gas.
(iron sulphide)		(from the air)				

The iron oxide which remains after burning pyrites is used in iron-works. The possibility of making use of this by-product naturally cheapens the price of sulphuric acid.

The applications of sulphuric acid are extraordinarily many. This acid expels most other acids from their compounds. We have already used it in this way for making hydrochloric acid, by causing it to react with common salt (see p. 67); it is also employed for decomposing phosphates, as we shall find when we come to the manufacture of artificial manures. The acid is used in making ammonium sulphate, $(NH_4)_2 SO_4$, a salt which is now manufactured in large quantities and is almost wholly employed in agriculture. Sulphuric acid is employed in obtaining hydrofluoric acid (of which we know something), nitric acid, and also stearic acid, which is used in candle-making. Sulphuric acid is indispensable in the manufacture of phosphorus, nitroglycerin, and gun-cotton, substances to be considered by us in later parts of the book. The manufacture of aniline uses large quantities of this acid. Parchment paper is made by immersing paper in sulphuric acid for a short time, and then removing the acid by continued washing in water. The other applications of sulphuric acid (some of them of minor importance) are innumerable.

Sulphuric acid is clearly one of those substances which are manufactured in enormous quantities. About 2,156,000 *tonnes** were made in Europe in 1890: this represents about 215,000 railway waggon loads; or about 600 loads (equal to, say, 20 goods trains) daily: and the manufacture has increased greatly since 1890.

Many of the salts of sulphuric acid are important. The salts which it forms with the heavy metals have long been called *vitriols*; iron vitriol [also called "green vitriol"] is iron sulphate, copper vitriol [also known as "blue vitriol"] is copper sulphate. As either iron, Fe, or copper, Cu, takes the place of two atoms of hydrogen in acids, the formula of iron sulphate is $FeSO_4$, and that of copper sulphate is $CuSO_4$.

ACID SALTS. DOUBLE SALTS. BASIC SALTS.

We have now sufficient knowledge to enable us to understand what yet remains to be said about salts, and especially about acid salts, double salts, and basic salts.

Acid salts are those in which only part of the hydrogen of acids is replaced by metals. To take an example. We know that the formula of the neutral [or normal] sodium sulphate is Na_2SO_4; this salt is formed by replacing both atoms of hydrogen in sulphuric acid, H_2SO_4, by sodium; but, as one atom of the metal sodium always replaces one atom of

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* As a metric tonne = ·98 ton (approximately), the number in the text represents about 2,113,000 tons. [TR.]

hydrogen, it is easy to see that another salt might exist having the formula $NaHSO_4$. That salt is an acid salt, because it still contains one atom of the hydrogen of the acid.

The atom of hydrogen in the acid salt $NaHSO_4$ can be replaced by another metal—by potassium, for example. If this is done we obtain the salt $KNaSO_4$, which is a *double salt,* and is called potassium sodium sulphate. To prepare this salt, caustic potash is added to a solution of acid sodium sulphate; the base (potash) neutralises the acid salt completely, and we obtain a neutral double salt. The reaction is expressed by the equation :—

$NaHSO_4$	+	KOH	=	$KNaSO_4$	+	H_2O.
Acid sodium sulphate	+	caustic potash	=	potassium sodium sulphate	+	water.

But there is another kind of double salts—namely, such as are produced when two salts crystallise from a solution wherein they are present, not one after another, as happened with benzoic acid and common salt (see p. 54), but combined together as a double salt. The number of salts which crystallise from solutions as double salts is, however, very small compared with the number of those which always crystallise by themselves alone.

The alums are the best known of all double salts. The name of the class is taken from common alum, which is a double salt of aluminium sulphate and potassium sulphate. One atom of aluminium always takes the place of three atoms of hydrogen. Now, as there are only two atoms of hydrogen in sulphuric acid, the adjustment can be brought about only by the replacement of six atoms of hydrogen, from three molecules of sulphuric acid, by two atoms of aluminium. Hence the formula of aluminium sulphate is $Al_2(SO_4)_3$. The formula is written $Al_2(SO_4)_3$ to indicate that three SO_4 [atomic groups] are combined in this salt with two Al [two atoms of aluminium]. This aluminium salt, which crystallises very imperfectly, combines eagerly with potassium sulphate, whose formula is K_2SO_4, to form an easily crystallisable double salt, which has long been known by the name *alum.* If the two salts are present in a solution, they do not crystallise separately, one after the other, but they crystallise out in combination, as the double salt $Al_2(SO_4)_3K_2SO_4$. We may write this formula as $Al_2K_2(SO_4)_4$; we may then halve this, and so obtain the formula $AlK(SO_4)_2$ for alum. But it is much more difficult to understand this shortened formula, because it does not make apparent the way wherein the aluminium and potassium, together, replace the four hydrogen atoms of two molecules of sulphuric acid.

Quite a number of other metals (and also *ammonium,* concerning which we shall learn something shortly) can take the places of aluminium and potassium in the common alums. *Iron alum,* for instance, is $Fe_2K_2(SO_4)_4$. The potassium in this double salt may be replaced by ammonium, acting as a metal; we thus obtain *iron ammonia alum,* $Fe_2(NH_4)_2(SO_4)_4$. Almost all those double salts which are called alums crystallise very readily, so that it is an easy matter to obtain them pure (compare p. 56). All alums crystallise with 24 molecules of "water of crystallisation." If one examines a crystal of common alum, one finds that, besides $Al_2K_2(SO_4)_4$, it contains water, and indeed 24 molecules of water. If this water is driven out by heating, what is called *burnt alum* is obtained. Burnt alum is a white amorphous powder; the crystals of alum are only obtained when $Al_2K_2(SO_4)_4$ is combined with $24H_2O$. As in alum, so in very many other crystalline salts, there is found water of crystallisation. In all such cases the crystalline form is impossible without the water. The quantity of water of crystallisation can be calculated in the same way as the quantity of any other constituent of a chemical compound. Let us calculate the water in alum. The atomic weight of aluminium is 27, of potassium 39, of sulphur 32, of oxygen 16, and of hydrogen 1. The molecular weight of alum given by the formula $Al_2K_2(SO_4)_4 24H_2O$ is—

$$\begin{array}{cccc} Al_2 & K_2 & (SO_4)_4 & 24H_2O \\ (2 \times 27) + & (2 \times 39) + & (4 \times 96) + & (24 \times 18) = 948. \end{array}$$

In 948 parts by weight of alum crystals there are $24 \times 18 = 432$ parts by weight of water. The proportion—

$$948 : 432 = 100 : x; \text{ or, } x = \frac{432 \times 100}{948}$$

shows that alum contains 45·5 per cent. of water of crystallisation.

Chrome alum, $Cr_2K_2(SO_4)_4\ 24H_2O$, wherein chromium takes the place of the aluminium of common alum, crystallises in especially large and well-formed crystals.

Acid salts are those salts which are able to combine with more alkali, after the manner of acids; *basic salts*, on the other hand, are those salts wherein the whole of the base is not saturated by acid. Basic salts are, therefore, prepared to combine with more acid. The formula of one of these salts must indicate exactly the quantity of base therein which is not saturated by acid; and as the relations of the parts of such salts to one another vary much, the chemical compositions, and hence, of course, the formulæ, of basic salts are often very complicated.

The two elements *selenion* and *tellurium* are chemically like sulphur. Both occur only in small quantities. Their likeness to sulphur is very marked. They burn in air to the compounds SeO_2 and TeO_2 (selenious oxide and tellurous oxide), which correspond to SO_2; in other words, each of these elements, like sulphur, combines with two atoms of oxygen from the air. The two oxides SeO_2 and TeO_2 can be oxidised to selenic and telluric acids [H_2SeO_4 and H_2TeO_4]. If hydrochloric acid reacts with iron selenide or iron telluride, *selenuretted hydrogen gas* or *telluretted hydrogen gas* is obtained, just as sulphuretted hydrogen gas is produced by the reaction of hydrochloric acid with iron sulphide. These two gases resemble sulphuretted hydrogen; but they smell much more abominably and they are much more poisonous than that gas.

(i) $FeS + 2HCl = FeCl_2 + H_2S$.
Iron sulphide + hydrochloric acid = iron chloride + sulphuretted hydrogen gas.

(ii) $FeSe + 2HCl = FeCl_2 + H_2Se$.
Iron selenide + hydrochloric acid = iron chloride + selenuretted hydrogen gas.

(iii) $FeTe + 2HCl = FeCl_2 + H_2Te$.
Iron telluride + hydrochloric acid = iron chloride + telluretted hydrogen gas.

We pass now to another group of elements, the nitrogen group. This group contains four elements—nitrogen, phosphorus, arsenic, and antimony.

NITROGEN.

We know (see p. 120) that more than 77 per cent. of the atmosphere is composed of nitrogen. The symbol for nitrogen is N; the name nitrogen [nitre-producer] is connected with *nitrum*, the Latin name for saltpetre. We obtained nitrogen by burning phosphorus in a bell-glass standing over water: the phosphorus combined with the oxygen in the air, forming phosphoric anhydride (P_2O_5), and the nitrogen, which had formed part of the air under the bell-glass, remained. The nitrogen thus prepared was mixed with carbon dioxide, argon, etc. (see analysis of air on p. 120), for we made no attempt to remove these substances. But we have always sought to obtain the substances we have examined in a state of purity, and we must do the same in the case of nitrogen, because even small quantities of impurities may greatly modify the properties of a substance.

To obtain pure nitrogen we employ a method very different from that we used for making impure nitrogen from the air.

We know that the formula of nitric acid is HNO_3. There exists an acid, called *nitrous acid*, which is related to nitric acid in the same way as sulphurous acid (H_2SO_3) is related to sulphuric acid (H_2SO_4): as sulphurous acid contains one atom of oxygen less than sulphuric acid so nitrous acid is poorer in oxygen than nitric acid by one atom. The formula of nitrous acid must, then, be HNO_2. This acid reacts with bases and forms salts; with ammonia it forms *ammonium nitrite*, NH_4NO_2. We must know something of ammonia (we come to that compound in a few pages) before we are

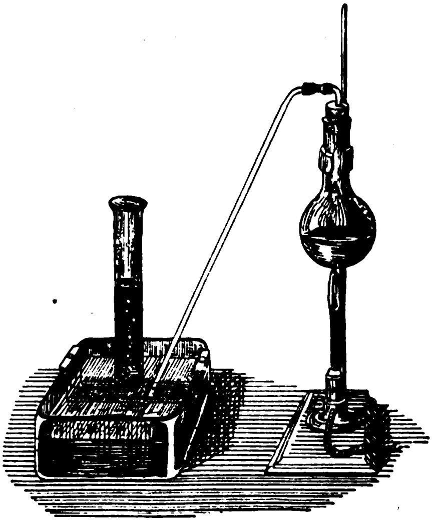

Fig. 42.—Preparation of nitrogen gas.

in a position to understand why the salts of ammonia are spoken of as *ammonium salts*. Looking more clearly at the formula of ammonium nitrite, NH_4NO_2, we notice that the salt is composed of two atoms of nitrogen, united to four atoms of hydrogen and two atoms of oxygen—that is, to twice two hydrogen atoms and one oxygen atom. But the formula of water, H_2O, is two hydrogen and one oxygen atoms. Hence we can very well understand that ammonium nitrite might decompose to two molecules of water ($2H_2O$) and one molecule of nitrogen (N_2). This decomposition is, indeed, easily effected by heat. It is only necessary to boil a solution of the salt in water; the nitrogen comes off plentifully from the boiling liquid, and may be collected in the way shown in fig. 42, where A represents the flask wherein the solution of ammonium nitrite is heated. The equation that expresses the reaction is the following:—

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2} = \underset{\text{nitrogen gas}}{N_2} + \underset{\text{water.}}{2H_2O.}$$

This reaction yields pure nitrogen.

The simplest way of stating the behaviour of nitrogen is to say that it is just the opposite of that of oxygen. For example, a glimmering chip of wood takes fire in oxygen, but a brightly burning chip is extinguished when it is immersed in a cylinder filled with nitrogen.

In speaking of the preparation of nitrogen we learned that nitric acid is richer in oxygen by one atom than nitrous acid; hence *ammonium nitrate* is richer in oxygen by one atom than ammonium nitrite, and must therefore have the formula NH_4NO_3. Now what will happen when this salt is heated? How will the atom of oxygen behave that is in this salt over and above the number of atoms of oxygen in ammonium nitrite? Experiment shows (as was to be expected) that the water is not further oxidised by the extra oxygen atom, but that this oxygen holds to the nitrogen, and, combined therewith, forms N_2O. The compound that is obtained thus without difficulty is called *nitrous oxide gas.*

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{nitrous oxide gas}}{N_2O} + \underset{\text{water.}}{2H_2O.}$$

Nitrous oxide is sometimes called "laughing gas." When breathed, it produces a condition of semi-unconsciousness, which lasts for a short time—long enough, for instance, to allow of the extraction of a tooth. This gas has been used, and is still to some extent used, in dentistry, although more convenient substances are now at our disposal—ethyl chloride, for example—which cause insensibility only around the tooth to be operated on, and have the great advantage of not requiring that complete unconsciousness should be produced for the performance of a slight operation. And so it is that the interest in nitrous oxide gas of those who are not chemists is gradually passing away.

In the preparation of nitrogen and nitrous oxide we had two exceedingly clear examples of how it is sometimes possible to tell, from the inspection of the formula of a compound, what are likely to be the products of the decomposition of that compound. In the cases in question the compounds were ammonium nitrite (NH_4NO_2) and ammonium nitrate (NH_4NO_3).

We shall now return to our usual custom of becoming acquainted with the most important hydrogen compound of the element we are considering. *Ammonia* is the chief compound which nitrogen forms with hydrogen. The name has come down from old times. Ammonia is a compound of one atom of nitrogen and three atoms of hydrogen; its formula is NH_3. This compound is formed whenever dry nitrogenous materials are heated or are allowed to putrefy. It was by one of these methods—namely, by heating a mixture of camel's dung and salt (sodium chloride) in earthen jars —that ammonium chloride, or *salammoniac* as it has been called since ancient times, was prepared long ago in the East.

Ammonia—the compound NH_3—is a gas with basic properties, and hence it turns red litmus paper blue. This gas is quite the reverse of such a gas as hydrochloric acid, which has acid properties. These two gases combine to form a salt—namely, ammonium chloride or salammoniac. We are not at all surprised to find that the solid body salammoniac should be composed of two gases; we know that water, and hence, of course, ice, consists of two gases.

Like most other gases, ammonia is colourless. It has a very penetrating smell. The compound is obtained by heating, in a flask, a mixture of salammoniac and a base stronger than ammonia. As we regarded common salt as sodium hydrochloride (p. 67), so may we look on salammoniac as ammonium hydrochloride. The stronger base will drive out the ammonia gas, and

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[*] This is a contraction either of *sal ammoniacum* or of *sal armeniacum*. There are doubts as to which is correct.

will combine with the hydrochloric acid in place of the ammonia. To do this we shall use that base which is at once the cheapest and the most effective—namely, burnt lime that has been slaked by a little water. In the reaction of this base with salammoniac the base combines with the hydrochloric acid, taking the place of the ammonia and producing calcium chloride, while the ammonia which is set free escapes as a gas from the flask. The following equation represents the reaction :—

$$\begin{array}{ccccccccc} 2NH_4Cl & + & Ca(OH)_2 & = & 2NH_3 & + & CaCl_2 & + & 2H_2O. \\ \textbf{Salammoniac} & + & \textbf{slaked lime} & = & \textbf{ammonia gas} & + & \textbf{calcium} & + & \textbf{water.} \\ & & & & & & \textbf{chloride} & & \end{array}$$

Ammonia gas is exceedingly soluble in water, and therein it resembles hydrochloric acid gas ; hence, like hydrochloric acid gas, it cannot be collected over water, as it would dissolve in the water instead of collecting in the cylinder. If we wish to examine ammonia gas, we must collect it over mercury, using that liquid in place of water. Fig. 43 shows an apparatus suited for this purpose. The cylinder is filled with mercury, and inverted in mercury in a pneumatic trough (made as small as possible to save mercury, which is expensive), and the ammonia is led into this cylinder from the mixture in the flask A, wherefrom it is produced.

If ammonia gas is led into water, which may be placed in a washing-flask (in an arrangement similar to that shown on p. 68), the water absorbs a large quantity of the ammonia, and we obtain *ammonia liquor*—that is, an aqueous solution of the gas. A litre of such a solution contains more than 300 grams of ammonia [nearly 20,000 grains per gallon]. An aqueous solution of ammonia is popularly known as "spirit of hartshorn."

Practically all the ammonia that is used nowadays is obtained from the products of the gas-works, so that it is not necessary to have recourse to salammoniac from the East. We shall discover the reason for this when we consider the manufacture of coal-gas; and we shall also see, in a later part of the book, why almost all the ammonia that can be produced by the gas-works in all parts of the world is used as artificial manure.

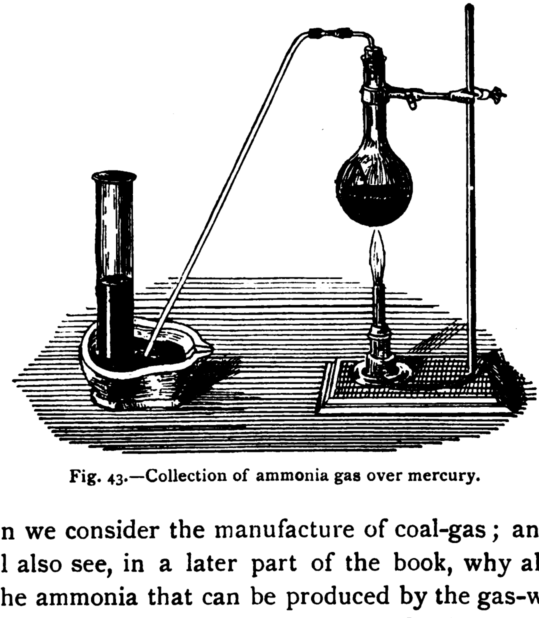

Fig. 43.—Collection of ammonia gas over mercury.

Ammonia combines with sulphuric acid to form sulphate of ammonia, or, as it is now called, *ammonium sulphate.* The formula of this salt is $(NH_4)_2SO_4$, corresponding closely to that of potassium sulphate, K_2SO_4.

Ammonia gas has the formula NH_3; *it may be regarded as the anhydride of a base, just as* SO_2 *is regarded as the anhydride of the corresponding sulphurous acid*, H_2SO_3. The behaviour of an aqueous solution of ammonia towards acids is as if the ammonia had combined with the water and the solution contained the compound NH_4OH. This corresponds with the behaviour of an aqueous solution of SO_2 towards bases. When an aqueous solution of ammonia is added to diluted sulphuric acid,* we may regard the reaction as taking place thus:—

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O;$$

Ammonia + sulphuric acid = ammonium sulphate + water;

just as the reaction between solutions of caustic potash and sulphuric acid is this:—

$$2KOH + H_2SO_4 = K_2SO_4 + 2H_2O.$$

Caustic potash + sulphuric acid = potassium sulphate + water.

If the formula of ammonia is written in the foregoing equations as that of the gas, NH_3, then the equations represent the changes as being direct additions of the ammonia to the acids; thus:--

$$NH_3 + HCl = NH_4Cl.$$

Ammonia + hydrochloric acid = salammoniac.

$$2NH_3 + H_2SO_4 = (NH_4)_2SO_4.$$

Ammonia + sulphuric acid = ammonium sulphate.

But this is against the generalisation (see p. 150) that the reaction between an acid and a base always

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* The sulphuric acid is diluted to moderate the reaction between the acid and the base.

produces water as well as a salt. Such an insufficient way of writing the reactions of ammonia with acids as is used in the two preceding equations is often a stumbling-block which beginners in chemistry do not know how to remove. It is therefore much better for beginners always to write ammonia in such equations, not as the anhydride NH_3, but as NH_4OH, for by doing so all difficulties disappear.

The atomic complex NH_4, *which, however, cannot itself be isolated* (see later, under *valency*), is called *ammonium*, reminding one of potassium and sodium, which it closely resembles; and the salts that are formed from ammonia and acids are called *ammonium salts* (ammonium sulphate, ammonium acetate, etc.).

The compound of ammonia gas with carbonic anhydride gas (CO_2) is sometimes used for making cakes light and spongy, instead of the more tedious process of fermentation by yeast. The action of the salt in causing dough to rise is as follows. Although the two gases ammonia and carbonic anhydride unite at the ordinary temperature to form a solid white salt, yet at the temperature of a baking oven the salt is decomposed into its two constituents; and it is these two gases (ammonia and carbon dioxide) which bubble through the dough and so make it rise.*

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* The salt generally employed as a baking powder is not at all the normal ammonium carbonate. The acid anhydride CO_2 and the basic anhydride NH_3 cannot form the normal salt [which would be $(NH_4)_2CO_3$], as water is not present. Their reaction may be expressed thus :—

$$\underset{\text{Carbonic anhydride}}{CO_2} + \underset{\text{ammonia}}{2NH_3} = \underset{\text{ammonium amido carbonate.}}{(NH_4)CO_2NH_2.}$$

Two other compounds of nitrogen and hydrogen have been prepared recently: one has the formula N_3H, and is called *hydrazoic acid*; the other has the formula N_2H_4, and is named *hydrazine*.

Nitrogen combines with oxygen in five proportions. We have already become acquainted with one of the compounds, N_2O, nitrous oxide; and we have also alluded to nitrous and nitric acids. We must now study nitric acid pretty fully; but we shall leave on one side, as not particularly important for our purposes, the two oxides NO (nitric oxide) and NO_2 (nitrogen dioxide).

NITRIC ACID.

We should not expect to find nitric acid uncombined on the earth's surface; so strong an acid will always meet with bases wherewith it can combine. Two salts of nitric acid are found very abundantly—potassium nitrate in India and sodium nitrate in Chili. The former is called *potash saltpetre* [or *nitre*], and the latter *soda saltpetre* [or *Chili saltpetre*]. The name saltpetre is used to include both. These two salts, both of which are soluble in water, are found in the soil of certain districts in India and Chili; if these soils are boiled with water, the salts dissolve, and are obtained as crystals by pouring off the solutions from the soils, evaporating, and allowing to cool.

Potash saltpetre has been known in Europe since about the fifth century. Its composition is expressed by the formula KNO_3, from which we calculate the percentage of oxygen in the salt to be 47·5. For, the atomic weights of potassium, nitrogen, and oxygen being 39, 14, and 16 respectively, we have :—

$$\begin{array}{c} \mathrm{K} \quad \mathrm{N} \quad \mathrm{O_3} \\ 39 + 14 + (3 \times 16) = 101\,; \end{array}$$

$$\text{hence } 101 : 48 = 100 : x\,; \quad x = \frac{48 \times 100}{101} = 47{\cdot}5.$$

The salt is evidently rich in oxygen.

To prepare nitric acid from nitre the salt is heated with sulphuric acid; the sulphuric acid drives out the nitric acid and combines with the potassium in its place. The reaction is expressed in the following equation :—

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4.$$

Potassium nitrate + sulphuric acid = nitric acid + acid potassium sulphate.

As nitric acid is a liquid which can be distilled, we use a retort in preparing it, and this makes it easy to separate the acid from the acid potassium sulphate. The potassium nitrate and the sulphuric acid are placed in a retort (R, fig. 44), which is then heated; vapours soon come off, and condense to a liquid in the receiver A, which is placed in a basin filled with cold water, and is thereby cooled sufficiently for our purpose. The liquid that condenses in the receiver is nitric acid; the acid potassium sulphate remains in the retort.

In preparing nitric acid we meet with an acid salt—namely, acid potassium sulphate. This is a salt formed by replacing only a portion of that hydrogen of the acid which is replaceable by metal; hence the salt $KHSO_4$ is still acid, and is able to react with bases after the manner of an acid. This salt is also able to decompose potassium nitrate after the manner of free sulphuric acid; producing, finally, neutral potassium sulphate, and setting free the nitric acid which was combined with the second potassium atom that seized the acid potassium sulphate in order to convert it into the neutral salt.

$$\begin{array}{ccccccc} HKSO_4 & + & KNO_3 & = & K_2SO_4 & + & HNO_3. \\ \text{Acid potassium} & + & \text{nitre} & = & \text{neutral potassium} & + & \text{nitric acid} \\ \text{sulphate} & & & & \text{sulphate} & & \text{(red fuming).} \end{array}$$

As one would expect, acid potassium sulphate, with its half-neutralised sulphuric acid, does not react with nitre so readily as free sulphuric acid reacts. Hence, if acid potassium sulphate is to expel nitric acid from nitre (in accordance with the equation given above), the temperature of the mixture of nitre and acid potassium sulphate must be made much higher than is required when sulphuric acid itself is employed. This is a matter of no moment in itself. But nitric acid is no longer completely stable at this higher temperature; it cannot suffer this high temperature without taking hurt. A portion of the acid, it is true, distils over as such, as HNO_3; but another portion decomposes to simpler compounds, and particularly to nitrogen dioxide, NO_2. The nitrogen dioxide, which is a red gas, dissolves in

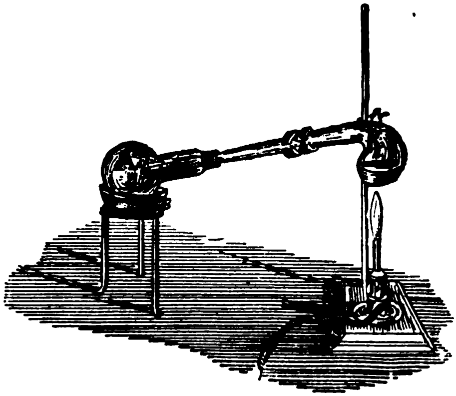


Fig. 44.—Preparation of nitric acid.

that part of the nitric acid that distils over unchanged. Hence the nitric acid in the receiver appears red; and the liquid fumes if the flask is opened, because the red gas evaporates into the air from the liquid. The liquid in the receiver is called *red fuming nitric acid.*

The final result of these considerations is as follows. If it is desired, as it generally is, to make colourless nitric acid, the quantities of nitre and sulphuric acid must be such that the whole of the nitre is decomposed by the sulphuric acid, and, consequently, acid potassium sulphate remains in the retort. The equation, which has been given already—

$$\begin{array}{ccccccc} KNO_3 & + & H_2SO_4 & = & HKSO_4 & + & HNO_3 \\ \text{nitre} & + & \text{sulphuric acid} & = & \text{acid potassium sulphate} & + & \text{nitric acid} \end{array}$$

tells that—

$$\begin{array}{ccccccl} K & & N & & O_3 & & \\ 39 & + & 14 & + & (3 \times 16) & = & 101 \text{ parts by weight of nitre, and} \\ H_2 & & S & & O_4 & & \\ 2 & + & 32 & + & (4 \times 16) & = & 98 \text{ parts by weight of sulphuric acid} \end{array}$$

(or 97 parts by weight of sulphuric acid for 100 parts of nitre) must be used. But if it is desired to prepare the red fuming nitric acid, which is often used as an oxidising agent, the formation of neutral potassium sulphate must be kept in view, and half as much sulphuric acid must be employed for the same quantity of nitre as before [or twice as much nitre for the same quantity of sulphuric acid], in accordance with the equation:—

$$\begin{array}{ccccccc} 2KNO_3 & + & H_2SO_4 & = & K_2SO_4 & + & 2HNO_3. \\ \text{Nitre} & + & \text{sulphuric acid} & = & \text{neutral potassium sulphate} & + & \text{red fuming nitric acid.} \end{array}$$

In this case it is necessary to use 2 × 101 = 202 parts by weight of nitre to 98 parts of sulphuric acid, or only 48·5 parts by weight of sulphuric acid for 100 parts of nitre; for when the sulphuric acid has driven out the first half of the nitric acid, and has thus been changed to acid potassium sulphate, then this acid salt must react with the second half of the nitre, with the total result that red fuming nitric acid is obtained.

Nitric acid is a very strong acid. It dissolves all metals except gold and platinum. As it dissolves silver, nitric acid may be used to separate silver from gold; hence its older name, *parting acid.* The readiness wherewith silver dissolves in nitric acid is shown by the following experiment. As it has been found in practice that concentrated nitric acid diluted with 20 per cent. of water is the most suitable for the purpose, acid of that concentration is put in the flask A (fig. 45), the flask is very slightly warmed, and a little piece of silver foil is thrown into it. The silver dissolves in the liquid, and disappears almost instantly. The acid and the metal interact to form silver nitrate; hence it is only necessary to evaporate the contents of the flask to dryness—in other words, to remove the acid over and above what was used in the reaction—in order to obtain the silver nitrate as a solid residue.

Fig. 45.—Dissolving silver in nitric acid.

Silver nitrate is white, like so many salts; its formula is $AgNO_3$. This salt, an aqueous solution whereof we have already often used (see pp. 9, 50, 146), was once called *lapis infernalis,* an astonishing name derived from the fact that anything touched with a solution of the substance very soon becomes black. The blackening effect is due to the decomposition of the salt into its constituents by light, and hence the separation of the silver as an exceedingly fine black powder on any surface which has been rubbed with the salt and exposed to light.

AQUA REGIA.

We have just learned that gold and platinum are insoluble in nitric acid; there is no single acid which dissolves these metals, but a mixture of nitric and hydrochloric acids brings them into solution: as the alchemists called gold the king of metals, they gave the name *aqua regia* to this mixture. Nitric acid (HNO_3) is very rich in oxygen, and hydrochloric acid (HCl) consists of hydrogen and chlorine; when these two are mixed, the oxygen of the nitric acid exerts an oxidising action on the hydrogen of the hydrochloric acid, combining with it to form water, so that the chlorine becomes available. We know that chlorine is extraordinarily active—or, to use a better expression, that chlorine possesses much chemical energy; hence we are not surprised that the chlorine, as it is produced in the nascent state, should attack gold and platinum. If a solution of gold or platinum in *aqua regia* is evaporated to dryness, gold chloride or platinum chloride is obtained. These salts dissolve in water very easily.

We must just mention that it has been found, in recent years, that a solution of potassium cyanide (which substance will be considered when we come to the compounds of carbon) dissolves gold, but not platinum. This method of extracting gold from the finely powdered rock is now used in South Africa, almost to the exclusion of all others.

EXPLOSIVES.

We know that the salts of nitric acid are very rich in oxygen. It is its richness in oxygen that has caused potassium nitrate—a substance which does not differ in appearance from a thousand other white salts—to have a greater influence on the history of peoples than any other chemical compound. For the history of a people has often depended on a battle won or lost, and it is this nitre which has helped to decide innumerable battles of the later middle ages and of modern times. Nitre has been the foundation of all sorts of gunpowder until very recently. For about fifteen years attempts have been made to replace powder made with potassium nitrate by smokeless explosives based on nitric acid.

The connection between nitre and gunpowder is as follows. A mixture of nitre with such combustible substances as charcoal, pitch, or sulphur continues to burn once it has been ignited. In distinction to ordinary combustibles, such a mixture does *not* require to get oxygen from the air for its combustion, but it finds the required oxygen in the nitre. Hence such a mixture can do what an ordinary combustible body cannot do: it can burn in an enclosed space without the entrance of oxygen from outside; it can burn under water, for instance.

We have here a mixture of 25 parts ordinary gunpowder, 50 parts nitre, 40 parts charcoal, and 10 parts sulphur, which has been moistened with spirit (this removes the risk of explosion during the rubbing), well mixed by rubbing, packed as tightly as possible into a paper covering, and kept for some time in a chamber at 110°, whereby the spirit has been removed. This cartridge will be about 7 cm. long by 4 mm. diameter [say, 3 in. by $\frac{1}{6}$ in.]; if we hold it by a pair of tongs, ignite it, and bring it under a cylinder filled with water and inverted in water in the pneumatic trough, as shown in fig. 46, we shall see that the cartridge continues to burn under the water, and that the cylinder is filled rapidly with the gases that are produced by burning our mixture. In this experiment the cylinder should not stand on the shelf of the trough, but should be supported by a clamp (as shown in fig. 46). Ordinary gunpowder is not suitable for the experiment, because it burns much too rapidly, and one does not get sufficient time to bring a cartridge filled with that powder under the water after it has been ignited.

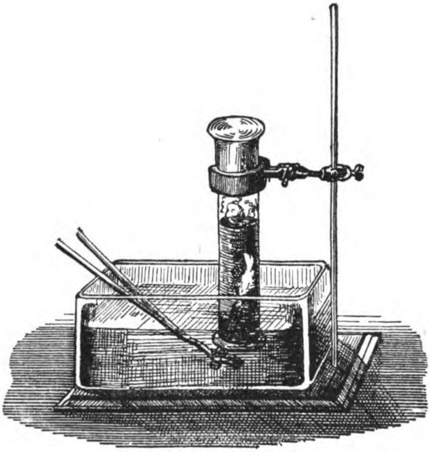


Fig. 46.—Burning gunpowder under water, and collecting gases produced.

As long ago as the seventh century, pots filled with a mixture of nitre and combustible bodies, which was set on fire, were thrown as dreadful weapons against the enemy or the enemy's ships. This was called "*Greek fire.*" It was hundreds of years after this, however, that men came to recognise the fact, and to turn it to practical account, that there was something in this mixture besides its astonishing combustibility—that the mixture had an explosive power. By *explosive power* we mean a power which is suddenly developed and is capable of scattering the surrounding objects in all directions. Records dating from the thirteenth century show that it had been discovered by that time that the best mixture for explosive purposes was one of nitre, charcoal, and sulphur, the same mixture as that we now call gunpowder. A military gunpowder made in the eighties of the nineteenth century consisted of 74 per cent. nitre, 16 per cent. charcoal, and 10 per cent. sulphur.

There is nothing now mysterious about the fact that such a mixture of nitre, charcoal, and sulphur drives a shot from a cannon or splits the rock around the hole wherein it is placed. The reason is easy to understand. The mixture of the three substances is placed behind the shot or in the bore-hole in the rock; there it occupies comparatively a very small space. But when the mixture is fired, there is suddenly formed carbonic acid gas (CO_2) from the carbon (C), and sulphur dioxide gas (SO_2)—along with some sulphuric acid—from the sulphur (S). The nitre, KNO_3, gives the necessary oxygen. This compound is, of course, decomposed, and its nitrogen is set free as gas. The potassium of the nitre reacts with the gases, and most of it is changed to potassium carbonate and sulphite (some of the latter becoming sulphate), which are thrown into the air. As these salts are in a state of extremely fine division, they float in the air for some time, and form the white smoke of powder. To sum up: a small quantity of powder, when burnt, produces a very large quantity of gases, leaving the powder-vapour out of account. As these gases, at the moment of their formation, are tremendously compressed in a small space, they seek every opportunity of expanding. The movable shot lies on one side of the gases; hence, to gain space, they drive the shot out of the gun. The strength of the cannon, or the gun, withstands the shock; but if the gases are produced in a bore-hole, they shatter the surrounding materials.

It should be noticed that experiments have shown that sodium nitrate cannot be substituted for potassium nitrate in gunpowder. Although the two salts are very like one another, yet they are not identical in their behaviour.

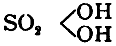
The preparation of gunpowder from its three constituents has been so perfected in the last forty years that further improvements are scarcely conceivable, and, indeed, for many reasons, are not necessary. Cannon shots can be projected, by the help of gunpowder, through distances greater than twenty kilometres [over twelve and a half miles].

On the other hand, the conditions regarding guns are very different. It was demonstrated, in the fifties, by purely mathematical deductions, that, if the diameter of projectiles were diminished as much as possible, such projectiles could be sent to much greater distances than before, provided an impulse could be given to the considerably reduced shots stronger than that generally obtainable from the explosive power of the old powder.

Now, explosives have long been known in chemical laboratories whose power is much greater than that of the gunpowder now in use. For instance, a substance called *fulminating mercury* is obtained by the action of nitric acid on mercury in the presence of alcohol. (We shall not concern ourselves with the composition and the formula of this very complex compound.) This substance is exploded by any blow; hence it is too dangerous as a substitute for gunpowder: moreover, it explodes so suddenly that if it were used in a gun it would burst the gun before it set the shot in motion. It is not every explosive that can be used in place of gunpowder, or as a bursting material in mining operations.

A substance was discovered in the forties which made possible, at a later time, the preparation of a new powder, more powerful, and relatively less dangerous to manipulate, than the old gunpowder. Cellulose is required for the preparation of this substance. We have already mentioned cellulose when speaking of paper (see p. 121), and we know that the formula of this compound is $C_6H_{10}O_5$. Cellulose is a constituent of all plants. Paper is made from rags which have come from substances manufactured from plant-fibres —from linen rags, for instance—so that the presence of cellulose in paper is not astonishing. Cotton wool is nearly pure cellulose.

To understand what follows we must once more recall the formulæ of acids and bases; for example, the formulæ of sulphuric acid, H_2SO_4, and nitric acid, HNO_3, and the formulæ of caustic potash and caustic soda, KOH and NaOH. In all of these we find the atomic group OH, composed of an atom of oxygen and an atom of hydrogen. To recognise this group in the formulæ of the two acids we must group the atoms that form these acids in certain ways, and write—



$SO_2 \langle {}^{OH}_{OH}$ in place of H_2SO_4, and

$NO_2 — OH$ in place of HNO_3.

We shall soon become acquainted with the hypotheses which enable us to form a clear mental picture of the grouping of atoms in compounds; we shall discover that these hypotheses are not hard to grasp—not so hard, indeed, as the doctrine of atoms and their weights. The group OH is very ready to combine with another atom of hydrogen, so forming water, H_2O. The group OH may be called the residue of water. Special names are given to such residues, or *rests*, which, as we shall see, play a very important part, as the formulæ of many complicated compounds would be unintelligible without them. The water residue—that is, the atomic complex OH—is called *hydroxyl* (from the Greek ὕδωρ = water). *All the commoner acids and bases, with the exception of hydrochloric, hydrobromic, hydriodic, and hydrofluoric acids, contain the hydroxyl group, OH.* Nitric acid contains this group once, sulphuric acid twice, as we saw from the "dissected" formulæ of these acids. This same group OH—hydroxyl—is found in cellulose, $C_6H_{10}O_5$, which behaves towards several acids as a base. One molecule of caustic potash, $K—OH$, reacts with one molecule of nitric acid, $NO_2—OH$, to form the salt potassium nitrate, $NO_2—OK$, besides a molecule of water; and one molecule of sulphuric acid, $SO_2{<}^{OH}_{OH}$, reacting with two molecules of caustic potash, $2K—OH$, forms the neutral salt $SO_2{<}^{OK}_{OK}$ and two molecules of water. The reaction of cellulose with nitric acid is similar to these; three molecules of nitric acid interact with the three hydroxyl groups in a molecule of cellulose, and the products are a salt-like compound and water. The following equations express these reactions:—

(i) $K—OH + NO_2—OH = NO_2—OK + H_2O.$

One molecule caustic potash + nitric acid = potassium nitrate + one molecule water.

(ii) $2K—OH + SO_2{<}^{OH}_{OH} = SO_2{<}^{OK}_{OK} + 2H_2O.$

Two molecules caustic potash + one molecule sulphuric acid = neutral potassium sulphate + two molecules water.

(iii) $C_6H_7O_2(OH)_3 + 3NO_2—OH = (NO_2—O)_3C_6H_7O_2 + 3H_2O.$

One molecule cellulose + three mols. nitric acid = one molecule gun-cotton + three mols. water.

The compound produced by the action of nitric acid on cellulose (in practice cotton wool is employed) would be properly called *cellulose nitrate*; but it is generally known as *nitrocellulose*, or, in ordinary life, as *gun-cotton.*

The water residue, the hydroxyl group OH, also occurs in glycerin. Glycerin is a constituent of animal and vegetable fats, all of which are glycerin salts of fatty acids. In these fats glycerin behaves towards the fatty acids like a base. Glycerin also reacts with nitric acid, and, like cellulose, with three molecules of that acid. The formula of glycerin is $C_3H_8O_3$; written so as to indicate three hydroxyl groups, this formula becomes $C_3H_5(OH)_3$. The reaction with nitric acid is expressed thus by an equation:—

$$\underset{\substack{\text{One molecule}\\ \text{glycerin}}}{C_3H_5(OH)_3} \underset{+}{+} \underset{\substack{\text{three mols.}\\ \text{nitric acid}}}{3NO_2\text{—}OH} \underset{=}{=} \underset{\substack{\text{one molecule}\\ \text{nitroglycerin}}}{(NO_2\text{—}O)_3C_3H_5} \underset{+}{+} \underset{\substack{\text{three mols.}\\ \text{water.}}}{3H_2O.}$$

The compound which is thus produced is an oily liquid; it might be called *glycerin nitrate*, but it is usually known as *nitroglycerin*. The names nitroglycerin and nitrocellulose are derived from the fact that the group NO_2, which is the *rest* of nitric acid (NO_2—OH), is called the *nitrogroup*.

Forty years ago it was supposed, wrongly, that the nitrogroup, NO_2, entered into cellulose and glycerin in the reactions we have just considered; hence the products of these reactions were called nitrocellulose and nitroglycerin. But that is not what really occurs. It is not the rest NO_2 which forms a part of the new compounds; but the reactions of nitric acid with cellulose and glycerin are exactly similar to the reactions of that acid with bases (such as potash) whereby salts are produced, as is shown in the equations already given. The names originally given to the two compounds have, however, remained in ordinary use. We shall learn later something about the true nitrocompounds.

The nitric acid used for making guncotton and nitroglycerin must be as free from water as possible. The equations that have been given show that three molecules of water are produced in the preparation of these compounds (the weight of water formed can be calculated easily); hence the concentrated nitric acid used gets gradually diluted as the action proceeds. The remedy for this is found by allowing a mixture of nitric and sulphuric acids to act on cotton wool or glycerin, in place of nitric acid alone. As we know (see p. 45), sulphuric acid draws water to itself; it seizes hold of all the water that is formed in the chemical reaction which results in the preparation of the explosive substance. The addition of sulphuric acid insures that the nitric acid is not diluted by water at any stage of the *process of nitration*, as the action is called. We have already referred to the great demand for sulphuric acid for the manufacture of nitroglycerin and guncotton (p. 157); the reason for that demand is now apparent.

Guncotton and nitroglycerin are the main foundations of the newer powders and explosives. The empirical formulæ * of guncotton and nitroglycerin are $C_6H_7N_3O_{11}$ and $C_3H_5N_3O_9$ respectively. Let us suppose these compounds to be burning, and let us consider what will be the products of combustion of the carbon, hydrogen, nitrogen, and oxygen. As there is plenty of oxygen in the compounds, the carbon will be burnt to carbon dioxide, an invisible gas, the hydrogen will become water, which will also be an invisible gas at the high temperature of the reaction, and the nitrogen will be set free, also as an invisible gas. In a word, all the products of the explosion of either of the two substances are invisible gases. The substances burn, therefore, without smoke, in distinction to gunpowder, the smoke of which consists (as we have seen, p. 181) of potassium salts. The application of these two explosives to gunnery has led to the preparation of smokeless powders.

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* An empirical formula states the total number of atoms of each element in a compound, without indicating in any way the supposed arrangement of the atoms. [TR.]

Guncotton and nitroglycerin are much more powerful explosives than the old powder. That powder is a mixture of substances, and it burns away, as other mixtures do. But guncotton and nitroglycerin are not explosive mixtures of substances; the molecule of each itself falls to pieces when explosion occurs. Whereas a kilogram of the old powder required, perhaps, a hundredth of a second for its combustion, a kilogram of guncotton is decomposed in the fifty thousandth of a second; and this difference of itself makes the guncotton a much superior explosive.

We know that nitroglycerin is a liquid. To get it into the form of cartridges, for use as an explosive, it has long been customary to mix the liquid with a fine sand called *kieselguhr*; this mixture is called *dynamite*. The explosive force of the nitroglycerin is tempered by the sand. At a later time it was found that if guncotton is mixed with nitroglycerin the mixture sets to a jelly-like mass; in this case the explosive force of the nitroglycerin is not modified by sand, but, rather, it is added to that of the guncotton. There are many solvents for *blasting gelatin* (as the jelly-like mixture of guncotton and nitroglycerin is called)—for instance, *acetone*, a compound we shall meet when we come to the compounds of carbon. If blasting gelatin diluted with acetone is passed between rollers placed near together, it comes out in the form of sheets; and as the acetone evaporates quickly, the explosive is obtained in plates. When these plates are cut into very small pieces they form the modern smokeless powder. The non-formation of smoke has been explained already;

to put it in a word, it is due to the absence of potassium salts in the explosive. The results of using smokeless powder in small arms are extraordinary: the bullets are propelled for more than three kilometres [over one and three-quarters miles].

If nitrate of potassium or nitrate of sodium is fused with lead, the lead is oxidised, by the oxygen of the nitrate, to lead oxide, PbO; and the nitrate, giving up an atom of oxygen, becomes a nitrite (compare p. 164).

(i) $KNO_3 + Pb = KNO_2 + PbO.$
Potassium nitrate + lead = potassium nitrite + lead oxide.

(ii) $NaNO_3 + Pb = NaNO_2 + PbO.$
Sodium nitrate + lead = sodium nitrite + lead oxide.

The salts of nitric acid are called nitrates; the salts of nitrous acid are called nitrites. Sodium nitrite, which is cheaper than potassium nitrite, because Chili saltpetre is cheaper than potash saltpetre, is much used in the manufacture of coal-tar colours. The preparation of this salt is a not unimportant branch of chemical industry.

PHOSPHORUS.

PHOSPHORUS was discovered in 1670.

Phosphorus was one of those casual results which accrued to the world of these times from the unmeaning investigations of the alchemists. A Hamburg merchant, Brandt by name, went to the goldmakers to repair his straitened circumstances. Everyone in those days believed in *transmutation*, as the process of turning the base metals into gold and silver was called. This transmutation was to be effected by some methods and tinctures, which, however, were still to be discovered. The important question was, who should be the first to find the stone of wisdom? Brandt worked for a long time before he came to the conclusion that nothing was to be gained by him as long as he followed the ordinary methods. At last he hit on the notion of extracting the mysterious principle from the products of the living organism, and he thought that urine would be the most suitable starting-point for his investigations. We laugh at such a conception nowadays. But in those days, when no accurate examinations had been made of life-processes, when phrases and empty jingles of words passed for learning, and faith and intention for knowledge, and when laws were made before observations, there was something plausible, especially to a dilettante like Brandt, about the notion that man was the most perfect machine, the machine in which all substances and forces were brought to the highest development and action. What was separated and disengaged from this quintessence of creation, this world in miniature, from the microcosm, that must be the most excellent and the most active of all things. Urine was evidently the only source whence the stone of wisdom could be obtained.

There is a small quantity of calcium phosphate in urine; for albumin contains phosphorus; and the albumin that is used in the body yields phosphates among its products of decomposition. All such decomposition-products can be removed from the body only in the urine; hence the existence therein of calcium phosphate, from which Brandt prepared phosphorus.

Phosphorus is prepared nowadays from bones, because these are rich in calcium phosphate. The phosphoric acid is reduced to phosphorus by heating strongly with charcoal in retorts, from which the phosphorus distils over. Phosphorus is a wax-like body of a pale yellow colour. Its most striking property is its extraordinary inflammability—that is, great readiness to combine with oxygen—which makes it possible to raise phosphorus to the ignition point with the greatest ease. Phosphorus cannot be left in the air without at once beginning to oxidise; hence it must be kept under water (see fig. 47); preserved thus from contact with the air, it remains unchanged for any length of time. The name *phosphorus* is derived from the Greek, and means *light-bearer*. The name was given because, when exposed to the air, the substance glows in the dark, owing to the slow oxidation that goes on: the glowing is so slight that it is not visible in daylight. Slight rubbing, which, like all friction, raises the temperature, soon causes ignition—that is to say, changes the slow oxidation into rapid oxidation, accompanied by the phenomena of fire. We have already

Fig. 47.—Phosphorus kept under water.

more than once ignited phosphorus, and seen it burn to a white smoke, which is an oxide of phosphorus. That oxide is composed of two atoms of phosphorus and five atoms of oxygen; its formula is, therefore, P_2O_5. It is called either phosphorus pentoxide or phosphoric anhydride, as we already know (p. 117).

The ready inflammability of phosphorus has been known, of course, since the substance was discovered; nevertheless, a long time passed before a convenient method was found for using this property to obtain fire. It was not till the thirties of the nineteenth century—that is, not till nearly two hundred years after the discovery of phosphorus—that phosphorus matches were made, which at last enabled everyone to obtain fire without trouble. We cannot now properly picture to ourselves a time when there were no matches. At first some phosphorus was fastened to little slips of wood which had been dipped in sulphur. The small quantity of phosphorus was ignited by rubbing; the flame passed to the easily ignited sulphur, which in turn set fire to the wood.

A sad trouble accompanied the manufacture of these phosphorus matches; the workpeople became gradually seriously diseased from constantly handling the poisonous yellow phosphorus. A remedy was urgently called for. The discovery of red phosphorus made a remedy possible. The conditions are these: if ordinary yellow phosphorus is heated for a considerable time to 250°, it is gradually changed into a red powder which is not poisonous.

We can bring about this change in the manner represented in fig. 48. A small piece of ordinary yellow, easily inflammable phosphorus has been placed in the inner tube A, which has then been closed by fusing the glass and allowing it to run together. The quantity of air in the tube is so small that the phosphorus is practically cut off from the air; hence the phosphorus cannot burn when it is heated, for lack of oxygen. If the tube with the phosphorus in it were heated directly over a flame, the tube would very probably break; and if that happened, the experimenter would be exposed to the danger of being very badly burnt by some of the glowing pieces of phosphorus which would be scattered in all directions. It is less dangerous to heat the tube in a bath kept at the proper temperature. For this purpose we shake some *phenanthrene* into the outer, wide tube B—phenanthrene is a compound obtained from coal-tar, which melts easily and boils at 360° C. [680° F.]—and

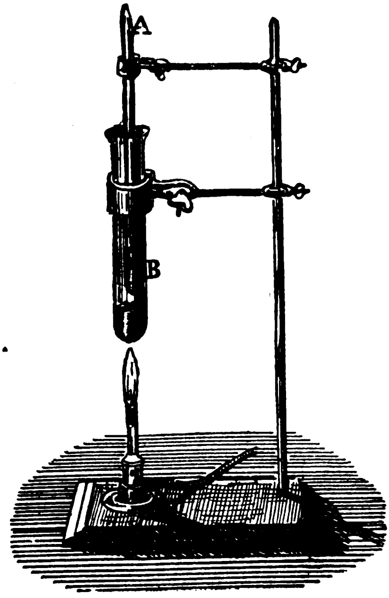

Fig. 48.—Change of yellow into red phosphorus.

we then cause the phenanthrene to boil by means of the flame placed below the tube. The phosphorus which is surrounded by the vapour of phenanthrene, and is kept at 360° C., soon begins to be coloured red, for the change proceeds very quickly at this high temperature.

The red phosphorus thus produced is not poisonous, and it is also much less inflammable than yellow phosphorus. It cannot be ignited by mere rubbing; on the contrary, it takes fire only when it is rubbed with substances which are very rich in oxygen. The preparation of "safety matches" is based on this property of red phosphorus. The heads of these matches contain no phosphorus (in contradistinction to the older phosphorus matches), but are composed of substances very rich in oxygen, such as potassium chlorate, $KClO_3$, potassium bichromate, $K_2Cr_2O_7$, and lead peroxide, PbO_2, wherewith lead sulphide, PbS, is often mixed, because this substance has been found very suitable. The rubbing surface whereon the safety matches are ignited consists of red phosphorus, made to adhere to the box by means of glue.

A third modification of phosphorus has been obtained. If the tube wherein we prepared red phosphorus had been heated, not to 360° only, but to a temperature as high as 530°, crystals of phosphorus would have sublimed in the upper, and therefore cooler, part of the tube. These crystals form a third variety of phosphorus; they are not so easily inflammable as ordinary phosphorus, and are less active than that substance.

THE VARIOUS MODIFICATIONS OF CERTAIN ELEMENTS.

We have seen that phosphorus exists in more than one form, or modification. Several other elements are like phosphorus in this respect. Such a behaviour of an element seems at first sight unthinkable; it cannot be understood off-hand: for an element—a something which exists, so to speak, alone and by itself, as a thing in itself—can surely have but one kind of qualities, can surely exist only in one form, which cannot vary.

We cannot suppose that there are several kinds of gold, several kinds of lead, or several kinds of sodium. Chemically pure gold—the element gold—is once for all gold, exhibits now and always the same chemical behaviour, etc. This apparently incontestable demand of our perceptive faculties seems to be contradicted by what we have found to be the facts regarding phosphorus. The apparent contradiction can be easily removed, however, by the aid of the atomic theory, and an elucidation of the facts can be arrived at in the following way. The atomic weight of phosphorus is 31, as determined by the analysis of phosphorus pentachloride, for example. As ordinary phosphorus is easily gasified, there is no difficulty in determining the specific gravity, and hence the molecular weight, of phosphorus gas (see p. 111). The specific gravity of gaseous phosphorus is sixty-two times greater than that of hydrogen at the same temperature. For the reasons laid down in the page already referred to, it follows that the molecular weight of phosphorus gas is 124, which is four times 31—four times the atomic weight of phosphorus. Hence the molecule of [the gaseous phosphorus obtained by heating] ordinary phosphorus consists of four atoms; the molecule of red phosphorus may consist of [a number of atoms different from the number whereof the molecule of ordinary phosphorus is composed, say] perhaps twenty atoms; and the molecule of the crystalline phosphorus produced at a high temperature may perhaps consist of, say, forty atoms.

We can only make an approximate guess at the number of atoms in the molecules of red and crystalline phosphorus; for we have at present no method for finding the molecular weights of substances which cannot be gasified and are insoluble in all menstrua. The two kinds of phosphorus—red and crystalline—are insoluble in all menstrua, nor can they be gasified as such.

We must not pass over the fact that methods have been developed, in the last ten years, for finding the molecular weights of bodies which cannot be gasified, from the behaviour of these bodies in solutions. The principles of the methods are, briefly, these. Everyone knows that water freezes at 0° C. [32° F.]. Now, if we dissolve common salt in water, we obtain a solution which freezes considerably under 0°; a saturated solution of salt, for instance, freezes at −20·37° C. [−4·66° F.]. If such *lowerings of freezing points* are examined more closely, it is found that they are not chance occurrences; it is found that, if a weighed quantity of a substance is dissolved in a weighed quantity of any solvent, the freezing point of the solvent is not only lower than that of the pure solvent, but that the lowering bears a perfectly definite relation to the freezing point of the pure solvent. Experiments have shown that *the molecular weight of the body in solution can be calculated from the observed lowering of the freezing point of the solvent.* It has also been found that, when a weighed quantity of a body is dissolved in a weighed quantity of a solvent—let us say water—and the boiling point of the solution is determined, this boiling point is higher than that of the pure solvent—in this case is higher than 100° C. [212° F.]. The boiling point of a saturated solution of common salt, for instance, is 109·25° C. [228·65° F.]. *The molecular weight of the body in solution can be calculated from the observed raising of the boiling point of the solvent.*

These methods for determining molecular weights give results which agree well and are trustworthy only when very dilute solutions are used; for example, solutions containing about ·3 gram of substance in 40 grams of solvent. The depression of freezing point or increase of boiling point does not amount to more than a few tenths of a degree in such solutions; hence it is necessary to work with very delicate thermometers and in specially constructed apparatus, protected, for instance, from all air-draughts. We see that the very remarkable law which states that equal volumes of all gases contain equal numbers of molecules finds its counterpart in the influence of any dissolved body on its solvent which can be measured once for all, and serves as the basis of a method of calculating the weights of molecules.

We have only appraised the number of atoms in the molecules of red and crystalline phosphorus, as contrasted with the four atoms whereof the molecule of yellow phosphorus is formed. At any rate, it is easily seen that the appearance of an element in several modifications finds an explanation in terms of the fact, established experimentally, that the molecule of an element may consist sometimes of a greater and sometimes of a smaller number of atoms, according to the conditions of preparation of the element.

One can see at once that there is nothing peculiar about this explanation, nothing which clashes with our general conception of an element. Rather it is the other way round, as one sees after a little careful attention; for without the conception of the atomic condition of the elements, and the possibility (connected therewith) of elementary molecules being sometimes larger and sometimes smaller, the existence of elements in different modifications, which are now greater, now smaller, atomic complexes, would be quite inexplicable. This appearance of the elements in various modifications is, indeed, a support of the atomic hypothesis, for this hypothesis is alone able to explain it.

OZONE.

We are now in a position to give an explanation of ozone.

Ozone is a modification of oxygen. While the ordinary oxygen that is found in the atmosphere consists of molecules of the composition O_2 (see p. 111), ozone consists of molecules of the composition O_3, molecules composed of three atoms. Ozone is most conveniently obtained by passing electric sparks through oxygen; the great shock changes three molecules of ordinary oxygen, O_2, into two molecules of ozone, O_3. Ozone has a peculiar smell. This smell can sometimes be perceived after a severe thunderstorm, wherein the lightning has brought about the formation of ozone. Ozone soon changes back to ordinary oxygen.

PHOSPHORETTED HYDROGEN.

Of the three compounds of phosphorus and hydrogen which are known—PH_3, P_2H_4, and P_4H_2—we shall consider only one, namely, the compound PH_3, the composition of which corresponds with that of ammonia,

NH_3. Like ammonia, this phosphoretted hydrogen is a gas. The gas is spontaneously inflammable ; that is to say, it takes fire as soon as it comes into contact with the air. We shall, therefore, prepare this compound. The inflammability of this gas is due to the rapid union of its phosphorus and its hydrogen with the oxygen of the air to form phosphorus pentoxide, P_2O_5, and water, H_2O, respectively.

$2PH_3$	+	$8O$	=	P_2O_5	+	$3H_2O$.
Phosphoretted hydrogen	+	oxygen (from the air)	=	phosphorus pentoxide	+	water.

This phosphoretted hydrogen is obtained by boiling caustic potash solution with phosphorus.

The products of this reaction are phosphoretted hydrogen and a salt called potassium hypophosphite :—

$4P$	+	$3KOH$	+	$3H_2O$	=	PH_3	+	$3PO_2H_2K$.
Phosphorus	+	caustic potash solution	+	water	=	phosphoretted hydrogen gas	+	potassium hypophosphite.

Were we to put phosphorus in caustic potash solution contained in the retort A of the apparatus shown in fig. 49, and to warm, we should have an explosion. Phosphoretted hydrogen so readily causes explosions that an unskilled person had much better not attempt to prepare it. The phosphoretted hydrogen that formed in the retort would at once react with the air therein with explosive violence, and the retort would be shattered. To prevent this mishap we fill the apparatus, at the beginning of the experiment, with a gas wherewith phosphoretted hydrogen does not react—with hydrogen gas, for instance. This is done, in the way shown in fig. 49, by connecting the retort with a Kipp's apparatus for generating hydrogen, and allowing the hydrogen to flow through the apparatus. As soon as the whole of the air has been driven out of the apparatus, the potash solution may be warmed without danger. The phosphoretted hydrogen passes through the tube B into water, and rises through the water in bubbles. Each bubble takes fire as it comes into contact with the air at the surface of the water, and the white smoke of phosphorus pentoxide which is formed ascends in the form of a ring. It looks almost as if the water had caught fire by chance.

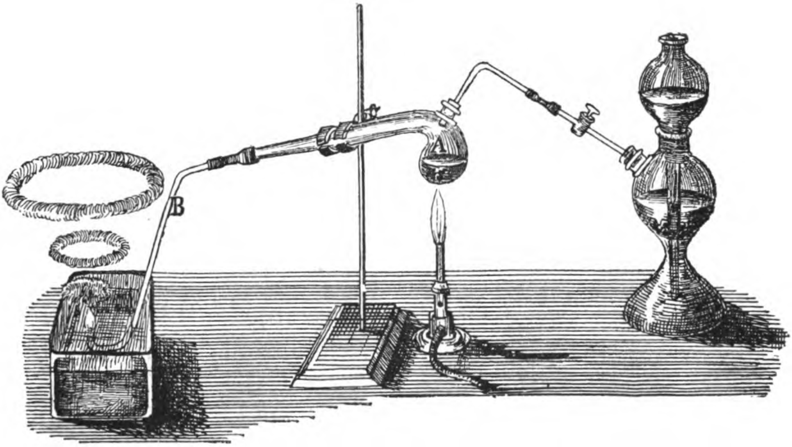

Fig. 49.—Preparation of spontaneously inflammable phosphoretted hydrogen.

Phosphorus, like sulphur, combines directly with chlorine, bromine, and iodine. *Phosphorus pentachloride*, PCl_5, is much used in the laboratory, because it enables us to effect the replacement of the hydroxyl group (see p. 183) by chlorine in the most different kinds of compounds. Phosphorus pentachloride is prepared by passing chlorine gas over phosphorus gently warmed in a retort:—

P	+	$5Cl$	=	PCl_5.
Phosphorus	+	chlorine gas	=	phosphorus pentachloride.

If we wished to replace one hydroxyl group (one OH) in sulphuric acid by an atom of chlorine, we would allow one molecule of PCl_5 to react with one molecule of sulphuric acid, H_2SO_4. As $P = 31$ and $Cl = 35{\cdot}5$, it follows that $\overset{P}{31} + (5 \times \overset{Cl_5}{35{\cdot}5}) = 208{\cdot}5$ parts by weight are equivalent to one molecule of phosphorus pentachloride; and as $H = 1$, $S = 32$, and $O = 16$, it follows that $(2 \times \overset{H_2}{1}) + \overset{S}{32} + (4 \times \overset{O_4}{16}) = 98$ parts by weight are equivalent to one molecule of sulphuric acid.

$SO_2{<}\begin{smallmatrix}OH\\OH\end{smallmatrix}$	+	PCl_5	=	$SO_2{<}\begin{smallmatrix}Cl\\OH\end{smallmatrix}$	+	$POCl_3$	+	HCl.
one mol. sulphuric acid	+	one mol. phosphorus pentachloride	=	chlorosulphonic acid	+	phosphorus oxychloride	+	hydrochloric acid.
98 parts by weight		208·5 parts by weight		116·5 parts by weight		153·5 parts by weight		36·5 parts by weight.

The equation shows that phosphorus oxychloride and hydrochloric acid are obtained in the reaction, besides chlorosulphonic acid; these substances must be separated from one another. As there is no water present, gaseous hydrochloric acid will be produced. If the operation is conducted in a draught-chamber, the acid gas will be carried away through the flue into the open air, and will thus be got rid of. In order to separate the chlorosulphonic acid and the phosphorus oxychloride, both of which are liquids that can be distilled, we make use of the process called "*fractional distillation.*" That process is conducted with such an apparatus as is represented in fig. 5 (p. 7). Phosphorus oxychloride boils at 107° C. [224·6° F.], and chlorosulphonic acid at 158° C. [316·4° F.]. As long as phosphorus oxychloride is distilling over, the thermometer will not rise above 107°; when that compound has been removed, the thermometer will rise to 158°: hence it is only necessary to collect separately the liquid that distils over at 158° in order to obtain chlorosulphonic acid. *Substances that can be distilled are separated from one another by distillation, using a thermometer—that is, by taking advantage of the differences between their boiling points: solid bodies are purified, as we know, by re-crystallisation* (see p. 55).

In phosphorus pentachloride we have a means for replacing an atomic complex—in this case the hydroxyl group—by an atom of chlorine. This is the first example we have had of the possibility of replacing, not only single atoms, but atomic groups, in compounds, by other atoms, according to definite rules. Phosphorus pentachloride is a "*group re-agent.*"

There are two oxides of phosphorus; two atoms of phosphorus combine with three atoms of oxygen, forming the trioxide P_2O_3, and also with five atoms of oxygen, forming the pentoxide P_2O_5, which has been so often mentioned already. Both of these oxides react with water to form acids: but we shall consider only the *phosphoric acids* derived from the pentoxide; *phosphorous acid*, which is derived from phosphorus trioxide (or phosphorous anhydride), is of little interest to us.* Phosphorus pentoxide yields three acids—called *metaphosphoric acid*, *pyrophosphoric acid*, and *orthophosphoric acid*—by combining with one, two, or three molecules of water. Orthophosphoric acid is by far the most important of these acids: it is also called ordinary phosphoric acid; and when phosphoric acid is spoken of without any qualifying word, it is always this acid that is meant.

P_2O_5	+	H_2O	=	$H_2P_2O_6$ (or, halved, HPO_3).
Phosphoric anhydride	+	one molecule water	=	metaphosphoric acid.
P_2O_5	+	$2H_2O$	=	$H_4P_2O_7$.
Phosphoric anhydride	+	two molecules water	=	pyrophosphoric acid.†
P_2O_5	+	$3H_2O$	=	$H_6P_2O_8$ (or, halved, H_3PO_4).
Phosphoric anhydride	+	three molecules water	=	orthophosphoric acid.

Orthophosphoric acid, or simply phosphoric acid, has the formula H_3PO_4; for it is not necessary to write the formula as $H_6P_2O_8$—that is used only to make perfectly clear the formation of the acid from phosphoric anhydride. The simpler formula, H_3PO_4,

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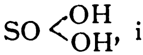
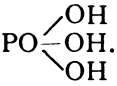
* There is a third oxide of phosphorus, P_2O_4. A solution of this oxide in water contains both phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4). [Tr.]

† This formula cannot be halved; the half formula would contain a half atom of oxygen.

shows the proportion wherein the phosphorus, hydrogen, and oxygen are combined. The three atoms of hydrogen are replaceable by metal; the acid is *tribasic* (as the expression is). According as one, two, or three atoms of hydrogen are replaced by a metal, very different salts are obtained. The basicity of an oxy-acid [very often] agrees with the number of hydroxyl groups in the acid; for it is [generally] the hydrogen of the hydroxyl groups that is replaceable by metal. Nitric acid, $NO_2—OH$, is monobasic; sulphuric acid,  $SO{<}^{OH}_{OH}$, is dibasic; and phosphoric acid is tribasic,  $PO{\lt}\begin{matrix}OH\\OH\\OH\end{matrix}$. A similar state of affairs holds good for [many] bases: the number of hydroxyl groups in a base measures what is called the "*acidity*" of that base.*

We are acquainted with mono-acid bases, such as caustic potash, K—OH, and caustic soda, Na—OH; and there are also bases which are di-acid, tri-acid, etc. It is not necessary that all the replaceable atoms of hydrogen in a polybasic acid should be replaced by the same metal (or by the ammonium group, see p. 171); but the atoms of hydrogen may be replaced by different metals (compare p. 159). The metal magnesium, for instance, always replaces two atoms of hydrogen; hence, if we replace two atoms of hydrogen in phosphoric acid by magnesium, we

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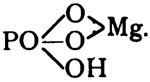
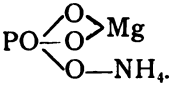
* Of course, it is ridiculous to talk of the *basicity of an acid* and the *acidity of a base*. Most unfortunately, these expressions have been in common use for many years. [TR.]

get a salt which has the formula $MgHPO_4$, or, written more fully,  $\mathrm{PO}\begin{array}{l} \diagup \mathrm{O} \searrow \\ - \mathrm{O} \nearrow \mathrm{Mg}. \\ \diagdown \mathrm{OH} \end{array}$ This salt is found in urine. When urine putrefies, ammonia is formed therein; and this reacts with the magnesium salt, and replaces the atom of hydrogen by ammonium, NH_4. Stale urine, then, always contains ammonium magnesium phosphate, $MgNH_4PO_4$, or, written more fully,



$$\mathrm{PO}\begin{array}{l} \diagup \mathrm{O} \searrow \\ - \mathrm{O} \nearrow \mathrm{Mg} \\ \diagdown \mathrm{O}-\mathrm{NH_4}. \end{array}$$

THE BUILDING UP OF PLANTS FROM INORGANIC SUBSTANCES.

Now that we are acquainted with phosphoric acid, we know something of all the inorganic substances and compounds that are required for the growth of plants—of all with the help whereof plants live. Plants live on inorganic substances—on the constituents of non-living materials; whereas the animal world cannot use such material for their growth, but can live, directly or indirectly, only on the substances that are produced by plants. For when we eat flesh, etc., it has always come from animals which have been nourished on plants. A survey of the nutrition of plants, at this point in our course, besides being interesting in itself, will afford an opportunity for the elucidation of some occurrences which are important from a purely chemical point of view.

The connection between the plant world and non-living matter—first enunciated by Liebig—may be set forth briefly somewhat as follows. If a plant, or a part of a plant—wood, for instance—is burnt, ashes remain. These ashes, which were formerly thought to be merely chance constituents of the plant, represent what the plant took by its roots from the soil wherein it grew, as being absolutely necessary to its existence.

If a soil does not contain the main constituents which an analysis of such plant-ash shows to be contained therein, the plant in question cannot thrive in that soil. The ashes of different plants are not of the same composition; hence one plant may grow and thrive on a plot whereon another plant does not grow or grows badly. Every crop raised on a field withdraws from the soil of the field a considerable number of kilos. of inorganic salts. Since Liebig made this clear, people have realised that these inorganic salts must be given back to the soil. This is done by using artificial manures. Strange though it sounds, nevertheless it is the case, that all agriculture was more or less a robbing of the soil before the true state of affairs was made known by Liebig; for the inorganic constituents of the soil that were carried away in the marketable products of agriculture were not given back to the soil. The stable manure, and the like, that were put on the soil carried back thereto much smaller quantities of inorganic salts than were sold in the form of agricultural produce.

The following table presents analyses of the ashes of some products of the vegetable kingdom :—

		Ash of rye grains.	Ash of barley grains.	Ash of potatoes.
Phosphoric acid*	P_2O_5	47·52 per cent.	38·8 per cent.	17·4 per cent.
Potash . .	K_2O	34·50 "	21·1 "	60·4 "
Magnesia . .	MgO	11·38 "	7·0 "	4·7 "
Lime . . .	CaO	2·75 "	1·7 "	2·4 "
Silicic acid* .	SiO_2	2·75 "	29·3 "	2·1 "
Soda . . .	Na_2O	0·52 "	—	2·6 "
Iron oxide . .	Fe_2O_3	0·20 "	2·1 "	1·2 "
Chlorine . .	Cl	0·38 "	—	3·0 "
Sulphuric acid* .	SO_3	—	—	6·2 "
		100·0	100·0	100·0

These analyses exhibit the requirements of certain plants as regards various inorganic compounds. Every soil suited for agriculture contains in itself most of these compounds. Experience shows that phosphoric acid and potash salts are almost the only compounds, of those found in plant ashes, which must be supplied to such soils in order to maintain their fertility, or to bring them to a higher degree of productiveness by increasing in them the quantities of the inorganic compounds which are absolutely necessary for plant growth.

Many sources of phosphoric acid are within our

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* The names phosphoric acid, silicic acid, and sulphuric acid are here applied to the anhydrides of these acids; and the percentage amounts of those acids are calculated as these anhydrides. This is a custom which has come from the older analyses of plant-ashes, and is retained in this department of analysis.

reach. Besides bones, which we already know (p. 190) to consist for the most part of calcium phosphate, there is the mineral *phosphorite*, which is more or less pure calcium phosphate; and we could hardly even enumerate the less important sources of this compound.

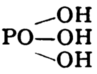
The calcium phosphate in bones and in phosphorite is quite insoluble in water; but the roots of plants are able to absorb only bodies that are dissolved by water. By the process called disintegration nature provides for the rendering soluble of those rock-fragments which are present in every soil and represent the supply of calcium phosphate insoluble in water. That process is somewhat as follows. The carbonic acid which circulates through the soil with the air—for carbonic acid is a constituent of the air—acts, along with the moisture in the soil, on the rock-fragments, and, attacking the insoluble calcium phosphate therein, converts it into a calcium salt of phosphoric acid which is soluble in water.

This natural process takes place very slowly in soils. If a soil is to be manured with the calcium phosphate of bones, or phosphorite, that salt must be changed to a soluble calcium phosphate before it is put into the soil. The roots absorb this phosphate dissolved in the moisture of the soil, and the good results of the manuring are apparent in the next crop that is taken from the soil.

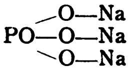
This change of one calcium phosphate into another which is soluble in water is known as making "*superphosphate*"; the phosphoric acid in the product is in a condition wherein it is more valuable to the agriculturists than when it is in the raw material.

The production of soluble phosphate can be accomplished only by chemical methods. The finely powdered raw material is covered with sulphuric acid, which, being the stronger acid, seizes the calcium, and, replacing part of the phosphoric acid, causes the formation of a calcium phosphate that is soluble in water and is, therefore, fitted for absorption by the roots of the plants.

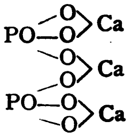
The following considerations will enable us to follow this process, and will also give us an opportunity of examining more fully than before the conception of the *basicity of an acid.* Metal can take the place of hydrogen atoms in phosphoric acid (H_3PO_4), as in all other acids. Sodium, for instance, produces the salt Na_3PO_4, sodium phosphate. As the three atoms of hydrogen in phosphoric acid are all replaceable, the acid is said to be tribasic. Now, the metal calcium does not, like sodium, replace one atom of hydrogen from an acid, but always two atoms of hydrogen. Hence the formula of the calcium salt of the tribasic phosphoric acid must be $Ca_3(PO_4)_2$; for three atoms of calcium correspond to six atoms of hydrogen, and two molecules of phosphoric acid--two molecules of H_3PO_4 —are required to yield six atoms of hydrogen. As calcium always takes the place of two atoms of hydrogen, and half an atom of calcium is impossible, the formula $Ca_3(PO_4)_2$ is the only possible expression for the neutral calcium phosphate. This is seen more clearly if we expand the formulæ (compare p. 183) so as to show the three hydroxyl groups and the replaceable hydrogen atoms of the phosphoric acid.



Tribasic
phosphoric acid.

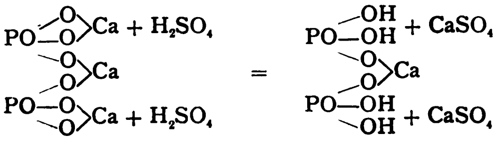


Sodium salt of tribasic
phosphoric acid.



Calcium salt of tribasic
phosphoric acid.

These formulæ make clear to us the replacement of the three hydrogen atoms of the three hydroxyl groups of phosphoric acid by three atoms of sodium, and the replacement of six atoms of hydrogen by three atoms of calcium. The calcium salt of tribasic phosphoric acid, which is found native, is a neutral salt, and is insoluble in water; but if we remove two of the three atoms of calcium, by acting on the salt with sulphuric acid, an acid calcium phosphate is produced: for a salt which contains replaceable atoms of hydrogen in addition to a metal—in this case one atom of calcium—is called an acid salt (see p. 158); and in this case the sulphuric acid which is made to react with the neutral calcium phosphate brings about the replacement of calcium by hydrogen. The sulphuric acid exchanges hydrogen for calcium, and forms calcium sulphate, a salt that is commonly known as *gypsum*. The following equation shows this exchange of atoms:—



One mol. neutral calcium phosphate + two mols. sulphuric acid = one mol. acid calcium phosphate + two mols. calcium sulphate.

The acid calcium phosphate which is formed by the reaction of two molecules of sulphuric acid with one molecule of the salt present in bones, or *phosphorite,* is soluble in water; hence it can be absorbed by the plant roots, and is capable of acting as an artificial manure. If three molecules of sulphuric acid were allowed to react with one molecule of the salt in the raw material, the whole of the calcium would be removed by the sulphuric acid, and free phosphoric acid would, of course, be obtained. But phosphoric acid is so corrosive that it would destroy the roots of the plants. What is called *manuring with phosphoric acid* is really manuring with acid monocalcium phosphate, which is the substance in "*superphosphate*" that acts as a fertiliser. The phrase in common use, "manuring with phosphoric acid," is, therefore, incorrect.

It is easy to calculate the quantity of sulphuric acid which must be added to a specified quantity of phosphorite in order to produce superphosphate. The formula of neutral tricalcium phosphate is $Ca_3P_2O_8$; and as $P = 31$, $Ca = 40$, and $O = 16$, the molecular weight of this salt is—

$$\overset{Ca_3}{(3 \times 40)} + \overset{P_2}{(2 \times 31)} + \overset{O_8}{(8 \times 16)} = 310.$$

As two molecules of sulphuric acid must be used, and as the molecular weight of sulphuric acid (H_2SO_4) is 98, it follows that 196 parts by weight of sulphuric acid must be poured on to 310 parts by weight of phosphorite [assuming the phosphorite to be pure tricalcium phosphate]: stated in percentages, 63·2 kilos.

sulphuric acid must be added to 100 kilos. phosphorite* [or 63·2 lb. or cwts. sulphuric acid to 100 lb. or cwts. phosphorite].

In manufacturing superphosphate, finely ground phosphorite is thoroughly mixed with the calculated quantity of sulphuric acid; the mass is heated by the heat produced in the reaction, and after cooling [and breaking into pieces, and powdering] it is obtained in the form of a powder which may be spread on the fields. The gypsum that is produced by decomposing the crude phosphate remains mixed with the soluble acid phosphate: but that does not matter, as the gypsum does not injure the plants; indeed, the presence of calcium salts may be useful in the cases of soils that are poor in lime, for we know, from the analyses of plant ashes, that compounds of calcium are required by plants. "Superphosphate," then, is a mixture of monocalcium phosphate and calcium sulphate.

The potash salts that are needed for artificial manuring may be obtained from the Stassfurt salts (compare p. 58). The main potassium compound in these salts is the double salt of potassium chloride and magnesium chloride, which has the composition $KCl . MgCl_2 . 6H_2O$. Before it can be sold to the farmers the potassium chloride must be separated from the magnesium chloride, as the latter is harmful to plant growth. This is effected by re-crystallising the *carnallite*, which is the mineralogical name of the double salt.

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* Calculated by the proportion, $310 : 196 = 100 : x$, whence $x = 63·2$.

Potassium chloride and magnesium chloride both dissolve in water, but potassium chloride is much less soluble in cold water than magnesium chloride. In order to obtain potassium chloride, therefore, the crude salt from the mines is dissolved in hot water, and potassium chloride crystallises out as the solution cools, while magnesium chloride remains dissolved in the mother-liquor. As there is very little demand for magnesium chloride, this mother-liquor must be allowed to run into the nearest stream. A relatively small quantity of the mother-liquor suffices to yield all the bromine that is required on the market (compare p. 59); what remains after the bromine has been extracted is thrown away. A double sulphate of potassium and magnesium, called *kainite*, and having the composition $K_2SO_4 . MgSO_4 . 6H_2O$, is one of the salts found at Stassfurt. Potassium sulphate is obtained from this salt.

Now that we have considered the constituents of plant-ashes sufficiently for our purpose, we shall turn to the other substances that are required for the growth of plants. The most important of these is the element carbon, which, indeed, is the very foundation of the existence of plants. This carbon makes its appearance when parts of plants are heated out of contact with air, that is, under conditions such that complete combustion is impossible because of lack of oxygen. If wood is heated out of contact with air, carbon remains in the form of charcoal, and we have a visible demonstration of the fact that carbon forms a large part of the substance of a plant. It is clear why carbon cannot be present in plant ashes, and is not therefore found among those constituents of plant ashes which are discovered by analyses thereof: for, as the ashes are obtained by burning the plant in a crucible in contact with the air, the carbon is burnt to carbon dioxide, which passes away into the atmosphere. As with the carbon, so with the nitrogen and the water that are contained in plants; these also pass away during the process of burning, and therefore they are not found among the constituents of the ashes.

Plants obtain their carbon from the atmosphere Although the air contains only three parts of carbon dioxide gas per ten thousand, nevertheless this quantity, which seems so small, is amply sufficient for the needs of plants. The plants absorb the carbonic acid gas by their leaves, and the surface presented by these is very large compared with that of the whole of the other parts of a plant. It is the green colouring material of the leaves, called *chlorophyll*, which is able to make the carbonic acid gas of the atmosphere available for the plants. That gas seems to be changed directly into starch, a substance which is present in all green leaves. It is, of course, impossible to manure fields with carbonic acid gas, to supply the soil artificially with this gas; fortunately it is unnecessary, for no one has noticed at any time that plants suffer from want of carbon dioxide.

Plants take the hydrogen they require from the moisture in the soil, and the supply of moisture is replenished by the rain. They receive sufficient oxygen in the carbonic acid gas (CO_2) and the water (H_2O) which they absorb; indeed, they get more oxygen than they need, and so they discard some of it through their leaves. The oxygen which is expired in that way is a portion of that taken from the carbon dioxide, not that taken from the water: thus it is that plants breathe in carbon dioxide (CO_2) and breathe out oxygen.

As we know, the reverse of these processes occurs in the animal kingdom. Animals inspire air, and hence oxygen, by their lungs or gills, and expire carbon dioxide. It is the oxygen which is breathed in with the air that forms this carbon dioxide. The oxygen acts on compounds in the animal bodies which contain carbon, and, combining with their carbon, produces carbonic acid gas.

The circumstances connected with the absorption of nitrogen by plants are very remarkable. Ten thousand parts of air contain only three parts of carbon dioxide, but nearly eight thousand parts of nitrogen (see p. 120). Although that small quantity of carbon dioxide is quite sufficient to supply the demands of plants, yet plants often lack nitrogen, and their growth is stopped for want of that element, notwithstanding the vast quantities of it that are present in the air. The reason for this must be that the absorption of the nitrogen of the air is attended with difficulties.

Nitrogen is required by plants, because it is absolutely necessary for the production of albuminous substances. *Egg-white is the type of a large class of extraordinarily complex nitrogen-containing substances, called albuminoids, which are produced in living organisms, and are necessary for the continuance of life both* *in the animal and the vegetable world. It is impossible to think of life without the presence of such nitrogenous substances.*

Plants are not furnished with an organ adapted for taking up the nitrogen of the air directly quite in the same way as they absorb carbon dioxide. On the contrary, they only absorb nitrogenous substances by their roots from the soil. Such substances which are to act as nourishment to plants must be soluble in water, just as phosphates must be soluble in water. Nitrogen itself is practically insoluble in water. For a long time we did not know the processes whereby nitrogen, which is so little disposed to combine with other elements, is changed into compounds that are soluble in water, and therefore can be absorbed by the roots of plants. On the other hand, experience showed that the fertility of a soil was increased by the addition of nitrogenous bodies, a fact not to be wondered at considering what we know of the albuminoids of plants. There are two main materials suitable for this purpose, and with both of these we are already acquainted. One is Chili saltpetre—that is sodium nitrate, $NaNO_3$ (see p. 172)—a compound which is very soluble in water, and therefore very suitable for absorption by the roots of plants, and is also sufficiently cheap for manuring purposes; the other is ammonium sulphate, $(NH_4)_2SO_4$, which is obtained from the gas-works (see forward p. 271).

The method whereby the nitrogen of the air is converted, in nature, into compounds that are soluble in water has been elucidated only in the course of the last fifteen years. The help of bacilli is required for effecting this change. Arable soils contain bacilli which are able, by their life-processes, to combine nitrogen with oxygen and to produce compounds allied to nitric acid. These compounds, as one would suppose, immediately react with the lime or the potash compounds in the soil to form calcium nitrate and potassium nitrate [or compounds allied to these], which are soluble in water: in this way the nitrogen which was before in the atmosphere becomes capable of absorption by the plant-roots. But such bacilli do not collect on the roots of all kinds of plants in quantities sufficient to render unnecessary the use of nitrogenous manures; hence the increase in growth which results from adding soluble nitrogenous compounds, in the form of artificial manure, to the supply of such compounds which nature provides by the processes we have described. It is for this reason that Chili saltpetre, and the like, are found to be so useful in increasing the fertility of soils. The bacilli which are found on the roots of the leguminous plants are the best nitrogen-collectors.

Certain nitrogenous compounds which are insoluble in water are good manures; such are dried and powdered blood, and shavings of horn, both of which must be classed with the albuminoids, for they consist of very complex nitrogenous compounds produced by changes in living organisms. These manures act more slowly than Chili saltpetre or ammonium sulphate, which are soluble in water, because they have to be changed into compounds soluble in water, and this is done gradually as the substances decay in the soil.

We have dwelt at some length on the connections between non-living materials and the plant-world, which is the foster-mother of the animal world. It is easy to see that it was only by such purely chemical knowledge that agriculture could cease to be an empirical and mechanical trade and become a skilled art. The chemical investigations that have led to this knowledge are not yet fifty years old; and that is the reason why the thorough application of that knowledge has not long ago spread over the whole world, but is still confined to a few highly civilised countries, and even there to that part of the agricultural population which is really intelligent.

ARSENIC.

Arsenic is related to phosphorus and nitrogen. Notwithstanding its metal-like appearance, it belongs to the same group as these two non-metallic elements; in the first place because it combines with hydrogen to form a gaseous compound—arsenuretted hydrogen—whereas metals do not form such hydrogen compounds, and secondly because its compounds with oxygen yield acids, whereas most of the oxides of the true metals are bases.

It is only those metals which combine with very large quantities of oxygen that form both basic oxides and also compounds very rich in oxygen which show acidic properties. For instance, manganese forms not only manganous oxide, manganic oxide, and manganese peroxide, but also both manganic and permanganic acids (see forward, under MANGANESE).

Arsenic itself is found native. Compounds of arsenic with sulphur, with oxygen, and with metals also occur in rocks; and these, as well as native arsenic, are worked in mines.

Arsenuretted hydrogen, AsH_3, can be formed by a reaction similar to that which yields sulphuretted hydrogen. As iron sulphide reacts with hydrochloric acid to give sulphuretted hydrogen gas (see p. 144), so zinc arsenide (which is more easily made than iron arsenide) reacts with hydrochloric acid to give arsenuretted hydrogen. The equation which expresses the latter reaction is this:—

$$\underset{\text{Zinc arsenide}}{Zn_3As_2} + \underset{\text{hydrochloric acid}}{6HCl} = \underset{\text{arsenuretted hydrogen gas}}{2AsH_3} + \underset{\text{zinc chloride.}}{3ZnCl_2.}$$

Many other compounds of arsenic yield arsenuretted hydrogen gas when they are brought into a mixture which is producing hydrogen—that is, when they come into contact with nascent hydrogen (see p. 106). It is on this reaction that the process for detecting arsenic in cases of poisoning is based. That process, which is more certain and easier of performance than the detection of almost any other poison, is conducted as follows. Pure hydrogen is produced in a flask (A, fig. 50), and the liquid to be tested for arsenic is poured into the flask, by the funnel B. The gas which issues from the flask is ignited at C, and a porcelain plate is held in the flame. If arsenic is present it is deposited on the plate in black spots. The tube through which the gas passes has been narrowed at D; that tube is now heated by a Bunsen burner placed a little behind the narrow part. Arsenuretted hydrogen is decomposed, at a moderately high temperature, into its constituents, arsenic and hydrogen. The hydrogen escapes, and the arsenic appears on the cooler part of the tube, in front of the flame, as a lustrous deposit known as *"an arsenic mirror."* As this mirror is obtained even when a mere trace of arsenic is placed in the vessel wherein hydrogen is generated, the detection of arsenic is easy and certain.

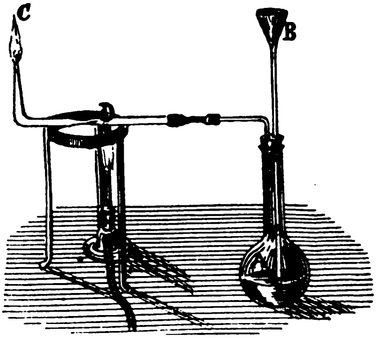

Fig 50.—Detection of arsenic.

Arsenic combines with chlorine, bromine, and iodine Two compounds of arsenic with oxygen are known, corresponding with the two oxides of phosphorus, namely, As_2O_3, called *arsenic trioxide*, and As_2O_5, called *arsenic pentoxide.* As these bodies combine with bases, in the presence of water, to form salts, they are also called *arsenious anhydride* and *arsenic anhydride* respectively.

Arsenious anhydride, As_2O_3, is popularly known as "*white arsenic*"; it is often used as a poison for rats. It is produced in quantity as a bye-product in the working of arsenical ores, which contain such metals as cobalt, nickel, tin, and silver in addition to arsenic. The ores are heated in furnaces in a stream of air; the arsenic is burnt to arsenic trioxide, which is volatile at the high temperature of the furnaces :—

$$\begin{array}{ccccc} 2As & + & 3O & = & As_2O_3. \\ \text{Arsenic} & + & \text{oxygen} & = & \text{arsenic trioxide.} \\ & & \text{(from the air)} & & \end{array}$$

The vapours that come from the furnace are passed through long chambers before reaching the chimney, and the arsenic trioxide settles on the bottoms and sides of these chambers. In this way the poisonous substance is prevented from passing out by the chimney. The price of arsenious oxide is very low, as the substance is almost a waste product in certain metallurgical operations.

ANTIMONY.

The symbol for antimony, Sb, is derived from the Latin name, *stibium*. Antimony is more metallic than arsenic. Its applications are those of a metal; it is employed chiefly for melting with lead, to which it imparts a greater hardness. In its chemical relations antimony is classed with the non-metals, inasmuch as, like nitrogen, phosphorus, and arsenic, it forms a gaseous compound with hydrogen—antimonuretted hydrogen, SbH_3. The behaviour of this gas is very similar to that of arsenuretted hydrogen. Like phosphorus and arsenic, antimony forms two compounds with oxygen—antimony trioxide, Sb_2O_3, and antimony pentoxide, Sb_2O_5. The composition of the trioxide, Sb_2O_3, corresponds with that of phosphorus trioxide or phosphorous anhydride, P_2O_3: but antimony trioxide does *not* show acidic properties, although it is the oxide of a non-metal; it reacts with acids to form salts, like the oxides of metals; for instance, with sulphuric acid it forms *antimony sulphate*; hence it is classed with the bases. The higher oxide of antimony—that is, the oxide richer in oxygen—Sb_2O_5, which corresponds with phosphorus pentoxide or phosphoric anhydride, P_2O_5, is, however, an acid anhydride; it forms salts by reacting with bases in the presence of water; for instance, with caustic potash solution it forms the fairly insoluble salt *potassium antimonate.*

Nature, as is her custom, has drawn no hard and fast line between the metals and the non-metals. Antimony belongs to both classes; in the gaseous compound antimonuretted hydrogen and in the acidic pentoxide it behaves like a non-metal, and in the basic trioxide it behaves like a metal.

WE now come to the last group of elements we shall consider which contains non-metals. Some of the members of this group are distinctly metallic. The group comprises the four elements carbon, silicon, germanium, and tin.

CARBON.

Carbon, the symbol for which is C, is found in nature in three modifications. One of these has no definite form; it is amorphous: this modification of carbon is found in wood charcoal. The two other modifications are crystalline, and occur in very much smaller quantities. If the crystals take the form of black leaflets they are called *graphite*, if they are clear and transparent they are called *diamond*.

The most convenient method of proving that diamond and graphite are pure carbon is to burn them in pure oxygen gas, and to show that the sole product in either case is carbon dioxide, CO_2; hence neither can be anything but carbon. Both these forms of carbon are exceedingly difficult to burn in air: we may recall the use of graphite crucibles in melting metals.

Let us perform the combustion of a diamond, in the manner shown in fig. 51. The flask A is closed by a cork, through which passes a glass tube that reaches to the bottom of the flask. Oxygen is passed through the flask, from a gasholder, G, and then into an open vessel, B (by the glass tube D, which passes only a little way through the cork into the flask A). Some clear, filtered lime water is placed in the flask A. As long as oxygen only is passing through the apparatus, the lime water is not changed, although the oxygen bubbles through it; for what can be formed by the mutual action of these two materials? Two stout wires of copper pass through the cork of the flask, and these are connected, within the flask, by a spiral of thin

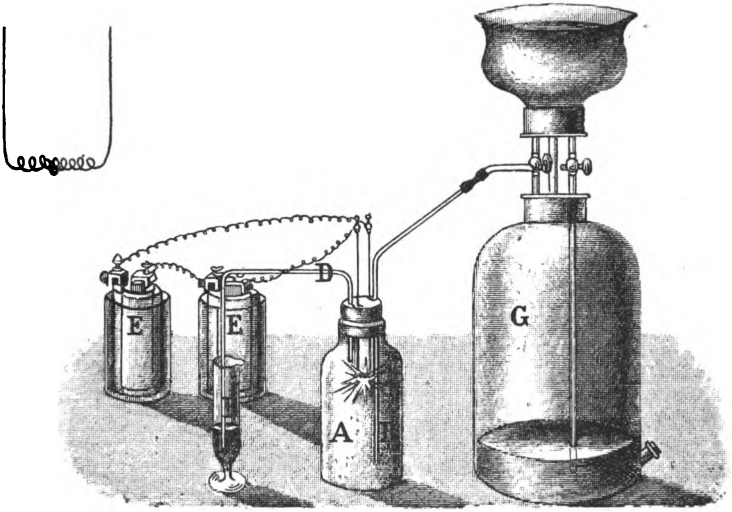

Fig. 51.—Burning diamond in oxygen, and detection of the carbon dioxide produced.

platinum wire. When, at a later stage of the experiment, an electric current is passed through the copper wire—such a current as is obtained from a couple of Bunsen elements* (E, fig. 51) is quite sufficient—the platinum spiral becomes red hot. We use platinum because we know that our spiral will not melt, notwithstanding the thinness of the wire, inasmuch as platinum fuses only at the very highest temperatures. A small fragment of diamond is fastened in the platinum spiral, as shown on an enlarged scale in fig. 51, the cork is placed tightly in the flask A, and oxygen gas is passed through the apparatus. After a short time all the air will have been driven out of the flask. We then allow the stream of oxygen to pass more slowly, and we close the electric circuit. The platinum spiral gets red hot and glows; the heat is conducted to the diamond, and we see this burning brilliantly in the atmosphere of oxygen and gradually disappearing. At the same time we notice the lime water becoming turbid; we see the bubbles of gas producing a white solid, which gives a milky appearance to the liquid. This white solid gradually settles to the bottom of the flask; when it is examined it is found to be nothing but calcium carbonate. As we already know (p. 134), calcium carbonate is insoluble in water; therefore it is formed by the reaction between the gas in the flask, which is no longer oxygen but carbon dioxide, and the calcium hydroxide, $Ca(OH)_2$, present in the lime water.

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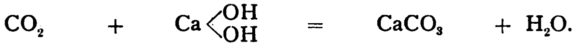
* The word *element* has here a meaning entirely different from that given to it in other parts of this book. In this case the word has nothing to do with chemistry.



$$CO_2 + Ca\begin{cases}OH\\OH\end{cases} = CaCO_3 + H_2O.$$

Carbon dioxide gas + calcium hydroxide = calcium carbonate + water.

The carbon dioxide gas, CO_2, must be produced from the diamond, for the oxygen gas did not cause the lime water to become turbid before the diamond began to burn. Hence the diamond must have been converted into carbon dioxide by burning, and must, therefore, have consisted of carbon.

The reason for setting fire to the diamond by the somewhat unusual method of placing it in a platinum spiral and making the spiral red hot by an electric current is, of course, that it is necessary to avoid the use of a flame, or anything of that sort; for a flame would have formed combustion-products which would have mixed with the products of the combustion of the diamond, and it would not have been possible, without further complications, to decide what part of the products of combustion came from the diamond and what part came from the material which was burnt to produce the flame.

If a small piece of graphite were burnt in place of the diamond, and in the same manner as we have burnt the diamond, we should notice exactly the same phenomena; hence graphite also is nothing but carbon.

This process of burning carbon is expressed by the following equation:—

$$C + O_2 = CO_2.$$

Carbon + oxygen = carbon dioxide.

As the atomic weight of carbon, C, is 12, and that of oxygen, O, is 16, it is evident that when 12 parts by weight of carbon are burnt to carbon dioxide 44 parts by weight of that gas are produced $[CO_2 = 12 + (2 \times 16) = 44]$. If these numbers are calculated to percentages, it is seen that 100 kilos. of carbon yield 366 kilos. of carbon dioxide. The 266 kilos. of oxygen which are required to combine with the 100 kilos. of carbon are mixed in the air with four times as much nitrogen—in round numbers, with 1066 kilos. of nitrogen. Hence 366 + 1066 = 1432 kilos. [about 1_2 tons] of gaseous products escape by a chimney into the air when 100 kilos. [about 11 cwts.] of carbon are burnt in a fire, assuming that no more air is drawn through the fire than suffices to burn all the carbon. The work done by the chimney of a furnace in which many thousand kilos. of carbon may be burnt daily is evidently considerably greater than we are accustomed to suppose.

If there were a suitable solvent for carbon, there would be no reason why the carbon should not crystallise therefrom in the form of diamond. But no such solvent is known. Melted iron is the best solvent of carbon; but the carbon crystallises as graphite as the iron cools. Nevertheless, it has been found possible, of late years, to cause carbon to separate from this somewhat extraordinary solvent in the form of diamonds—of almost microscopic smallness, it is true. If the melted iron is allowed to cool under great pressure, instead of by free exposure to the air, minute diamonds are found in the cold block, along with graphite. The method is simple enough. The melted iron is thrown into water while it is red hot; the surface solidifies at once, and as it contracts on cooling it exerts an enormous pressure on the inner parts, which are still molten, and small diamonds are thus produced. In order to get the graphite and the diamonds out of the iron the piece of iron is dissolved in hydrochloric acid; the crystallised carbon remains, and the artificial diamonds are separated from the graphite by picking.

ORGANIC CHEMISTRY.

The capacity of carbon to form compounds is greater than the combining capacities of all the other elements taken together: the compounds of this one element are more numerous than those of all the others. Nature has also used this element in forming living beings, the most complicated of all things. Carbon is found in all materials that are connected with the world of living things. The analyses made by chemists had shown this long ago; hence the chemistry of carbon was designated "*organic chemistry*," and this special name has remained in use till to-day. It is the custom in the universities and colleges to begin the study of chemistry by attending lectures on inorganic chemistry, which deal with all the elements except carbon, and to follow these by lectures on *organic chemistry*.

After what has been said it is not surprising to be told that very great efforts have been required to set in order the vast number of compounds of carbon which form the subject-matter of organic chemistry. Nevertheless, there is no very great difficulty in understanding the fundamental principles by the application whereof this order has been attained. We may, indeed, often be inclined to think that the formulæ of the organic compounds, wherein "*rests*" [or radicles] are made use of (compare p. 183), recall the moves of the pieces on a chess-board. At any rate, it will not do to hurry through the following thirty-five pages.

THE VALENCIES OF THE ELEMENTS.

In order to obtain a clear understanding of this, the most pregnant part of the whole domain of chemistry, we must turn back to those hydrogen compounds of the non-metallic elements which we have already considered so fully. The hydrogen compounds of the four elements chlorine, bromine, iodine, and fluorine, which we have already recognised to be most important aids in determining atomic weights, are these :—

$$ClH \qquad BrH \qquad IH \qquad FH.$$

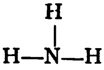
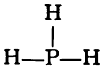
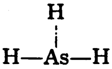
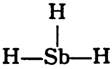
The second group of elements wherewith we concerned ourselves consisted of oxygen, sulphur, selenion, and tellurium. The hydrogen compounds of these elements have the formulæ :—

$$OH_2 \qquad SH_2 \qquad SeH_2 \qquad TeH_2.$$

Nitrogen, phosphorus, arsenic, and antimony formed our third group of elements. The hydrogen compounds of these are :—

$$NH_3 \qquad PH_3 \qquad AsH_3 \qquad SbH_3.$$

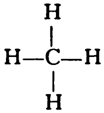
If we place the formulæ of these compounds together, writing them in a somewhat different fashion, we have the following presentation :—

First Group.	Second Group.	Third Group.
$H—Cl$	$H—O—H$	 $H—\overset{\overset{H}{\vert}}{N}—H$
$H—Br$	$H—S—H$	 $H—\overset{\overset{H}{\vert}}{P}—H$
$H—I$	$H—Se—H$	 $H—\overset{\overset{H}{\vert}}{As}—H$
$H—F$	$H—Te—H$	 $H—\overset{\overset{H}{\vert}}{Sb}—H$

The mere inspection of this arrangement shows that the elements of these three groups have something in common. This common property is that [single atoms of] the elements of the first group bind to themselves one atom of hydrogen, [single atoms of] the elements of the second group hold fast two atoms of hydrogen, and [single atoms of] the elements of the third group unite themselves to three atoms of hydrogen. The lines joining the symbols of the elements and the symbols of hydrogen are the outward expressions of these reactions. Chemists are accustomed to use the word *valency* to designate the power possessed by the atom of an element to hold to itself atoms of other elements, and to measure the valency [of an atom] by the number of atoms of hydrogen which it can bind to itself. The [atoms of the] elements of the first group are said to be *monovalent,* those of the second group *divalent,* and those of the third group *trivalent.*

It is evident from what has been said that the atom of hydrogen, which is the standard of valency, is itself monovalent. For, in the first place, the attracting power of the elements is reciprocal—one atom of hydrogen is able to hold fast one atom of chlorine, just as one atom of chlorine holds fast one atom of hydrogen. In the second place, the atoms of the chlorine group are themselves monovalent, because they can bind each but one atom of hydrogen; the atoms of the oxygen group are divalent, because they bind each two atoms of hydrogen; and the atoms of the nitrogen group are trivalent, inasmuch as they can hold fast each three atoms of hydrogen.

Chemists had got about as far as this in their knowledge of these relations in the forties of the nineteenth century. Kekulé (who died in 1896) put the coping-stone on the edifice in the year 1857 by showing that organic chemistry—the chemistry of the innumerable array of carbon compounds—follows the same law, inasmuch as the [atom of] carbon is tetravalent. With the insight of genius, Kekulé showed that all the carbon compounds, vast though their number is, can be derived from the hydrocarbon CH_4. It is to him we owe the representation of this hydrocarbon by the formula which puts before our eyes the tetravalency of the carbon atom :—



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—H} \\ | \\ \mathrm{H} \end{array}$$

This hydrocarbon is a gas; it is called *marsh-gas*, or, more generally nowadays, *methane*.

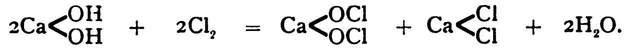
As thus presented, the theory of the valency of the elements appears so simple that one might almost regard it as self-evident. It is difficult to comprehend the endless trouble which had to be taken by generations of the most expert chemists before this clear insight was obtained into the nature of the mutual combinations of the atoms.

Although we have said but little as yet regarding the linking of atoms, we are in a position to give an opinion concerning the possible existence of compounds, a thing which it would have been impossible to do with our previous knowledge. For instance, we can assert that an attempt to isolate the atomic complex OH, which we know as the radicle (or rest) of water (p. 183), would be fruitless. For, as one atom of oxygen (O) is able to hold fast to itself two atoms of hydrogen (2H), the compound OH cannot exist by itself. Because there is only one atom of hydrogen for the one atom of oxygen in this substance OH, the second *valency* of the oxygen atom (as it is called) has no outlet; it must remain suspended in the air, as it were; and, as thousands of investigations have shown, this is a thing which never occurs. Just as little could the *rests* of ammonia, NH or NH_2, exist as complete compounds: one could not get hold of them. For in these combinations only one atom or only two atoms of hydrogen are present for one atom of nitrogen: but the nitrogen atom is trivalent, and its three valencies require three atoms of hydrogen for their saturation, as we see in ammonia, NH_3.

The construction of all chemical compounds, whether inorganic or organic, proceeds in accordance with the following simple rule, wherein is found the key by means of which chemists are able to enter and survey the immense field of their activity. The construction of all chemical compounds, from the simplest (such as hydrochloric acid, HCl) to the most complicated, takes place in such a way that *in the place of any monovalent atom or group there enters only some other monovalent atom or group, in the place of a divalent atom or group there enters only some other divalent atom or group, in the place of a trivalent atom or group there enters only some other trivalent atom or group.* The monovalent, divalent, and trivalent bodies may be monavalent, divalent, and trivalent atoms, or mono-, di-, or trivalent *rests* or atomic complexes.

The readiest method for making clear the bearing of this simple rule on the linking of the atoms in all known compounds, and in all compounds yet to be discovered, is to give some examples. Chlorine is a monovalent element; hence it is able to replace hydrogen, which is also monovalent. Consider water, for example, H—O—H. By replacing an atom of hydrogen by chlorine we obtain the compound Cl—O—H, which we may write as ClOH, without the joining lines. We should expect this compound to exist, and we should expect to be able to isolate it. The compound is, indeed, well known; it is called *hypochlorous acid.*

The calcium salt of this acid—calcium hypochlorite—is the active substance in bleaching powder; hence we should expect to obtain hypochlorous acid by the reaction of this salt with a stronger acid. As we have learned (p. 48), bleaching powder is formed by passing chlorine over slaked lime: this reaction produces calcium chloride besides calcium hypochlorite. The equation which expresses this reaction also indicates that calcium is a divalent metal; for an atom of calcium holds two atoms of chlorine in calcium chloride, and two atomic groups of hydroxyl (OH) in slaked lime :—



$$2\mathrm{Ca}\left<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + 2\mathrm{Cl}_2 = \mathrm{Ca}\left<\begin{matrix}\mathrm{OCl}\\ \mathrm{OCl}\end{matrix}\right. + \mathrm{Ca}\left<\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. + 2\mathrm{H}_2\mathrm{O}.$$

Slaked lime + chlorine = calcium hypochlorite + calcium chloride + water.

Bleaching powder is a compound of calcium hypochlorite and calcium chloride.

By replacing the atoms of hydrogen in ammonia, NH_3, by chlorine, we obtain the three compounds NH_2Cl, $NHCl_2$, and NCl_3. These compounds (called chlorides of nitrogen) are characterised by their great readiness to explode.

By similar operations we can replace three atoms of hydrogen in methane, CH_4, a compound from which all the compounds studied in organic chemistry can be derived. One of these derivatives of methane is the compound $CHCl_3$, which is called *trichloromethane.* This compound was known long before Kekulé declared the "*constitution*" of the organic compounds: it is generally called *chloroform,* the name given to it by Liebig, who discovered it in the year 1831. Chloroform is much used in medicine as a sleep-producing agent. It can be obtained directly from methane by the reaction of that compound with chlorine:—

$$CH_4 \quad + \quad 6Cl \quad = \quad CHCl_3 \quad + \quad 3HCl.$$

Methane + chlorine = chloroform + hydrochloric acid.

The equation shows that hydrochloric acid is formed in this reaction, besides chloroform. As chloroform can be distilled, it is easily separated from the other product of the reaction (compare p. 201).

Now let us suppose that three of the atoms of hydrogen in methane are replaced by an atom of trivalent nitrogen. The rule that has been stated shows that this can be done. The product of this reaction is the compound $H{-}C{\equiv}N$ (or, written more shortly, HCN). This compound is well known; it is the extremely poisonous *prussic acid.* We have here another example of the actual existence of a compound which we have constructed theoretically on paper. The potassium salt of this acid, KCN, is called potassium *cyanide*,* and hence the systematic name of the acid, HCN, is *hydrocyanic acid.*

Now that we have considered the replacement of hydrogen atoms, singly or repeatedly, by the atoms of other elements, we must consider their replacement by radicles (or *rests*). This will give us an opportunity of showing that all the compounds of carbon—and the number of them is enormous—follow the universal rule. It must be admitted that there is some special property belonging to carbon which makes it possible for that element to form a greater number of compounds than all the other elements together. This special property is the following. *The atoms of carbon are able to combine with one another in any numbers, whereas the atoms of the other elements are either unable to do this or do it only to a very limited extent.* Atoms of carbon are able to take part in the formation of molecules of great size—that is to say, molecules that are composed of a very large number of atoms—whereas molecules that are formed entirely of atoms of other elements are never formed of very many atoms. Examples will best show us how molecules of great complexity are formed with the aid of atoms of carbon.

It is evident that only one compound, H—Cl, can be formed by the union of monovalent chlorine with monovalent hydrogen; any other compound is impossible. Two compounds of divalent oxygen with hydrogen are known: water, H_2O or H—O—H, and hydrogen peroxide, H_2O_2 or H—O—O—H. No other compound of these two elements has been formed. Three com-

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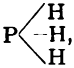
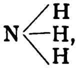
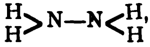
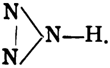
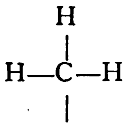
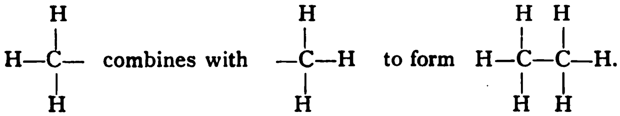
* From the Greek κύανος = dark blue.

pounds of hydrogen with trivalent phosphorus are known: PH_3 or  $P\begin{cases}-H\\-H\\-H\end{cases}$, P_2H_4 or  $\begin{matrix}H\\H\end{matrix}\!>P-P<\!\begin{matrix}H\\H\end{matrix}$, and P_4H_2 or H—P═P—P═P—H. Trivalent nitrogen also forms three compounds with hydrogen: ammonia, NH_3 or  $N\begin{cases}-H\\-H\\-H\end{cases}$, hydrazine, N_2H_4 or  $\begin{matrix}H\\H\end{matrix}\!>N-N<\!\begin{matrix}H\\H\end{matrix}$, and hydrazoïc acid, N_3H or  $\begin{matrix}N\\|\\N\end{matrix}\!>N-H$. The expanded formulæ of these compounds exhibit the arrangements of the valencies between the atoms of hydrogen and those of oxygen, phosphorus, and nitrogen respectively. We see as many as four atoms of phosphorus arranged in a chain, some of them held by double bonds (compare p. 239); and we notice the same kind of combination between atoms of nitrogen in hydrazoïc acid. No other compounds of nitrogen and hydrogen or of phosphorus and hydrogen have been obtained save the three in each case. We find at most four atoms of phosphorus or three atoms of nitrogen held together in the molecules of these phosphorus or nitrogen compounds: all attempts that have been made to bind together more than these numbers have been fruitless. On the other hand, we shall see immediately that the number of compounds formed of hydrogen and carbon only—the hydrocarbons—is very great.

If we suppose that one atom of hydrogen is taken away from the molecule of methane, CH_4, we obtain the radicle CH_3, or  $\begin{array}{c}H\\|\\H-C-H\\|\end{array}$, which cannot exist by itself.

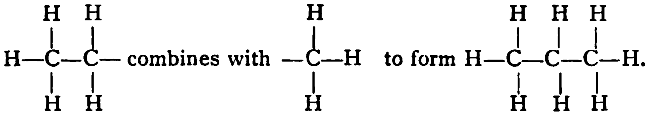
This radicle requires the addition of an atom of hydrogen to convert it into a body which can exist; hence it can bind to itself an atom of hydrogen. And so the universal rule holds good here also, in what may be called an inverted sense: that which can hold fast one atom of hydrogen is monovalent. Hence CH_3 is a *monovalent radicle.* Now, in the compounds of carbon almost any monovalent atom or group can take the place of another monovalent atom or group; hence, for example, the radicle CH_3 is able to take the place of H. This radicle is monovalent, hence it can combine with other monovalent radicles or atoms; it is able to combine with itself—to bind itself to itself, so to speak. In the latter case two monovalent CH_3 radicles hold together by their carbon atoms; thus:—



$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}- \text{ combines with } -\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \text{ to form } H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H.$$

The new hydrocarbon, C_2H_6, which is thus obtained is called *ethane.*

Evidently we can repeat this process, as the number of carbon atoms which are able to hold together in a molecule is very great, in contradistinction to the atoms of the other elements.



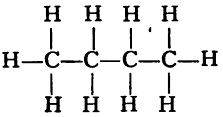
$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}- \text{ combines with } -\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H \text{ to form } H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H.$$

Monovalent radicle of ethane.

Monovalent radicle of methane.

Propane.

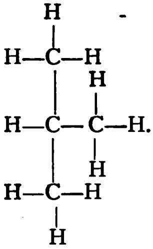
The hydrocarbon, C_3H_8, which is thus produced is called *propane.* By replacing an atom of hydrogen in the molecule of propane by the radicle CH_3 we obtain a new hydrocarbon, called *butane.*



$$\begin{array}{ccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

Butane.

and



Isobutane.

A closer examination of the formula of butane shows that another way of linking the atoms in this molecule is possible, without disturbing the tetravalency of the carbon atoms or the monovalency of the hydrogen atoms. There are thus two bodies each of which has the empirical formula C_4H_{10}. Such compounds are called *isomerides*; hence the designation of the second butane as *iso*butane. Isomeric compounds are composed of the same numbers of the same atoms (in the present case of four carbon atoms and ten atoms of hydrogen); nevertheless, they are different from one another, inasmuch as the arrangements of the atoms in their molecules are not the same. This fact makes possible the existence of a vast number of carbon compounds which did not come into our consideration before. For instance, eighteen isomeric octanes are possible, all having the formula C_8H_{18} (see forward, p. 247). Chains containing as many as sixty atoms of carbon have been constructed in the laboratory. The formula of the hydrocarbon which contains this number of atoms of carbon is $C_{60}H_{122}$.

Before proceeding farther with the consideration of the formulæ wherein the atomic complexes seem to be moved about in a manner that recalls the movements of the pieces in chess we shall pay attention to certain actual relations between compounds, and especially to a method which is used in the laboratory for forming propane, starting with methane and ethane. For this purpose chlorine is allowed to react with methane and ethane, which hydrocarbons are directly attacked by that element :—

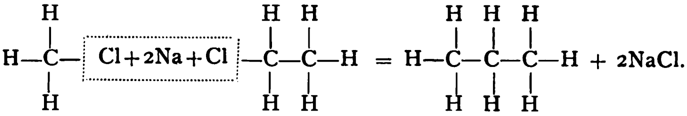
$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

Methane + chlorine = methyl chloride + hydrochloric acid.

$$C_2H_6 + Cl_2 = C_2H_5Cl + HCl.$$

Ethane + chlorine = ethyl chloride + hydrochloric acid.

As the equations show, the products of these reactions are methyl chloride and ethyl chloride respectively. The monovalent radicles (or "rests") of such hydrocarbons as methane, ethane, propane, etc., are named *methyl*, *ethyl*, *propyl*, etc. If a mixture of methyl chloride and ethyl chloride is heated with sodium, the sodium withdraws the chlorine, forming sodium chloride, and the two radicles—methyl and ethyl—combine to form propane :—



$$H—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—\boxed{Cl+2Na+Cl}—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—H = H—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}—H + 2NaCl.$$

Methyl chloride + sodium + ethyl chloride = propane + sodium chloride.

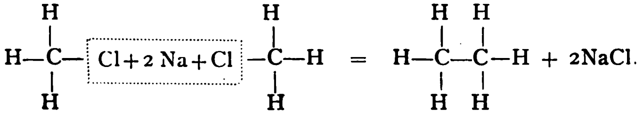
In this reaction we recognise the *synthesis* of propane.

The foregoing reactions suggest the process whereby we can pass from methane to ethane. For this purpose all that is needed is to heat methyl chloride with sodium. Two molecules of methyl chloride react with sodium, as shown in the following equation :—

$$2CH_3Cl + 2Na = H_3C—CH_3 + 2NaCl.$$

Methyl chloride + sodium = ethane + sodium chloride.

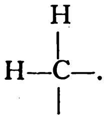
If the formulæ are expanded, we have :—



$$H-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\boxed{Cl+2\,Na+Cl}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-H = H-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}-H + 2NaCl.$$

Methyl chloride + sodium + methyl chloride = ethane + sodium chloride.

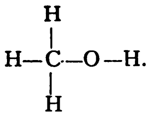
We shall shortly become acquainted with the method for preparing methane, which is the starting point wherefrom all the compounds of organic chemistry are theoretically obtained.

Let us suppose that two atoms of hydrogen are taken away from methane; we obtain the "rest," or radicle, CH_2, which is thus written in an expanded formula  $H-\underset{|}{\overset{\substack{H\\|}}{C}}-$. This radicle is, of course, divalent, for it is able to combine with two atoms of hydrogen. As two methyl groups are able to combine with one another, so can this radicle CH_2 combine with itself. The product is C_2H_4, which is generally written $H_2C{=}CH_2$, the divalency of the CH_2 group being expressed by the double bond. This hydrocarbon, C_2H_4, is called *ethylene*; in the same series we have *propylene*, $H_3C—CH{=}CH_2$, etc. It is evident that propylene may be represented as *methyl-ethylene*. If we think of methane deprived of three atoms of hydrogen, we have the monovalent radicle $HC\equiv$. If one atom of the trivalent nitrogen combines with this radicle $HC\equiv$, we get HCN, which is prussic acid, a compound whose formula has been already deduced in a somewhat different way (compare p. 233). If $HC\equiv$ combines with itself, which must be possible, we obtain a hydrocarbon called *acetylene*, $HC\equiv CH$ or C_2H_2. We shall return to this hydrocarbon, which has been so much talked of recently, when we are dealing with coal-gas; meanwhile we have learnt its formula and "constitution."

The appearance and external qualities of the hydrocarbons are determined by the numbers of carbon atoms in the molecules of these compounds. Methane is a gas, so are ethane and propane ; but hydrocarbons with more carbon atoms in their molecules than propane are liquids—some of these occur in petroleum ; and as the number of carbon atoms increases, the hydrocarbons become butter-like and then solid. Vaseline consists of hydrocarbons of the consistency of butter, paraffin-wax of solid hydrocarbons.

So far we have confined our attention almost completely to compounds of carbon and hydrogen, that is, to hydrocarbons. At the most we have considered compounds formed by the replacement of hydrogen atoms in hydrocarbons by monovalent chlorine, Cl, or by trivalent nitrogen, N. But the fundamental rule holds good : in organic chemistry any monovalent atom or group can replace another monovalent atom or group, any divalent atom or group can replace another divalent atom or group, any trivalent atom or group can take the place of another trivalent atom or group.

Let us return to the formula of water, H—O—H. The group —O—H (hydroxyl) is a monovalent radicle, inasmuch as it is able to bind to itself a single atom of hydrogen. If an atom of hydrogen in methane (CH_4) is replaced by hydroxyl, the compound that is obtained is $CH_3—OH$, or, written more fully,



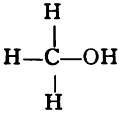
$$\begin{array}{c} H \\ | \\ H—C—O—H. \\ | \\ H \end{array}$$

This compound is an alcohol. All carbon compounds whose molecules contain hydroxyl groups united to carbon in the way shown in the above formula are called alcohols. The word *alcohol* is used by the chemist as a specific name, in contradistinction to the practice of ordinary life. The special alcohol we are dealing with at this moment is called *methylic alcohol*: evidently it is the simplest alcohol that can exist.

Methylic alcohol has been known for many years, as it is obtained by heating wood in closed vessels—by the dry distillation of wood, as this process is called (see p. 269). Because of its preparation from wood, this alcohol was called *wood spirit.* At the time of its discovery nothing was known of tetravalent carbon, or methyl, or ethyl. The names wood spirit and methylic alcohol are now synonymous.

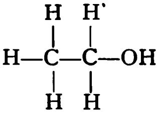
If one hydrogen atom in the methyl group of methylic alcohol, $H_3C—OH$, is replaced by another methyl group (CH_3), we obtain *ethylic alcohol,* $H_3C—CH_2—OH$. But, in accordance with our rule, it is evident that we might replace the hydrogen of the hydroxyl group in methyl alcohol ($H_3C—OH$) by a methyl group. The result of that replacement would be $H_3C—O—CH_3$. This compound, which is called *methylic ether,* is easily prepared.

We are constantly being presented with examples of the way wherein the radicles, or "rests," can be moved here and there. Ethylic alcohol is, so to speak, the next older brother of methylic alcohol. Such a relationship as that of these two compounds is called an *homologous* relation in organic chemistry. Ethylic alcohol is the next higher homologue of methylic alcohol; and, as we can now easily perceive, *propylic alcohol,* $CH_3—CH_2—CH_2—OH$, is the next higher homologue of ethylic alcohol. The process may be extended immensely; in a word, there is a vast number of alcohols possible to the chemist.



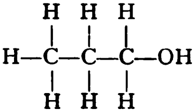
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & — & C & — & OH \\ & & | & & \\ & & H & & \end{array}$$

Methylic alcohol.
Empirical formula, CH_4O.



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & — & C & — & C & — & OH \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Ethylic alcohol.
C_2H_6O.



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & — & C & — & C & — & C & — & OH \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

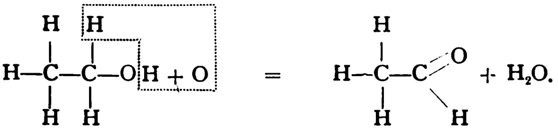
Propylic alcohol.
C_3H_8O.

Whisky and other spirits consist [chiefly] of diluted ethylic alcohol. This alcohol is present in all fermented drinks, and gives them their intoxicating effects. It is contained in wine, beer, cider, etc. In all these drinks it is produced by the fermentation of fruit sugar, which is easily obtained from other sugars, such as cane sugar, and is produced in fermentable liquids. The [principal] change produced in fruit sugar during fermentation is expressed by the equation:—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2.$$

Fruit sugar = ethylic alcohol + carbon dioxide.

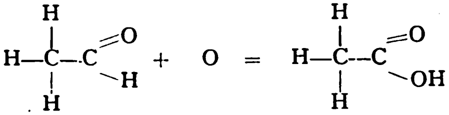
Groups or classes of compounds, such as the alcohols, have definite class properties. For instance, all these alcohols behave similarly towards oxygen: when oxidised, they lose two atoms of hydrogen, and these combine with an atom of oxygen to form water, H_2O. A single atom of oxygen, which is divalent, then takes the place of the two atoms of hydrogen that leave the molecule. In the case of ethylic alcohol the first part of this change is presented thus:—



Ethylic alcohol + oxygen = ethylic aldehyde + water.

We have again symbolised the divalency of the atom of oxygen, in the compound produced in this reaction, by a double line. We have placed the name of the compound that is produced under the formula of that compound. The compound is an *aldehyde* (abbreviated form of *alcohol dehydrogenatus*). This special compound is ethylic aldehyde. Methylic alcohol, as one would suppose, yields methylic aldehyde, propylic alcohol gives propylic aldehyde, and so on.

The aldehydes are able to take up more oxygen, whereby the hydrogen atom that is present in the aldehydic group $\left(-\mathrm{C}\begin{array}{l}\!=\mathrm{O}\\ \!\diagdown\mathrm{H}\end{array}\right)$ is changed into hydroxyl, OH. By this reaction the aldehydes are changed into acids; for example:—



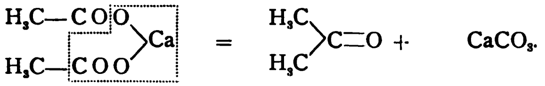
$$\mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{C}\begin{array}{l}\!=\mathrm{O}\\ \!\diagdown\mathrm{H}\end{array} + \mathrm{O} = \mathrm{H}-\underset{\underset{\mathrm{H}}{|}}{\overset{\overset{\mathrm{H}}{|}}{\mathrm{C}}}-\mathrm{C}\begin{array}{l}\!=\mathrm{O}\\ \!\diagdown\mathrm{OH}\end{array}$$

Ethylic aldehyde + oxygen = acetic acid.

The acid that is produced in this case is the well-known acetic acid, the empirical formula whereof is $C_2H_4O_2$. The formula is generally written $H_3C—COOH$, because this formula is at once more convenient than the fully expanded formula, and indicates that the acid is monobasic, inasmuch as it contains only one hydroxyl group. It has been known for ages that acetic acid is formed by the oxidation of alcohol. Wine or beer becomes sour when it is allowed to stand in the air, wine-vinegar or beer-vinegar being produced. The air, or, more accurately, the oxygen of the air, converts the alcohol immediately into the acid, without the formation of the intermediate substance aldehyde; but aldehyde is readily prepared in the laboratory by the oxidation of alcohol.

Two salts of acetic acid demand our attention—acetate of lead, and acetate of lime, or, more accurately, acetate of calcium. As lead (Pb, from the Latin, *plumbum*) is divalent, the formula of the lead salt is $(H_3C—COO)_2Pb$. It retains from olden times the name *sugar of lead*, because it has a sweet taste ; but, despite its tempting name, like all other lead compounds, it is very poisonous.

Calcium acetate, $(H_3C—COO)_2Ca$, is the material which serves for the preparation of acetone, a compound we met with in the manufacture of smokeless powder. If calcium acetate is subjected to dry distillation—for instance, if it is heated in a retort—it decomposes into calcium carbonate ($CaCO_3$), which remains in the retort, and acetone, C_3H_6O, which easily distils over, as it is a liquid that boils at 58° C. [136·4° F.]. This decomposition of calcium acetate is more easily followed if the formulæ are expanded, thus :—



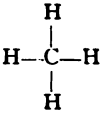
Calcium acetate = acetone + calcium carbonate.

In this sufficiently expanded formula of acetone we again recognise the tetravalency of the atom of carbon. It is not necessary to expand the CH_3 groups ; we already know that CH_3 is a monovalent radicle, and we know why this is so.

Ethylic alcohol, $H_3C—CH_2—OH$, yields acetic acid, $H_3C—COOH$. Methylic alcohol, $H—CH_2—OH$, of course, yields the corresponding acid $H—COOH$; this compound is called *formic acid*, because it is found in ants (Latin, *formica* = an ant). Propylic alcohol gives propionic acid, and so on. We see that to each of these alcohols there belongs an aldehyde and an acid.

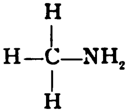
The replacement of hydrogen by radicles of various kinds, in the manner already illustrated, is carried on very extensively in organic chemistry.

Ammonia has the formula NH_3; hence NH_2 is a monovalent radicle, for it wants one atom of hydrogen, and this radicle may replace one atom of hydrogen. Let us take the simplest case. Let this radicle NH_2 replace an atom of hydrogen in methane, CH_4; then from methane, CH_4, we obtain *methylamine*, CH_3NH_2.



$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$

Methane.

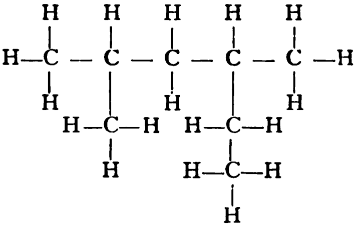


$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -NH_2 \\ & | & \\ & H & \end{array}$$

Methylamine.

The empirical formula of methylamine is CNH_5.

Chains of carbon atoms need not be arranged in one line; they may have lateral ramifications; for hydrogen atoms in a single chain of carbon atoms may be replaced by methyl groups, etc. The following hydrocarbon is an example wherein the carbon chains divide at two places:—

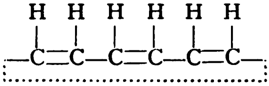


The empirical formula of this hydrocarbon is C_8H_{18};

the compound is an *octane.* The single chain contains five carbon atoms; it is, therefore, a pentane chain. As one hydrogen atom is replaced by the methyl group CH_3, and another by the ethyl group C_2H_5, the hydrocarbon is called *methyl ethyl pentane.* It is one of the eighteen possible octanes (compare p. 237).

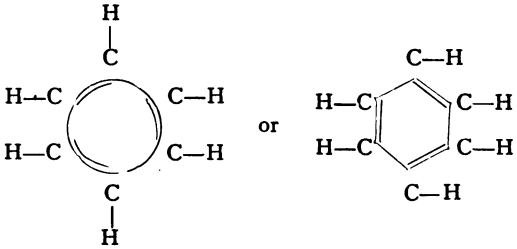
It has been said that any monovalent atom or group is replaceable by any other monovalent atom or group, etc. If this possibility is fully taken advantage of, a vast number of compounds may be formed, all of which can be traced back to chains of carbon atoms with lateral ramifications.

From what has been said, we may form some notion of why it is that carbon is able to form a greater number of compounds than any other element; an almost indefinitely large number of atoms of this element may be held together in a molecule. But not only are there single chains of carbon atoms and chains with side branches; there are also ring-formed chains; and the number of compounds derived from these is greater than the number of those derived from what are called "open chains." There are very many compounds in the chemistry of carbon from which a hydrocarbon can be obtained that has the formula C_6H_6, and is called *benzene,* because benzoic acid is one of the bodies wherefrom it is obtained. As this compound contains only six atoms of hydrogen, combined with six atoms of carbon, it seems scarcely possible to bring it into accordance with the tetravalency of carbon. This was done, however, by Kekulé in 1866, who thereby placed the coping stone on his building of organic chemistry. For nothing has since been found in the domain of carbon chemistry, and we may assert that nothing will be found, which does not or will not fit into this wonderful structure. What remains to be done is to work out all the consequences that follow from the conceptions of Kekulé. Following Kekulé, let us regard the six hydrogen atoms of benzene as equally distributed among the six carbon atoms, a fact which has been established by experimental investigations of the derivatives of benzene (with some of which we shall soon become acquainted), and let us suppose that the carbon atoms of benzene are alternately singly and doubly linked to one another. We arrive at the following single chain formula:—



$$-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-$$

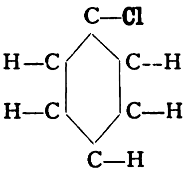
The four middle carbon atoms are here tetravalent; for each is bound to its two adjacent carbon atoms by three valencies, and the fourth valency of each is satisfied by hydrogen. But the two carbon atoms at the ends of the chain seem to be only trivalent, for they are bound to neighbouring carbon atoms by double linkings, and their third valencies are saturated by hydrogen atoms. These two atoms of carbon have still each one valency to be disposed of; the fourth valency seems to flutter in the air. Now comes in Kekulé's stroke of genius. The two carbon atoms at the ends of the chain dispose of their fourth available valency between themselves, as we have indicated above by a broken line. These atoms no longer stand at the ends of a chain, for, as the following scheme shows, all the six atoms of carbon are bound together in the form of a ring. This scheme represents all the carbon atoms, and also all the hydrogen atoms, as behaving in the same way, for all are arranged in exactly similar relative positions.



Formula of the hydrocarbon benzene.

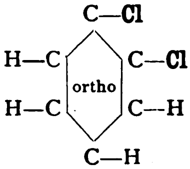
Kekulé's hypothesis presents a ring-formed combination of the six carbon atoms; hence the expression "chemistry of rings"—that is, of compounds which are supposed to contain an atomic complex whose atoms are arranged in a ring. As it is somewhat inconvenient to draw rings, it is customary to retain the straight lines between the carbon atoms, and to use a hexagon formula in place of a ring. As everyone who is acquainted with the subject knows that the carbon atoms in the ring are alternately singly and doubly linked—in the manner shown in the above formulæ—it is usual to omit the double lines, and to use a hexagon only. We constantly meet this hexagon formula in those books which are concerned with the chemistry of compounds that contain ring-formed atomic complexes.

The possibility of replacing any monovalent atom or group by another monovalent atom or group, etc., holds good when we start from benzene. If one atom of hydrogen in benzene is replaced by chlorine, we obtain *chlorobenzene.* Only one chlorobenzene (C_6H_5Cl) can exist, for the result is the same which of the six atoms of hydrogen is replaced by an atom of chlorine.

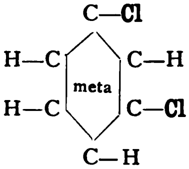


Chlorobenzene.

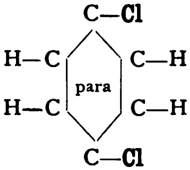
But if two atoms of hydrogen in benzene are replaced by two atoms of chlorine, it is evident from the formulae that three isomeric dichlorobenzenes are possible. These three modifications are:—



(I)
Dichlorobenzene.



(II)
Dichlorobenzene.



(III)
Dichlorobenzene.

The two chlorine atoms in the first dichlorobenzene are attached to contiguous carbon atoms, in the second they are attached to carbon atoms which are separated by another atom of carbon, and in the third the carbon atoms whereto the chlorine atoms are attached are separated by two other atoms of carbon. It may be seen by trying that other modifications are impossible.

Suppose, for example, that the second chlorine atom in III is attached to the next carbon atom to the left. We get the same arrangement as is presented in II; for we get an arrangement wherein the two chlorine atoms are attached to carbon atoms that are separated by one other atom of carbon.

Diderivations of benzene of the kind shown in I are called *ortho compounds*, diderivations of the kind shown in II are called *meta compounds*, and diderivations of the kind shown in III are called *para compounds*. We speak of orthodichlorobenzene, metadichlorobenzene, and paradichlorobenzene.

What holds good when we are dealing with two atoms of chlorine also holds good for any other two monovalent atoms or atomic groups which may be brought into the benzene ring.

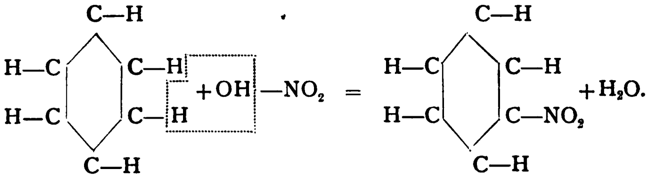
Before the promulgation of Kekulé's theory, no reason could be given for the existence of three isomeric diderivatives such as the dichlorobenzenes, and no reason could be given why there should not be four or five such derivatives of benzene.* Now it is all self-evident. The number of diderivatives of benzene known to-day is very great, but of none have more than three isomeric forms been obtained,

---

* A model may be used, in place of the hexagon formula, to express Kekulé's hypothesis; black balls may represent the carbon atoms, white balls the hydrogen atoms, and so on, and the joining lines may be made with pieces of wire. The various consequences that flow from the valencies of the different atoms, etc., may be demonstrated by the aid of such a model, in the way indicated by von Baeyer in his lecture, delivered at the Kekulé anniversary, on the use of such models in the development of theoretical conceptions in chemistry. Such models show to some

notwithstanding the endless trouble that has been taken to prepare more; hence this consequence of the theory of Kekulé has become one of the main supports of that theory. The theory declares with certainty what nature allows and what she does not allow. In speaking of the incompleteness of science, it is sometimes said, half in fun, that "the exception proves the rule"; but this is one of those rules to which not a single exception has been observed.

Nitrobenzene is obtained by treating benzene with nitric acid. In this reaction there is not produced a salt-like compound, such as is formed, for example, by the reaction of nitric acid on cellulose (see p. 184), but a true *nitro*-compound. The group NO_2 is called the nitrogroup. The nitro-compounds are not comparable with the salts of nitric acid; in these compounds nitric acid has lost its hydroxyl group, OH.



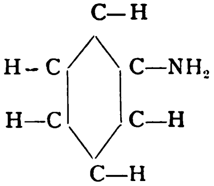
Benzene + nitric acid = nitrobenzene + water.

C_6H_6 + $HO—NO_2$ = $C_6H_5—NO_2$ + H_2O.

extent that what Hertz (the discoverer of electric waves) said of Clerk Maxwell's electromagnetic theory of light is true also of Kekulé's theory:—"One cannot study this wonderful theory without feeling at times as if mathematical formulæ had a life of their own, as if there was in them a special understanding, as if they were more subtle than we are, more subtle than their discoverer, as if they gave us back more than was put into them at the time."

In the formation of a salt or a salt-like compound from nitric acid the hydrogen atom of the hydroxyl group of the acid is replaced by a metal, as in the formation of potassium nitrate, NO_2—OK, or by a monovalent organic radicle, as in the formation of methyl nitrate, NO_2—O(CH_3). All such compounds contain the group NO_3 (or NO_2—O—), which is the monovalent radicle of nitric acid when hydrogen has been removed. The nitro-compounds, on the other hand, contain another monovalent radicle of nitric acid, namely NO_2—, which is nitric acid wherefrom hydroxyl has been removed. Nitric acid can be obtained from the salts of that acid by their reactions with a stronger acid (compare p. 173); but the acid cannot be obtained in that way from the nitro-compounds.

If we replace an atom of hydrogen in benzene by the monovalent radicle of ammonia—by NH_2—we obtain the well-known compound *amidobenzene*, or *aniline*, the compound which gives its name to the modern coal-tar colour industry.



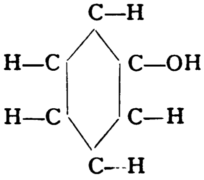
Aniline.

Benzene, which is the starting point of our considerations, the mother-substance of all ring-formed atomic arrangements, besides being obtained from benzoic acid and many other compounds, is found in coal-tar. When this black waste product of the gas-works is distilled, clear oil passes over: this oil contains benzene, besides carbolic acid, naphthalene, and many other useful substances. The benzene is purified by fractional distillation (see p. 201)—it boils at 80° C. [176° F.]—and is converted into aniline. The following method is employed for doing this. First of all the benzene is transformed into nitrobenzene, and the nitrobenzene is then changed to aniline by the reaction with it of nascent hydrogen (see p. 107).

Colours are obtained from aniline under all sorts of conditions. To mention one set of conditions only: if aniline is mixed with methyl aniline and the mixture is heated with substances very rich in oxygen, a process of oxidation occurs, and a red mass is obtained, which is fuchsine:—

$$\begin{array}{ccccccccc} 2C_6H_5NH_2 & + & C_6H_4(CH_3)NH_2 & + & 3O & = & C_{19}H_{19}N_3O & + & 2H_2O. \\ \text{Aniline} & + & \text{methyl aniline} & + & \text{oxygen} & = & \text{fuchsine} & + & \text{water.} \end{array}$$

If an atom of hydrogen in benzene is replaced by hydroxyl, OH, we obtain *phenol*, $C_6H_5—OH$. This compound is generally called *carbolic acid*, which name was given to it by its discoverer in the thirties of the nineteenth century. The expanded formula of this compound is:—

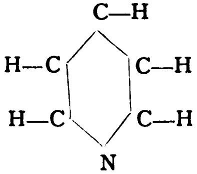


Phenol, or carbolic acid.

The name carbolic acid implies that the compound reacts as an acid and forms salts—that the hydrogen of the hydroxyl group is replaceable by metals. Carbolate of calcium, carbolate of silver, etc., have been prepared. The atom of carbon whereto the hydroxyl group is attached in this compound is connected with the other carbon atoms in a way which is very different from that of the linkings in those open chains of carbon atoms which yield true alcohols that do not show any acidic properties. The differences between the behaviours of the hydroxyl groups in C_6H_5OH and in the true alcohols is connected with the ring formation of the carbon atoms in phenol.

In the eighties of the nineteenth century chemists had slowly come to the conviction that a ring-formed atomic complex need not necessarily be formed of CH groups, as is the case with benzene. Each of the carbon atoms that form the ring is connected to other carbon atoms by three valencies—by two valencies on one side and by one on the other side—while the fourth valency of each is satisfied by an atom of hydrogen. Now the atom of nitrogen is trivalent; and it was found that such a trivalent atom was able to close the ring by taking the place of the trivalent group CH. No atom of hydrogen can be attached to the atom of nitrogen, inasmuch as the three valencies of that atom are required for closing the ring.

The arrangement of the atoms in a molecule of the body we are considering will be as follows:—



Pyridine.

This compound, *pyridine*, can be obtained from certain alkaloids. But what are *alkaloids*? Methods have long been known for obtaining indifferent substances from plants—substances which do not change vegetable colouring matters, and are neither acids nor bases; we recall, for instance, starch, sugar, and the like. Acids, such as citric, malic, and tartaric acid, were also prepared from plants. But the fact was long overlooked that many plants contain substances which have an alkaline reaction, colour red litmus blue, and combine with acids to form salts. It was in 1817 that the existence of such substances was finally proved by the preparation of the alkaline compound *morphine* from opium. Attention being thus called to the subject several substances resembling morphine were soon obtained—for instance, *quinine, coniine, veratrine*, etc. The very convenient specific name *alkaloid* was applied to all these "alkalis from plants": the name implies a compound, obtained from plants, which reacts like an alkali. The investigation of the alkaloids has shown that, with few exceptions, they are derivatives of pyridine. But pyridine itself can be prepared from coal-tar (see forward); hence it can be obtained in abundance.

In the sense in which we spoke of a chemistry of benzene we may also speak of a chemistry of pyridine; that is to say, the hydrogen atoms in the molecule of pyridine may be replaced by radicles of different kinds, and a great number of compounds may be obtained. The alkaloids are among the most important compounds derived from pyridine. The study of certain individual alkaloids has advanced so far that the relative arrangements of all the atoms in their molecules have been worked out. In such cases it is known how many methyl or other groups have taken the places of hydrogen atoms in pyridine; and several alkaloids have been made artificially in the laboratory by introducing the proper atomic groups into the pyridine molecule. The alkaloids from plants usually act very energetically on the bodies of animals and human beings; many are strong poisons, such as strychnine and morphine. But these poisonous substances often act as most important remedies when they are administered in extremely small doses. Quinine, especially, has been used for many years as a medicine, because it lowers the bodily temperature during fever; and as fever accompanies many kinds of illness, quinine may be employed in very different ailments.

The chemical study of quinine is not yet completed. The empirical formula of quinine, $C_{20}H_{24}N_2O_2$, shows that the molecule of this compound is composed of forty-eight atoms. The arrangement of these atoms, which is very complicated, has not yet been fully elucidated—we do not yet know how the atoms are linked to one another in the molecule. So long as the arrangement of the atoms is unknown, it is not possible to make quinine artificially; for how can we link together atoms as they are linked in quinine if we do not know what the linkings are in the molecule of that compound?

Nevertheless, the many investigations that have been made of pyridine derivatives have led to the recognition of bodies in whose molecules atoms and atomic groups are linked together in such a way that these bodies most probably resemble the natural alkaloids; and experiments made on animals in a state of fever have shown that these artificially made preparations lower the temperature. In this way we have been able to make artificial febrifuges, such as *antipyrine*, which are useful in the illnesses of human beings.

We have now gained some conception of "organic chemistry." We have become acquainted with the two classes of compounds which are considered in that branch of chemistry—those wherein the carbon atoms are arranged in open chains, and those wherein the arrangement is ring-formed. These two classes contain all the compounds of carbon.

THE CHEMISTRY OF ORGANISED SUBSTANCES.

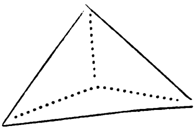
Organic chemistry is not to be confused with the chemistry of organised substances—that is, those substances which make life possible, and in which and with the help of which life proceeds. We already know that those organised bodies which contain nitrogen and have a very complex composition are classed as *albuminoids*. Crystallisation is the best way of purifying solid substances. But only very few albuminoids can be crystallised, and so obtained completely pure. The red colouring substance in blood is an albuminoid; it is called *oxyhæmoglobin.* The oxyhæmoglobin from human blood crystallises with great difficulty; it is scarcely possible to purify this body thoroughly by crystallisation: but oxyhæmoglobin from the blood of horses may be crystallised, and so purified, readily. An analysis of oxyhæmoglobin leads to the formula $C_{555}H_{881}N_{149}S_2O_{177}Fe$. From what we know of organic chemistry, we can understand that there is practically no hope of our being able to find out how these 1765 atoms are linked together. Even supposing that this question, which seems insolvable, were solved in the course of time, we should still have to face the extremely difficult task of properly linking together all the atoms and atomic groups present in oxyhæmoglobin in order to prepare that substance artificially.

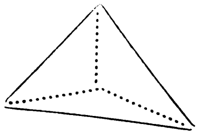
Most of the albuminoids do not crystallise; hence but few of the bodies can be obtained chemically pure in a satisfactory way: this makes the problems of determining their constitution and synthesising them quite insolvable at present. What knowledge we have seems to indicate that these problems will never be solved.

The Asymmetric Carbon Atom.

If we inquire in what manner the four hydrogen atoms in the molecule of methane are arranged *in space* around the atom of carbon, we must suppose that these four atoms are placed symmetrically about the carbon atom. Such an arrangement is obtained if we think of the four hydrogen atoms as joined by lines that form the sides of triangles, and of a pyramid formed of four equal triangles, with the atom of carbon in the middle.

As the four atoms of hydrogen are grouped quite symmetrically as regards the atom of carbon, we obtain a regular pyramid, that is, a tetrahedron. Now, if one of the hydrogen atoms is replaced by something else, the attractive force exerted by the atom of carbon will cause the replacing atom (or group) to occupy a position not exactly the same as that which was occupied by the hydrogen atom that has been replaced. If we think of this replacing atom (or group) as one of the summits of the tetrahedron, the other three summits being atoms of hydrogen, then the arrangement is no longer exactly symmetrical; it is no longer a tetrahedron. If an atom of carbon is united to four different atoms or atomic groups, the pyramid becomes quite irregular; it is asymmetric. An atom of carbon thought of as so situated is called an *asymmetric carbon atom*. The name is rather infelicitous, for all carbon atoms are, of course, always identical. It is not the carbon atom that is asymmetrical in the case we are considering; it is the positions of the four atoms or groups (which may be called A, B, C, and D), relatively to the atom of carbon whereto they are bound, that are asymmetrical. Such asymmetric pyramids can exist in two forms, that are alike in all respects save that one bears to the other the relation that an object bears to its image in a mirror, and the two cannot be superimposed on one another. The relation between the two is the same as that between a right-hand and a left-hand glove. The following figures show such a right-handed pyramid and its left-handed counterpart:—

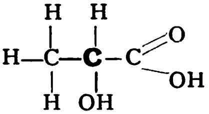




Now, many chemical compounds possess what seems to be the accidental property of rotating the plane of polarisation of a ray of light. These compounds act in a certain definite way on what is called polarised light when solutions of them are examined in a polarisation-apparatus. It would seem as if there could be no connection between the arrangement of atoms in molecules and polarised light. But this assumption is incorrect;

for it has been found that solutions of carbon compounds that contain an asymmetric carbon atom or several asymmetric carbon atoms are able to act on polarised light. *Lactic acid* is a fairly simple example of such a compound. Although methods are known whereby many compounds have been prepared in the laboratory containing asymmetric carbon atoms and rotating the plane of polarisation of a ray of light, nevertheless it is at present impossible even to think of applying such complicated methods to so complex a substance as oxyhæmoglobin. In a word, this apparently secondary property seems to make impossible the artificial preparation of an oxyhæmoglobin which should be the same as the natural product.

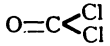
Lactic acid can be obtained both from milk and the flesh of animals. The empirical formula of this acid is $C_3H_6O_3$. The lactic acids prepared by different methods are not identical, but isomeric in a certain sense. While lactic acid from milk does not act on polarised light, the acid from flesh rotates the plane of polarisation in a right-handed direction. A close examination of *sarcolactic acid* has shown that the arrangement of the atoms in the molecule of this compound is such that an asymmetric carbon atom comes between the two other carbon atoms. The following is the expanded formula of the compound:—



The **C** is the asymmetric atom; for the four valencies of this atom are saturated, one by the group CH_3, another by an atom of hydrogen, another by the group OH, and the fourth by the group COOH. This sarcolactic acid has been prepared artificially, and the product of this synthesis exerts the same influence on polarised light as the naturally occurring acid. However remarkable is this synthesis, yet it is easy compared with the synthesis of the complex of 1765 atoms of oxyhæmoglobin, wherein there may be perhaps 300 asymmetric carbon atoms, some of which may cause right-handed rotation and others left-handed rotation of the plane of polarisation of a ray of light.

We have still to deal with the two oxides of the element carbon, compounds which it is not customary to class as organic. We shall also consider coal-gas, and, finally, we shall say a little about acetylene gas. Carbon combines with oxygen in two proportions only: one atom of carbon combines with one atom of oxygen to form *carbon monoxide* gas, CO, and with two atoms of oxygen to form *carbon dioxide* gas, CO_2. The second of these compounds is also called *carbonic anhydride*, and also, although not quite correctly (see p. 49), carbonic acid gas, or carbonic acid.

Carbon monoxide is the only compound wherein the carbon atom is not tetravalent. For, as the oxygen atom is divalent, and one atom of carbon holds only one atom of oxygen in the molecule of this compound, the carbon atom is only divalent in $C{=}O$. In all the vast number of carbon compounds, with this single exception, the carbon atom is tetravalent. This exception must be accepted as a fact by itself; we cannot attempt to give an explanation of it in this place. Carbon monoxide impresses us as "an unsaturated compound": for example, if carbon monoxide gas and chlorine gas are mixed, they combine to form carbon oxychloride, in which compound the carbon atom is tetravalent.



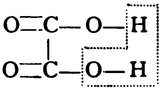
$$\mathrm{CO} \quad + \quad \mathrm{Cl_2} \quad = \quad \mathrm{O{=}C{<}^{Cl}_{Cl}}$$

Carbon monoxide + chlorine = carbon oxychloride.

Carbon monoxide gas is formed when coal or charcoal burns in a limited supply of air, that is, when there is not enough oxygen to burn the fuel completely. Hence this gas issues from badly constructed stoves, and especially when such stoves are full of red hot fuel and the valves are closed. Carbon monoxide is very poisonous, and fatal accidents have been caused by the escape of this gas into rooms. The poisonous action of carbon monoxide depends on the following considerations. We have become acquainted with oxyhæmoglobin, the red colouring matter of blood. The prefix *oxy* denotes that this substance is rich in oxygen; it is this compound which, in the lungs, takes the oxygen from the air (see p. 132). Now, if the air of a room contains carbon monoxide gas, this gas also is absorbed by the red colouring matter of the blood, and carbon oxide hæmoglobin is formed, besides oxyhæmoglobin. While the oxyhæmoglobin that circulates in the blood is ready to part with oxygen to the body—constantly taking up oxygen again in the lungs in place of that which it has given to the body—carbon oxide hæmoglobin, on the contrary, is a very stable compound, and it can be decomposed only very slowly by the body; hence the quantity of this compound in the blood is increased by every breath that is taken in an atmosphere which contains carbon monoxide. When there is a certain amount of this compound in the blood, the vital functions of the blood can no longer be exercised, and death results. The stability of the compound of carbon monoxide with hæmoglobin is shown by the fact that it can be detected in blood from a corpse several months after death. It is, therefore, easy to determine whether death has been caused by carbon monoxide, a matter which is sometimes of legal importance. Ordinary blood is wholly decomposed in the course of a few months.

The preparation of carbon monoxide gas by burning charcoal in a limited supply of air is not a convenient laboratory method for making that compound. The product of the reaction is a mixture of carbon monoxide with the nitrogen of the air wherein the carbon has been burnt. We shall prepare the gas by another, very convenient, method.

Oxalic acid is an organic acid; it contains carbon. Sorrel plants contain salts of oxalic acid, from which the acid may be prepared; but the process now employed consists in fusing caustic soda with sawdust, whereby the sodium salt of oxalic acid is produced. The acid is very cheap: its chief applications are in the colour industries. The formula of oxalic acid is $H_2C_2O_4$. If this acid is treated with reagents that withdraw water—with concentrated sulphuric acid, for instance (which, as we know, is a strong dehydrating substance)—water is formed, and there remain two atoms of carbon and three atoms of oxygen. This reaction may be expressed as follows, using an expanded formula and indicating the decomposition by a dotted line:—



$$\begin{array}{l} O{=}C{-}O{-}H \\ \quad\;\; | \\ O{=}C{-}O{-}H \end{array}$$

The group of five atoms (C_2O_3) falls to pieces, forming a molecule of carbon monoxide, CO, and a molecule of carbon dioxide, CO_2. To put the matter more briefly: when a mixture of oxalic acid and sulphuric acid is warmed, the oxalic acid decomposes to water, which is held by the sulphuric acid, and a mixture of the two gases carbon monoxide and carbon dioxide, which issues from the flask wherein the operation is conducted.

$$H_2C_2O_4 = CO + CO_2 + H_2O.$$

Oxalic acid = carbon monoxide + carbon dioxide + water.

If the stream of gas is led through a solution of caustic potash in a washing-bottle, the carbon dioxide is retained by the alkali, wherewith it forms potassium carbonate, and pure carbon monoxide gas passes on, and may be collected in a cylinder over water.

$$CO_2 + CO + 2KOH = K_2CO_3 + H_2O + CO.$$

Carbon dioxide + carbon monoxide + potash = potassium carbonate + water + carbon monoxide.

By bringing a light to a jarful of carbon monoxide, we see that this gas is combustible, and that it burns with a bluish and very slightly luminous flame. The product of combustion is carbonic acid gas.

$$CO + O = CO_2.$$

Carbon monoxide + oxygen = carbon dioxide.

If carbon is burnt in much air, or, as we have done already (p. 118), in pure oxygen gas, one atom of carbon combines with two atoms of oxygen, and carbon dioxide (or carbonic anhydride) is produced. The carbon atom in this molecule is tetravalent, as two divalent atoms of oxygen are held by one atom of carbon, $O=C=O$.

Carbon dioxide is not prepared in the laboratory by burning carbon in air: the product of this reaction would contain the whole of the nitrogen that was present in the air used for burning the carbon. There is no difficulty in preparing the pure compound by another method. Carbon dioxide is readily driven out of its salts by the action of the stronger acids. Carbonates, especially calcium carbonate, are found plentifully in nature. Limestone is impure calcium carbonate; marble is a purer form of the same compound. If pieces of marble are placed in a Kipp's apparatus and hydrochloric acid is allowed to mix with the marble (in the manner described on p. 35), a regular stream of carbon dioxide gas is obtained by simply opening the stopcock of the apparatus. The other product of the reaction—calcium chloride—is very soluble in water; it therefore remains dissolved in the aqueous solution of hydrochloric acid used in the process. The following equation expresses the decomposition:—

$$\underset{\text{carbonate}}{\overset{CaCO_3}{\text{Calcium}}} + \underset{\text{acid}}{\overset{2HCl}{\text{hydrochloric}}} = \underset{\text{dioxide}}{\overset{CO_2}{\text{carbon}}} + \underset{\text{chloride}}{\overset{CaCl_2}{\text{calcium}}} + \overset{H_2O.}{\text{water.}}$$

When an acid is set free from its salts, the acid usually contains hydroxyl groups: we recall the case of sulphuric acid. In the present case the hypothetical carbonic acid, H_2CO_3, which we should expect to obtain, decomposes into carbonic anhydride and water. The true carbonic acid, $CO\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$, which we should expect to be formed in accordance with the reaction $CaCO_3 + 2HCl = H_2CO_3 + CaCl_2$, has not been isolated. We cannot attempt an explanation why this is so; the fact must be accepted. We shall return to carbonic acid when we are dealing with the formulæ of the carbonates of the light metals.

As has been already noticed, carbon dioxide is the gas which is contained in all effervescing fermented liquors—in beer and champagne, for instance. The carbon dioxide in these liquors is formed by the fermentation of the sugar which is a necessary ingredient of all liquids capable of being fermented. The formula of this sugar, called *grape sugar* by chemists, is $C_6H_{12}O_6$. Yeast consists of small cells which, like the cells of moulds, are always present in the air. If yeast is present in a liquid that also contains grape sugar (and as yeast-cells are always in the air, they readily fall into any liquid that is exposed to the air), the yeast grows rapidly in the liquid, and decomposes the sugar, in accordance with the equation :—

$$\begin{array}{cccccc} C_6H_{12}O_6 & = & 2C_2H_6O & + & 2CO_2. \\ \text{Grape sugar} & = & \text{alcohol} & + & \text{carbon dioxide.} \end{array}$$

This process is called fermentation. All fermented drinks, then, contain alcohol. The carbon dioxide that is produced in the fermentation escapes into the air when the fermentation proceeds in open vessels, as in making wine; but this gas is retained in such drinks as beer and champagne. Artificial seltzer water and other "aerated liquids" are charged with carbon dioxide, which is generally made from marble and hydrochloric acid, by pumping in the gas under pressure.

As carbon and oxygen combine to form carbon dioxide, CO_2, so do carbon and sulphur combine, when they are heated together, to form *carbon disulphide*, which is a liquid that boils at 45° C. [113° F.]. This reaction is another instance of the chemical likeness of sulphur and oxygen. The equation which expresses the combination of carbon and sulphur is as follows:—

$$\begin{array}{ccccc} C & + & S_2 & = & CS_2. \\ \text{Carbon} & + & \text{sulphur} & = & \text{carbon disulphide.} \end{array}$$

Our reason for especially mentioning carbon disulphide is the following. We have seen that all the compounds of organic chemistry, and, in the final analysis, also the compounds which form the substance of living things, can be referred to and derived from the hydrocarbon methane, CH_4. Hence it is of especial interest to prepare this compound, to which all organic substances are referable, from inorganic materials, and so to find a way of passing from the inorganic to the organic. Of the many processes for preparing methane, the following is that which enables us to make that compound from its elements—that is to say, from inorganic, non-living materials. As we know, carbon disulphide is obtained by directly combining the two elements carbon and sulphur. Sulphuretted hydrogen also can be made from inorganic substances. The preparation of this compound from its elements is already known to us: it is only necessary to melt together sulphur and iron, and to pour hydrochloric acid on the iron sulphide that is so formed (compare p. 144). Now, if a mixture of carbon disulphide and sulphuretted hydrogen is passed over red hot copper (just as we passed water-vapour over red hot iron, on p. 31), the hot copper lays hold of the sulphur of both compounds, sulphide of copper is produced, and the carbon which was combined with sulphur in one of the compounds combines with the hydrogen which was united to sulphur in the other compound, thereby forming the hydrocarbon methane, CH_4. The following equation expresses the reaction :—

$$\begin{array}{ccccccccc} CS_2 & + & 2H_2S & + & 8Cu & = & CH_4 & + & 4Cu_2S. \\ \text{Carbon disulphide} & + & \text{sulphuretted hydrogen} & + & \text{copper} & = & \text{methane} & + & \text{copper sulphide.} \end{array}$$

In this reaction, then, we find what we are seeking—a means of passing from inorganic to organic substances.

The Manufacture of Coal-Gas.

When any sort of material is placed in a retort, or in a closed vessel (which need not necessarily take the form of a retort), and is subjected to the action of a source of heat outside the vessel, any substances contained in the material which are volatilised by heat, or any volatile substances which are produced by the action of heat on the material, are driven out, and escape from the retort in the form of gases. Such a process is called *dry distillation.*

The dry distillation of coal, for the purpose of making coal-gas, is conducted on a very large scale. The coal is shot into tubular vessels made of fire-clay, which are placed in a furnace where they can be heated to redness. Although the coal is raised to a very high temperature, it cannot burn in the retorts, because of the absence of air.

Coal is what is left of very ancient forests, the wood of which has been gradually changed into coal by the action on it of water and of the varying external conditions to which it has been subjected during the millions of years it has been embedded in the earth. Carbon is the main constituent of coal (compare p. 212); it also contains hydrogen, oxygen, nitrogen, and sulphur, as well as incombustible matters of different kinds which are grouped together under the common name of *ash*.

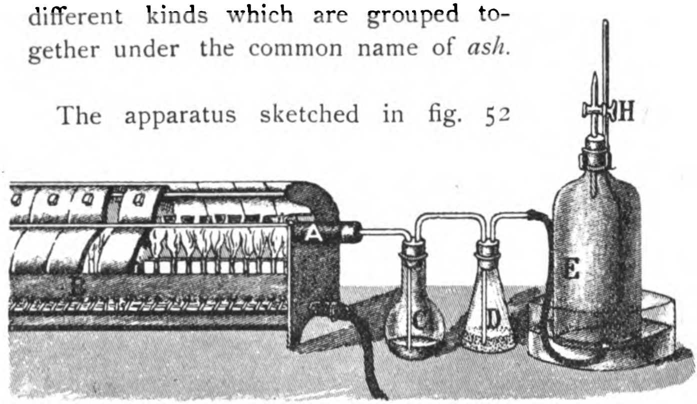


Fig. 52.—Gas-making apparatus for lecture purposes.

The apparatus sketched in fig. 52 represents the essential parts of a manufactory of coal-gas. Coal has been placed near one end of the tube A, and this tube has been arranged in a long gas furnace (B) wherein it can be strongly heated. The open end of the tube projects from the furnace. This end carries a cork, through which passes a glass tube for the escape of any volatile bodies that may be formed when the coal in the tube is heated.

Let us consider what constituents of the coal can be volatilised from it by this treatment. Let us begin with the hydrogen. Part of the hydrogen of the coal will immediately escape in the state of gas; another portion will be volatilised after combining with carbon to form hydrocarbons. We know that the number of hydrocarbons is immense; hence we shall not be surprised if hydrocarbons of all kinds are formed at the high temperature to which the coal is raised in the retorts. Moreover, the oxygen in the coal will react with the carbon. As there is only a little oxygen, the main product of this reaction will be carbon monoxide gas: a little carbon dioxide may also be produced. As regards the nitrogen, part of it will escape as nitrogen gas, but part will combine with hydrogen to form ammonia, which will pass away as a gas. Almost all of the sulphur will leave the retort in combination with hydrogen, as sulphuretted hydrogen gas. The main constituent of coal is carbon; and as only a small part of this will be removed, in combination with hydrogen as hydrocarbons and in combination with oxygen as carbon monoxide, the greater part of the carbon will remain in the retorts, as carbon itself is quite non-volatile. When the coal has been heated for a long time and the production of gas has ceased, the carbon which has not been volatilised in combination with other elements will be found in the retorts, along with the ash of the coal. This carbon is known as *coke.* As coke consists almost wholly of carbon, it may be burnt in furnaces and stoves; for carbon will burn when it is ignited and sufficient air is supplied; and it is the lack of the necessary air which makes impossible the burning of the coke in the retorts.

How will the volatile products behave when they leave the retorts? Although these bodies were all gaseous at the temperature of the retorts, and escaped as gases from the retorts, they will not all remain in the gaseous state at the ordinary temperature. Several of these substances will condense to liquids in the cooler parts of the apparatus almost as soon as they leave the retorts. This part of the products of distillation will collect, in the form of tar, in the vessel c (fig. 52). In a manufactory of gas, the volatile substances coming from the retorts are very thoroughly cooled, for the purpose of removing all the tar, as if any of that were left it would tend to stop the street-mains. Everything that is not very volatile is thus removed from the gaseous products of the distillation. The stream of gas is now passed through a tower containing coke (compare p. 69), on to which a stream of water trickles from above. (This tower is not shown in fig. 52). The water is thus made to present a very large surface to the gas. We know (see p. 168) that ammonia gas is extraordinarily soluble in water, hence we are not surprised that all the ammonia in the coal-gas should be removed by this process of washing. Because of this washing whereto the gas must be submitted, the gas-works become the sources of the ammonia water from which ammonia compounds are prepared for use as artificial manures (compare p. 215).

The gas which has been freed from ammonia now passes over layers of hydrated oxide of iron. One of our first experiments (p. 11) showed how readily iron and sulphur combine. In the present case the sulphuretted hydrogen in the crude gas reacts with the hydrated oxide of iron and forms sulphide of iron; in this way the gas is freed from sulphur, in the flask D (fig. 52). If sulphur were left in the gas, it would be burnt to sulphur dioxide, SO_2 (compare p. 140), and the smell of this compound would make it impossible to remain in a room lighted by such gas.

The purification of the gas is now completed. The purified gas collects in the gasholder (E, fig. 52), wherein it is stored and from which it is distributed to the consumers. To test the gas we have made, we ignite a jet of it, after opening the stopcock H, and we see that it burns with the customary, clear, luminous flame of coal-gas.

An analysis of coal-gas, prepared as has been described, gave the following results:—

Hydrogen (H)	45·2	volumes	per cent.
Methane (CH_4)	35·0	"	"
Other hydrocarbons . . .	4·4	"	"
Carbon monoxide (CO) . .	8·6	"	"
Carbon dioxide (CO_2) . .	2·0	"	"
Nitrogen (N)	4·8	"	"
	100·0		

The most important of the compounds that are classed as "other hydrocarbons" are ethylene, $H_2C{=}CH_2$, and acetylene, $HC{\equiv}CH$, hydrocarbons containing doubly linked and trebly linked atoms of carbon.

Considering what we have now learned, we shall not be surprised to find that very many hydrocarbons are obtained from tar. By distilling tar, in an apparatus like that represented on p. 7, benzene is obtained—the hydrocarbon having the composition C_6H_6 and boiling at 80° C. [176° F.], which we have already considered so fully. Among the other hydrocarbons obtained from tar may be mentioned *naphthalene.* This compound, which has the formula $C_{10}H_8$, solidifies on cooling. Some of the oxygen in the coal reacts with constituents of the tar, and (besides benzene) there is formed, among other bodies, the compound C_6H_6O, or $C_6H_5—OH$. This compound is none other than carbolic acid (see p. 254). We see, then, how easy it is to obtain carbolic acid from tar: it is only necessary to distil the tar. Ammonia is not the only nitrogenous compound obtained by distilling coal. At the high temperature of the retorts a small portion of the nitrogen in the coal goes to produce ring-formed compounds, among which is pyridine (see p. 256).

ACETYLENE GAS.

Of late years there has come into use for lighting purposes a gas which is much more easily prepared than coal-gas. Notwithstanding this apparent advantage, this gas has not been a serious rival to coal-gas; it has not taken the place of coal-gas, as that has been replaced by the electric light, or as coal-gas replaced candles.

It is almost self-evident that many chemical compounds should be formed at high temperatures which cannot be produced at lower temperatures. For the last ten years or so it has been possible to attain temperatures in manufacturing processes much higher than those that could be reached before that time. In order to obtain high temperatures, we now make direct use of the arrangement which is employed in the electric arc light for raising the carbon points to a full white heat. In almost all the methods of heating formerly used, the heat was conducted to the contents of a vessel through the walls of the vessel, and only a portion of the heat of the external fire reached the substance to be heated. But in the new method the carbon points can be placed in contact with the substance to be heated, so that the substance shall be exposed to the full heat of the electric arc. The remarkable results obtained by the use of the *electric furnace* depend on this fundamental difference between the new method and all the older methods of heating (see fig. 53). For instance, if a mixture of carbon and lime is heated in the electric furnace, the two substances readily react, a result which can hardly be obtained by any other method.

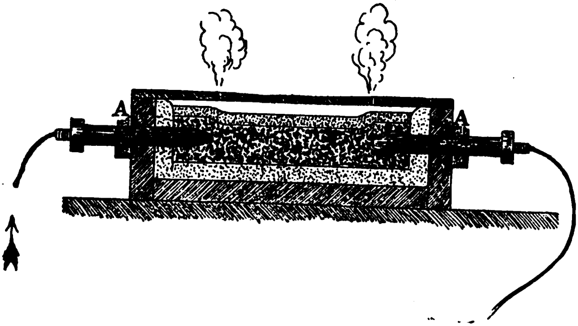


Fig. 53.—Electric furnace.

Lime is calcium oxide, CaO. When a mixture of carbon and lime is exposed to the high temperature of the electric arc, the calcium and carbon combine, and the oxygen, which was held by the calcium, enters into union with another portion of the carbon to form carbon monoxide gas, which passes away. The product of this reaction in the electric furnace is a compound of calcium and carbon, called *calcium carbide*, and having the composition CaC_2. Calcium carbide is now an important commercial article. This compound, which is perfectly stable at the high temperature of the electric furnace, is very sensitive to the action of cold water. As soon as calcium carbide comes into contact with cold water, a reaction occurs, in accordance with the following equation :—

$$\underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{water}}{H_2O} = \underset{\text{acetylene gas}}{C_2H_2} + \underset{\text{calcium oxide.}}{CaO.}$$

To obtain acetylene gas, nothing more is needed than to pour water on to calcium carbide. The gas may be produced very conveniently by using a Kipp's apparatus (see pp. 36 and 199). Pieces of calcium carbide are put into the middle bulb, the stoppers are placed in the openings, and water is poured into the apparatus, the stopcock F being kept closed. As soon as the stopcock is opened, water flows into the bulb containing the calcium carbide, and acetylene gas is produced, in accordance with the equation given above.

Acetylene gas burns with a very clear flame, which, however, smokes very readily, because of the extremely large amount of carbon contained in the gas. It is easy to calculate the quantity of carbon in acetylene.

As the atomic weights of carbon and hydrogen are 12 and 1 respectively, the molecular weight of acetylene is

$$\overset{C_2}{(2 \times 12)} + \overset{H_2}{(2 \times 1)} = 26.$$

Twenty-four parts by weight of carbon are contained in twenty-six parts of acetylene. Calculating to percentage, we have $26 : 24 = 100 : x$; hence $x = 92{\cdot}3$. Acetylene thus contains 92·3 per cent. of carbon and 7·7 per cent. of hydrogen.

The most annoying thing about acetylene gas is the presence in it of gaseous impurities, especially phosphoretted hydrogen. We know that all commercial kinds of carbon contain ash, and that calcium phosphate is one of the constituents of such ash (see p. 206). That compound reacts with carbon at the high temperature of the electric furnace, forming carbon monoxide, which passes off, and calcium phosphide; and when calcium phosphide comes into contact with water, phosphoretted hydrogen is evolved. We have already noticed that phosphoretted hydrogen gas is spontaneously inflammable (p. 198). Although the minute quantity of phosphoretted hydrogen in acetylene may not cause the gas to take fire spontaneously, yet when the acetylene is ignited for the purpose of giving light, the phosphoretted hydrogen burns to phosphoric acid and water. The phosphoric acid makes itself visible, in a room lighted by acetylene, in the form of a white smoke, which causes headaches and other ailments. Acetylene cannot be generally used until a suitable means of purifying it has been found. If the gas is passed over calcium chloride, the phosphoretted hydrogen is retained: but much remains to be done in improving the methods of purification.

PETROLEUM.

Liquid combustible material is obtained in many places by forming suitable bore-holes in the earth's surface. The natural product is called crude petroleum; when this is distilled, a liquid is obtained which is suitable for burning in lamps. The examination of this substance shows that it is composed of a great many hydrocarbons belonging to the class of open chain compounds (see p. 249). As petroleum is quite free from oxygen and sulphur, the metal sodium, which so eagerly combines with oxygen, may be kept in it without undergoing change. As the only products of the combustion of petroleum are carbon dioxide and water, the burning of this substance does not vitiate the surrounding air. No satisfactory explanation has yet been given of the formation of petroleum in the interior of the earth.

FLAME.

We have always used gas-flames for heating apparatus; but the flames we have used, unlike the ordinary gas-flames, have been non-luminous, and have not deposited soot on the surfaces exposed to them.

The luminosity of ordinary gas-flames is brought about in the following way. So high a temperature is attained by the burning of the hydrocarbons in the gas that a portion of these hydrocarbons is decomposed, with the separation of carbon, and the formation of hydrogen, which burns more rapidly than the carbon. It is only in the outer edges of the flame that the separated carbon finds oxygen enough to burn it, and it is not till it reaches the outside of the flame that this carbon disappears as it is changed into carbonic acid gas. The carbon which separates in the interior of the flame is raised to a full red heat, and (like all glowing bodies) emits light, which we use for the purpose of illumination.

The readiness of the hydrocarbons to undergo this decomposition increases as the amount of carbon in them increases. The richer a hydrocarbon is in carbon, the more easily is carbon separated from it. This readiness reaches its maximum in acetylene. The carbon that is separated in a hot flame cannot burn in the interior of the flame for want of oxygen, but must pass towards the outer edge, where it may be burnt. During this brief time the carbon is raised to the high temperature that is needed to make it luminous. What has been said of the flame of coal-gas holds good of other luminous flames, such as those of oil lamps and candles. In the case of an oil lamp or a candle, the wick sucks up liquid or melted material, which is gasified in the flame, wherein it suffers a kind of dry distillation (compare p. 269), and then burns luminously. Every lamp and every candle is a gas-works in itself, and produces the gas which it requires.

To show that a luminous gas-flame contains free carbon, it is only necessary to hold a porcelain plate in such a flame. By the sudden cooling of the flame thus effected, and also by the opposition which the plate presents to the passing outwards of the particles of carbon, some of the particles that are floating about are prevented from reaching the outside of the flame. These particles cannot, therefore, be burnt; they settle on the plate in the form of soot, which is very finely divided carbon.

It is such hydrocarbons as acetylene and ethylene which cause the luminosity of an ordinary gas flame.* The greater the quantity of such hydrocarbons in coal-gas, the greater will be the luminosity of the gas, until at last there is a danger of the flame smoking; that is to say, so many particles of carbon may be separated in the interior of the flame that they do not find sufficient oxygen for their complete combustion even when they have travelled to the outer edge of the flame, so that some of them get cooled below their temperature of ignition and float about as soot.

If coal-gas, before it is burned, is mixed with so much air that there will be enough oxygen in the flame, when the gas is ignited, to burn all the carbon to carbon dioxide inside the flame, there will be no separation of carbon—there will be no formation of carbon which, being heated very strongly, would make the flame luminous; in other words, the flame will not

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* In the analysis of coal-gas (on p. 273) these and other hydrocarbons are grouped together under the heading "other hydrocarbons."

emit light, nor will it smoke. Such a flame will be suitable for heating all sorts of vessels, and especially for cooking, as it will not blacken the utensils that are used.

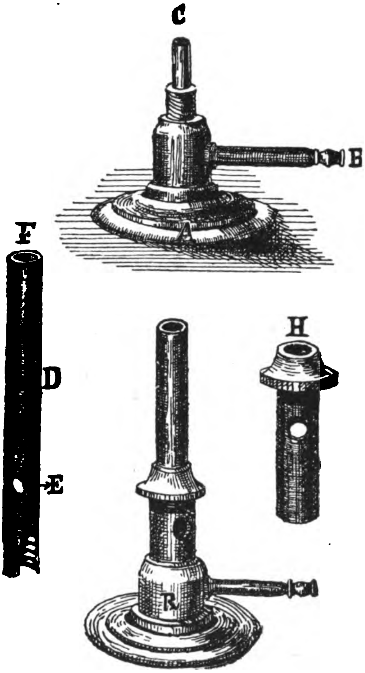

Fig. 54.—The Bunsen burner and its several parts.

Bunsen solved this problem soon after the introduction of lighting by gas, and the principle he employed is the foundation of all the apparatus that is used to-day for cooking by means of non-luminous gas-flames. The method is based on the arrangements shown in fig. 54, which represent the special form of apparatus that is used in chemical laboratories. The gas is admitted at B, and issues from a fine opening at C. The burner is mounted on a heavy foot, which gives it the necessary stability. If the stream of gas is ignited at C, it burns in the usual way, that is to say, luminously. But the gas is not ignited at C: a long metal tube (D) is placed over the opening C, and is fastened by a screw-thread (shown on A and also on D). The peculiarity of this metal tube is that it is pierced near its lower end by holes (E). If the tube D is fixed over the burner and gas is led in at B, the gas, streaming upwards through D, will draw air in by the holes E; hence a mixture of gas and air will issue at the upper end of the tube, that is, at F. When the mixture of gas and air is ignited, at F, there will be air, and therefore oxygen, in the interior of the flame; hence the minute particles of carbon that are produced in an ordinary gas-flame will not be formed in this flame, for all the carbon will be burnt by the oxygen that is mixed with the gas. The flame cannot, therefore, become luminous. The apparatus H is an outer case which can be pushed over D. The amount of air admitted through the holes E can be regulated by turning this case. The flame produced by such a burner as this—a burner we have made use of repeatedly—heats vessels without dirtying them, because there is no separation of carbon in the flame.

The flame of such a burner as that just described is much hotter than an ordinary gas-flame, because of the rapid combustion of the whole of the carbon in the gas. If a bundle of platinum wire is held in this flame—platinum is quite unchanged at this temperature—it becomes red hot and emits light. The modern incandescent gas-light exhibits this process in an extremely complete way. This arrangement resembles a Bunsen lamp. There are holes (generally four) near the place where the gas enters, so that it is a mixture of gas and air that is burnt, and the flame is non-luminous and very hot. The *mantle* is suspended in the non-luminous flame (see fig. 55). The mantle is made of cotton which has been thoroughly steeped in solutions of nitrate of thorium and nitrate of cerium [these are salts of two comparatively rare metals]; the cotton is then strongly heated, when it burns, and the nitrates are decomposed, nitrogen and oxygen are given off, and a mixture of oxides of thorium and cerium remains in the form of a mantle, which, unfortunately, is so perishable. If the mixture of oxides contains 99 per cent. thorium oxide and 1 per cent. cerium oxide (and this is easily attained by steeping the cotton mantle in a properly mixed solution of the two nitrates), it emits an extremely clear white light when it is strongly heated by the non-luminous flame obtained by making use of the principle of the Bunsen burner.

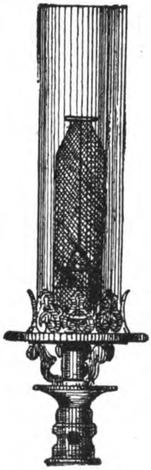

Fig. 55.—Incandescent gas-light.

A temperature higher than that of the Bunsen burner is obtained by blowing air into a gas flame. The gas blow-pipe is represented in fig. 56. Gas enters at A, and burns with a luminous flame: air is driven in by bellows, at B, and passes along a tube which terminates in a point inside the flame. As soon as air is driven into the flame, the luminosity vanishes, and a very high temperature is attained, whereat glass, for instance, melts easily. Should the temperature thus attained not be high enough for some special purpose, oxygen gas may be blown into the flame in place of air;* but it is not often necessary to do this in the laboratory. This flame is so hot that it may take the place of the oxyhydrogen flame (see page 137) in almost every case; and it has the advantage of using coal-gas, whereas hydrogen must be especially prepared if the oxyhydrogen flame is to be employed.

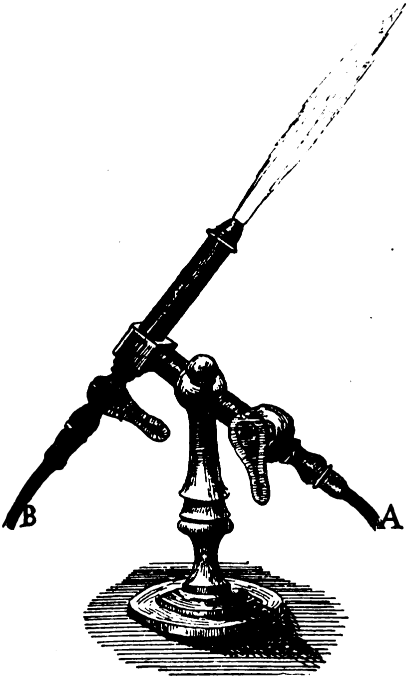

Fig. 56.—Blow-pipe.

SILICON.

Silicon is an element that is chemically very like carbon; compounds of it are found very widely distributed on the earth. The oxygen compound, SiO_2, called *silicon dioxide* [or, more commonly, *silica*], corresponds with carbon dioxide. As the latter is often named carbonic acid, so is SiO_2 called silicic acid, although the more correct name is *silicic anhydride*. Ordinary sand is [more or less pure] silica, SiO_2.

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* Oxygen may be bought in steel tubes.

This oxide shows its acidic character by combining with bases to form salts; for instance, it combines with lime to form *calcium silicate*, with alumina to form *aluminium silicate*, and with potash to form *potassium silicate* (see p. 74). Silicates play an important part in nature: most of the rocks whereof mountains are formed consist of mixtures of these salts; granite, for instance, is a mixture of three minerals—felspar, quartz, and mica. Felspar is composed of the silicates of aluminium, calcium, and potassium; quartz is crystallised silica; and the chief constituents of mica are silicate of aluminium and silicate of magnesium.

Of the many attempts that have been made to prepare a compound of one atom of silicon with one atom of oxygen (SiO, corresponding with CO), none has yet been successful.

Silicon forms a compound with hydrogen, SiH_4. This compound, which is called *silicon hydride*, corresponds with methane, CH_4. Silicon hydride is a gas; it is prepared by the reaction of hydrochloric acid with a compound of silicon and magnesium (*magnesium silicide*). The preparation is similar to that of arsenuretted hydrogen (p. 218). In place of zinc silicide, the more easily prepared compound of silicon and magnesium is used.

$$\underset{\substack{\text{Magnesium}\\\text{silicide}}}{SiMg_2} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{4HCl} = \underset{\substack{\text{silicon hydride}\\\text{gas}}}{SiH_4} + \underset{\substack{\text{magnesium}\\\text{chloride.}}}{2MgCl_2.}$$

$$\underset{\substack{\text{Zinc}\\\text{arsenide}}}{As_2Zn_3} + \underset{\substack{\text{hydrochloric}\\\text{acid}}}{6HCl} = \underset{\substack{\text{arsenic}\\\text{hydride gas}}}{2AsH_3} + \underset{\substack{\text{zinc}\\\text{chloride.}}}{3ZnCl_2.}$$

Silico-chloroform, $SiHCl_3$ (analogous to chloroform,

$CHCl_3$, p. 233), can be obtained by replacing three atoms of hydrogen in silicon hydride by chlorine.

Silicon atoms have not the property of combining together in long, branching chains in so marked a way as atoms of carbon; hence the number of silicon compounds is much smaller than the number of carbon compounds, notwithstanding that the two elements are similar and that the atoms of both are tetravalent.

This shortcoming in the behaviour of silicon, if such an expression may be used, is particularly helpful in making clear to us that it is not the tetravalency of carbon alone which gives to that body its peculiar position among the elements. This special position depends much more on the capability which the atoms of carbon possess of combining with one another to form chains that ramify in various directions.

We shall now pass from the consideration of non-metallic elements to consider some of the metals.

THE METALS.

THE metals may be divided into two main classes, the heavy metals and the light metals. Such metals as iron, lead, silver, etc., belong to the first class; and the second class contains those which have a specific gravity less than 5. Most of the lighter metals have been discovered in the present century.

The terms *noble* and *base* are sometimes used to designate different classes of metals. The noble metals are found in the earth uncombined with other elements. Although they have been in contact with the air for endless ages, they have not combined with the oxygen of the air—they have not changed into oxides. Gold, platinum, and considerable quantities of silver are found "native." The base metals, on the other hand, are generally found combined with oxygen or sulphur. In the older periods of the earth's history the metals must have had many opportunities of forming compounds with sulphur, whose chemical likeness to oxygen we already know (see p. 267). Those sulphides of metals which are found in the earth are spoken of as pyrites, glance, or blende; for instance, there is *copper pyrites*, *lead glance*, and *zinc blende*. Many other compounds of the base metals occur more complex than the oxides and sulphides—for instance, carbonate of lead and sulphate of magnesium.

When a metal or a compound of a metal is found in the earth in such quantities that the preparation of the metal from the raw material is technically remunerative, the substance found in the earth is spoken of as an *ore* of the metal. Whether any material is or is not considered an ore of a certain metal depends entirely on the commercial value of the material. For instance, the dust of the streets always contains iron; no one, however, would think of extracting iron therefrom; but if the street dust contained as much gold as it contains iron, it would be a first-rate gold ore.

Metallurgy is concerned with the extraction of metals from their ores. In the case of a noble metal, the operation is confined, for the most part, to the mechanical separation of the metal from the soil or rock wherein it is embedded. All the platinum and a good deal of the gold that is used is thus obtained. Although some silver is got in this way, it is generally necessary to use more complicated methods for obtaining that metal, as most of it is found in combination with other elements. In the case of a base metal, it is always necessary to use a more or less complex process. The processes used consist, in broad outline, in so treating the ores, however complicated they may be, that the metals in them are finally converted into oxides. The oxides are then mixed with carbon and strongly heated. The carbon seizes the oxygen and is converted into carbon monoxide gas, and the metals are obtained freed from oxygen. In this process the carbon is said to reduce the metallic oxide to metal. The following equations present instances of such processes of reduction :—

$$CuO + C = Cu + CO.$$

Copper oxide + carbon = copper + carbon monoxide gas.

$$NiO + C = Ni + CO.$$

Nickel oxide + carbon = nickel + carbon monoxide gas.

$$Fe_2O_3 + 3C = 2Fe + 3CO.$$

Ferric oxide + carbon = iron + carbon monoxide gas.

We notice that the carbon which reduces the metallic oxides is always oxidised to carbon monoxide (CO), never to carbon dioxide (CO_2). At the high temperatures of the furnaces wherein the operations are conducted the carbon cannot bind to itself more than a single atom of oxygen.

There is no process for obtaining the metals directly from their sulphur compounds, corresponding with that whereby they are obtained from their oxides, which is applicable in metallurgy. An indirect method must be employed. A method often used is known as *roasting* the ore. The sulphide is strongly heated in a stream of air; the oxygen of the air burns the sulphur to sulphur dioxide gas (SO_2), which escapes (see p. 149), and the metal is converted into oxide, which remains: the oxide is then reduced by heating with carbon. The roasting of zinc blende (which is the source of most of the zinc used for various purposes) and its conversion into zinc oxide is an example of this process.

$$ZnS + 3O = ZnO + SO_2.$$

Zinc blende (zinc sulphide) + oxygen (from the air) = zinc oxide + sulphur dioxide gas.

The reduction of metallic oxides by heating them with carbon is sometimes conducted in a blast furnace. The blast furnace is a tubular erection, into which ore and carbon [in the form of coal, coke, or charcoal] are thrown from above, along with certain substances which serve as fluxes and are necessary for properly conducting the smelting process, while a blast of air is forced in from beneath, whereby the carbon is burnt in the furnace. The melted metal, and the other molten substances known as *slag*, are drawn out from below, from time to time, while fresh material is thrown in from above.

Iron is one of the most remarkable of the heavy metals, inasmuch as it can be obtained in three very different modifications, which seem to be three different metals—namely, *pig-iron*, *steel*, and *malleable iron*. The chemical differences between these are dependent on the different quantities of carbon they contain. All iron that is technically useful must contain a definite quantity of carbon; chemically pure iron is too soft to be of any technical use. The quantities of carbon in the three kinds of iron are as follows:—

Pig-iron contains 2·3, or more than 2·3, per cent. of carbon.

Steel contains 1·6, or less than 1·6, per cent. of carbon.

Malleable iron contains not more than 0·5 per cent. of carbon.

Iron containing between 1·6 and 2·3 per cent. of carbon finds no technical applications.

Pig-iron can be melted, and can, therefore, be cast in moulds. Malleable iron and steel can be forged; that is to say, these substances do not become fluid at a full red heat, but they become so soft that they can be worked with the hammer, or some other form of pressure, and brought into any shape that is desired. Articles of steel become extraordinarily hard when they are cooled suddenly after having been worked under the hammer, but malleable iron does not harden when treated in this way. Steel and malleable iron can be welded; that is to say, although they do not melt at a very high temperature, two pieces can be united to form one homogeneous substance by hammering them together at a white heat.*

All the heavy metals commonly used, except mercury and zinc, are obtained by reducing their oxides by heating with carbon in furnaces. It is well known that mercury volatilises comparatively easily. If an attempt were made to obtain this metal by heating in a blast furnace, the metal would simply escape, as a gas, into the air at the top of the furnace. Mercury must be distilled from retorts, like any other liquid, like water, for instance. The retorts used for distilling mercury are made of fire-clay. The metal is obtained by heating its ores in such retorts, and cooling the vapour in suitable vessels. Zinc also must be got by a similar process; for zinc is a comparatively easily volatilised metal, although one is not accustomed to think of it as such. If zinc oxide is heated with carbon, the metal is

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* More details concerning the domestic and economic applications of iron will be found in the author's *Chemistry in Daily Life*, pp. 274–302 (2nd Ed.)

produced; but it volatilises at the high temperature which is required for the reduction of the oxide: hence, if the process were conducted in a blast furnace, the zinc would escape, as gas, from the top of the furnace, and would there be burnt to oxide by the oxygen in the air. For these reasons zinc oxide is heated with carbon in fire-clay retorts, and the vapour of zinc is conducted into suitable vessels, wherein it condenses. Under these conditions the vapour of the metal does not come into contact with the air, and has no chance of being burnt again to oxide.

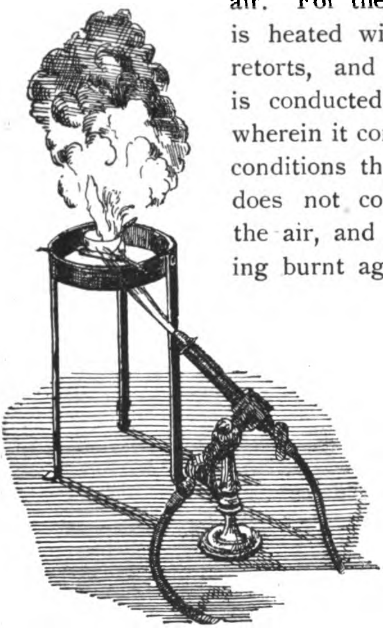

Fig. 57.—Burning zinc by a blow-pipe flame.

The following experiment shows how readily zinc may be volatilised, and how easily its vapour may be burnt in the air. A few small pieces of zinc-foil are placed in a porcelain crucible, which is then heated by the flame of a blow-pipe (see fig. 57). The zinc soon melts, and, as the heating is continued, a flame appears at the mouth of the crucible, and zinc oxide rises into the air as a white smoke.

Alloys are formed by heating mixtures of metals.

The alloys that are formed by dissolving metals in mercury (and mercury dissolves most of the metals) are called *amalgams*. Bronze is obtained by melting together copper and tin, brass by melting together copper and zinc. Gold and silver are soft metals—so soft that they are worn away by much use; but if mixtures of about ninety parts of gold or silver with about ten parts of copper are melted, the very hard alloys are obtained of which our gold and silver coins are made.*

We know (compare p. 217) that bases are oxides of metals: these bases react with acids, which are derived from oxides of non-metals, to form salts. Many metals, like some of the non-metals we have considered, combine with oxygen in more than one proportion (we recall the two oxides of sulpur, SO_2 and SO_3). Iron, for instance, forms the oxide FeO, called *ferrous oxide*, and the oxide Fe_2O_3, called *ferric oxide*. Halogen compounds of the metals generally exist corresponding with such oxides; these are designated *-ous* and *-ic* chlorides, bromides, and iodides. *Ferrous chloride* has the composition $FeCl_2$, and *ferric chloride* has the composition $FeCl_3$. As the valency of an elementary atom is measured by the number of monovalent atoms it can hold fast (compare p. 229), we see that in one of

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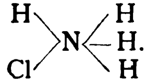
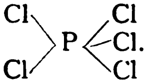
* The English gold coinage alloy contains 91⅔ per cent. of gold and 8⅓ per cent. of copper; the silver coinage alloy contains 92½ per cent. of silver and 7½ per cent. of copper. The German gold coins are made of an alloy of 90 per cent. gold and 10 per cent. copper, and German silver coins of an alloy of 90 per cent. silver and 10 per cent. copper. [Tr.]

these chlorides the iron atom is divalent, while in the other it is trivalent. Some metals exhibit *varying valency*. There is no abrupt distinction between the metals and the non-metals in this respect. Nitrogen and phosphorus generally act as trivalent atoms, but in some compounds the atoms of these elements are pentavalent; for instance, when ammonium chloride, NH_4Cl, is formed from ammonia, NH_3, and hydrochloric acid, HCl, the nitrogen atom must hold together the five monovalent atoms, thus  $\begin{matrix} H & & H \\ & N & -H \\ Cl & & H \end{matrix}$. The atom of phosphorus is pentavalent in the molecule of phosphorus pentachloride,  $\begin{matrix} Cl & & Cl \\ & P & -Cl \\ Cl & & Cl \end{matrix}$. But while nitrogen and phosphorus are pentavalent only in a proportionately small number of compounds, many metals show one valency in one series of compounds and another valency in another series of compounds, so that one may say that changing valency is the rule with them, while it is something exceptional with nitrogen and phosphorus.

Manganese, which is a metal resembling iron, is an especially instructive example of changing valency. In the oxide MnO, called *manganous oxide*, the atom of manganese is divalent, inasmuch as oxygen is divalent. This oxide forms salts—for instance, $MnSO_4$—by reacting with acids.

$$MnO + H_2SO_4 = MnSO_4 + H_2O.$$

Manganous oxide + sulphuric acid = manganous sulphate + water.

Manganese also forms the oxide Mn_2O_3, *manganic oxide.* As two atoms of the metal are here combined with three atoms of divalent oxygen, each atom of manganese in this compound is trivalent. As two atoms of manganese take the place of six atoms of hydrogen, the sulphate corresponding with this oxide will be $Mn_2(SO_4)_3$.

Mn_2O_3	+	$3H_2SO_4$	=	$Mn_2(SO_4)_3$	+	$3H_2O$.
Manganic oxide	+	sulphuric acid	=	manganic sulphate	+	water.

The compounds derived from mangan*ous* oxide are called mangan*ous* compounds; those derived from mangan*ic* oxide are called mangan*ic* compounds. Similarly, $FeSO_4$ is ferr*ous* sulphate (FeO is ferr*ous* oxide), and $Fe_2(SO_4)_3$ is ferr*ic* sulphate (Fe_2O_3 is ferr*ic* oxide). The equations which present the formations of these two sulphates of iron from their corresponding oxides are as follows:—

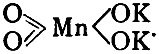
FeO	+	H_2SO_4	=	$FeSO_4$	+	H_2O.
Ferrous oxide	+	sulphuric acid	=	ferrous sulphate	+	water.
Fe_2O_3	+	$3H_2SO_4$	=	$Fe_2(SO_4)_3$	+	$3H_2O$.
Ferric oxide	+	sulphuric acid	=	ferric sulphate	+	water.

Besides ferrous and ferric oxides, an oxide of iron intermediate between these is known; it is called *ferroso-ferric oxide*, and has the composition Fe_3O_4 [$FeO . Fe_2O_3$]. This oxide is found abundantly in nature; its mineralogical name is *magnetic ironstone.* There are no salts corresponding with this oxide.

Returning to manganese, mention must be made of the oxide MnO_2, called *manganese peroxide*: here the manganese atom is tetravalent. No salts corresponding with this oxide have been isolated. We are now in a position to examine more fully the reaction between this oxide and hydrochloric acid which we used for the preparation of chlorine. The two atoms of oxygen in MnO_2 are able to oxidise four atoms of hydrogen to water; one molecule of MnO_2 reacts, therefore, with four molecules of hydrochloric acid, HCl. It is probable that the first product of the reaction is a tetrachloride, $MnCl_4$ (and water). If this salt is formed, it is very unstable, and at once decomposes to manganous chloride, $MnCl_2$ (corresponding with manganous oxide, MnO), and chlorine. The equation which expresses the preparation of chlorine is:—

MnO_2	+	$4HCl$	=	Cl_2	+	$MnCl_2$	+	$2H_2O$.
Manganese peroxide	+	hydrochloric acid	=	chlorine gas	+	manganous chloride	+	water.

There are two other highly oxidised compounds of manganese—*manganic acid*, wherein the manganese atom seems to be hexavalent, and *permanganic acid*. Manganic acid has not itself been isolated, but its composition may be deduced from that of its potassium salt, K_2MnO_4, the expanded formula of which may be written thus:



$$\begin{matrix} O \\ O \end{matrix} \gg Mn \lessdot \begin{matrix} OK \\ OK \end{matrix}.$$

The anhydride of permanganic acid, Mn_2O_7, has been isolated, by adding sulphuric acid to potassium permanganate; it is called also *manganese heptoxide*. The salt *potassium permanganate* is often used [as a disinfectant and deodoriser; a solution of it is known as "Condy's fluid"]. The formula of this salt is $K_2Mn_2O_8$ (but the half-formula $KMnO_4$ is often used);

and the composition of permanganic acid, from which it is derived, is given by the formula $H_2Mn_2O_8$.

The technical productions of potassium manganate and potassium permanganate are closely connected. When manganese peroxide, MnO_2, is fused with potash, KOH, and potassium chlorate, $KClO_3$ (the mineral *pyrolusite* is used; it is more or less pure MnO_2), the oxygen of the chlorate oxidises the MnO_2, and the product of the reaction—a green solid—contains the salt K_2MnO_4, potassium manganate. If this is dissolved in water (it dissolves easily) and chlorine is passed into the solution, one atom of the potassium of the manganate combines with chlorine, forming potassium chloride, KCl, and the solution becomes pinkish red, because of the formation of potassium permanganate.

$$\begin{array}{ccccccccc} 2K_2MnO_4 & + & Cl_2 & = & K_2Mn_2O_8 & + & 2KCl. \\ \text{Potassium manganate} & + & \text{chlorine} & = & \text{potassium permanganate} & + & \text{potassium chloride.} \end{array}$$

As potassium permanganate is less soluble in water than potassium chloride, the two salts may be separated by crystallisation. After evaporation the permanganate crystallises out, while the chloride remains in the mother-liquor. The addition of an acid to a (green) solution of potassium manganate withdraws potassium [forming a potassium salt of the acid used], and produces a (red) solution of potassium permanganate. Manganic acid cannot, then, be obtained by the reaction of potassium manganate with an acid.

We shall not attempt to treat of the remaining heavy metals; we shall content ourselves with giving the formulæ of the oxides of the better known of them. If the formulæ of the oxides, and hence the valencies of the elements, are known, it is easy to deduce the formulæ of the other compounds and salts of these elements.

Zinc, Zn, reacts only as a divalent element; the formula of its oxide is ZnO. Two oxides of *mercury* are known—Hg_2O, mercurous oxide, and HgO, mercuric oxide; the former yields the mercurous salts, and the latter the mercuric salts. *Copper* forms cuprous oxide, Cu_2O, and cupric oxide, CuO: cuprous and cupric salts are known. The oxides of *gold* are aurous oxide, Au_2O, and auric oxide, Au_2O_3, and from these aurous and auric salts are derived. The only oxide of *silver* which forms salts is Ag_2O: there is another oxide known—silver peroxide, AgO—but salts corresponding with this oxide have not been isolated. The oxide of *tin*, SnO_2, reacts with strong acids as a base, but with strong bases it acts as an acid; it is called stannic oxide, or stannic anhydride. *Lead* forms three oxides: PbO, (known as litharge), which reacts with acids to form salts; PbO_2, called lead peroxide [corresponding with which only one salt, lead tetracetate, $Pb(C_2H_3O_2)_4$, has been isolated]; and Pb_3O_4, known as red lead. Of the three oxides of *cobalt*, CoO, Co_2O_3, and Co_3O_4, only the first and second form salts. *Nickel* forms nickelous oxide, NiO, which is salt-forming, and nickelic oxide, Ni_2O_3.

THE LIGHT METALS.

While many of the heavy metals have been known for a very long time, most of the light metals, such as potassium, sodium, and aluminium (which have been referred to on p. 287), were prepared for the first time in the nineteenth century. The alkalis and the soluble bases, those exact opposites of the acids, are compounds of certain of the light metals; potash, for instance, which has been used as an alkali for centuries, is a compound of the metal potassium. The oxide of potassium has the formula K_2O; the atom of potassium is monovalent, and that of oxygen is divalent. This oxide reacts with water to form the alkali *caustic potash*, according to the equation:—

$$\underset{\text{Potassium oxide}}{K_2O} + \underset{\text{water}}{H_2O} = \underset{\text{caustic potash.}}{2KOH.}$$

An aqueous solution of a caustic alkali may be used as the exact reverse of an aqueous solution of an acid, say, sulphuric acid. The solution of such an acid is neutralised by adding to it a solution of a caustic alkali. A piece of paper soaked in litmus solution and dipped into the liquid serves to indicate when sufficient alkali has been added, for a neutral liquid does not alter the colour of either red or blue litmus. If carbonic anhydride gas or sulphur dioxide gas is passed into a solution of caustic potash, potassium carbonate or potassium sulphate is soon formed.

The oxides of the heavy metals also react with the acids to form salts: iron oxide and sulphuric acid form sulphate of iron. But most of the oxides of the heavy metals (ferric oxide, for instance) are not soluble in water, whereas the oxides of potassium and sodium dissolve very easily in water, forming caustic potash and caustic soda solutions respectively. Hence, because of their insolubility in water, it is not nearly such an easy and rapid process to neutralise acids by the oxides of the heavy metals as to neutralise them by solutions of caustic potash, soda, or ammonia.

Very many compounds of certain light metals have been known for long. Oxide of calcium, CaO, for instance, is obtained by strongly heating limestone (calcium carbonate, $CaCO_3$), which is a very widely distributed and common substance. When this compound is strongly heated, it decomposes into calcium oxide and carbon dioxide gas:—

$$\begin{array}{ccccc} CaCO_3 & = & CaO & + & CO_2. \\ \text{Calcium carbonate} & = & \text{calcium oxide} & + & \text{carbon dioxide.} \\ \text{(limestone)} & & \text{(burnt lime)} & & \end{array}$$

Burnt lime has long been known and used in making mortar; but neither the alchemists nor the early chemists were able to separate it into oxygen and a metal. Chemists were thus in the awkward position of having to deal with a substance which did not give one the impression of being an element—for burnt lime certainly does not seem to be an elementary substance—but yet mocked every attempt to separate it into simpler constituents, and had, therefore, to be classed among the elements. It had often been remarked that burnt lime resembled the oxides of the metals; that, for instance, like these compounds, it neutralised acids. Because of this likeness, it was customary, before the discovery of oxygen, to speak of what we now call metallic oxides as metallic calces. Lavoisier (see p. 127) was the first to prove that the calx of tin was an oxide of tin. We can perhaps form some conception of the sensation that was caused by the isolation of the first light metal by Davy in the year 1806. The metal was potassium, obtained by Davy from caustic potash. The isolation of that metal was not effected by purely chemical methods, but by the help of electricity, obtained by using the "Voltaic pile," sixteen years after the discovery of the galvanic current. As is well known, the Voltaic pile has long been superseded by the galvanic cell, and that is being now replaced by the dynamo. The sensation which was caused by the isolation of the first alkali metal, with its remarkable properties, was no less than that caused in our own day by the discovery of the Röntgen rays.

PREPARATION OF THE LIGHT METALS BY ELECTRICITY.

On p. 33 we learnt that the electric current decomposes water into oxygen and hydrogen. If we use an aqueous solution of a metallic salt—say, copper sulphate—in place of water, the current causes the separation of the metal, in this case copper, at the negative pole (in place of hydrogen), and the radicle SO_4, which was combined with copper, travels to the positive pole.

This process is applied technically; it is called *electroplating.* Suppose it is wished to cover a piece of zinc with nickel (to repeat on a small scale a process which has extended greatly of late years), the operation is carried out in the manner shown in fig. 58. The zinc plate A, whereon nickel is to be deposited, is fastened to the negative pole of an electric circuit, and a plate of nickel is attached to the positive pole B. Both plates are immersed in a solution of a salt of nickel, say, nickel sulphate, and the electric current is sent through this nickel bath. After a short time we see that the zinc plate is covered with a film of nickel.

If the current were sent through a solution of a salt of a light metal, through a solution of common salt (sodium chloride), for instance, the reaction would, of course, be similar. Sodium would be separated at the negative pole. But we know (p. 29) that sodium instantly decomposes water; therefore it is not possible that sodium should be actually separated in this experiment: the sodium will decompose water, and hydrogen will be obtained at the negative pole. If, then, it is desired to prepare one of the alkali metals by means of the electric current, not a trace of water must be present, and an aqueous solution of a salt of the alkali metal must not be used. Now, not only do aqueous

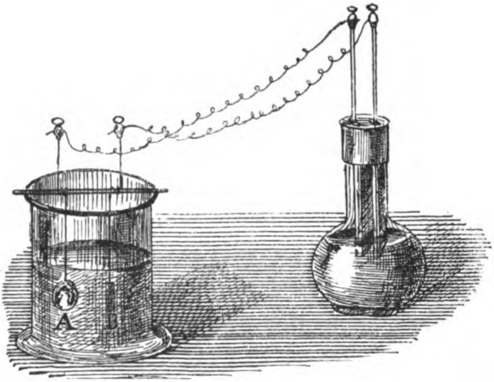


Fig. 58.—Electroplating.

solutions of the salts of the alkali metals conduct electricity, but the melted salts themselves do the same. As there is no water in the liquid formed by melting one of these salts, the alkali metal which is separated by the electric current remains unchanged therein, and collects at the negative pole, from which it may be removed. This was the method employed by Davy.

POTASSIUM.

Potassium hydroxide (caustic potash) is the most convenient compound of potassium from which to obtain the metal electrolytically. The compound is melted, and the current is sent through the melted substance; potassium collects at the negative pole.

Potassium is a silver-white metal; its specific gravity is 0·86. One litre of this metal weighs 860 grams, while one litre of water weighs 1000 grams. The metal therefore floats on water. It decomposes water into its constituents; the hydrogen is given off, and the metal combines with the oxygen, forming potassium oxide, which dissolves in the rest of the water with the production of potassium hydroxide.

Because of its readiness to combine with oxygen, potassium cannot be kept exposed to the air. The surface of a freshly cut piece of potassium is silver-white, but if exposed to the air it is very soon covered with a greyish film of oxide. The metal is much softer than lead; it can be cut by a knife very easily. Potassium is generally kept under petroleum (as sodium is, see p. 29), which is a mixture of hydrocarbons (p. 278), and protects the potassium from the oxidising action of the air.

We have already made mention of the existence of potassium salts in the ashes of plants, and also of the immense deposits of these salts which are worked at Stassfurt. Until the Stassfurt salts began to be worked, about forty years ago, the ash of plants was the only available source of potassium compounds. When plants or wood are burnt, the carbon forms carbon dioxide; and this combines with potassium, if compounds of that metal are present, to form potassium carbonate. The formulæ of carbon dioxide and hypothetical carbonic acid are these:—

CO_2	$CO_2 + H_2O = H_2CO_3$
Carbon dioxide.	Hypothetical carbonic acid.

Although carbonic acid has not been isolated (compare p. 266), we must regard carbonates as derived from this compound. If we suppose that the two hydrogen atoms of carbonic acid are replaced by potassium, we obtain potassium carbonate, K_2CO_3. This salt used to be called pot-ashes, for the following reasons. The lixiviation of the ashes of wood, for the purpose of obtaining a substance that was much used in making soap (p. 313), glass (p. 319), and in other industries, is a very ancient process; the liquor (containing potassium carbonate) was evaporated to dryness in iron vessels, and the solid residue was used for the purposes we have mentioned. This residue—impure potassium carbonate—is very hygroscopic; it rapidly attracts moisture from the air, and after a time becomes a liquid; it could not, therefore, be kept in bags or casks, but it was necessary to pack it in pots which could be closed securely. Hence the name *pot-ashes*.

Besides the normal potassium carbonate, K_2CO_3, an acid salt exists, produced by replacing one atom of hydrogen in the hypothetical carbonic acid by potassium. The formula of this salt is $KHCO_3$; it is called *potassium hydrogen carbonate*, or *acid carbonate of potassium*, or sometimes *bicarbonate of potash*. This salt is produced by passing carbon dioxide into a concentrated solution of the normal carbonate: as the acid salt is much less soluble than the normal salt, it soon begins to separate out from the solution into which carbon dioxide is passed.

$$\begin{array}{ccccccc} K_2CO_3 & + & CO_2 & + & H_2O & = & 2KHCO_3. \\ \text{Potassium carbonate} & + & \text{carbonic anhydride} & + & \text{water} & = & \text{acid potassium carbonate.} \end{array}$$

Potassium carbonate is the material from which caustic potash is prepared. Potash lye, as a solution in water of caustic potash is sometimes called, has been used for centuries, especially in the preparation of soap. In order to understand the preparation of this compound from potassium carbonate, we must consider for a moment the following reactions. We know that lime, CaO, is produced by strongly heating limestone (p. 300). When water is added to lime, the two combine to form *slaked lime*:—

$$\begin{array}{ccccc} CaO & + & H_2O & = & Ca(OH)_2. \\ \text{Lime} & + & \text{water} & = & \text{slaked lime.} \end{array}$$

This reaction, like many other chemical reactions, is accompanied by the production of heat. In this case so much heat is produced that a portion of the water is driven off as steam. When one who is unacquainted with chemical changes sees steam produced by pouring cold water on to lime, he is apt to think there is something mysterious about the operation. Slaked lime is a white powder that may be stirred up with water; when it is treated in this way it forms the lime-plaster used by masons. But slaked lime is only slightly soluble in water. If a thin milk of lime (lime stirred with water) is filtered, the clear filtrate contains one part of calcium hydroxide (or slaked lime) dissolved in 760 parts of water. Clear lime-water contains but a very little of the alkali calcium hydroxide, but thick milk of lime is very rich in alkali.

Milk of lime is used for making caustic potash in the following way. When fairly thin milk of lime is poured into a solution in water of potassium carbonate, the calcium hydroxide seizes the carbon dioxide of the carbonate, and calcium carbonate (which is insoluble in water) and potassium hydroxide are produced.

$$K_2CO_3 + Ca(OH)_2 = 2KOH + CaCO_3.$$

$$\begin{array}{ccccccc} \text{Potassium carbonate} & + & \text{calcium hydroxide} & = & \text{potassium hydroxide} & + & \text{calcium carbonate.} \end{array}$$

If a concentrated solution of potassium carbonate is decomposed by milk of lime and the liquid is separated from the calcium carbonate which precipitates, a concentrated solution of potassium hydroxide (caustic potash) is obtained. Solid caustic potash is produced by evaporating this liquid to dryness, and heating the residue strongly to remove the whole of the water.

The potash is melted by the heat; on cooling it remains as a hard, white solid. By pouring the melted potash into moulds, it solidifies in the form of sticks, which are convenient for use in the laboratory. Potassium hydroxide is a strongly caustic substance; hence the name *caustic* potash.

The most important technical application of solutions of caustic potash in water is in making soap. All soaps are prepared from fats, which are compounds of certain organic acids with glycerin. As fats are compounds of these acids, the acids are grouped together under the common name *fatty acids*; they all contain single chains of carbon atoms. The acids most commonly found in soaps are *stearic*, *palmitic*, and *oleïc acid.* The fats are decomposed by boiling with potash lye. These glycerin compounds of the fatty acids react with caustic potash to form potassium compounds of the fatty acids (which are soaps) and glycerin. The soaps produced by using caustic potash are soft [hard soaps are obtained by using caustic soda].

Potassium chloride is another important salt of potassium; it is obtained from the Stassfurt deposits, and finds its chief application as an artificial manure.

We have already become acquainted with potassium bromide when considering bromine, and potassium iodide when considering iodine.

The salt *potassium chlorate*, which we used when we prepared oxygen gas, is formed when chlorine gas is passed into a hot solution of caustic potash. The chlorine seizes the potassium and forms potassium chloride. The hydroxyl groups (OH) which thus become available cannot exist alone; they must enter into some reaction whereby stable bodies are produced. Six of these groups form three molecules of water and three atoms of oxygen; and the three atoms of oxygen react with a molecule of potassium chloride to produce potassium chlorate, which separates from the liquid, as it is much less soluble in water than potassium chloride. The reaction may be expressed in the following equation:—

$$\begin{array}{ccccccccc} 6KOH & + & 6Cl & = & KClO_3 & + & 5KCl & + & 3H_2O. \\ \begin{array}{c}\text{Potassium}\\ \text{hydroxide}\end{array} & + & \text{chlorine} & = & \begin{array}{c}\text{potassium}\\ \text{chlorate}\end{array} & + & \begin{array}{c}\text{potassium}\\ \text{chloride}\end{array} & + & \text{water.} \end{array}$$

We already know something about potassium nitrate and potassium nitrite (p. 188).

Potassium silicate is obtained by the reaction between potassium hydroxide and sand, which is approximately pure silica (compare p. 284). This salt is soluble in water; it is sometimes called "potash soluble glass." On the large scale the salt is prepared by fusing a mixture of potassium carbonate and sand.

Very small quantities of compounds of the two metals *rubidium* and *cæsium* are found in nature. These metals are very similar chemically to potassium; their compounds are exceedingly like those of potassium both in composition and properties.

SODIUM.

While the Stassfurt mines are the main source of potassium compounds, inexhaustible supplies of compounds of sodium are found in many parts of the earth. Vast quantities of common salt, which, as we know, is sodium chloride, occur in salt mines, besides what is present in the sea.

Sodium resembles potassium in its chemical behaviour. Both metals can be prepared by similar methods; decomposition of sodium hydroxide by the electric current produces sodium, just as potassium is obtained by electrolysing caustic potash. The surface of freshly cut sodium is silver-white. Heated in dry air, sodium forms Na_2O_2, a compound which is called *sodium peroxide.* Hydrogen peroxide (p. 141) is obtained by the action of a dilute acid on this compound; for example:—

$$\begin{array}{ccccccc} \mathrm{Na_2O_2} & + & \mathrm{2\,HCl} & = & \mathrm{H_2O_2} & + & \mathrm{2NaCl.} \\ \text{Sodium peroxide} & + & \text{hydrochloric acid} & = & \text{hydrogen peroxide} & + & \text{common salt.} \end{array}$$

Sodium decomposes water; hydrogen is set free, and the sodium combines with the oxygen of the water (compare p. 30).

In the course of time methods have been discovered for transforming sodium chloride, which occurs so plentifully in nature, into sodium carbonate, which is scarcely found native. Sodium carbonate has long been known commercially as "soda." The process whereby "soda" is made from sodium chloride is exceedingly ingenious; but it is so complicated, both technically and chemically, that we shall not consider it in this INTRODUCTION TO CHEMISTRY.*

Sodium carbonate (or "soda") is very similar to potassium carbonate in its chemical behaviour: but the salts differ in some respects; for example, the potassium salt is very hygroscopic, and it is so soluble in water that to obtain the solid salt a solution of it must be evaporated to dryness. Sodium carbonate is also easily soluble in water, but it is much more soluble in hot water than in cold. If a solution which has been made by saturating hot water with sodium carbonate is allowed to cool, the salt separates in crystals from the cold liquid. The "soda crystals" prepared in this way contain ten molecules of water of crystallisation; the formula of the crystalline compound is $Na_2CO_3 . 10H_2O$. Let us calculate the percentage of water in "soda crystals." The atomic weights of sodium, carbon, and oxygen are 23, 12, and 16 respectively—the atomic weight of hydrogen being 1; hence the molecular weight of the crystalline salt is:—

$$\begin{array}{ccccccccc} Na_2 & & C & & O_3 & & 10 \quad H_2O & & \\ (2 \times 23) & + & 12 & + & (3 \times 16) & + & 10([2 \times 1] + 16) & = & 286. \end{array}$$

As 286 parts by weight of "soda crystals" contain 180 parts of water, it follows, from the proportion $286 : 180 = 100 : x$, that x (that is, the percentage of water in the crystals) is 62·9. Almost two-thirds of

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* Details of this process are given in *Chemistry in Daily Life*, pp. 199–211 (2nd Ed.).

the weight of any quantity of "soda crystals" is water.

If the crystallised sodium carbonate is heated, the water is driven off, and the anhydrous "soda" remains in the form of a white powder. As dry "soda" contains much more sodium carbonate than an equal weight of "soda crystals," it is more economical, from considerations of the cost of transport, to manufacture "soda" than "soda crystals." When a compound which contains water of crystallisation is deprived of that water by heating, the process is called calcination; hence dry "soda" is often spoken of as *calcined soda.*

The water cannot be seen in crystals of sodium carbonate. If the crystals are exposed to the air, they gradually change to a white powder. The water of crystallisation, which is present in such large quantity, slowly evaporates, as any other water would do; and as the crystallised form is dependent on the presence of the ten molecules of water, the crystals crumble to powder when the water is removed. The loss of water of crystallisation is called the *efflorescence* of crystals. We must not, however, suppose that all compounds which contain water of crystallisation effloresce; some of them, on the contrary, retain their water permanently at ordinary temperatures.

Sodium carbonate may be used in place of potassium carbonate for many purposes; is is often employed nowadays where potassium carbonate was once used. The latter is much more expensive than "soda," because "soda" can be manufactured cheaply. from common salt. If we wish to know what weight of sodium carbonate is required to replace a determinate weight of potassium carbonate in performing some chemical reaction, we obtain this information by using the following proportion :—

$$K_2CO_3 : Na_2CO_3 = 1 : x.$$

The molecular weight of K_2CO_3 is 138 ($K_2 = 78 + C = 12 + O_3 = 48$), and the molecular weight of Na_2CO_3 is 106 ($Na_2 = 46 + C = 12 + O_3 = 48$) ; hence 106 parts of sodium carbonate will replace 138 parts of potassium carbonate. Substituting these values in the proportion already given, we have $138 : 106 = 1 : x$; hence $x = 0{\cdot}74$. That is to say, 74 kilos. of sodium carbonate will replace 100 kilos. of potassium carbonate.

As potassium carbonate combines with a molecule of carbonic anhydride and forms acid potassium carbonate when the gas is passed into a solution of the salt, so is acid sodium carbonate produced when a solution of the normal salt is caused to react with carbonic anhydride.

$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{carbonic anhydride}}{CO_2} + \underset{\text{water}}{H_2O} = \underset{\text{acid sodium carbonate.}}{2NaHCO_3.}$$

The reaction between calcium hydroxide (slaked lime) and a solution of sodium carbonate is similar to that between calcium hydroxide and a solution of potassium carbonate : calcium carbonate is formed, and precipitates, as it is insoluble in water, and the solution contains sodium hydroxide.

$$\underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{calcium hydroxide}}{Ca(OH)_2} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{sodium hydroxide.}}{2NaOH.}$$

By removing the calcium carbonate by filtration, a solution of sodium hydroxide, or caustic soda, is obtained. Solid caustic soda remains as a white mass when the solution is evaporated to dryness and the residue is heated. Like caustic potash, caustic soda may be melted and cast in sticks.

Much use is made of caustic soda in manufacturing processes; thousands of hundredweights of it, indeed, are used daily. Fats are decomposed by caustic soda; hence it is employed in making soaps. The process is precisely similar to that which occurs when caustic potash is used :—

$$\begin{array}{c}\text{Glycerin compound}\\ \text{of fatty acid}\end{array} + \begin{array}{c}\text{caustic soda}\\ \text{solution}\end{array} = \begin{array}{c}\text{sodium salt of}\\ \text{fatty acid}\\ \text{(soap)}\end{array} + \text{glycerin.}$$

Potash soaps are soft; soda soaps are hard.

Caustic soda is also used for boiling with rags in making paper; also for decomposing wood, and getting cellulose therefrom, in the same manufacture. Acid sulphite of calcium is a keen competitor against caustic soda in paper-making, for a solution of this salt is able to break up wood and produce cellulose. The formula of this salt is $CaH_2(SO_3)_2$: sulphurous acid is H_2SO_3; and as an atom of calcium is divalent and takes the place of two atoms of hydrogen, the formula of normal calcium sulphite is $CaSO_3$. This salt combines with sulphurous acid to form the acid salt $CaSO_3 . H_2SO_3$, or $CaH_2(SO_3)_2$.

Caustic soda is much used in dyeing, and in many other chemical industries.

Of the other salts of sodium, mention must be made of the sulphate. The formula of *sodium sulphate* is, of course, Na_2SO_4. The crystals which are deposited as a hot aqueous solution of this salt cools have the composition $Na_2SO_4 . 10H_2O$; the crystalline salt is sometimes called *Glauber's salt*, after the name of its discoverer. The salt is still prepared by the method given by Glauber more than two hundred years ago; sodium chloride is decomposed by sulphuric acid. As a fairly high temperature is needed to complete the reaction, the two substances are heated together in a furnace.

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

Common salt + sulphuric acid = sodium sulphate + hydrochloric acid.

We became acquainted with this reaction when we were preparing hydrochloric acid; we did not then pay attention to the sodium sulphate which is produced (see p. 67).

We have already learnt something of *sodium thiosulphate* (p. 151), and also of *sodium nitrate* and *sodium nitrite* (p. 188).

Sodium silicate is obtained by a process similar to that whereby potassium silicate is made. Sodium hydroxide is caused to react with silica, or sodium carbonate is melted with sand. The salt dissolves in water; it is commonly called "soda soluble glass."

Borax is a sodium compound; it is a sodium salt of boric acid. The element *boron* (the symbol for which is B) is generally placed among the non-metals, although some of its reactions are those of a metal. It is a trivalent element; it is able, therefore, to hold to itself three hydroxyl groups, and to form $B(OH)_3$, a compound which, as it has acidic properties, is called *boric* (or *boracic*) *acid*. The acidic properties of this compound are very feebly marked; it does not form normal salts [the normal sodium salt would be Na_3BO_3]. Borax is the sodium salt of an acid which has the composition $H_2B_4O_7$; this compound, which is called *pyroboric acid*, may be regarded as formed by removing five molecules of water from a complex boric acid, thus:—

$$4B(OH)_3 - 5H_2O = H_2B_4O_7.$$

Borax is used in soldering, an operation which consists in causing two pieces of metal to adhere. It is necessary that the surfaces of the metals to be soldered should be perfectly clean; the slightest film of oxide prevents the joining of the metals. When borax is strewed on the metals to be soldered and they are heated till the borax melts, that salt acts like an acid, and, dissolving any traces of oxides that may be present, insures the perfect contact of the metallic surfaces.

The metal *lithium*, and also the group *ammonium* (NH_4), are chemically closely allied to sodium. It is not necessary for us to consider lithium. We have already studied ammonium somewhat fully (p. 171).

The metals potassium, sodium, rubidium, cæsium lithium (and ammonium) are commonly classed together under the name *alkali metals*. The *metals of the alkaline earths* are allied to the alkali metals; they are *calcium*, *barium*, and *strontium*. It is only the first of these which is of special interest to us; the two others are very like calcium in their chemical behaviours.

CALCIUM.

The metal calcium is obtained by the electrolysis of calcium chloride, $CaCl_2$; the electric current decomposes this salt into calcium and chlorine gas. Calcium is a pale yellow metal, somewhat heavier than water; its specific gravity is 1·6. Calcium oxidises rapidly by exposure to air; and as it decomposes cold water, it must be kept under a liquid, such as petroleum, which is free from oxygen.

Many compounds of calcium are found abundantly in nature; we know that limestone and marble are calcium carbonate (p. 300); alabaster and gypsum are calcium sulphate; phosphorite is calcium phosphate.

Burnt lime, CaO, is obtained, as we know, by strongly heating limestone (or marble); lime is slaked by adding water to it, whereby calcium hydroxide, $Ca(OH)_2$, is produced (p. 305). Mortar is formed by mixing slaked lime and sand with water to the consistency of a paste. Mortar, laid between the stones or bricks of a building, hardens, and binds the stones together; during the hardening process carbon dioxide is absorbed from the air, and calcium carbonate is formed.

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{carbon dioxide}}{CO_2} = \underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{water.}}{H_2O.}$$

We notice that water is formed in this reaction. Mortar does not become thoroughly dry—does not stop exuding water—until the whole of the calcium hydroxide in it has been changed to calcium carbonate. Remembering that the air contains only ·03 per cent. of carbon dioxide (by volume), we can understand why the walls of a new building take such a long time to become dry. The drying process may be hastened by burning coke in the rooms of a newly built house while the doors and windows are closed. The air of the rooms becomes charged with carbon dioxide, and the conversion of the calcium hydroxide in the mortar into calcium carbonate proceeds more rapidly.

As carbon dioxide is necessary for the hardening of mortar, ordinary mortar does not harden under water, because there is very little carbon dioxide in water. In making mortar that will harden under water—such mortars are called *hydraulic mortars*, or *cements*—it is necessary to burn a mixture of limestone with sand, and clay, which is a silicate of aluminium (see under *aluminium*). If such a mixture is burnt, and then ground into fine powder, and mixed with water, it hardens under water; calcium silicate and calcium aluminate (see forward, p. 327) are gradually formed, and the formation of these compounds produces a hard mass. Carbon dioxide is not required for the hardening of such a mixture.

Calcium chloride, $CaCl_2$, is obtained by dissolving calcium hydroxide (slaked lime) in hydrochloric acid, and evaporating the solution to dryness. The salt is thus obtained as a white solid, suitable for use as a drying agent. We know that when gases are passed over this salt they are robbed of any water that may be mixed with them (p. 138).

$$Ca(OH)_2 + 2HCl = CaCl_2 + 2H_2O.$$

Calcium hydroxide + hydrochloric acid = calcium chloride + water.

Chloride of lime is quite a different substance from calcium chloride. It is prepared by leading chlorine gas over calcium hydroxide, after the manner described on pp. 49 and 232, where we became acquainted with the composition of this substance.

An aqueous solution of chloride of lime bleaches slowly. But the full bleaching effect of such a solution is only obtained when acid is added to it. The acid decomposes the substance, and sets free the chlorine that was used in the preparation of the chloride of lime, and this chlorine bleaches (compare p. 108). If hydrochloric acid is used, the reaction that occurs may be expressed thus :—

$$Ca(OCl)_2 + 4HCl = 4Cl + CaCl_2 + 2H_2O.$$

Calcium hypochlorite + hydrochloric acid = chlorine + calcium chloride + water.

Chloride of lime contains calcium chloride, $CaCl_2$, besides calcium hypochlorite, $Ca(OCl)_2$. The hydrochloric acid reacts with the latter compound only.

Calcium sulphate, $CaSO_4$, occurs native. When this compound is found without water of crystallisation, it is called *anhydrite*; generally, however, it occurs with two molecules of water of crystallisation, and is called *gypsum*, or *alabaster* when it has a peculiarly fine texture and a beautiful surface. When gypsum is heated slightly above 100° C. [212° F.], it loses its water of crystallisation. If this burnt gypsum is mixed with water to the consistency of a paste, it re-combines with two molecules of that compound. The paste may easily be made to fill a mould completely; it hardens rather rapidly, re-forming crystalline gypsum. This process is much used for making casts, etc. [calcium sulphate used for such purposes is generally called "plaster of Paris"].

If gypsum is too strongly heated, it will not re-combine with water; it is said to be "overburnt." Such gypsum is, of course, useless for making casts.

We must now glance at the salt *calcium silicate.* This compound is of no great importance in itself; but when it is melted with certain other silicates, *glass* is produced, which is an exceedingly unchangeable substance. Chemically considered, glass is a double silicate; ordinary glass generally consists of calcium silicate and sodium silicate, because these are the cheapest materials from which glass can be made.

Glass is not made by mixing these two silicates and melting the mixture; the materials used are sand (which is more or less pure silica, SiO_2), calcium carbonate, and sodium carbonate ("soda"). These materials are mixed and heated till the mixture melts. The silica, which is non-volatile at high temperatures, drives out the carbonic anhydride of the two carbonates when the mixture is strongly heated in a furnace, and, combining with the calcium and the sodium, forms calcium silicate and sodium silicate. The substance we call glass is thus formed in the furnace directly from the materials placed therein.

Sodium sulphate, which is cheaper than "soda," is much used in glass-making, instead of sodium carbonate. If this salt is employed, it is necessary to add carbon to the mixture in the furnace. The reactions proceed as follows. The carbon reduces the sodium sulphate to sodium sulphite, and is itself oxidised to carbon monoxide gas, which passes off.

$$Na_2SO_4 + C = Na_2SO_3 + CO.$$

Sodium sulphate + carbon = sodium sulphite + carbon monoxide gas.

The silica then reacts with the sodium sulphite; sodium silicate is produced, while sulphur dioxide (which is a gas, see p. 149) escapes from the furnace. Although a sulphur compound (sodium sulphate) was put into the furnace, the glass contains no sulphur, nor does it contain any of the carbon that was added to reduce the sodium sulphate to sulphite.

If potassium carbonate is used in place of sodium carbonate in glass-making, a double silicate of calcium and potassium is produced. Such *potash glass* is much less easily melted than *soda glass*; it is used for special purposes by chemists and glass-cutters.

Lead glass is obtained by melting mixtures of lead oxide and sodium carbonate with silica. This glass is a double silicate of lead and calcium; it is very lustrous when cut, and is sometimes used for making artificial precious stones.

MAGNESIUM.

Magnesium is a member of the group of metals beryllium, magnesium, zinc, cadmium. *Beryllium* is one of the rare elements; its most commonly occurring compound is *beryl*, which is a double silicate of beryllium and aluminium. If this compound is coloured green by the presence of a very little oxide of chromium, it forms the precious stone called *emerald*. *Zinc* and *cadmium*, which belong to the same group as magnesium, are heavy metals, so that magnesium forms a kind of stepping stone from the heavy to the light metals.

Magnesium compounds are found very abundantly in nature; they are generally associated with compounds of calcium. Magnesium carbonate is called *magnesite* by mineralogists. Various ranges of mountains are formed of *dolomite*, which is a double carbonate of magnesium and calcium. Almost all naturally occurring waters contain compounds of magnesium, besides compounds of calcium. Magnesium phosphate is found, along with calcium phosphate, in the bones of all animals.

Magnesium is obtained, like the other light metals, by the electrolysis of its chloride; the electric current decomposes that compound into magnesium and chlorine. Magnesium is a silver-white, lustrous metal; its specific gravity is only 1·7. The metal is easily set on fire: in burning it emits extremely white light; for this reason magnesium powder is used for taking instantaneous photographs in darkened rooms. As magnesium does not react with cold water, it may be kept under water, unlike sodium and potassium. [Hot magnesium, however, decomposes steam, forming magnesium oxide and hydrogen.]

Magnesium oxide, MgO, may be obtained by strongly heating magnesium carbonate, as calcium oxide is obtained by strongly heating calcium carbonate.

$$MgCO_3 = MgO + CO_2.$$
Magnesium carbonate = magnesium oxide + carbon dioxide.

$$CaCO_3 = CaO + CO_2.$$
Calcium carbonate = calcium oxide + carbon dioxide.

Magnesium oxide is generally called *magnesia*, a name which has come down from former times; in pharmacy it is known as *magnesia usta* (or burnt magnesia, from the method of its preparation). If magnesium carbonate is not "overburnt," the oxide that is formed combines with water, just as calcium oxide does, and forms magnesium hydroxide.

$$MgO + H_2O = Mg(OH)_2.$$
Magnesium oxide + water = magnesium hydroxide.

Large quantities of *magnesium chloride*, $MgCl_2$, are found in the Stassfurt deposits, along with calcium chloride (compare p. 24). *Magnesium sulphate* has long been known under the name of *bitter salt*, because of its bitter taste. [In this country it is often called *Epsom salts*.] It is found in many waters; at Stassfurt it occurs in large quantities. A great number of *magnesium silicates* is known. *Talc* and *meerschaum* are silicates of magnesium; *asbestos*, which is used for its fire-resisting property, is a double silicate of magnesium and calcium.

ALUMINIUM.

The last metal we shall consider is aluminium. *Silicates of aluminium* are found in the earth in vast quantities, forming the various kinds of *clay*. The impurer clays—those which contain iron and sand—are used for making bricks and pottery; better varieties are employed in the manufacture of stoneware and majolica-ware; and the purest clays are used in making porcelain.*

Compounds of aluminium are evidently very widely distributed; but it is only in comparatively recent times that the metal has been prepared. Of course, it has long been possible to prepare silica and aluminium oxide from clay—that is, from aluminium silicate. But no method was found for decomposing aluminium oxide (compare what was said regarding calcium oxide on p. 300).

Wöhler isolated aluminium in 1827, by heating the chloride of the metal with sodium.

$$\underset{\text{Aluminium chloride}}{AlCl_3} + \underset{\text{sodium}}{3Na} = \underset{\text{aluminium}}{Al} + \underset{\text{sodium chloride.}}{3NaCl.}$$

This method is not suited for the cheap production of aluminium, because the preparation of anhydrous aluminium chloride is a troublesome affair. There would be no difficulty in preparing this chloride could it be made by a method similar to those whereby

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* More details concerning these various wares will be found in *Chemistry in Daily Life*, pp. 235-243 (2nd Ed.).

we prepared sodium chloride and calcium chloride—that is to say, by dissolving the oxide or hydroxide of the metal in hydrochloric acid, evaporating, and crystallising. It is easy to obtain aluminium oxide; the mineral *bauxite* contains this oxide [and ferric oxide]. If aluminium oxide is dissolved in hydrochloric acid, aluminium chloride is formed, as one would expect.

$$Al_2O_3 + 6HCl = 2AlCl_3 + 3H_2O.$$

Aluminium oxide + hydrochloric acid = aluminium chloride + water.

But when the solution is evaporated, the aluminium chloride and the water react to re-form aluminium oxide and hydrochloric acid, so that anhydrous chloride of aluminium cannot be obtained by this method.

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl.$$

Aluminium chloride + water = aluminium oxide + hydrochloric acid.

In order to obtain anhydrous aluminium chloride, chlorine gas is passed over a mixture of aluminium oxide and carbon (charcoal) while the mixture is kept red hot.

$$Al_2O_3 + 3C + 6Cl = 2AlCl_3 + 3CO.$$

Aluminium oxide + carbon + chlorine = aluminium chloride + carbon monoxide gas.

Aluminium oxide is not reduced by carbon, even at the highest attainable temperature; if it were reduced, this would be the most convenient method of preparing aluminium (as lead is obtained by heating its oxide with carbon). But when chlorine is passed over a strongly heated mixture of aluminium oxide and carbon, the tendency of aluminium to combine with chlorine is added to the striving of the carbon to remove oxygen from the oxide: the result of this double attraction is the combination of the carbon with the oxygen of the aluminium oxide to form carbon monoxide, and the combination of the chlorine with the aluminium to form aluminium chloride. As all the materials are dry and are raised to a high temperature, the chloride of aluminium that is produced is anhydrous. When this salt is heated with sodium, in the manner practised seventy years ago, metallic aluminium is produced.

We know that sodium can be obtained electrolytically (p. 301.) Instead of causing sodium to react with anhydrous aluminium chloride, which is costly to prepare, aluminium is prepared to-day by a direct electrolytic method, similar to that whereby sodium can be obtained.

If aluminium oxide could be melted, it would only be necessary to pass an electric current through the melted substance in order to obtain aluminium; oxygen would also be formed, but that, being a gas, would pass off. This process cannot be applied directly, because aluminium oxide does not melt at the highest attainable temperature. But it is possible to produce a fusible substance by mixing aluminium oxide with fluorspar (calcium fluoride, see p. 76) and similar materials. This mixture, if properly made, melts at the temperature of the electric furnace; and at the same time the aluminium oxide is separated, by the electric current which flows through the furnace, into aluminium and oxygen. (For a description and representation of the electric furnace, see p. 275).

It is by the application of this method that aluminium has been produced at a moderate cost in recent years. The hopes that aluminium would take the place of certain other metals, because of its low specific gravity, have not been realised so fully as was anticipated. The want of hardness and rigidity of the metal necessitates the use of comparatively large quantities of it, so that what might be gained in lightness is more than counterbalanced in other ways.

We learnt something of the *alums*, which are compounds of aluminium (the name of the metal being derived from that of the compound), when we were considering the double salts. The alum which has been known for the longest time is potash alum—potassium aluminium sulphate, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$ (see p. 160).

Alumstone is found in certain parts of the earth—near Rome, for example; if this mineral is heated, and then lixiviated with hot water, alum crystallises from the solution as it cools. This is the oldest method for making alum; the process is easily conducted, and, as alum crystallises very readily, there is no difficulty in purifying the product. Alum has been used in dyeing for a very long time. The goods are soaked in an *alum bath*, and the alumina in the alum causes the colour to be held fast in the fibres of the fabric. Most colours show no tendency to adhere to the fibres of textile fabrics; the colours can be washed out by water. But if the fabric is dipped in a solution containing alumina, that compound is deposited in the fibres; and when the fabric is then immersed in a solution of a colouring substance, the colour enters into union with the alumina, and is so firmly held that it cannot be removed by washing with water.

It should be remarked that, although alumina is the most important *mordant*, it is by no means the only one in use. The action of all mordants is similar to that of alumina.

Alum is manufactured to-day, on the large scale, by other methods. As alum is valuable only because of the aluminium compound it contains, and the potassium sulphate in it is unnecessary and increases its cost, pure aluminium sulphate is prepared (and the price is not great, as sulphuric acid is so cheap) and used as a substitute for alum. To prepare this salt, a silicate of aluminium (see p. 323), which is found native in a state of purity, is heated with sulphuric acid; sulphate of aluminium is formed, and silica remains undissolved. The mixture is then treated with hot water: aluminium sulphate dissolves, and silica remains; the liquid is filtered, and evaporated to dryness.

There are many other salts of aluminium, but most of them are of no special importance for our purposes. We must, however, say something regarding *calcium aluminate*, which we mentioned when considering cement (see p. 317). We know that alumina is a very weak base; for instance, when a solution of the oxide in hydrochloric acid is evaporated, the aluminium chloride in the solution is decomposed. If all bases are to be looked on as hydroxyl compounds (compare

p. 203), we must think of aluminium oxide as combining with water and forming the base $Al_2O_3 . H_2O$, or $Al_2O_2(OH)_2$. This hydroxide reacts with strong bases as a weak acid. (Tin dioxide behaves similarly; see p. 300.) If we suppose that the two hydrogen atoms in this hydroxide are replaced by an atom of calcium (which is a divalent element), we obtain the compound Al_2O_4Ca. Such compounds are called *aluminates*. This calcium aluminate is found in cement, after that is treated with water, and, along with calcium silicate, causes the hardening of the cement.

The precious stone *chrysoberyl* is composed of *beryllium aluminate*, Al_2O_4Be. *Sodium aluminate*, $Al_2O_4Na_2$, and *potassium aluminate*, $Al_2O_4K_2$, are also known; the formulæ of these salts are generally halved, and written AlO_2Na and AlO_2K respectively.

THE SYSTEMATIC ARRANGEMENT OF THE ELEMENTS.

We have now become acquainted with the principal elements, and their chemical behaviour in broad outline. The general conclusions and the theories we deduced from that survey led to a system, an arrangement, of all the material things around us considered from the chemical point of view. What a wonderful order was introduced when the facts were regarded in the light of the theory of atoms and molecules!

We must now inquire, in conclusion, whether it is necessary to suppose that the elements are particular kinds of matter, each quite distinct from the others. We have found that there are resemblances between some of the elements; we noticed certain groups, each of four similar elements: we recall chlorine, bromine, iodine, and fluorine; and oxygen, sulphur, selenion, and tellurium.

The question we have suggested is so natural that it must have engaged the attention of chemists long ago. In the year 1826 Prout suggested that hydrogen is the foundation of all the elements; that the others are only condensed hydrogen, and have been formed by the coalescence of atoms of hydrogen to produce larger groups of atoms. But it was made evident in the sixties of the nineteenth century that the hypothesis of Prout was not in keeping with facts, however simple it might seem when it was not inquired into too narrowly. If that hypothesis was correct, the atomic weights of all the elements must be whole numbers, multiples of the atomic weight of hydrogen, because we are bound to regard the atoms of hydrogen as indivisible. But, by using extremely fine methods and delicate balances, it was shown to be impossible to express the atomic weights of all elements by whole multiples of the atomic weight of hydrogen taken as unity. The atomic weight of chlorine, for instance, is 35·5, that of silver is 107·9, and so on.

After the abandonment of Prout's hypothesis, the question of the interdependence of the elements remained at rest for some time; it was, however, again approached from different sides almost simultaneously, and it has at last found its final [?] expression in the table of Mendelejeff. That table appears on pp. 338 and 339. Both the full names and the symbols of the elements are given, as the latter render easier a general survey of the arrangement, and because the symbols and the names of many elements have not been given in this book, except in the tables on pp. 22 and 88, and there are many who are not familiar with all the elementary symbols.

This table is drawn up on what seems the simplest principle. As we see, the elements are arranged one after the other in the order of the increasing values of their atomic weights. It must not be forgotten that we do not yet know all the elements. Hence it was necessary to leave spaces for elements yet to be discovered, and to know exactly where such spaces should be left if the continuity of the system was to be brought into proper distinctness.

Considering this arrangement of the elements in the order of their atomic weights as a whole, we notice, following the seventh member of a series, an eighth element, which therefore begins a new series, and has a marked similarity with the first member of the series which precedes that whereof the eighth element is the first member. Newlands had remarked this before Mendelejeff; and this circumstance led him to speak of the *law of octaves* of the elements, an elegant but not particularly helpful expression.

Hydrogen does not fit well into the system; we must assign an exceptional position to this element. The same thing must be said of helium, an element recently discovered and not yet sufficiently examined. (We have already [p. 136] laid stress on the peculiar position of this element). Taking series 2 and 3, it is certain that the character of the elements therein changes regularly and gradually as their atomic weights increase, and also that the character of these elements changes periodically—that is to say, it rises and falls in much the same way in the two series, so that corresponding members of these series are analogous, and their chemical behaviours are similar. For instance, lithium is very like sodium; both are light metals, both are monovalent, and so on. We have already considered in detail the marked similarity between carbon and silicon (p. 284); both are tetravalent. Not less marked is the likeness between oxygen and sulphur; both are divalent, etc. Because of their equal valencies, the corresponding members of these two series produce compounds of the same form, as is indicated by the formulæ of oxides placed at the heads of the several groups. This similarity of properties of the elements of the several groups is certainly remarkable, for the table is arranged solely on the basis of the atomic weights of the elements, and not, for instance, in accordance with their valencies. Nevertheless, the elements fall into their proper positions as regards their valencies. One would not suppose that atomic weight is connected with valency; but the table shows that such a connection exists.

One circumstance is of special importance: when the oxides and hydrides are considered (the formulæ of these compounds are placed at the heads of the several groups in the table), such regularities are noticed in the forms of the compounds, in many series, in passing from one element to the next in the series, that it is necessary to conclude that such regular series are complete—that all the elements belonging to them are already known. The seven elements of the third series, for instance, form the following oxides:—

Na_2O	$Mg_2O_2(MgO)$	Al_2O_3	$Si_2O_4(SiO_2)$	P_2O_5	$S_2O_6(SO_3)$	$(?Cl_2O_7)$
Sodium	**Magnesium**	**Aluminium**	**Silicon**	**Phosphorus**	**Sulphur**	**(?Chlorine**
oxide.	**oxide.**	**oxide.**	**oxide.**	**oxide.**	**oxide.**	**oxide.)**

We see that the quantity of oxygen in these oxides increases regularly in passing from the first to the seventh member of the series.* The four last members of this series form the following hydrogen compounds:—

SiH_4	PH_3	SH_2	ClH
Silicon hydride.	Phosphorus hydride.	Sulphur hydride.	Chlorine hydride.

If we inquire into the chemical properties of these four hydrides, we find that chlorine hydride is a strong acid, and is not readily decomposed by heat; that sulphur hydride is a very weak acid, which is decomposed at a red heat; that phosphorus hydride has no acidic characters, but is decomposed at a lower temperature than sulphur hydride; and that silicon hydride is not acidic, and is easily separated by heat into silicon and hydrogen.

The elements in the several series exhibit a regular continuity, not only as regards the forms of certain compounds, but in all their chemical and physical properties. The metals come towards the beginnings of the series, and the non-metals towards the ends; for instance, the third series begins with sodium and ends with chlorine, and copper and bromine are at the beginning and the end respectively of the fifth series. As an example of regularity in physical properties, we may take the specific gravities of the elements in the seventh series:—

Specific gravity .	10·5	8·6	7·4	7·2	6·7	6·2	4·9
Name of Element.	Silver.	Cadmium.	Indium.	Tin.	Antimony.	Tellurium.	Iodine.

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* I have bracketed chlorine oxide, Cl_2O_7, and put a query before it, because this oxide has not yet been isolated with certainty, although the corresponding acid ($H_2Cl_2O_8$) is known. [Tr.]

A careful consideration of the table shows that, when the elements are arranged in periods of seven, there is always a marked difference between the last member of the series with even numbers and the first member of the odd-numbered series—between manganese and copper, for instance. Moreover, all those elements whose atomic weights and properties prevent their being placed in the periods of seven elements—these are called *short periods*—are found between the last members of the series with even numbers and the first members of the series with odd numbers. For instance, the three elements iron, nickel, and cobalt are found at the end of the fourth series—that is, between manganese and copper—and ruthenium, rhodium, and palladium come at the end of the sixth series. When we take these elements into account, we obtain the *long periods* of seventeen elements each [for instance, the long period beginning with potassium and ending with bromine, and the other long period beginning with rubidium and ending with iodine]. The similarities between the corresponding members of these long periods are greater than those between the corresponding members of the short periods.* Potassium, rubidium, and cæsium ought to be very much alike; on p. 315 we learnt that these three elements are very similar. The table indicates that close resemblances should exist between sulphur, selenion, and tellurium, and between chlorine, bromine, and iodine; we know that the elements in each of these triplets are very closely allied.

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* It is easy to overlook the arrangements of the long periods when the table is inspected.

The elements in the eighth group, which seems to stand somewhat apart, show strongly marked similarities; they are all exceedingly infusible, and the only elements which form oxides of the form RO_4 belong to this group.

We have seen that conclusions can be drawn regarding certain properties of elements from the positions occupied by these elements in the table. Hence it is possible in this way to declare the properties of an element which has not been isolated; for these properties must correspond, on the whole, with those of the element which is separated from it by a long period of seventeen members. Mendelejeff established the possibility of doing this. The names of three elements are printed in the table in heavy type; these three elements have been isolated since the publication of Mendelejeff's memoir in 1869. Mendelejeff applied his table in this way, and in his first memoir gave a detailed account of the properties of elements which were then unknown. As it would have been somewhat hazardous to have given names to unknown elements, which might perhaps never be discovered, as they might not be found anywhere on the earth's surface, Mendelejeff designated his unknown elements by the names of those to which they ought to show the closest analogies, placing the Sanscrit prefixes *eka* and *dui* before the names of the analogues of the undiscovered elements. The element whose properties he announced in the greatest detail was that which is placed in the fifth series and the third group, and was called by him *eka-aluminium*. In the year 1875 Lecoq de Boisbaudran discovered a new element, which he named *gallium*. This element was obtained from a specimen of zinc blende; and as the mineral contained only very small traces of the new element, the first accounts of it given by its discoverer were not very exact. Mendelejeff, however, at once recognised that the new element was his eka-aluminium. Thereupon he, living in St. Petersburg, described very accurately the properties of this element, which had been in the hands of only one chemist, in Paris. As the element followed zinc in the table, Mendelejeff assigned to its atomic weight the approximate value of 68. As aluminium oxide has the formula Al_2O_3 (p. 324), gallium oxide must be Ga_2O_3; and as the atom of gallium must be trivalent, since the element belongs to Group III., the formula of its chloride must be Ga_2Cl_6 (or $GaCl_3$). As this chloride must be composed of 68 parts by weight of gallium (the atomic weight of the element being 68), and $3 \times 35{\cdot}5 = 106{\cdot}5$ parts of chlorine, the chloride must contain 39 per cent. of gallium and 61 per cent. of chlorine. In this way Mendelejeff was able to announce the quantitative composition of a compound of an element before that compound had been seen by anyone.

From the position of the new element in the table, it follows that sulphuretted hydrogen must precipitate sulphide of gallium from solutions of salts of the metal, and also that gallium will not be oxidised by exposure to the air. Mendelejeff also predicted the specific gravity of this element; he gave the value 5·9, which is almost exactly the true value. The fuller examination of gallium, after it had been obtained in larger quantities, confirmed the accuracy of everything that had been predicted by Mendelejeff with regard to its physical and chemical properties.

The two elements *scandium* and *germanium* were discovered at a later time. They also were found to fit into the places left for them in his table by Mendelejeff; and the trustworthiness of that arrangement was thus confirmed.

The sure prediction of the properties of undiscovered elements, and the foreknowledge of the *quantitative* compositions of their compounds when none of these had been actually prepared, will always rank as one of the most brilliant pieces of work in the domain of chemistry; for it shows that trustworthy conclusions of all kinds, in chemical matters, may be drawn from those hypotheses regarding the constitution of matter which are made use of in chemistry. In many cases it was only after several years that an opportunity occurred for demonstrating, by the use of the balance, and therefore in a perfectly certain manner, the justness of conclusions that had been drawn from these hypotheses. The composition of gallium chloride, which we have considered, is a case in point.

SYSTEMATIC ARRANGEMENT OF

General formulæ of (i) hydrogen compounds. (ii) salt-forming oxides richest in oxygen.	*Group I.* R_2O*	*Group II.* R_2O_2	*Group III.* R_2O_3	*Group IV.* RH_4 R_2O_4
Series 1.	Hydrogen = 1	… …	… …	… …
,, 2.	Lithium = 7	Beryllium = 9	Boron = 11	Carbon = 12
,, 3.	Sodium = 23	Magnesium = 24	Aluminium = 27	Silicon = 28
,, 4.	Potassium = 39	Calcium = 40	**Scandium = 44**	Titanium = 48
,, 5.	Copper = 63	Zinc = 65	**Gallium = 70**	**Germanium = 72**
,, 6.	Rubidium = 85	Strontium = 87	Yttrium = 89	Zirconium = 90
,, 7.	Silver = 108	Cadmium = 112	Indium = 114	Tin = 119
,, 8.	Cæsium = 133	Barium = 137	Lanthanum = 138	Cerium = 139
,, 9.	… …	… …	… …	… …
,, 10.	… …	… …	Ytterbium = 173	… …
,, 11.	Gold = 197	Mercury = 200	Thallium = 204	Lead = 207
,, 12.	… …	… …	… …	Thorium = 232

Using the symbols in

Series 1.	H = 1	… …	… …	… …
,, 2.	Li = 7	Be = 9	B = 11	C = 12
,, 3.	Na = 23	Mg = 24	Al = 27	Si = 28
,, 4.	K = 39	Ca = 40	Sc = 44	Ti = 48
,, 5.	Cu = 63	Zn = 65	Ga = 70	Ge = 72
,, 6.	Rb = 85	Sr = 87	Yt = 89	Zr = 90
,, 7.	Ag = 108	Cd = 112	In = 114	Sn = 119
,, 8.	Cs = 133	Ba = 137	La = 138	Ce = 139
,, 9.	… …	… …	… …	… …
,, 10.	… …	… …	Yb = 173	… …
,, 11.	Au = 197	Hg = 200	Tl = 204	Pb = 207
,, 12.	… …	… …	… …	Th = 232

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* R = one atom of any element in the group.

THE ELEMENTS (MENDELEJEFF).

General formulæ of (i) hydrogen compounds, (ii) salt-forming oxides richest in oxygen.	*Group V.* RH_3 R_2O_5	*Group VI.* RH_2 R_2O_6	*Group VII.* RH R_2O_7	*Group VIII.* R_2O_8
Series 1.	Helium = 4	... ...	... ...	... ...
,, 2.	Nitrogen = 14	Oxygen = 16	Fluorine = 19	... ...
,, 3.	Phosphorus = 31	Sulphur = 32	Chlorine = 35·5	
,, 4.	Vanadium = 51	Chromium = 52	Manganese = 55	Iron = 56 Nickel = 58·5 Cobalt = 59
,, 5.	Arsenic = 75	Selenion = 79	Bromine = 80	
,, 6.	Niobium = 94	Molybdenum = 96	... ...	Ruthenium = 101 Rhodium = 103 Palladium = 106
,, 7.	Antimony = 120	Tellurium = 126·5	Iodine = 127	
,, 8.	Praseodym. = 140	Neodymium = 144	... ...	... ...
,, 9.	Erbium = 166	... ...	... ...	... ...
,, 10.	Tantalum = 183	Tungsten = 184	... ...	Osmium = 191 Iridium = 193 Platinum = 195
,, 11.	Bismuth = 208	... ...	... ...	
,, 12.	... ...	Uranium = 240	... ...	... ...

place of names.

Series 1.	He = 4	... ...	... ...	... ...
,, 2.	N = 14	O = 16	F = 19	... ...
,, 3.	P = 31	S = 32	Cl = 35·5	... ...
,, 4.	V = 51	Cr = 52	Mn = 55	Fe = 56 Ni = 58·5 Co = 59
,, 5.	As = 75	Se = 79	Br = 80	
,, 6.	Nb = 94	Mo = 96	... ...	Ru = 101 Rh = 103 Pd = 106
,, 7.	Sb = 120	Te = 126·5	I = 127	
,, 8.	Pr = 140	Ne = 144	... ...	
,, 9.	Er = 166	... ...	... ...	
,, 10.	Ta = 183	W = 184	... ...	Os = 191 Ir = 193 Pt = 195
,, 11.	Bi = 208	... ...	... ...	
,, 12.	... ...	U = 240	... ...	... ...

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