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INORGANIC CHEMISTRY

BY

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PREFACE TO THE FIRST EDITION

Of late years the teaching of Chemistry in schools has tended to assume more and more the character of "research work," each pupil "discovering" his own facts (with a little guidance), and also interpreting them in their mutual connections. This method is admittedly of great value in cultivating the pupil's powers of accurate observation and manipulation; but from the point of view of the student who proceeds to a College or University, there to continue the subject as part of a course in Science or Medicine, it leaves something to be desired. In even an elementary University course, the student is suddenly confronted by a bewildering multitude of details, which he must learn from his lecture-notes or a text-book, for now the limited time at his disposal for practical work makes it impossible for him to acquire his material on the leisurely school lines to which he has become accustomed.

This little volume has been written to help in bridging the gap here apparent. In it I have emphasised general principles, which shall enable the student to extend his first-hand laboratory knowledge in various directions, and to connect and correlate apparently isolated facts. No instructions for practical work are given, as any teacher can easily select from the many excellent manuals at his disposal those experiments which best typify the principles referred to.

Although I have written the book throughout from the point of view of modern theory (so that the student on pursuing his studies shall have as little as possible to unlearn), I have studiously placed theoretical matters in the background, for the reason that in my own experience the beginner does not appreciate their proper significance. The school is, in my opinion, no place for "chemical philosophy": that should only come at the end of an elementary University course, when the student has a good grip of the facts and principles, *i.e.* the realities, of Chemistry.

J. W.

November 1901.

PREFACE TO THE ELEVENTH EDITION

THE little book of which this is an enlarged version was first issued in 1901, and has passed through a considerable number of editions. From time to time I have been asked if it might not be possible to widen its scope without sacrifice of simplicity or essential change in the mode of presentation. As my own teaching experience warranted me in considering this step both practicable and advisable, some four years ago I set about recasting the original book, but the revised issue, owing to war conditions, has been delayed until now.

The general and the systematic portions are in the new version less strictly separated than in the old. All the common elements now receive brief systematic treatment, and the theoretical portion has been considerably enlarged. By these changes I trust that the book will become useful to a larger number of elementary students in colleges, without losing its utility for school classes in which the study of Chemistry is now carried much further than when the book was originally written.

J. W.

October 1918.

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INORGANIC CHEMISTRY

CHAPTER I

EXAMPLES OF CHEMICAL ACTION

If a piece of limestone is heated to bright redness, it undergoes a complete change in its properties: it, in fact, ceases to be limestone, and becomes what we call quicklime. The change here produced by the action of heat is a **chemical change**, and one of a comparatively simple character, so that some time may be profitably devoted to its study.

When we say that a substance has been changed into something else, we mean that the properties of the material before and after the change are recognisably different. In some cases of change it is easy to observe the difference in properties. For example, if we put a piece of paper into a flame, the paper burns and chars: from being white coherent paper it becomes a brittle black mass of obviously different properties. On the other hand, there are many cases of change where the difference in properties of the changed and unchanged substances is by no means so easily detected by simple inspection. A piece of quicklime is not unlike the piece of limestone from which it was derived by heating, but if we observe its properties more closely, we find that it must be regarded as an entirely different kind of substance. One important respect in which it differs from limestone is that when treated with a small quantity of water, it becomes warm, cracks, and breaks up into a bulky friable mass. The original limestone exhibits none of this behaviour, being practically unaffected by water. We can use, then, the action of water as a **test** for distinguishing between limestone and quicklime. Chemical tests are in general of this nature: if we cannot tell offhand what a substance is, we try its action with something else, and see how it behaves.

Quicklime is produced from limestone on the large scale in the operation known as **lime-burning**. The operation is conducted in a lime-kiln, which is a kind of furnace of stone or brickwork, the internal cavity being usually conical or egg-shaped. This cavity is filled with alternate layers of fuel (small coal or coke) and limestone, air being admitted at the bottom. When the fuel burns in the air, the limestone is raised to such a temperature that it is converted into quicklime. The quicklime falls as the fuel burns away, and may be raked out through the air-holes, while fresh fuel and limestone are supplied from above, to take its place, the process thus being made to go on continuously.

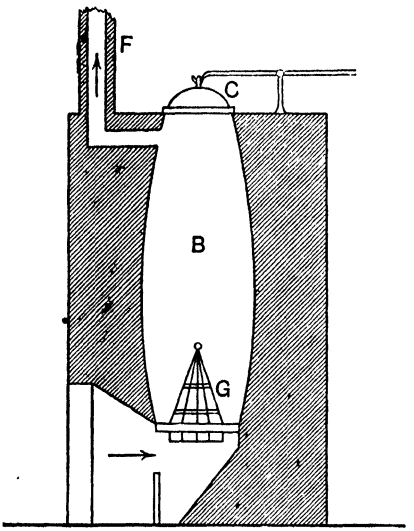


Fig. 1.—Kiln for Lime-Burning.

The body of the kiln *B* is fed with alternate layers of fuel and limestone, introduced at the top by removing the cover *C*. The gases escape by the flue *F*. The conical grating *G* directs the pieces of burnt lime so as to facilitate withdrawal at the bottom.

When limestone is burnt in this way it loses nearly half its weight, only about 11 cwts. of quicklime being obtained from a ton of limestone. It is clear that, to justify this loss of material, and the loss of fuel in producing it, the quicklime must possess some valuable property not possessed by the original limestone. The property in question is the power of being slaked by water. As has already been indicated, quicklime, when brought into contact with a small amount of water (about one-third of its weight), swells and crumbles, the mass becoming hot at the same time. The heat production may be so great that some of the water is converted into steam. The powder obtained from quicklime and water is called **slaked lime**, and its properties are plainly different from those of the substances from which it was produced. It bears no resemblance whatever to water, and differs from the quicklime used in its formation in being unaffected by

further amounts of water. No heat is produced when these substances are brought together, and the slaked lime is merely wetted by the contact, or dissolved away if a very large quantity of water is used. A paste of slaked lime and water is used in the preparation of mortar for building purposes, and it is to this end that limestone is chiefly burnt. The slaking of quicklime for mortar or plaster may be seen during the construction of almost any house, the materials being mixed in large wooden troughs, from which clouds of steam rise as the water is added.

Definite Weights.—If we take a portion of pure limestone, say 100 grams, and subject it in a crucible to a bright red heat, it will speedily begin to lose weight, but the loss of weight will not go on indefinitely. After the weight of the substance has been reduced to 56 grams no further loss occurs, however long the heating may be continued. The limestone has then been entirely converted into quicklime, which is quite unalterable by heat. Now, we shall always find that if we convert a pure limestone into quicklime, 100 parts of the limestone will give 56 parts of quicklime (*i.e.* about 11 cwts. per ton), no matter how the burning may have been conducted. Here, then, we have a definite and fixed proportion between the weight of limestone and the weight of quicklime derived from it; and we shall find that such definite relations by weight are characteristic of all chemical changes.

Should we, however, stop heating before the limestone has lost weight to the full extent—suppose, for example, that the 100 parts have become 78 parts—of what substance does the residue then consist? We have stopped the process when the loss of weight is only one-half the total possible loss—*i.e.* 22 parts instead of 44. Is the substance left behind exactly intermediate in properties between limestone and quicklime? In a certain sense it is, but on closer inquiry we find that the residue is not a single substance at all, but is really a mixture of two substances—namely, unchanged limestone and quicklime. This may be shown in various ways. For example, if we treat the mixture with water, the limestone half will be entirely unaffected, while the quicklime half will be slaked; and the slaked lime so produced may be entirely dissolved away if a sufficient quantity of water is taken.

There is thus really no intermediate step in the change from limestone to quicklime. Any limestone which has undergone alteration has been *completely* changed into quicklime: the rest is limestone with all its original properties. This sharp passage of one substance into another, as distinguished from a gradual transition, is always found in chemical change.

If we inquire as to the reason why limestone loses weight when converted into quicklime, we find it to be a well-known fact that the atmosphere in the immediate neighbourhood of limekilns is dangerous, inducing sleep and even causing death by suffocation. This is due to the presence near the kilns of a heavy vapour given off by the limestone during the burning, and usually called **carbonic acid gas.** If all the carbonic acid gas given off by the limestone on its conversion into quicklime were collected and weighed, its weight would be found to be exactly equal to the loss in weight experienced by the limestone — *i.e.* 44 parts for each 100 parts of the original limestone.

Consider now the slaking of lime. Again we meet with definite weights. The 56 grams of quicklime derived from 100 grams of limestone will only take up 18 grams of water to form dry powdery slaked lime. If we add less than 18 grams of water, the substance obtained is a mixture of quicklime and slaked lime; if we add more than 18 grams, a mixture of slaked lime and water remains — *i.e.* a wet mass or paste instead of the dry powder. There is thus once more a sharp transition of one substance into another of utterly different properties, no intermediate stages being formed.

We may now write the chemical actions involved in the burning and slaking of lime as follows:—

Limestone	gives	Quicklime	and	Carbonic acid gas
100 parts	=	56 parts	+	44 parts

Quicklime	and	Water	give	Slaked Lime
56 parts	+	18 parts	=	74 parts

These instances exemplify the fact that there is no loss of weight in chemical action if all the substances involved in the action are taken account of. The apparent loss of weight in the burning of limestone is due to the carbonic acid gas

being permitted to escape without being weighed. When it too is weighed, the sum of its weight and that of the quicklime is exactly equal to the weight of the limestone taken. Again, the weight of the slaked lime obtained from quicklime and water is exactly equal to the sum of the weights of these substances. Though, therefore, there may be great alterations in the properties of substances after a chemical change, there is no alteration in the total weight. This has been found to be strictly true for every chemical action that has been accurately investigated.

Varieties of the same substance.—There are other substances besides limestone which on heating become converted into quicklime and carbonic acid gas. Such are chalk, white marble, precipitated chalk, and Iceland spar. These substances are easily distinguished from limestone and from each other by even a superficial examination. Chalk is, as a rule, much softer than limestone, marble much harder and capable of acquiring a fine polish; Iceland spar forms perfectly clear transparent crystalline masses; precipitated chalk is a soft white powder. Yet if pure specimens of these bodies are heated, we find that in each case 100 parts of the substance will give 56 parts of quicklime and 44 parts of carbonic acid gas; and the quicklime produced by their calcination will unite with 18 parts of water to give slaked lime of exactly the same properties, whether it is prepared from chalk, marble, Iceland spar, or limestone.

We have here, then, five apparently different substances which behave chemically towards heat in precisely the same manner. These substances are said to be chemically identical, and are spoken of as different varieties of the same **chemical substance.** A greyhound and a bull-dog are very different in superficial appearance, yet they are both classed as varieties of dog, because they answer to certain zoological tests used to define and identify the species dog. In the same way limestone, marble, chalk, etc., are all classed as varieties of the chemical substance **calcium carbonate,** because they answer to certain chemical tests by means of which calcium carbonate may be identified—in particular, because they split up into quicklime and carbonic acid gas in the proportions by weight that have been indicated above.

Chemical Nomenclature and Equations.—Just as zoologists have found it convenient for systematic purposes to give animals names which differ from the common names of those animals—using for example *Canis familiaris* instead of dog—so chemists have devised a systematic nomenclature for substances regarded in the purely chemical aspect, with the result that one and the same thing has very frequently two names, one the common name, the other the systematic chemical name. Thus we have—

Common Name	Systematic Chemical Name
Marble, Chalk, Limestone, etc.	Calcium carbonate
Quicklime	Calcium oxide
Carbonic acid gas	Carbon dioxide
Slaked lime	Calcium hydroxide

The burning of limestone, chalk, or marble, is, then, chemically speaking, one action which may be represented as follows:—

Calcium carbonate	gives	Calcium oxide	and	Carbon dioxide
100 parts	=	56 parts	+	44 parts

Similarly for the slaking of lime we may write—

Calcium oxide	and	Water	give	Calcium hydroxide
56 parts	+	18 parts	=	74 parts

Such brief statements of chemical actions as those just given are called **chemical equations**, the total weights on the two sides being equal. As we shall see later, it is not customary to write chemical equations at length, giving both names and weights as above: chemical formulæ are used instead of the chemical names, and from the formulæ the weights can be calculated.

It should be noted that equations have only validity for *pure* chemical substances. Thus a limestone on complete burning may be found to give more or less than 56 parts of burnt lime for 100 of the original limestone. Such limestone, however, is impure—that is, the calcium carbonate of which the bulk of it consists is mixed with smaller quantities of other substances. The chemical equation in this case only applies to the calcium carbonate part of the impure limestone, nothing being stated as to how the impurities are affected by the burning.

The two chemical actions which we have just considered belong to two different and important types. The process of lime-burning is a **chemical decomposition**, or the splitting up of a substance into two or more others. The process of lime-slaking is a **chemical combination**, or the union of two or more substances to form a single chemical compound. We shall meet in the sequel with many examples of both of these types of chemical action.

CHAPTER II

CONDITIONS OF CHEMICAL ACTION

In the last chapter we saw under what conditions calcium carbonate is decomposed into calcium oxide and carbon dioxide: in order to effect the decomposition, the substance must be raised to a red heat. At the ordinary temperature calcium carbonate, if left to itself, undergoes no change; or, as chemists are accustomed to say, it is under these conditions perfectly *stable*. The high temperature is necessary before any decomposition occurs. This behaviour is very general; most substances which are stable at the ordinary temperature decompose when heated to a sufficiently high temperature. Sugar, for example, chars when heated, and gives off vapours, the decomposition being accompanied by the familiar smell of burnt sugar. Wood, too, if heated by itself, is converted into combustible vapours and charcoal. An instance of decomposition by heat very similar to that of limestone is afforded by slaked lime. If slaked lime be raised to a red heat, it decomposes into quicklime and water according to the equation—

Calcium hydroxide	gives	Calcium oxide	and	Water.
74 parts	=	56 parts	+	18 parts

the water at that temperature being in the form of highly superheated steam. A high temperature then is generally favourable to decomposition.

If we now consider what conditions are favourable to chemical combination, or in general, chemical action between two or more substances, we see in the first instance that the substances must be in **contact** with each other before they can interact at all. So long as they are separate, chemical action between them is impossible. Quicklime and water must be brought together before slaked lime can be produced by their union. It would appear reasonable, therefore, that

if we wish to promote chemical action between two substances, we should bring them into very close contact—*i.e.* mix them as thoroughly as possible. Large pieces of solid substances when brought together have only a very small surface of contact, but if each solid is reduced to a powder, the exposed surface is very great, and when the two powders are mixed, the surface of contact between them is much increased. Thus the charcoal, sulphur, and nitre which are the ingredients of gunpowder, would not form an explosive if mixed together in pieces the size of a pea. The surface of contact between the pieces would not be sufficiently great for that rapid chemical action to take place on which the explosion of gunpowder depends. In the manufacture of gunpowder, each ingredient is ground separately to a fine powder, and the powders are then intimately mixed and caked together by means of a small quantity of water, the cake being afterwards dried and broken up into grains of the requisite size. Each grain thus contains all the ingredients necessary for the rapid chemical action brought about when the gunpowder is fired.

If vigorous action is desired between a solid and a liquid, the solid should be powdered before being brought into contact with the liquid. This may be readily seen by noting the vigour of the action between quicklime and water when the quicklime is finely powdered. Even when the quicklime is in lumps, however, the action is still vigorous, because the quicklime is somewhat porous and soaks up the water into the interior of the lumps.

Solution.—A method which chemists very frequently employ for bringing about the very intimate contact of substances which are ordinarily solid, is to dissolve them in water and then mix the solutions together. In each solution the dissolved substance is distributed quite uniformly through the liquid, so that when the two solutions are mixed together, which can be done very simply and thoroughly by stirring, the dissolved substances are brought into a contact much closer than could generally be obtained by reducing them to a powder and then mixing. When water cannot be used as a solvent, some other liquid, such as alcohol or ether, may be employed; but in the laboratory, as in common life, water is used for the purpose in ninety-nine cases out of a hundred.

Temperature of Reaction.—Some substances act at once when brought into contact. Thus when quicklime and water are placed together, they immediately unite to give slaked lime. On the other hand, some substances which are capable of entering into vigorous chemical action do not affect each other under ordinary conditions, however long they may remain in contact. Thus the nitre, sulphur, and charcoal of gunpowder are absolutely without action on each other until the temperature is raised to a sufficient degree, when the ingredients suddenly react with such violence as to produce an explosion. Coal-gas and air, again, may be mixed at the ordinary temperature without anything occurring, but if a light is applied chemical action may take place with explosive violence. That a high temperature is necessary for the interaction of air and coal-gas may be verified by attempting to light a jet of the gas with a poker heated to dull redness. Notwithstanding the high temperature to which the gas in contact with the poker is raised, it may not ignite; but if the poker is heated more strongly or if a lighted taper is applied, ignition follows, the temperature of ignition being then surpassed.

If such a high temperature is necessary for the ignition of coal-gas, the student may ask: "Why does not the gas go out when the flame which lit it is removed?" The reason is simple. Vigorous chemical action is invariably accompanied by production of heat, and the heat produced by the chemical action of the coal-gas and air is sufficient to keep the temperature far above the ignition-point once the action is started. The case of gunpowder is similar. It is not necessary to heat the whole mass of the powder in order to fire it; if a light is applied to one portion, that is sufficient. The heat given out by the first portion as it explodes serves to raise the temperature of neighbouring portions to the exploding point, and so the explosion is propagated through the mass.

Some actions do not produce sufficient heat to keep themselves going once they are started. Thus a jet of ammonia gas will burn at the flame of a taper so long as the taper is kept at the jet, the heat from the lighted taper being sufficient to raise the mixture of ammonia gas and air to the ignition point. But as soon as the taper is removed, the action ceases, for the burning of the ammonia does not of itself produce

enough heat to keep the temperature of the ammonia and air up to the point at which they interact.

It may be said in general that chemical actions take place more rapidly as the temperature is raised. This circumstance explains the increase in vigour observed in many chemical actions which are at first comparatively slow. When cold water is poured on a lump of quicklime, nothing apparently happens for the first moment; but very soon a little steam makes its appearance, the action gets brisker, the evolution of steam becomes more rapid, and the mass cracks and crumbles to the powder of calcium hydroxide. This increase in vigour is chiefly due to the rise in temperature caused by the interaction of the first portions. The temperature of the neighbouring portions of water and quicklime is raised, with the result that they react much more rapidly than the first portions, and so produce more heat, which increases the rate of reaction of remaining portions, a constant acceleration of the reaction thus going on.

If the temperature at which the quicklime and water are brought into contact is above 100 degrees, the water is in the form of water-vapour or steam, but the action goes on just as before. Should the quicklime and water-vapour, however, be raised to a bright red heat, the action ceases, and no union takes place at all. This is in contradiction to the statement made above, that rise of temperature increases the vigour of chemical action, but a closer consideration shows that this exception is only apparent. We have already seen that calcium hydroxide decomposes at a red heat into calcium oxide and water-vapour. Now this is exactly the reverse of the reaction we have been considering, so that if calcium hydroxide were formed at the high temperature, it would at once be decomposed into the substances from which it was produced. We are, in fact, here dealing with a **reversible action**, the equation of which is—

Calcium oxide	+	Water	$\rightleftharpoons$	Calcium hydroxide
56	+	18	=	74

The oppositely directed arrows used instead of the sign of equality indicate that the action can proceed backwards as well as forwards. The forward action is a combination, the

reverse action a decomposition. Rise of temperature may increase the vigour of both reactions, but it favours the decomposition at the expense of the combination, so that at a bright red heat the direct action is altogether overpowered by the reverse action.

A similar instance of opposed reactions is afforded by the burning of limestone. At a bright red heat the action is one of decomposition, the calcium carbonate splitting up into calcium oxide and carbon dioxide. Carbon dioxide, at a lower temperature, is re-absorbed by calcium oxide with formation of calcium carbonate, so that we have the reversible action—

Calcium carbonate	$\rightleftharpoons$	Calcium oxide	+	Carbon dioxide.
100	=	56	+	44

Rise of temperature favours the decomposition, fall of temperature the recombination.

It must not be supposed that all chemical actions are reversible; indeed, most of the actions that the elementary student of chemistry encounters are irreversible. The charcoal and combustible vapours obtained by heating sugar will not recombine on cooling to reproduce the sugar from which they were formed, nor will the ash and gases from gunpowder which has been fired ever interact to form the original mixture of charcoal, sulphur, and nitre.

CHAPTER III

SOLUTIONS AND SOLUBILITY

IT has just been stated that chemists are in the habit of dissolving solid substances in liquids, especially water, in order to obtain them in a state suited to the production of many chemical actions. It is usually said in this connection that when a substance is dissolved in water, its chemical properties are not greatly changed; but this statement must not be taken too literally, and due allowance must be made for the properties of the water in the solution. For instance, a lump of sugar will burn if a light is applied to it; but if the same lump is dissolved in water we can scarcely expect it to burn then, were it only for the plain reason that the burning sugar would be extinguished by the water. We shall see in the sequel that water profoundly modifies the chemical properties of many other substances, such as nitric and sulphuric acids, and it will be necessary for us to know the properties of aqueous solutions of these substances, as well as those of the pure substances themselves, since the former are often of equal if not greater importance than the latter.

The solvent action of water varies very much with the substance on which it acts. Thus pure water will scarcely dissolve any calcium carbonate, whether in the form of chalk, marble, or limestone, whilst it will readily dissolve large quantities of sugar, salt, or nitre. To ascertain the extent of the action of water on a solid substance, the solid should be finely powdered and shaken up for a long time with the water, in order to get thorough contact between them. After a time (usually several hours) the water will take up no more of the solid, and is said to be **saturated** with it. The saturated solution is then decanted or filtered off from the excess of solid, and the water driven off from the solution at a gentle heat. If the quantity of solution which is evapor-

ated, and the residue which is derived from it, are both weighed, we can state in numbers the extent of the solvent action of the water, or, what is the same thing looked at from another point of view, the **solubility** of the salt in water.

Thus we find that at the ordinary temperature the quantities of water necessary to dissolve one part of substance are as follows:—

Substance	Parts water
Cane sugar	0·5
Salt	3
Saltpetre (nitre)	4
Slaked lime	800
Calcium carbonate	100000

To express the same results in another way, we may say that the following quantities of the various substances are dissolved by 100 parts of water:—

Substance	Solubility in 100 parts of water
Calcium carbonate	0·001
Slaked lime	0·13
Saltpetre (nitre)	25
Salt	36
Cane sugar	200

It is usually in this second way that solubilities are now stated.

From these tables it appears that cane sugar is extremely soluble in water, salt and saltpetre freely or easily soluble, calcium hydroxide sparingly soluble, and calcium carbonate practically insoluble. The solubility in water of a substance such as sulphur is too small to be measured, and it is therefore said to be insoluble in water.

We generally find that warm water dissolves things better than cold water, the difference in solubility being sometimes very great. Thus 100 parts of water at the boiling point (100°) will dissolve 39 parts of salt, and 250 parts of nitre, instead of 36 and 25 parts respectively at the ordinary temperature. The solubility of salt is therefore only slightly increased by the rise of temperature, but the solubility of the saltpetre is ten times as great in water at 100° as in cold water.

The variation of the solubility of substances with change of temperature is conveniently represented by means of a **solubility diagram** (fig. 2). Temperatures are measured along horizontal lines, and the amounts of substance dissolved along vertical lines. The solubility of the substance

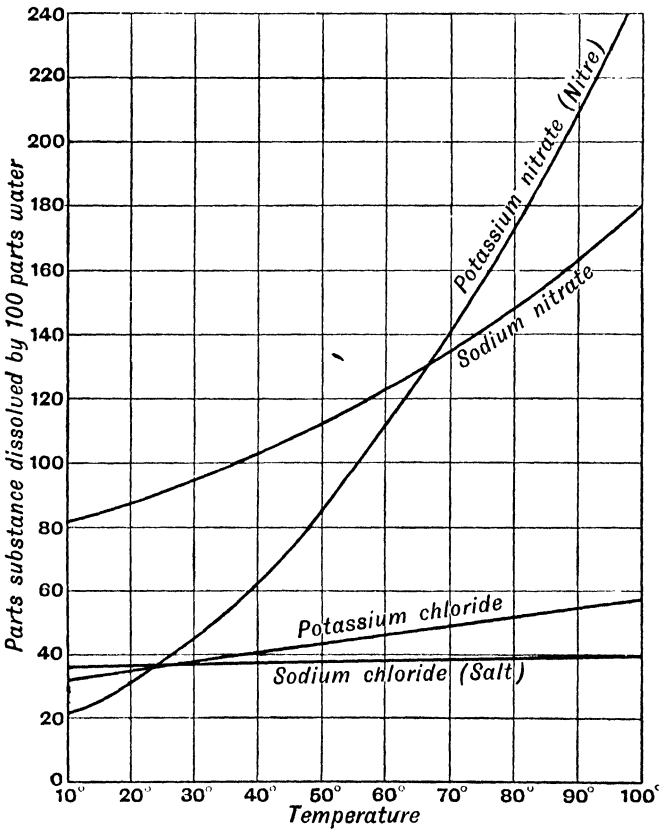


Fig. 2.—Diagram showing Variations of Solubility with Temperature.

at any one temperature is thus represented by a point in the diagram, the position of which indicates on the horizontal scale the particular temperature considered, and on the vertical scale the number of parts of substance dissolved by

100 parts of water. When these points for all the different temperatures are joined up, a **solubility curve** is obtained. Each of the substances considered in the diagram has its own solubility curve. The more nearly horizontal the curve runs (*e.g.* salt), the smaller is the variation with the temperature; the steeper the curve is (*e.g.* nitre), the greater is the variation with temperature. When the curves for two different substances cut, it shows the substances are equally soluble at the temperature represented by the point of intersection. Thus salt and nitre are shown by the diagram to have the same solubility (namely, 36 parts in 100 of water) at 24°.

Occasionally it happens that the solubility of a substance is less in hot than in cold water. The solubility of calcium hydroxide in boiling water is 0.06—*i.e.* only half the solubility in cold water. This diminution of solubility with rise of temperature can be easily shown experimentally as follows:—If the clear saturated solution of calcium hydroxide, commonly known as "lime water," is heated in a glass vessel to the boiling point, it is seen to become turbid, owing to separation of solid calcium hydroxide. The water at 100° being able to hold only half as much calcium hydroxide in solution as it could at the ordinary temperature, deposits the other half in the form of white solid particles which render the solution milky.

Since nitre is ten times as soluble at 100° as it is at the ordinary temperature of 15°, a solution saturated at the boiling point and then cooled will part with nine-tenths of the nitre it held dissolved. The nitre falls out from the solution if the cooling is rapid in the form of gritty particles technically known as "nitre meal." These particles are in reality small crystals: and if the hot solution is allowed to cool very slowly, large crystals of nitre may be obtained.

Nearly all chemical substances are crystalline, or may be made to assume the **crystalline state**. Crystalline substances, when properly investigated, are found to possess a definite form or shape of their own: non-crystalline or amorphous substances are formless. Sugar is an example of a substance which crystallises well, and nearly all the sugar used nowadays is in the form of small crystals. Clusters of large crystals of sugar grown together may be seen in sugar-candy. If a piece of sugar-candy is examined, it will at once be evident that the

same shape is repeated over and over again, and that the surfaces of the separate crystals are plane. This is characteristic: the faces of all perfect crystals are perfect planes. Frequently crystals are so small that the eye cannot tell if they possess any regular shape or if they are bounded by plane surfaces. In such a case recourse may be had to the reflection of light. Plane surfaces reflect light better than irregular surfaces, so that the small crystal faces may be made to appear as bright specks when they are held in the proper position with respect to the eye and a source of light. The small crystals of which a piece of lump sugar consists may easily be detected in this way if the lump is held so that the light from a window falls upon it and is reflected upwards to the eye.

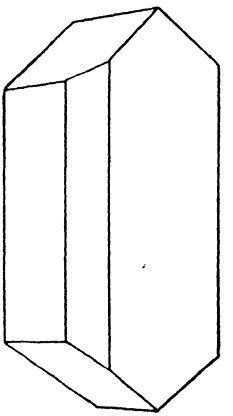


Fig. 3.
Crystal of Cane-Sugar.

Solids may almost always be made to crystallise either by fusing them and allowing them to solidify, or by dissolving them in some solvent and letting them separate from solution. If the separation is rapid, as in the above instance of nitre meal, the crystals are invariably small. When large crystals are desired, the separation of the substance must be allowed to go on slowly without much mechanical disturbance of the solution. This may be effected either by very slow cooling, or by letting the solvent evaporate slowly from the saturated solution. Good crystals may be obtained by allowing a cold solution of photographic hypo (sodium thiosulphate) to stand in an open vessel, the solvent being gradually lost by evaporation.

The process of crystallisation from solution in this way is a very important one, as it enables us to remove the impurities from impure substances. For example, if we grind together some alum and a little blue vitriol (copper sulphate) in a mortar, the mechanical separation of the two substances in the mixture is practically impossible. We can remove the copper sulphate, however, and obtain crystals of pure alum, by dissolving the mixture in hot water and allowing the solution to crystallise. The alum crystallises out in perfectly

colourless crystals, which are quite free from copper sulphate. Even if copper sulphate crystallises out at the same time as the alum, it will form separate crystals, which if the crystallisation takes place with the necessary slowness, may reach such a size as to be easily removed from the alum crystals by hand.

Some substances, when they separate from aqueous solution, do so as crystals which contain a definite amount of water. Thus, if we dissolve pure copper sulphate in water and allow the solution to crystallise, the substance which separates is not entirely copper sulphate, but a substance (blue vitriol) which contains copper sulphate and water in the proportions of 159 parts of the former to 90 parts of the latter. The water in such a case has none of the properties of liquid water, and is called **water of crystallisation.**

CHAPTER IV

SYMBOLS—FORMULÆ—EQUATIONS

In the splitting up of calcium carbonate by heat we have seen an instance of chemical decomposition. Similar decomposition is possible for most chemical substances, by heat or some other agency, and the question arises: Is there any limit to chemical decomposition? Are all substances decomposable? As an answer to these questions chemists have found by experiment that there are some seventy substances which have resisted all attempts to decompose them. These are called simple substances or **elements.** All other substances, which are known as **compounds,** are made up of these elements, and can be decomposed either directly or indirectly.

We can most readily express the composition of any chemical compound by stating of what elements it consists, and the quantities of these elements that are combined together to form the compound. Now, it has been found that without exception pure chemical substances have an invariable composition—*i.e.* they are made up of the same elements

combined together in the same proportions, no matter what the source of the compound may have been. This regularity is known as the **Law of Fixed Proportions.** For example, calcium carbonate, whether it is artificially prepared, or has been found in nature as marble, Iceland spar, etc., always contains the elements calcium, carbon, and oxygen; and its invariable composition in 100 parts is calcium 40 parts, carbon 12 parts, oxygen 48 parts.

We can express this and similar compositions very simply by making use of a system of symbols which chemists have devised for the purpose. A list of the commoner elements is given below. A complete list is given at the end of the book.

TABLE OF COMMONER ELEMENTS

Name	Symbol	Weight
Aluminium	Al	27
Barium	Ba	137
Bromine	Br	80
Calcium	Ca	40
Carbon	C	12
Chlorine	Cl	35·5
Copper	Cu	63
Gold (Aurum)	Au	197
Hydrogen	H	1
Iodine	I	127
Iron (Ferrum)	Fe	56
Lead (Plumbum)	Pb	207
Magnesium	Mg	24
Mercury (Hydrargyrum)	Hg	200
Nitrogen	N	14
Oxygen	O	16
Phosphorus	P	31
Potassium (Kalium)	K	39
Silicon	Si	28
Silver (Argentum)	Ag	108
Sodium (Natrium)	Na	23
Sulphur	S	32
Tin (Stannum)	Sn	118
Zinc	Zn	65·5

For each element there is a symbol, which consists of the first letter of the Latin name of the element, together sometimes with one of the subsequent letters, in order to prevent confusion when the names of several elements begin with the same letter. By writing these symbols alongside each other we can easily express what elements any given compound contains. Thus, to express that calcium carbonate contains calcium, carbon, and oxygen, we have only to write CaCO. But besides being mere shorthand for the names of the elements, these symbols are something more. **Each symbol expresses a definite amount of the element which it denotes.** These *combining weights* are given in the table after the symbols. Thus the symbol C not only indicates the element carbon, but 12 parts by weight of carbon: the symbol Ca represents not only calcium, but 40 parts of calcium, and so on. The complex symbol or **formula** CaCO represents, then, not only a compound containing the elements calcium, carbon, and oxygen, but a compound whose composition is

Calcium	40 parts
Carbon	12 „
Oxygen	16 „
	68 parts

This compound, which contains 40 parts of calcium in 68, cannot be calcium carbonate, which contains 40 parts of calcium in 100. If we compare the compositions

	CaCO	Calcium carbonate
Calcium . .	40	40
Carbon . .	12	12
Oxygen . .	16	48

we see that relatively to the other elements calcium carbonate contains three times as much oxygen as a compound of the formula CaCO. We may therefore write its symbol CaCOOO, which now expresses the correct composition.

In order to save repetition of symbols, it is customary to write the formula of calcium carbonate $CaCO_3$ instead of at length as above. The number affixed to the symbol of an

element indicates how often the symbol must be repeated. Thus the formula of sulphuric acid H_2SO_4 is a shorter form of HHSOOOO. This formula expresses the fact that sulphuric acid contains

Hydrogen .	H_2	$= 2 \times 1 =$	2 parts
Sulphur . .	S	$= 32 =$	32 ,,
Oxygen . .	O_4	$= 4 \times 16 =$	64 ,,
			98 parts

In the case of calcium carbonate, the formula of the substance expresses the percentage composition directly, as may be seen above, but this is merely a coincidence. In general the formula does not give the number of parts of each element in 100 parts, but in some other number. For sulphuric acid the formula expresses the number of parts of each element in 98. It is, of course, easy to calculate from this by simple proportion the number of parts in 100, or the percentage composition:

	Parts in 98	Parts in 100
Hydrogen . .	2	$2 \times \frac{100}{98} = 2.04$
Sulphur . . .	32	$32 \times \frac{100}{98} = 32.65$
Oxygen . . .	64	$64 \times \frac{100}{98} = 65.31$

Similarly, if we are told that the formula of sodium chloride is NaCl, we can calculate its percentage composition thus:

		Per cent.
Sodium . .	Na = 23	$23 \times \frac{100}{58.5} = 39.32$
Chlorine . .	Cl = 35.5	$35.5 \times \frac{100}{58.5} = 60.68$
	58.5	

In using these formulæ, the student must clearly understand that the composition of any chemical compound must be ascertained by actual experiment before a formula for it can be written at all. The formula is merely a brief and convenient

method of expressing the experimental results, and must never be conceived by the beginner in any other sense.

From a consideration of all well-defined compounds of two elements, it appears that their composition is regulated by the following **Law of Multiple Proportions :—When two elements unite in more than one proportion by weight, the quantities of one of the elements which combine with a fixed quantity of the other element stand to each other in proportions which can be expressed by the simple whole numbers.** Thus carbon combines with oxygen in two proportions to form two distinct compounds, carbon monoxide and carbon dioxide. Considering the composition of these compounds, we find that for a fixed weight of carbon in them there is twice as much oxygen in the dioxide as there is in the monoxide; or for a fixed weight of oxygen in them there is twice as much carbon in the monoxide as in the dioxide. Here the simple ratio is 2 : 1. In the five different oxides of nitrogen (compare Chapter XX.) we find that the quantities of oxygen united with a fixed quantity of nitrogen stand to each other as the whole numbers 5 : 4 : 3 : 2 : 1. It is really owing to the existence of this important law, which may be extended to compounds containing more than two elements, that chemists have been able to draw up a list of combining weights such as has been given on p. 19. By using these combining weights we can express the composition of compounds by means of formulæ, into which only the small whole numbers as a rule enter, and indeed we may give a generalised expression to the Law of Multiple Proportions in terms of the combining weights, as follows :—

Elements enter into the formation of compounds in such proportions as may be expressed by means of simple multiples of their combining weights.

It has already been indicated that chemical formulæ are used in equations instead of the names and weight of the substances involved. Thus the equation

Calcium carbonate	=	Calcium oxide	+	Carbon dioxide
100		56		44

can be expressed in formulæ as follows :—

$$CaCO_3 = CaO + CO_2$$

This symbolic equation gives us at once the correct weights, if we refer to our table of symbols :

$$\underbrace{CaCO_3}_{40+12+48} = \underbrace{CaO}_{40+16} + \underbrace{CO_2}_{12+32}$$

$$\underbrace{100}_{} = \underbrace{56}_{} + \underbrace{44}_{}$$

The equation, of course, presupposes that we know the composition of calcium oxide and of carbon dioxide to be represented by the figures corresponding to the above formulæ.

Similarly, if we know the composition of water and of calcium hydroxide to be given by the formulæ H_2O and CaH_2O_2, we can write the equation for the slaking of lime as follows :—

$$CaO + H_2O = CaH_2O_2$$

Reference to the weights expressed by the symbols will show that this equation indicates the combination of 56 parts of calcium oxide with 18 parts of water—*i.e.* the proportions actually found by experiment.

We can always test if an equation is *arithmetically* correct by adding up the weight values on the right and left of the equation, and seeing if they are in reality equal. A simpler plan of doing this, however, is to count the number of symbols of each element on the two sides. If the equation is arithmetically correct, the symbol of each element must appear the same number of times on the two sides, for it represents a fixed quantity of the element, and the elements are not transformable into one another. In the equation for the slaking of lime, we have on each side, one Ca, two O's, and two H's : the equation is therefore arithmetically correct. The testing of the arithmetical accuracy of an equation is very important, for the reason that an arithmetically incorrect equation cannot by any possibility be chemically correct. For an equation to be chemically accurate, the symbol of each element must appear the same number of times on the two sides, otherwise the total weight of the substances involved in the action would be changed, or else one element would have undergone transformation into another, both of which assumptions are chemically speaking impossible.

Of course, and the student must have this constantly before him, it does not follow that an equation which is arithmetically

correct is also chemically correct—*i.e.* that it is an expression for a chemical action which actually occurs. For example, the equation,

$$\underset{\text{Calcium carbonate}}{CaCO_3} = \underset{\text{Calcium peroxide}}{CaO_2} + \underset{\text{Carbon monoxide}}{CO}$$

is arithmetically accurate, and, moreover, involves only substances which are actually known; yet it is chemically quite inaccurate, for by no means at present known can we decompose calcium carbonate into calcium peroxide and carbon monoxide.

Before we can write an equation which shall be chemically accurate, we must know then not only the composition of all the substances involved, but also that the change implied by the equation actually takes place. A chemical equation ought always to be the expression of a chemical fact, and what is fact can only be ascertained by trial—*i.e.* by experiment.

The student will therefore do well to remember that though he can always write equations which are *arithmetically* accurate—an arithmetically inaccurate equation can only be the result of carelessness, for the accuracy can always be tested by counting the symbols—he cannot, without a real knowledge of the *facts* of chemistry, write equations which are *chemically* accurate.

There are one or two points concerning the use of figures in connection with chemical symbols with which the student must make himself familiar. The formula CaO expresses 56 parts of calcium oxide. Now, suppose we wish to write a formula expressing three times as much as this—*viz.* 168 parts. This can be done in two ways—either we can write Ca_3O_3, which still preserves the proper proportion between calcium and oxygen, and trebles the amount, or else we write 3CaO, the number prefixed to the formula applying to all the symbols in it. The latter method is almost invariably adopted by chemists, who prefer to keep the actual formula as simple as possible (compare Chapter XI.). The formula H_2O stands for 18 parts of water; $2H_2O$ stands for 36 parts; $3H_2O$ for 54 parts, and so on. It should be noted that fractional numbers never appear in chemical formulæ or equations.

Sometimes we find it convenient to group certain symbols together within a formula. Thus calcium hydroxide, which we have written CaH_2O_2, is usually written $Ca(OH)_2$ for a

reason which will appear in the sequel. A number affixed in this way to elements within brackets applies to all the symbols contained in the brackets: $Ca(NO_3)_2$ is the same as CaN_2O_6; $(NH_4)_2SO_4$ is the same as $N_2H_8SO_4$. Occasionally we find symbols in a complex formula separated by a point or a comma. The formula $CuSO_4,5H_2O$ or $CuSO_4.5H_2O$ is the formula of blue vitriol (p. 18), and indicates that the substance contains 159 parts of pure copper sulphate, together with $5 \times 18 = 90$ parts of water of crystallisation. If a number is prefixed to such a complex formula it only applies up to the point or comma. Thus $2CuSO_4,5H_2O$ is not twice the formula of blue vitriol, but the formula of a substance containing 2×159 parts of copper sulphate and 5×18 parts of water. If we wish to double the whole of the complex formula we put it all within brackets, and then prefix 2, thus: $2(CuSO_4,5H_2O)$, which indicates two formula-weights of blue vitriol.

As an example of equation writing we may take the following:—It is known that when sodium hydroxide and sulphuric acid react under certain conditions, sodium sulphate and water are the only products. It is further known that the composition of these substances may be accurately expressed by the following formulæ:—

Sulphuric acid	H_2SO_4
Sodium hydroxide. . . .	$NaOH$
Sodium sulphate	Na_2SO_4
Water	H_2O

Knowing these facts, we can proceed to write the equation as follows. First we write down the formulæ joined by the usual algebraic symbols,

$$H_2SO_4 + NaOH = Na_2SO_4 + H_2O$$

This is plainly not an equation, as we can see by counting the symbols on the two sides. On the left we have Na representing 23 of sodium; on the right we have Na_2 representing 46 of sodium. Since only whole numbers must appear in chemical equations, we cannot halve the amount of sodium on the right, for that would entail halving the single symbol S in order to keep the composition of sodium sulphate. We must therefore double the amount of sodium on the left, which we can only

do by doubling the whole formula of sodium hydroxide. We thus get—

$$H_2SO_4 + 2NaOH = Na_2SO_4 + H_2O$$

This is still not an equation, for we have four H's and two O's on the one side, as against two H's and one O on the other. To remedy this we double the quantity of water on the right, and so obtain the real equation—

$$H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O$$

in which the symbols are properly balanced. This equation is arithmetically correct, and tells us that 98 parts of sulphuric acid react with 80 parts of sodium hydroxide to give 142 parts of sodium sulphate and 36 parts of water. Here, by knowing the formulæ of the reacting substances and the products of the reaction, we have been able to calculate the proportions in which all these substances are involved in the chemical action by merely getting the chemical equation to balance. This is in general the case; if we know all the reacting substances and all the products of the reaction, and, further, know the formulæ which express their composition, we can, by a purely arithmetical process, write an equation which expresses the proportions by weight in which all the substances concerned participate in the reaction. It is sometimes not easy to arrive at the arithmetical solution of an equation in the manner indicated above, but it is always possible, and only requires a little expertness, which comes of practice. Examples of various methods of solving will be given as occasion requires.

In ordinary chemical equations the reacting substances are put on the left, and the products of reaction on the right. It is therefore necessary always to read chemical equations from left to right, unless the action is shown to be reversible by means of oppositely directed arrows. Thus the reversible equation

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

really gives expression to the two ordinary equations—

$$CaCO_3 = CaO + CO_2$$
$$CaO + CO_2 = CaCO_3$$

each of which is the reverse of the other.

CHAPTER V

COMBUSTION

THERE are a great many chemical reactions in which air plays a part. Atmospheric air consists of about one measure of *oxygen* and four measures of *nitrogen*. Although oxygen therefore occupies only one-fifth of the total volume of the air, it is nevertheless the active component of the mixture, the nitrogen merely serving to moderate the activity of the oxygen.

Familiar instances of actions in which air takes part are to be found in the processes of combustion. For example, when fuel such as wood or coal burns in the air, the chief action is the union of the components of these substances with the oxygen in the air, the combustion taking place with such vigour that heat and light are developed. Similarly, the burning of a taper or coal-gas in air consists in the union of the materials of these substances with oxygen. The principal components of such ordinary fuels and illuminating agents are the elements *carbon* and *hydrogen*. On combustion the carbon unites with the oxygen to form carbon dioxide, and the hydrogen unites with oxygen to form water, according to the equations—

C	+	O_2	=	CO_2
Carbon		Oxygen		Carbon dioxide
$2H_2$	+	O_2	=	$2H_2O$
Hydrogen		Oxygen		Water

That water is produced in the form of vapour may be easily shown by holding a cold bright object such as a polished piece of metal a little distance over a candle or gas flame. The cold metal cools the gases which rise from the flame, and the water-vapour condenses to minute drops of moisture on its surface, which in consequence immediately becomes dim. The presence of carbon dioxide in the gases produced

by the combustion can also be simply shown as follows:—If a drop of lime water is taken up on the end of a glass rod, and held some distance over the flame, it will at once become milky, by the production in it of insoluble calcium carbonate formed according to the equation—

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Calcium carbonate}}{\underline{CaCO_3}^*} + \underset{\text{Water}}{H_2O}$$

Many elements when heated in the air to a sufficiently high temperature take fire and burn, combining with the oxygen of the air to form oxides. Thus sulphur, when heated, burns with a characteristic blue flame to form the gas sulphur dioxide,

$$\underset{\text{Sulphur}}{S} + O_2 = \underset{\text{Sulphur dioxide}}{SO_2};$$

and phosphorus burns with a brilliant white flame to form clouds of phosphorus pentoxide P_2O_5, a solid which is produced according to the equation—

$$\underset{\text{Phosphorus}}{4P} + 5O_2 = \underset{\text{Phosphorus pentoxide}}{2P_2O_5}$$

Even metals may burn in air if sufficiently heated. Thus magnesium in the form of band or wire burns, when lit at an ordinary flame, with a dazzling white light, and gives rise to the oxide MgO according to the equation—

$$\underset{\text{Magnesium}}{2Mg} + O_2 = \underset{\text{Magnesium oxide}}{2MgO}$$

the oxide appearing in the form of a brittle white solid. Iron wire, too, when raised to a very high temperature burns readily with production of showers of sparks produced by the vigorous union of the iron with oxygen to form the oxide Fe_3O_4,

$$\underset{\text{Iron}}{3Fe} + 2O_2 = \underset{\text{Magnetic oxide}}{Fe_3O_4}$$

The evolution of light does not necessarily accompany the process of combustion, even when this is attended by con-

* The production of an insoluble substance (*precipitate*) may be conveniently represented in a chemical equation by underlining the formula of the substance.

siderable production of heat. If a red-hot iron rod is allowed to cool in the air, a scale will be found on the surface of the rod where it has been raised to a high temperature. Although no process of combustion is here evident, yet union has taken place between the iron and the oxygen with production of the same oxide as before. Again, if lead is melted in an iron vessel, it will be found that the surface very soon becomes covered with a solid scum. If this scum is raked off and a fresh bright surface of lead exposed, a fresh scum makes its appearance, which can in turn be removed. This solid scum is an oxide of lead formed by the union of the metal with atmospheric oxygen.

$2Pb$	$+$	O_2	$=$	$2PbO$
Lead				Lead monoxide (litharge)

In the same way, when copper is moderately heated in air it loses its metallic appearance and becomes covered with a coating of oxide of copper by gradual union with the oxygen of the air.

In animals a process of slow combustion constantly goes on, which is in all essential respects closely related to the combustion of fuel. The animal organism, like vegetable fuels, consists very largely of substances containing carbon and hydrogen, which are slowly burned in the body by means of the oxygen abstracted by the blood from the air, and conveyed by it from the lungs to all parts of the body. The products of this slow combustion in the body are carbon dioxide from the carbon, and water from the hydrogen — that is, the same substances as were produced by the rapid combustion of ordinary fuel. These products are carried in the blood back again to the lungs and leave the body in the expired air. That they are contained in expired air in considerable amount may easily be tested in the same way as before. If we breathe gently on a cold bright object held in front of the mouth, the surface will immediately become dim by the deposition of moisture (which, however, is not all obtained from the combustion of the tissues), and if we blow through a tube the end of which is immersed in lime water, the lime water will speedily become milky by the production of insoluble calcium carbonate. Here the process of combustion goes on at the low temperature of the animal body—namely, about 37°.

Although no light is evolved, so much heat is given out in the process that the temperature of the body is kept permanently above the ordinary temperature of the atmosphere.

Heat of Combustion.—A given quantity of a given substance burning in air will always give out the same amount of heat, no matter whether it burns slowly or rapidly. This, of course, does not imply that the same temperature will be reached in all cases. If the combustion goes on slowly, the evolution of the fixed amount of heat is spread over a long time, and the temperature at any one instant is therefore not raised to a high degree on account of the continual loss of heat by conduction and radiation. On the other hand, if the combustion of the substance takes place very rapidly, the same amount of heat as before is produced in a much shorter time, and consequently raises the reacting substances to a much higher temperature. The temperature obtainable by the combustion of a given amount of fuel depends, therefore, on whether the combustion is made to take place slowly or rapidly—in a large space, where the cooling effect is great, or in a small space, where the cooling effect is small. The combustion in the animal body is a good example of a slow combustion spread over a large space, the consequence being that the temperature of the body is never raised to any high degree, although very considerable quantities of material are burned.

This constancy of the heat of combustion of a substance only occurs if the products of combustion are the same. A gram of carbon burning to carbon dioxide gives out quite a different amount of heat from that evolved when a gram of carbon burns to form carbon monoxide (compare Chap. IX.). What is said here of combustion applies to chemical actions generally. The action between given weights of reacting substances is accompanied by the evolution (or absorption) of a fixed amount of heat if the products of the reaction are always the same.

CHAPTER VI

FLAME

WHEN iron burns in air or oxygen, much heat is given out in the combustion, small incandescent particles being shot off in the form of sparks. Similarly, when pure carbon is burned, although the temperature is raised to a very high degree, there is little or no flame. On the other hand, when coal-gas, or oil, or a candle is burned in the air, the combustion is accompanied by the production of flame.

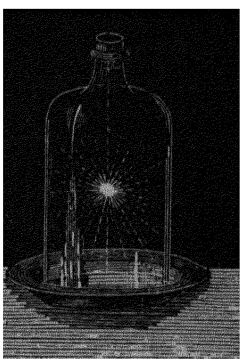


Fig. 4.
Iron wire burning in Oxygen.

If we inquire into the nature of flame, we find that what generally goes under that name is really a mixture of *reacting gases raised to a very high temperature* by the heat generated in the action, so that unless the reacting substances are, during combustion, in the gaseous state, the combustion is not accompanied by the production of flame. When iron burns in oxygen, the oxygen is of course a gas, but the iron is not, so that we have reaction between a gas and a solid, which produces no flame. In the same way, when charcoal, or better, diamond, burns in air or oxygen, although the oxygen is gaseous, the carbon of which these substances almost entirely consists remains solid at the temperature of the combustion, and so no flame is produced.

In the case of coal-gas burning in the air, both the reacting substances are gaseous, and the hot gases in the zone of reaction form what we usually call a flame. If oil is burned instead of coal-gas, notwithstanding that oil is a liquid, the combustion is attended by flame production. It must be

remembered, however, that although oil is liquid at the ordinary temperature, it is a gas at the temperature at which combustion takes place.

The oil, then, before reacting with the oxygen of the air, is converted into a gas, and so the reaction in reality takes place between gases, with consequent production of flame. Similarly, although the wax of a candle is a solid, yet by the heat of the reaction it is converted first into a liquid and then into a gas, and a flame is therefore the result of the combustion. Sulphur and phosphorus burn in air with production of flame on account of the heat of the combustion of these solid substances melting them, and converting them into vapour before they actually burn.

When fresh coal is put on a fire the combustion of the coal is accompanied by the production of flame. Coal, besides the element carbon as such, contains a considerable quantity of compounds of carbon with hydrogen, which are generally called *hydrocarbons*. These compounds are decomposed with production of combustible gases as the coal is heated, and the gases thus produced react with the oxygen of the air, the zone of reaction being marked by a luminous flame. As the combustion proceeds the hydrocarbons are practically all destroyed, and then there is nothing combustible left behind but carbon, which, as we have seen, is not volatile at the temperature of combustion, so that now there is interaction between a solid and a gas, and the fire which is what we call a bright or clear fire, simply glows without production of flame.

Coal-gas burned in an ordinary burner gives a brightly luminous flame. When burned in a bunsen burner, however, which has the air holes open, it burns with a non-luminous flame. If we shut off the air supply at the bottom of the bunsen, the luminosity reappears.

If we inquire into the cause of the **luminosity** of a coal-gas flame burned at an ordinary burner, we find that it is produced by hydrocarbons which are present in the gas. At the high temperature of the combustion, these hydrocarbons are partially decomposed with separation of **solid particles** of carbon within the flame, which, being heated to whiteness, render the flame luminous.

When air is admitted through the air holes of a bunsen

burner, we have seen that the luminosity of the flame disappears. There are two possible reasons for this. In the first place, the flame may be cooled, because the coal-gas is diluted with a considerable proportion of nitrogen from the air, which takes no part in the chemical action. This nitrogen must be heated

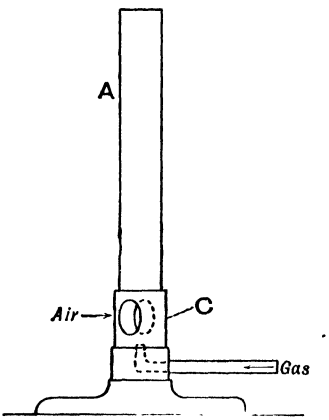


Fig. 5.—Bunsen Burner.

Gas is supplied through the side tube, and is delivered rapidly upwards through a small orifice, air being thereby sucked up through the air-hole, so that a mixture of gas and air passes up the tube *A*. The collar *C*, which contains a hole corresponding with that in the tube, may be made to admit or shut off air by rotating it round *A*. In the figure the air-hole is partially closed.

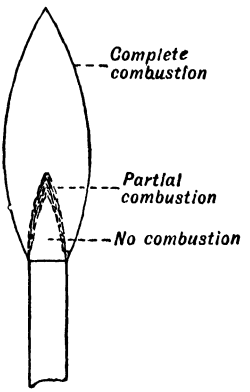


Fig. 6.—Non-luminous Bunsen Flame.

In the zone of no combustion the mixture of gas and air is below its ignition temperature; in the zone of partial combustion water vapour and carbon dioxide are formed, the combustible gases hydrogen and carbon monoxide being, however, still present; in the zone of complete combustion there is excess of air, and the gas is entirely burned to carbon dioxide and water.

along with the other gases present; and since the heat given out by the combustion of a given quantity of coal-gas is always the same, the temperature produced will not be so high as when no nitrogen is present. In the second place, oxygen is supplied along with the coal-gas. The coal-gas has therefore a better chance of meeting the requisite quantity of oxygen for its complete combustion (that is, the combustion of both carbon and hydrogen) when oxygen is supplied within as well as without the flame, than when the oxygen supply is derived entirely from the atmosphere outside the flame. In the latter

case, there is an insufficient supply of oxygen within the flame for burning both the hydrogen and the carbon, so that some of the carbon at first escapes combustion, and is therefore seen in a solid state at a white heat.

A luminous coal-gas flame may be made non-luminous by mixing it with pure nitrogen, which plays no direct part in the combustion at all, and in no way assists the combustion of the coal-gas. Its action is merely a cooling action: the temperature of the flame is kept so low by the admixture of nitrogen, that it never reaches the point necessary to decompose the illuminating hydrocarbons with separation of carbon. That cooling alone is able to destroy the luminosity in flame can be shown by holding a piece of fine copper wire gauze in a slanting position, so that a feebly luminous bunsen flame plays against it. If the luminosity of the flame is not too great, it disappears entirely when the flame is thus brought into contact with the wire gauze, which conducts away the heat very rapidly, and thus lowers the temperature. That heat, on the other hand, confers luminosity on a non-luminous flame may be seen by heating the tube of a bunsen burner to redness. Although, before heating, the flame was non-luminous, after the tube has been heated the flame becomes luminous. Here the illuminating hydrocarbons have been decomposed with production of particles of carbon, which in the flame are heated to whiteness and consequently emit light.

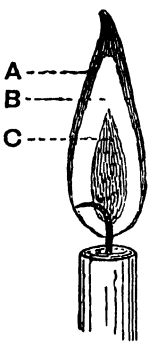


Fig. 7.
Candle Flame.

A. Area of no combustion.
B. Area of partial combustion.
C. Area of complete combustion.

In an ordinary gas burner, matters are so arranged that all the carbon which separates is burned in the outer regions of the flame, and no smoke is produced. If a large flame of coal-gas is burned in a bunsen with the air supply completely shut off, the flame will be seen to be smoky. Some of the carbon particles have here escaped combustion altogether, and are sent into the air as smoke, which may coalesce to what we call soot.

The separation of solid particles is not the only possible

cause of luminosity in flame. Even though no particles separate at all, a luminous flame may still be obtained by sufficiently increasing the pressure on the reacting gases. Thus hydrogen gas at the ordinary pressure of the atmosphere burns with a non-luminous flame, the reacting substances and all possible products of the reaction being gases at the temperature of the flame; but if the pressure of both gases is increased to several atmospheres, the hydrogen flame becomes luminous, notwithstanding the impossibility of the separation of solid particles.

It has already been indicated that the **effective temperature** obtained by the combustion of any substance depends upon the rate of combustion, and on the size of the space in which the combustion is effected. The actual temperature of the hottest portion of the bunsen flame is about 1800° C., but the effective temperature does not exceed about 1300°. Though the same quantity of gas is burned in the same time, if the combustion is made in one case to spread over a large area, and is in another case concentrated to a very small space, the effective temperature of the flame in the second case will be much higher than in the first. The same amount of heat is produced in a much smaller space, and there is more rapid and effective transmission to the object to be heated. If we want, therefore, to get a hotter flame from coal-gas than is given by complete combustion in the ordinary bunsen burner, we can obtain it by means of a blow-pipe, in which there is an arrangement for rapidly supplying the air necessary for the combustion of the gas. The coal-gas has not to spread out so far in order to meet the necessary oxygen, for it is already

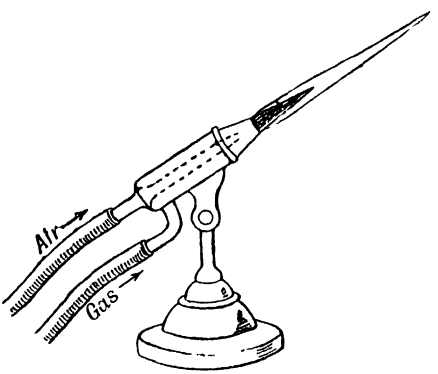


Fig. 8.—Blow-pipe.

Air is delivered rapidly from a bellows or air-blast through the narrow central tube, coal-gas passing up through the space between this and the outer tube: the two only mix at the mouth of the blow-pipe. By this arrangement a great amount of gas may be burned in a small space, with consequent high effective temperature.

mixed at the nozzle of the blow-pipe with all the oxygen it requires. The reaction thus takes place in a smaller space and the flame is much hotter than if no special air supply was given. To get a still higher effective temperature from coal-gas, oxygen may be supplied in the blow-pipe instead of air. Here the combustion takes place in a still smaller space, because the reacting gases are not diluted with nitrogen. If we lower a burning jet of coal-gas into a vessel filled with pure oxygen, we can see that the flame becomes much smaller than it was in the air, and if it is tested it will be found to be much hotter.

When a combustible gas and air, both under slight pressure, are passed through a porous solid, they may be made to burn in the pores at a rate greatly accelerated by the action of the solid, and thus produce locally a very high temperature. Such *surface combustion* is practically flameless, and its application is being developed on a technical scale.

When we consider that a flame consists of gases made visible by their chemical interaction, we see that if these gases were cooled below the temperature at which chemical action between them is possible, the flame would disappear.

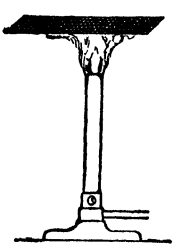


Fig. 9.

This can be shown readily by means of an ordinary non-luminous bunsen flame and a piece of fine wire gauze. The metal of the wire gauze exposes a large surface, and is a good conductor of heat. If it is brought into a flame the heat generated by the chemical action is conducted away along the wires of the gauze and dissipated. If the mesh of the gauze is fine enough, the gases are cooled below the ignition point, and can, in consequence, no longer interact.

Suppose the wire gauze to be brought down horizontally on the flame (fig. 9). It will be seen that the flame spreads slightly beneath the wire gauze, but that it does not penetrate to the upper surface of the gauze. That the mixture of coal-gas and air which constitutes the unburnt gases from the bunsen burner easily passes through the holes in the gauze, although the flame does not, may be proved by applying a light to the upper surface of the gauze, when the flame appears above the gauze as well as below it. A combustible

mixture must therefore have passed through the gauze, although the flame was unable to do so; in other words, below the gauze the gases were reacting chemically, but above the gauze they were not.

If the wire gauze is held an inch or so above the opening of an unlit bunsen burner, and a light is applied *above* the gauze (fig. 10), the gases which pass through take fire, but the flame is not transmitted downwards to the gases as they issue from the mouth of the burner. The reason is the same as before: the wire gauze lowers the temperature of the gases in its interstices to a point below that at which they can react chemically.

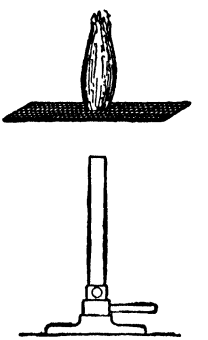


Fig. 10.

The same cooling action of wire gauze may be shown in another way. If burning alcohol is poured from a basin through the gauze, the part which passes through is extinguished, although the alcohol above and on the gauze is blazing freely.

Should a bunsen flame play against the under surface of a piece of wire gauze for a sufficient length of time to heat the gauze to redness, it will be found that suddenly the flame passes from beneath upwards through the gauze. This is due to the gauze having lost its cooling power by itself becoming red-hot.

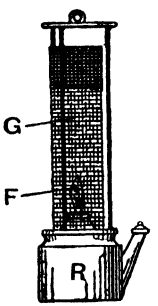


Fig. 11.—Safety Lamp.

The flame *F*, fed from the oil reservoir *R*, burns within the wire gauze cage *G*, which completely encloses it.

The principle of cooling reacting gases below their ignition point by means of wire gauze is applied in miners' **safety lamps**, which are usually named after their inventor, Davy. The Davy lamp (fig. 11) consists of a small oil lamp over which a cage or cylinder of wire gauze is screwed down. This cage, which entirely surrounds the flame, admits the free access of air and free removal of the products of combustion, but its cooling effect is such that a flame cannot in general pass through it. The reason why such safety lamps are used in mines is that the mine sometimes becomes filled with an inflammable mixture of fire-damp and air. When mixed with air in certain proportions this fire-

damp, or marsh gas, is not only inflammable, but explosive. If a naked flame were carried into such an explosive mixture a very serious accident might happen. If the flame, however, is guarded by a wire gauze cage it is only the part of the combustible mixture inside the cage that is inflamed, and the flame produced is incapable of passing outwards through the gauze.

The safety lamp is not an absolute protection against mine explosions, for the following reason. If a shot is fired in the neighbourhood of a safety lamp which is surrounded by an explosive mixture of fire-damp and air, there is such a sudden displacement of gas by the shot, that some of the burning gas within the cage is driven bodily through the wire gauze with such rapidity that the flame is not extinguished, and thus the mixture outside the cage is fired. This may be shown with a bunsen burner and a piece of wire gauze of somewhat coarse mesh. If the gauze is brought down slowly on the flame, the flame will not penetrate, and if we depress the gauze down to the actual mouth of the burner the flame may be extinguished altogether. If, on the other hand, we bring down the wire gauze rapidly on the flame by a smart blow, the flame will be found to penetrate it. In the latter case the reacting gases pass so rapidly through the gauze that they have not time to be cooled by it below the ignition point, and consequently they continue to react.

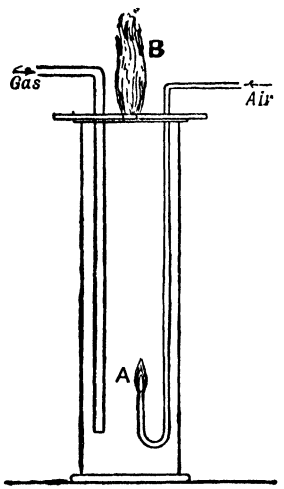


Fig. 12.—Combustion of Air in Coal-gas.

A. Flame of air burning in coal-gas.

B. Flame of coal-gas burning in air.

Since the combustion of coal-gas in air is a chemical reaction which takes place between the coal-gas and the oxygen in the air, it is apparent that we have been looking at this chemical reaction from one side only. Coal-gas and air will interact when heated to the requisite temperature, no matter in what way they are mixed. For practical reasons we usually have a jet of coal-gas issuing into the surrounding

air, but the combustion would take place equally well if a jet of air were made to issue into an atmosphere of coal-gas.

This may be shown experimentally by forcing a stream of air through a small jet or burner and lowering this into a jar filled with coal-gas, having previously lit the jet of air at the flame of the coal-gas burning in air at the top of the jar (fig. 12).

In a similar way we very frequently, on account of our every-day practice in conducting a chemical action, are one-sided in our terminology. Thus we say that coal-gas is a *combustible* substance and that air is a *supporter of combustion*; but as we have just seen, the terms might with equal propriety be reversed. When we say that a substance is *combustible*, without further qualification, we imply that it will burn in air or oxygen; and when we say that a gas is a *supporter of combustion*, we mean that it will react chemically with the same substances, and in the same way, as air does.

CHAPTER VII

NEUTRALISATION

In carbonic acid and calcium hydroxide we have met with examples of two very important classes of chemical substances —namely, **acids** and **bases**. They are, however, scarcely to be called typical examples, and in the present chapter we shall be concerned with the *soluble* acids and bases which are more commonly in use in the laboratory, and possess better defined properties. The common soluble acids are—

Chemical Name	Formula	Common Name
Sulphuric acid	H_2SO_4	Oil of vitriol
Nitric acid	HNO_3	Aquafortis
Hydrochloric acid	HCl	Muriatic acid

The common **soluble bases** or **alkalies** are—

Sodium hydroxide	NaOH	Caustic soda
Potassium hydroxide	KOH	Caustic potash
Ammonium hydroxide	NH_4OH	Ammonia

A convenient test for soluble acids and alkalies is their action on a solution of litmus, a purple colouring-matter extracted from certain lichens. Acids turn the purple litmus solution red, alkalies turn it blue. Papers impregnated with litmus are extensively used instead of litmus solution in testing for acids and alkalies, and are known on this account as *test-papers*. Acids and alkalies can be distinguished from each other not only by their action on litmus, but also by their taste. Acids have a sour taste; alkalies have a somewhat soapy flavour.

A curious characteristic of acids and alkalies is the power they possess of destroying or neutralising each other's properties. If we mix a solution of any of the above acids with a solution of any of the above alkalies in the proper proportions, the resulting solution will neither redden litmus nor turn it blue, and will be neither sour nor alkaline to the taste.

The characteristic properties of the original substances will have vanished, and new properties will have made their appearance. The solution obtained by the mixing of the acid and alkaline solutions leaves purple litmus unaffected, and possesses a taste resembling that of salt. The reciprocal action of acid and base is called **neutralisation**, and is a very important chemical process.

When we inquire more closely into the phenomena of neutralisation, we find that the definite proportions, which we have already seen to exist in the processes of burning and slaking lime, are equally evident in the reactions between acids and alkalies. For example, if we take two solutions of acids (say one of hydrochloric acid and the other of sulphuric acid) and find that three times as much of the sulphuric acid is required to neutralise a given weight of caustic soda as is required of the hydrochloric acid solution; then this same relation will be found with regard to any quantity of any alkali. That is, we may substitute caustic potash or ammonia for the caustic soda, and taking any quantity of them we please, we shall always find that three times as much of the given sulphuric acid solution is required to neutralise the alkali taken as is required of the given hydrochloric acid solution. The quantities of different acids which are capable of neutralising the same quantity of a given alkali are said to be **equivalent** to each other: in the above instance the quantity of hydrochloric acid in one volume of the hydrochloric acid solution is equivalent to the quantity of sulphuric acid in three volumes of the sulphuric acid solution. Using this conception of equivalence, we may say then that quantities of different acids which are equivalent with respect to one alkali are equivalent with respect to all alkalies.

Similarly, we find that quantities of different alkalies which are equivalent with respect to a given quantity of a given acid will neutralise the same quantity of any acid.

By an extension of the term equivalent we say that quantities of acid and alkali which are capable of neutralising each other are equivalent to each other; and still more generally, that *quantities of substances which are capable of reacting with each other chemically or of being substituted for each other in chemical actions are mutually equivalent.*

The substances formed by the mutual neutralisation of an acid and an alkali are **water** and a **salt**. The salts, of which ordinary salt is a typical example, form another very important class of chemical substances. They are solids under ordinary circumstances, generally possess a salt taste, and yield solutions which are mostly neutral to litmus.

As examples of salt-formation we may take the neutralisation of caustic soda by the three acids mentioned above, and express the reactions by means of equations.

$NaOH$	+	HCl	=	$NaCl$	+	H_2O
Sodium hydroxide		Hydrochloric acid		Sodium chloride		Water
40		36.5		58.5		18

$NaOH$	+	HNO_3	=	$NaNO_3$	+	H_2O
Sodium hydroxide		Nitric acid		Sodium nitrate		Water
40		63		85		18

$2NaOH$	+	H_2SO_4	=	Na_2SO_4	+	$2H_2O$
Sodium hydroxide		Sulphuric acid		Sodium sulphate		Water
80		98		142		36

Here the alkali is the same throughout, and the acid is varied. We may now write a similar set of equations for the neutralisation of hydrochloric acid by the various alkalies

HCl	+	$NaOH$	=	$NaCl$	+	H_2O
Hydrochloric acid		Sodium hydroxide		Sodium chloride		Water
36.5		40		58.5		18

HCl	+	KOH	=	KCl	+	H_2O
Hydrochloric acid		Potassium hydroxide		Potassium chloride		Water
36.5		56		74.5		18

HCl	+	NH_4OH	=	NH_4Cl	+	H_2O
Hydrochloric acid		Ammonium hydroxide		Ammonium chloride		Water
36.5		35		53.5		18

By taking the other pairs of acid-alkali we get still other salts, the equations representing the formation of which the student should write for himself. A list of all the salts formed

by the neutralisation of the common acids and alkalies is given below.

Chemical Name	Formula	Common Name
Sodium chloride	$NaCl$	Salt
Potassium chloride	KCl	Muriate of potash
Ammonium chloride	NH_4Cl	Sal-ammoniac
Sodium nitrate	$NaNO_3$	Chili saltpetre
Potassium nitrate	KNO_3	Saltpetre or nitre
Ammonium nitrate	NH_4NO_3	Nitrate of ammonia
Sodium sulphate	Na_2SO_4	Salt-cake
Potassium sulphate	K_2SO_4	Sulphate of potash
Ammonium sulphate	$(NH_4)_2SO_4$	Sulphate of ammonia

All of these salts are solids which are soluble in water, are neutral to litmus, and have a taste resembling that of ordinary salt.

If we now consider the quantities of substances taking part in the various actions, we see that to neutralise 40 parts of caustic soda are required—

36.5 parts of hydrochloric acid
63 „ nitric acid
49 „ sulphuric acid.

These quantities are therefore equivalent.

Again, in order to neutralise 36.5 parts of hydrochloric acid we require—

40 parts of sodium hydroxide
56 „ potassium hydroxide
35 „ ammonium hydroxide.

These quantities of the various alkalies are therefore equivalent to each other. Not only, however, are these quantities of the acids and alkalies equivalent as compared each with a substance of like kind—*i.e.* acid with acid, and alkali with alkali,—they are also equivalent when alkali is compared against acid. Thus 35 parts of ammonium hydroxide are equivalent to 63 parts of nitric acid—*i.e.* these quantities will exactly neutralise each other; and 56 parts of potassium

hydroxide are equivalent to 49 parts of sulphuric acid, as reference to the equations will show.

Using formulæ instead of the formula-weights connected with them, we see that NaOH, KOH, and NH_4OH are equivalent to one another. HCl and HNO_3 are also equivalent, not only to each other but also to NaOH, etc. It is different in the case of sulphuric acid. The formula H_2SO_4 represents 98 parts of sulphuric acid, which the equations show will neutralise twice as much caustic soda as 36.5 parts of hydrochloric acid. The formula H_2SO_4 is therefore equivalent to $2HCl$, and also to $2HNO_3$. When compared against alkalies, the quantity expressed by H_2SO_4 neutralises twice as much as the quantities expressed by the formulæ KOH, NaOH, and NH_4OH; H_2SO_4 is therefore equivalent to $2NaOH$, $2KOH$, and $2NH_4OH$.

Solutions are frequently made of such a concentration that one litre of the solution contains one equivalent weight in grams of the dissolved substance; these solutions are then said to be **normal**. A normal solution of sulphuric acid, for example, contains 49 grams of sulphuric acid in the litre; a normal solution of sodium hydroxide 40 grams, and so on. Normal solutions are much used in analysis, since they offer great convenience in the way of simplifying calculations. We can tell, for example, at once that 10 cc. of normal sulphuric acid solution will require exactly 10 cc. of normal caustic soda solution for neutralisation. Semi-normal solutions, of half the above concentrations, and deci-normal solutions of one-tenth concentration, are also in common use.

CHAPTER VIII

THE COMMON ACIDS AND BASES

THE three common acids—sulphuric acid, nitric acid, and hydrochloric acid—are usually called the *strong mineral acids*, to distinguish them from other acids of a weaker nature derived from minerals, and from the vegetable acids.

Sulphuric Acid, H_2SO_4.—This is the most important of all acids, and is prepared commercially on an enormous scale. It is not only the commonest acid, but the cheapest, and nearly all other acids are prepared from it by its action on certain salts. The crude commercial acid is known as *oil of vitriol*, and forms an oily liquid which is usually somewhat brown in colour. The concentrated oil of vitriol contains, besides other impurities, about 6 per cent. of water.

Sulphuric acid is a heavy, perfectly colourless liquid (sp. gr. 1.84). It is a powerfully corrosive substance, and destroys all animal and vegetable substances with which it comes in contact, blackening and charring them by partially converting them into charcoal. This charring may easily be observed by bringing sulphuric acid into contact with sugar, paper, or wood.

If it is poured into water, a great amount of heat is evolved, the rise of temperature being sufficient to convert a portion of the water into steam. In diluting it with water, care must therefore be exercised, as the production of steam may be so sudden as to cause portions of the corrosive liquid to fly about. The undiluted acid is often spoken of as *strong* sulphuric acid, and the diluted acid as *weak* sulphuric acid. It is better, however, to reserve the terms strong and weak to indicate the inherent strength or weakness of pure acids, using the terms **concentrated** and **dilute** to express the degree with which the pure substances are mixed with water.

Pure sulphuric acid boils at a temperature above 300°,

on which account it can be used to drive out more volatile acids from their salts, as will be seen below.

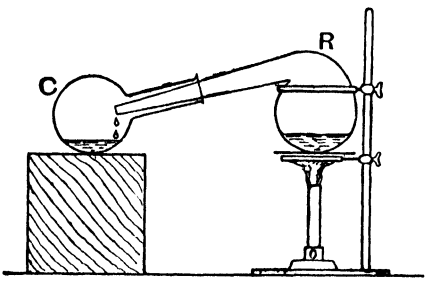


Fig. 13.—Laboratory Preparation of Nitric Acid.

A mixture of sodium nitrate and sulphuric acid is heated in the glass retort *R*, from which the nitric acid distils off, being condensed to the liquid form in the receiver *C*, which is kept cold by a jet of water playing on it.

Nitric Acid, HNO_3.—This acid is produced by the action of concentrated sulphuric acid on sodium nitrate. In the laboratory the two substances may be heated together in a retort. The sodium nitrate dissolves in the sulphuric acid on heating, and the nitric acid produced by their interaction boils off, the vapour being liquefied in a cooled receiver. The equation for the action is—

H_2SO_4	+	$NaNO_3$	=	$NaHSO_4$	+	HNO_3
Sulphuric acid		Sodium nitrate		Sodium hydrogen sulphate		Nitric acid
98		85		120		63

Nitric acid boils at a temperature below that of boiling water, whilst all the other substances concerned in the reaction boil

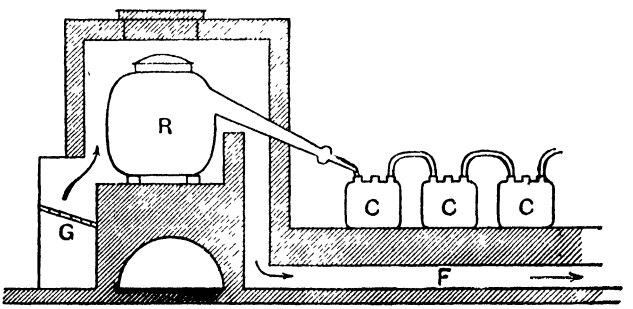


Fig. 14.—Commercial Preparation of Nitric Acid.

The cast-iron retort *R* is charged with sodium nitrate and sulphuric acid. It is entirely surrounded by brick-work, and is heated by the flames and hot gases from the grate *G*, which play round it and pass off through the flue *F*. The nitric acid which distils off is liquefied by passing through a series of earthenware condensers *C*.

at a much higher temperature; so that the nitric acid distils off and is thus separated from them.

Nitric acid produced in this way has always a reddish-yellow colour, which is due to the decomposition of a little of the acid by heat during the distillation. When freed from this impurity it is a colourless liquid of sp. gr. about 1.4. It mixes with water with considerable evolution of heat. The concentrated acid is powerfully corrosive, attacking both animal and vegetable substances, usually staining them bright yellow.

Hydrochloric Acid, HCl.—This acid is formed by the action of sulphuric acid on common salt (sodium chloride), the equation being—

H_2SO_4	+	$2NaCl$	=	Na_2SO_4	+	$2HCl$
Sulphuric acid		Sodium chloride		Sodium sulphate		Hydrochloric acid
98		117		142		73

It is a gas, so that when produced, it escapes from the other substances concerned, which are solid or liquid. As gases are extremely bulky and inconvenient to work with, pure hydrochloric acid is scarcely ever employed. The gas is led off as it is formed into water, which can absorb many hundred times its own volume. The solution of the gas in water is accompanied by a considerable rise in temperature. What is known as concentrated hydrochloric acid in the laboratory is an aqueous solution containing about 35 per cent. of the pure acid. Dilute hydrochloric acid contains not more than 20 per cent. The gas and the solution derived from it are without colour when pure, and are not nearly so corrosive in their action as sulphuric or nitric acid.

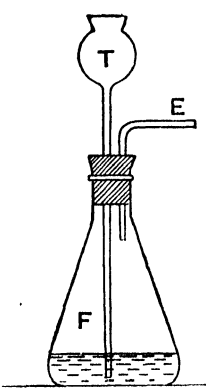


Fig. 15. —Preparation of Gaseous Hydrochloric Acid.

Salt is introduced into the flask *F*, and concentrated sulphuric acid poured through the thistle funnel *T*, the tube of which nearly reaches the bottom of the flask. The hydrochloric acid produced escapes through the exit tube *E*. Heat may be applied if necessary by means of a burner placed beneath the flask.

Sodium hydroxide, NaOH, and **Potassium hydroxide, KOH,** are the common fixed — that is, non-volatile — alkalies. They are white solids which are freely soluble in water. Their concentrated solutions are strongly caustic and corrosive, their dilute solutions less so.

Ammonium hydroxide, NH_4OH, only exists in aqueous solutions, which are prepared by dissolving ammonia gas in water, the equation for the action being—

$$\underset{\text{Ammonia}}{NH_3} + \underset{\text{Water}}{H_2O} \rightleftharpoons \underset{\text{Ammonium hydroxide}}{NH_4OH}$$

It was formerly called the *volatile* alkali on account of the ease with which it breaks up again into ammonia gas and water, according to an equation which is the reverse of that just given. The solution of ammonia may be easily distinguished from the solutions of the other alkalies by its characteristic smell, sodium hydroxide and potassium hydroxide being practically inodorous. The "strong ammonia" of the laboratory contains about 30 per cent. of ammonia.

These alkalies, as has already been mentioned, form a special subdivision of a much larger class of substances called **bases**. All bases are *hydroxides*, and have the power of reacting chemically with acids to form salts and water, just as the alkalies do. The other bases differ from the alkalies in not being freely soluble in water. Calcium hydroxide, for example, although not usually termed an alkali, is, like sodium hydroxide, a base, and capable of turning litmus blue and of neutralising acids. Thus, when calcium hydroxide is treated with hydrochloric or sulphuric acid, neutralisation takes place according to the following equations :—

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Calcium chloride}}{CaCl_2} + \underset{\text{Water}}{2H_2O}$$

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Water}}{2H_2O}$$

Calcium hydroxide, however, is only very sparingly soluble in water, and although its solution has an alkaline reaction, is not termed an alkali, but an **alkaline earth**. Strontium hydroxide $Sr(OH)_2$ and barium hydroxide $Ba(OH)_2$ are similar to calcium hydroxide in this respect, and are classed with it as alkaline earths. Owing to this classification of their hydroxides, the metals sodium and potassium are often referred to as metals of the alkalies, or alkali metals; and the metals calcium, strontium, and barium, as metals of the alkaline earths.

Some bases, such as zinc hydroxide $Zn(OH)_2$, possess no alkaline reaction, and are altogether insoluble in water. They

nevertheless react with acids to form salts in precisely the same way as the soluble bases. Thus zinc hydroxide and hydrochloric acid at once give zinc chloride and water:

$$\underset{\text{Zinc hydroxide}}{Zn(OH)_2} + \underset{\text{Hydrochloric acid}}{2HCl} = \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Water}}{2H_2O}$$

and similarly,

$$\underset{\text{Zinc hydroxide}}{Zn(OH)_2} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Water}}{2H_2O}$$

CHAPTER IX

OXIDES

THE process of ordinary combustion is a process of *oxidation*—that is, a process of union with oxygen; and if elements are the substances which are burned, the compounds produced are called **oxides.** Thus the element carbon burns to form carbon dioxide, hydrogen to form hydrogen oxide or water, zinc to form zinc oxide, iron to form an oxide of iron, phosphorus to form an oxide of phosphorus, and sulphur to form an oxide of sulphur.

Some elements form more than one oxide. Carbon, when burned in air or in oxygen, burns for the most part directly to carbon dioxide; but in some cases where there is not a sufficient supply of oxygen, another oxide, carbon monoxide, may be produced according to the equation—

$$2C + O_2 = \underset{\text{Carbon monoxide}}{2CO}$$

This monoxide differs altogether in its properties from the dioxide. The dioxide will not itself burn in air, and at once extinguishes a taper. The monoxide, although it extinguishes a taper, burns in air with a blue flame when a light is applied to it. The dioxide, as we have seen, turns lime-water milky: the monoxide has no effect on lime-water.

When we compare the equations

$$C + O_2 = \underset{\text{Carbon dioxide}}{CO_2}$$

$$2C + O_2 = \underset{\text{Carbon monoxide}}{2CO}$$

we see that for a given amount of carbon, twice as much oxygen is required to produce the dioxide as to produce the monoxide; and it is only when oxygen is present in insufficient quantity that the monoxide seems to be produced.

The production of carbon monoxide can easily be effected by passing a current of the dioxide over red-hot carbon. The

carbon and the carbon dioxide react with each other according to the equation—

$$\underset{\text{Carbon}}{C} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Carbon monoxide}}{2CO}$$

This action may be observed in the burning of a clear coal fire. The glowing coals consist almost entirely of carbon; and carbon is a substance which burns without flame. It will be seen, however, that little blue flames flicker on the top of the fire. These blue flames are due to the combustion of carbon monoxide. When air enters the fire at the bottom of the grate, its oxygen combines with the carbon of the coal to produce carbon dioxide, which, rising higher in the fire, comes into contact with red-hot carbon, and is converted into carbon monoxide. The carbon monoxide continues to ascend until it escapes at the top of the fire, where it mixes with more air, and once more produces carbon dioxide.

$$\underset{\text{Carbon monoxide}}{2CO} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Carbon dioxide}}{2CO_2}$$

The formulæ of the oxides of carbon indicate that the monoxide for a given quantity of carbon contains less oxygen than the dioxide. We therefore say that the carbon in carbon monoxide is at a lower **stage of oxidation** than the carbon in carbon dioxide, or that carbon in the monoxide is less highly oxidised than carbon in the dioxide.

Another example of an element which combines with oxygen in more than one proportion is to be found in sulphur. When sulphur burns in air or in oxygen under ordinary conditions, the chief product of the combustion is sulphur dioxide SO_2, but at the same time a small quantity of another oxide, sulphur trioxide SO_3, is formed. But even though there is a large excess of oxygen, very little of the oxide SO_3 is produced, by far the greater part of the sulphur remaining in the less highly oxidised stage of SO_2. In this respect sulphur differs altogether from carbon. The tendency for carbon is to pass on combustion into the higher stage of oxidation, while the tendency for sulphur is to remain at the lower stage of oxidation.

When an element unites with oxygen in more than one proportion, the various oxides produced are frequently distinguished from one another by means of the Greek numerals

prefixed to the word oxide. The numbers indicate the numbers of oxygen symbols contained in the formula, thus:

Carbon **Mon**oxide . . .	CO
Carbon **Di**oxide . . .	CO_2
Sulphur **Di**oxide . . .	SO_2
Sulphur **Tri**oxide . . .	SO_3
Nitrogen **Tetr**oxide . . .	N_2O_4
Nitrogen **Pent**oxide . . .	N_2O_5
Phosphorus **Pent**oxide . .	P_2O_5

Although many elements combine directly with oxygen when raised to a certain temperature, this is by no means invariably the case. The metal mercury when kept at its boiling point in presence of air or oxygen, slowly unites with the oxygen to form a quantity of mercuric oxide.

$$2Hg + O_2 = \underset{\text{Mercuric oxide}}{2HgO}$$

If we heat this oxide, however, to a slightly higher temperature than that at which it was formed, it breaks up again into metallic mercury and oxygen, which cannot be made to unite by further raising the temperature. This decomposition of mercuric oxide is sometimes used as a means of preparing a small quantity of oxygen (p. 86).

If instead of the metal mercury we take the metal silver and heat it, we find that at no temperature will it combine with oxygen at the ordinary pressure to form oxide of silver. At high pressures, however, silver may be made to combine with oxygen. Oxide of silver may also be formed easily by indirect methods. When heated it decomposes into metallic silver and oxygen.

$$\underset{\text{Silver oxide}}{2Ag_2O} = \underset{\text{Silver}}{4Ag} + \underset{\text{Oxygen}}{O_2}$$

The oxide MgO, on the other hand, formed by the combustion of magnesium, cannot be decomposed by heat, no matter how high the temperature is raised.

Magnesium is therefore an example of a metal which forms an oxide by direct combustion which is perfectly stable towards heat. Mercury is a metal which slowly oxidises at a moderate temperature to form an oxide, but this oxide easily decomposes again when the temperature is raised. Silver is an

example of a metal which will not form an oxide at ordinary pressures by direct union with oxygen, and is reproduced from the oxide by heating.

We have already had instances of the production of oxides by decomposition. We have seen that both calcium carbonate and calcium hydroxide decompose at a red heat with formation of calcium oxide, carbon dioxide, and water according to the equations—

$$\underset{}{CaCO_3} = \underset{\text{Calcium oxide}}{CaO} + \underset{\text{Carbon dioxide}}{CO_2}$$

$$\underset{}{Ca(OH)_2} = \underset{\text{Calcium oxide}}{CaO} + \underset{\text{Water}}{H_2O}$$

Many other carbonates and hydroxides decompose in a similar manner, giving off respectively carbon dioxide and water as gases, and leaving behind a residue of a metallic oxide.

Oxides may sometimes be formed by the careful decomposition of nitrates by heat. Lead nitrate when heated gives off gaseous nitrogen peroxide and oxygen, and leaves a residue of lead monoxide (litharge), the decomposition taking place according to the equation—

$$\underset{\text{Lead nitrate}}{2Pb(NO_3)_2} = \underset{\text{Lead monoxide}}{2PbO} + \underset{\text{Nitrogen peroxide}}{4NO_2} + \underset{\text{Oxygen}}{O_2}$$

Similarly, mercuric nitrate decomposes when heated to form mercuric oxide, the same gases being given off. In this case the heating must be done very gently, otherwise the temperature would rise to such a degree as to decompose the mercuric oxide which is formed.

The oxides of the elements form an extremely important class of substances, which may be divided into several subclasses, the chief of which are the **basic oxides**, and the **acidic oxides**. The basic oxides produce bases by union with water, or can be derived from bases by depriving them of water. Acidic oxides, on the other hand, produce acids by union with water, or can be formed by depriving acids of water.

An example of a basic oxide has already been met with in calcium oxide. This substance unites readily with water to form the base calcium hydroxide, and can be reproduced from calcium hydroxide by heating that substance to a red heat, the reversible equation being

$$CaO + H_2O \rightleftharpoons Ca(OH)_2$$

Zinc oxide is another example of a basic oxide. It, however, cannot be made to unite directly with water, to give the base zinc hydroxide $Zn(OH)_2$, but it can easily be derived from zinc hydroxide by heating, the equation being—

$$\underset{\text{Zinc hydroxide}}{Zn(OH)_2} = \underset{\text{Zinc oxide}}{ZnO} + H_2O$$

Examples of acidic oxides, or **acid anhydrides**, as they are sometimes called, have been seen in carbon dioxide and sulphur dioxide, which unite with water to form carbonic acid and sulphurous acid respectively, according to the equations—

$$\underset{\substack{\text{Carbon dioxide}\\\text{(Carbonic anhydride)}}}{CO_2} + H_2O \leftrightharpoons \underset{\text{Carbonic acid}}{H_2CO_3}$$

$$\underset{\substack{\text{Sulphur dioxide}\\\text{(Sulphurous anhydride)}}}{SO_2} + H_2O \leftrightharpoons \underset{\text{Sulphurous acid}}{H_2SO_3}$$

The acids formed from these anhydrides cannot, however, be obtained in the pure state, on account of the ease with which they decompose into the anhydrides and water, the equations for the decomposition being the reverse of those for their formation. Other acid anhydrides have a much greater tendency to remain combined with water—*e.g.* sulphuric anhydride SO_3, which unites with water as follows:—

$$SO_3 + H_2O = H_2SO_4$$

the sulphuric acid so produced only regenerating the anhydride with difficulty.

Some oxides, such as nitric oxide NO, are said to be **neutral oxides**—that is, neither acidic nor basic; but such oxides are exceptional, nearly all oxides possessing a more or less strongly marked acidic or basic character.

The *chemical* distinction between **metals** and **non-metallic elements** is chiefly based on the character of their oxides. *The non-metals form no basic oxides; every metal, on the other hand, forms at least one basic oxide.*

CHAPTER X

FORMATION AND DECOMPOSITION OF SALTS

We have seen in a previous chapter how salts may be produced by the mutual neutralisation of acids and bases. This is not the only way in which salts may be formed. Bases, which are metallic hydroxides, are related to metallic oxides by having in addition water in their composition. If now, instead of the base itself, we bring a basic oxide in contact with an acid, the two substances interact to produce a salt, the only difference from the ordinary production of salts by neutralisation being that less water is formed in the action. Thus zinc oxide is at once acted on by hydrochloric acid, and by sulphuric acid, the reactions taking place according to the following equations :—

$$ZnO + 2HCl = ZnCl_2 + H_2O$$
$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

Zinc chloride and zinc sulphate are the salts produced. If we compare these equations with the following, which show the production of the same salts from zinc hydroxide :—

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$
$$Zn(OH)_2 + H_2SO_4 = ZnSO_4 + 2H_2O$$

we see that twice as much water is produced in the second case as in the first ; but that the other products of the reaction are exactly the same.

All basic oxides are acted on by acids in this way, and produce the same salts as would be produced from the hydroxides which are derived from these basic oxides by the addition of water.

Another important method of salt production is by the **action of acids on metals.** Acids are frequently said to *dissolve* metals, but it must be noted that the metal is not dissolved by the acid in the same sense as salt is dissolved

by water. If we evaporate a solution of salt to dryness, the original salt is obtained as a residue. If we evaporate a solution of zinc in sulphuric acid to dryness, we do not obtain the metal zinc, but the salt zinc sulphate. A metal when it dissolves in acid is altogether changed; it is converted by the acid into a soluble salt of the metal, which then dissolves—*i.e.* the solution obtained by acting on an acid with a metal is a solution of a salt, and not a solution of the metal itself. The different acids vary in their action on metals. Hydrochloric acid and dilute sulphuric acid act in general least readily; nitric acid, and concentrated sulphuric acid, most readily. Heat in every case promotes the action of an acid on a metal.

Zinc is attacked by all three acids, whether dilute or concentrated. With dilute sulphuric acid the action is

$$\underset{\text{Zinc}}{Zn} + H_2SO_4 = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}$$

With hot concentrated sulphuric acid the action is

$$\underset{\text{Zinc}}{Zn} + 2H_2SO_4 = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Water}}{2H_2O}$$

When concentrated sulphuric acid acts on a metal, sulphur dioxide and water are produced at the same time as a sulphate of the metal, instead of the hydrogen gas which appears when dilute sulphuric acid is employed. Sulphur dioxide is a non-combustible gas which is moderately soluble in water, and can easily be recognised by its characteristic smell of burning sulphur. Hydrogen is a combustible gas, which, when pure, is free from smell. It will be noted that twice as much sulphuric acid is required to convert zinc into zinc sulphate when the acid is concentrated, as when the acid is dilute.

With hydrochloric acid, whether concentrated or dilute, the action is

$$\underset{\text{Zinc}}{Zn} + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + \underset{\text{Hydrogen}}{H_2}$$

This type of reaction is always met with when hydrochloric acid acts on a metal. The chloride of the metal and hydrogen gas are the only products.

The action of nitric acid on metals is usually somewhat complicated, a nitrate of the metal being almost always formed together with water and some compounds of nitrogen(pp. 174-7). The fact which the student should specially note is that, with rare exceptions, *hydrogen is not evolved when a metal dissolves in nitric acid.*

It has been stated above that hydrochloric and dilute sulphuric acid are usually somewhat less active, so far as the solution of metals is concerned, than nitric or concentrated sulphuric acid. The metals copper, mercury, and silver, for instance, are not attacked by dilute sulphuric or by hydrochloric acid, but will readily dissolve in nitric or in hot concentrated sulphuric acid, with formation of nitrates or sulphates. This difference in action will be referred to again in the sequel.

There are many other ways of producing salts; but those just given are the most important, and will suffice at present for the student.

Decomposition of salts by heat.—We have seen that the metallic salts may be derived on the one hand from an acid, and, on the other, from the hydroxide or basic oxide of a metal, or even from the metal itself. When such metallic salts are heated, they very frequently decompose with separation of the metallic or basic part from the acidic part. We have already had an instance of this in the action of heat on calcium carbonate, which decomposes into the metallic oxide CaO and the acidic anhydride CO_2, according to the equation—

$$CaCO_3 = CaO + CO_2$$

Practically all **carbonates** decompose in this manner at a red heat or below it, the chief exceptions being sodium carbonate Na_2CO_3, potassium carbonate K_2CO_3, and barium carbonate $BaCO_3$. Again, we have seen that mercuric nitrate, when heated, decomposes with production of mercuric oxide HgO, and gases originally derived from the nitric acid.

$$2Hg(NO_3)_2 = \underset{\text{Mercuric oxide}}{2HgO} + \underset{\text{Nitrogen peroxide}}{4NO_2} + \underset{\text{Oxygen}}{O_2}$$

Nearly all metallic **nitrates** decompose in a similar way, leaving behind a residue of a metallic oxide, the chief exceptions being

the nitrates of potassium and sodium KNO_3 and $NaNO_3$ (*see* p. 124).

The **chlorides** derived from hydrochloric acid contain no oxygen, and can therefore, when heated alone, leave no residue of a metallic oxide, although sometimes, when heated in air, they are partially converted into oxides by the action of the oxygen of the air. The metallic chlorides very frequently withstand a high degree of heat before any change occurs, and then they often merely vaporise without decomposition.

The **sulphates** of the metals usually withstand a considerable amount of heating without decomposition, but at a dull red heat they mostly decompose, giving off an oxide of sulphur, and leaving behind a residue of metallic oxide. The sulphates of potassium, sodium, calcium, barium, and lead may, however, be heated to redness without decomposition.

CHAPTER XI

THE GENERAL LAWS FOR GASES

If we wish to ascertain the quantity of a gas, we usually find it more convenient to measure its volume rather than to weigh it, as the weighing of gases is a troublesome operation. But it must be borne in mind, that while the weight of a given quantity of gas remains unchanged under all conditions, the volume varies very much according to the conditions under which we measure it. In the first place, the volume of a gas varies with the pressure upon the gas. The variation, however, takes place according to a fixed law, which is not only always the same for a given gas, but is the same for all gases. This law is known as **Boyle's law**, and states that *the volume of a given quantity of gas varies inversely as the pressure on the gas, if the temperature remains constant.* Thus, if we reduce the pressure on a gas to one-half, the gas will double its volume; if we double the pressure on a gas, the gas will be compressed to half its volume; if we quadruple the pressure on a gas, it will be compressed to one-fourth of its original volume; and so on. This law can be expressed otherwise by saying that the product of the pressure and volume of a given quantity of gas is constant at constant temperature. If the pressure on a gas be represented by p, and the volume by v, then we have the equation—

$$pv = \text{constant},$$

provided that the temperature always remains the same.

Not only are all gases affected equally by change of pressure, their volume is also affected equally by a given change in the temperature. The law regulating the change of volume of gases caused by change of temperature is known as **Gay Lussac's law**, and may be stated as follows:—

The volume of a given quantity of gas is directly proportional to its absolute temperature, provided the pressure remains constant. If we use the centigrade divisions, the absolute

temperature of a substance is equal to its centigrade temperature plus 273. Thus the absolute temperature corresponding

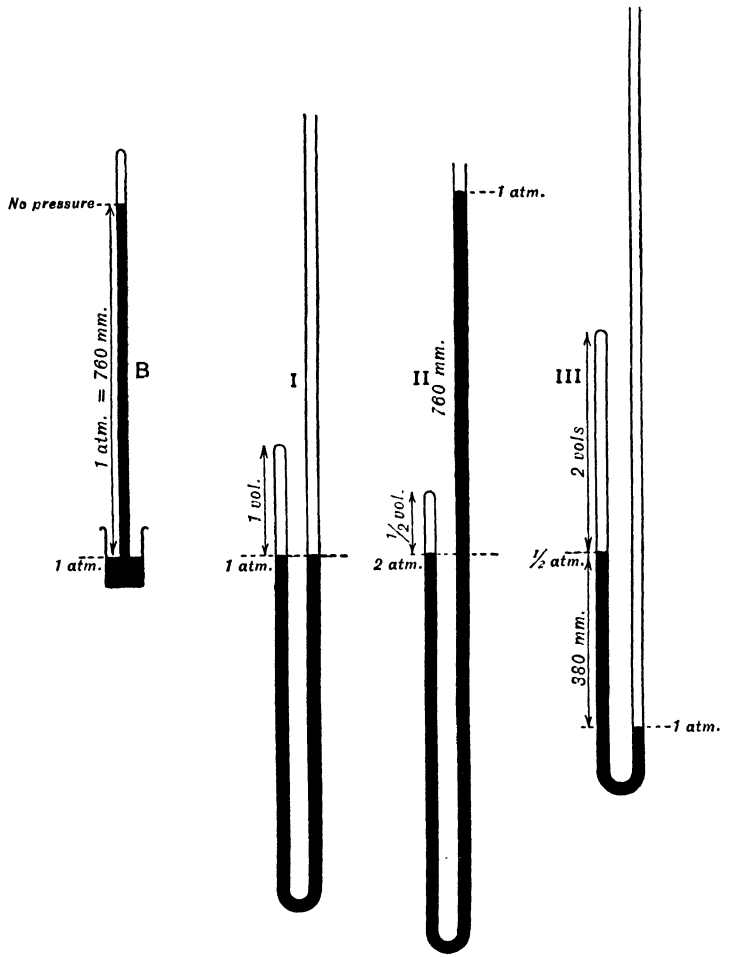


Fig. 16.—Diagram illustrating Boyle's Law.

B represents a mercurial barometer showing the average atmospheric pressure. *I*, *II*, and *III* show the volumes occupied by the same amount of gas at pressures of 1, 2 and ½ atmospheres respectively.

to 10°C. is 10 + 273 = 283. The volume of a given quantity of gas will be doubled if we heat from 0°C. to 273°C., for the

absolute temperatures corresponding to these are $0+273$ and $273+273$: the absolute temperature has been doubled, and consequently the volume of the gas is doubled.

Suppose now that the pressure and the temperature of a gas are both changed. By combining the above laws we arrive at the following expression:—If p_0, v_0, T_0, are the pressure, volume, and absolute temperature of a gas under one set of conditions; p_1, v_1, T_1, the corresponding magnitudes under another set of conditions, then

$$\frac{p_0 v_0}{T_0} = \frac{p_1 v_1}{T_1}$$

If any five of these six magnitudes are known, we can calculate the remaining magnitude. Thus we are in a position to solve a problem like the following:—"If a gas is heated from 10°C. to 20°C., by how much will the pressure on it have to be increased in order to bring it back to its original volume?"

Substituting the numerical values for the temperature in the above equation, and putting as the conditions of the problem require $v_1 = v_0$, then—

$$\frac{p_0 \cdot 273}{283} = \frac{p_1 \cdot 273}{293}$$

$$p_1 = p_0 \times \frac{293}{283}$$

and the increase of pressure is $\frac{10}{283}$ of the original value.

Knowing these simple laws for gases, it is possible to read the volumes of gases under any conditions which may be found convenient, and calculate from that volume and these conditions the volume which the gas would occupy under what we call normal conditions. **Normal pressure** we take to mean the average pressure of the atmosphere, which is equal to the pressure of a column of mercury 760 mm. high. The **normal temperature** is the temperature of melting ice—namely, 0°C. It is convenient to have these standard conditions (N.T.P.) for measuring the volumes of gases, for it enables us easily to pass from the volumes of gases to their weights.

On account of the gas laws holding for all gases—that is, on account of all gases being affected equally by changes in temperature and pressure, we can compare the volumes of gases with each other, not only under the standard conditions but under

any conditions, provided they are the same for the gases compared. Thus, if under one set of conditions the volume of a certain quantity of one gas is equal to twice the volume of a certain quantity of another gas, then, no matter how the conditions are changed, the volume of the first gas will always be double the volume of the second gas, if the volumes of the two gases are measured under conditions which are the same for both.

Concentration and Density of Gases.—The term **concentration** is used by chemists to express the weight of a substance contained in a given volume. Thus the concentration of solutions is frequently expressed as the number of grams of dissolved substance contained in a litre of the solution; and we say, for example, that the concentration of hydrochloric acid solution of constant boiling point is 223 grams per litre, meaning thereby that a litre of this solution contains 223 grams of hydrochloric acid.

The term may be applied similarly to gases, and we may say that oxygen at 0° and 760 mm. has a concentration which may be expressed as 1.43 grams per litre; in other words, the weight of a litre of oxygen at normal temperature and pressure (N.T.P.) is 1.43 grams (approximately).

The **density** of a substance is defined as the number of grams of it which is contained in 1 cubic centimetre and is thus proportional to its concentration. The absolute density of oxygen, then, according to this definition, would be 0.00143. Since, however, according to the gas laws, the volume of a gas changes greatly both with temperature and pressure, it follows that the concentration or density of the gas exhibits corresponding changes. It is seldom, therefore, that the absolute density of a gas is utilised, since even slight variations of temperature and pressure will change its value. The notion of **relative density** is, however, convenient, the densities of all gases being referred to that of some standard gas under the same conditions of temperature and pressure. Hydrogen, the lightest known gas, is frequently adopted as the standard gas to which the densities of other gases are referred. On this standard oxygen has the relative density 16 (approximately); in other words, oxygen will, bulk for bulk, always be sixteen times as heavy as hydrogen, if the two gases are measured at the same temperature and pressure.

The following table exhibits, in round numbers, the densities of various common gases referred to that of hydrogen as unity :—

		Density
Elements	Hydrogen	1
	Nitrogen	14
	Oxygen	16
	Chlorine	35·5
Mixture	Air	14·5
Compounds	Carbon monoxide	14
	Ammonia	8·5
	Carbon dioxide	22
	Hydrochloric acid	18.25
	Sulphur dioxide	32

It may be noted that gases with relative density less than 14.5 are lighter than air, whilst those with density greater than 14.5 are heavier.

Solubility of Gases.—When a gas is only moderately soluble in a liquid, the amount of it dissolved by a given quantity of the liquid depends upon the pressure, and the solubility is generally stated as the number of volumes of the gas dissolved by one volume of the liquid. The manner in which a quantity of gas dissolved varies with the pressure is very simple, and is known as **Henry's law.** *At a given temperature the weight of a gas dissolved by a given bulk of liquid is proportional to the pressure of the gas.*

Thus, at 0°C. water dissolves 4 per cent. of its own volume of oxygen at one atmosphere pressure; at two atmospheres pressure it would dissolve twice as much by weight; at three atmospheres three times as much; and so on. It must not be supposed, however, that at two atmospheres pressure the water will dissolve 8 per cent. of its own volume of oxygen, for at two atmospheres pressure each volume of oxygen gas will contain twice the weight of oxygen that it did at one atmosphere pressure. Thus, doubling the pressure doubles the weight of gas dissolved, but it halves the volume which the gas occupies before it is dissolved. If we then consider volumes, we may state Henry's law in the form that *the volume of a gas dissolved by a given volume of liquid is independent of*

the pressure. We can thus say that at 0°C. water will always dissolve 4 per cent. of its volume of oxygen, no matter what the pressure of the oxygen is, although, of course, the actual weight of oxygen dissolved varies directly with the pressure.

Another form in which Henry's law may be stated is that *at a given temperature the ratio of the concentrations of a gaseous substance in the gas and in its saturated solution is constant.* Thus the concentrations of oxygen in the gas itself and in water saturated with the gas at 0° are in the ratio of 100 to 4. This ratio is sometimes spoken of as a **distribution ratio,** as it shows how the oxygen is distributed between the gaseous and liquid portions.

In giving the solubility of a gas in water it is customary to reduce the dissolved volume, measured at the temperature of the experiment, to the volume which it would occupy at 0°. This reduced volume is usually spoken of as the **absorption coefficient** of the gas.

The solubilities of different gases in water are widely different, as the following table shows. The numbers given are the volumes of gas dissolved by one volume of water at 0° and 760 mm. :—

Ammonia, NH_3	1050	volumes.
Hydrochloric acid, HCl	505	,,
Sulphur dioxide, SO_2	80	,,
Sulphuretted hydrogen, H_2S	4.4	,,
Carbon dioxide, CO_2	1.8	,,
Argon, Ar	0.06	,,
Oxygen, O_2	0.04	,,
Nitrogen, N_2	0.02	,,
Hydrogen, H_2	0.02	,,

The solubility of gases almost invariably falls off as the temperature rises, and gases may usually be expelled from water by boiling, hydrochloric acid being an exception to this last statement. Gases which, like ammonia and hydrochloric acid, are excessively soluble in water, do not obey Henry's law.

CHAPTER XII

GAY LUSSAC'S LAW OF VOLUMES AND AVOGADRO'S PRINCIPLE

Reacting Volumes of Gases.—When we measure the volumes of gases which take part in chemical actions, we find that they are related in a very simple way to one another, provided that the volumes are all measured at the same temperature and pressure. Thus, when acidulated water is decomposed by an electric current, two volumes of hydrogen are produced at one pole (the cathode) for each volume of oxygen produced at the other (the anode). If we reverse this action, we find that exactly these proportions of oxygen and hydrogen unite to form water, and not only so, but that the volume of water vapour produced is exactly equal to the volume of hydrogen burned. Again, hydrogen and chlorine unite in equal volumes to produce hydrochloric acid gas, the volume of which is exactly equal to the sum of the volumes of the hydrogen and chlorine; and when carbon or sulphur is burned in oxygen, the volume of the carbon dioxide or sulphur dioxide produced is exactly equal to the volume of oxygen which has disappeared.

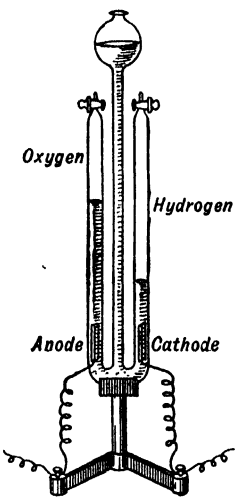


Fig. 17.—Volumetric Composition of Water.

When water, acidulated with sulphuric acid, is decomposed by an electric current, the volume of hydrogen produced may be seen in the above apparatus to be twice as great as the volume of oxygen produced simultaneously. The taps permit the gases to be tested. The water is forced by the accumulating gas to rise into the bulb on the middle tube.

This regularity, usually termed **Gay Lussac's Law of Volumes**, from its discoverer, is general, and may be stated as follows:—

When gases play a part in a chemical action, whether as reacting substances or as products of the reaction, the proportions by

volume in which they take part in the reaction may be expressed by means of the simple whole numbers.

Avogadro's Principle.—When we consider reactions involving gaseous substances we find then that the following regularities have been established:—

1. Gaseous substances always enter into chemical actions in simple multiples of their reacting weights (Law of Multiple Proportions).
2. Gaseous substances always enter into chemical actions in simple multiples when measured by their volumes (Gay Lussac's Law of Volumes).

It follows, therefore, that the volumes occupied by the characteristic reacting weights of different gases must be simply related to one another.

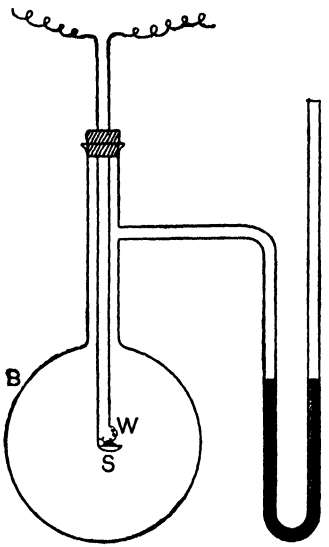


Fig. 18.—Volumetric Composition of Carbon Dioxide or Sulphur Dioxide.

A piece of charcoal or sulphur placed in the spoon *S* may be made to ignite in the oxygen with which the closed bulb *B* is filled by heating the wire *W* by means of an electric current. After the combustion is completed and the gas cooled to the temperature of the air, it will be found that the volume of the gas, as indicated by the levels of the columns of liquid in the bent tube, has remained unchanged.

Avogadro's principle consists in a definite fixing of this relationship. It may be stated as follows:—

The molecular weights of different gases are proportional to the weights of equal volumes of these gases measured at the same temperature and pressure. In other words, *the molecular weights of different gases are proportional to their relative densities.* Here we have a definition of the term **molecular weight**, which applies in the first instance only to gases. It is a special reacting weight chosen from several possible multiples in order that the relationship between reacting weight and reacting volume shall be expressed in a simple, general, and self-consistent manner.

The molecular weight in grams, or **molar weight**, may be defined numerically as follows. *The molar weight of a gas is*

equal to the number of grams of the gas which would occupy 22.4 litres at 0° and 760 mm.

The volume occupied by the gram molecular weight of a gas is often termed the **gram-molecular volume** or **molar volume**, and is equal to 22.4 litres at N.T.P.

Determination of Molar Weights

Gases.—In order to determine the molar weight of a gas—that is, the weight of the gas in grams which would occupy 22·4 litres at normal temperature and pressure—it is not necessary actually to weigh the gas under these conditions or to use a vessel of this inconveniently large volume. All that is necessary is to make simultaneous measurements of the weight, volume, temperature and pressure of any convenient quantity of the gas, and to calculate from them, by means of the simple gas laws, what the required weight would be.

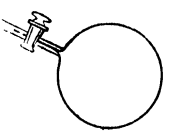


Fig. 19.

The operation can be carried out practically by means of a glass bulb of moderate dimensions, which is provided with a stop-cock as shown in the figure. The bulb is connected with an air-pump until the air has been completely exhausted from it. It is then weighed on an accurate balance. Next, the gas whose molar weight is to be determined is admitted into the bulb, usually at the atmospheric pressure, and the value of this pressure is noted. The bulb with its contents is accurately weighed again, and the difference between this weight and the original weight gives the weight of the gas in the bulb.

The temperature at which the bulb was filled is also noted, and finally the volume of the bulb is ascertained. This may be done by filling the bulb up to the stop-cock with a liquid of known specific gravity, such as water or mercury, and ascertaining what the weight of this liquid is. The following is an example of calculation of a molar weight. A bulb whose volume was 214 cc. contained 0.281 grams of oxygen at 19°C. and 744 mm. From these data the molar weight of oxygen may be ascertained by solving the following problem:—If 0.281 grams of a gas at 19°C. and 744 mm. occupy 0.214 litres, what weight of it will occupy 22.4 litres at 0°C. and

760 mm.? We may first reduce the volume under the given conditions to N.T.P. as follows:—

$$\frac{744 \times 0.214}{273 + 19} = \frac{760x}{273}$$

$$x = 0.196$$

Since 0.281 grams occupy 0.196 litres at normal temperature and pressure, the weight which would occupy 22.4 litres under the same conditions is

$$\frac{22.4 \times 0.281}{0.196} = 32.0.$$

The molar weight of oxygen is thus 32, and since the symbol O stands for 16, we take O_2 as the molar formula of oxygen.

Vapour Density.—In order that the molar weight of a substance may be determined, it is not necessary that it should exist as a gas under ordinary conditions. If the substance is liquid or solid at the ordinary temperature, we may, by raising the temperature, convert it into a gas or vapour, and then determine precisely as before the weight, volume, temperature and pressure of the substance whilst it is in the vaporous condition. If we wish, for example, to determine the molar weight of water, we may do so by placing some liquid water in a bulb whose volume is known, the quantity of liquid being greater than is requisite to fill the whole bulb with vapour. The bulb, with its liquid contents, is now immersed in a liquid of known temperature, which must be above the boiling point of water, say in an oil bath at 120°C. The water in the bulb boils and expels the air from the bulb, and the boiling is continued until all the liquid water has disappeared. The bulb is then closed by sealing off the end of the projecting stem in the blowpipe flame, and is removed from the bath, wiped clean, and allowed to cool. The temperature of the bath and the atmospheric pressure, which is equal to the pressure of the water vapour at the moment the bulb was closed, are accurately noted. On cooling, the water vapour in the interior of the bulb mostly condenses to

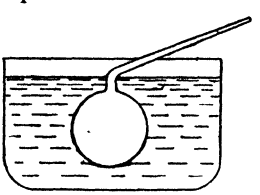


Fig. 20.

liquid water, but as the bulb is tightly closed, this change has no effect on the weight of the bulb and its contents, which is now accurately ascertained. By deducting the weight of the bulb and measuring its volume all the data necessary for calculating the molar weight are now known. The method here described is known as Dumas's method of vapour density determination.

Molecular Formulæ.—The practical advantage of molar weights as defined by Avogadro's principle is at once apparent when we come to deal with reactions which involve gases. In the first place, we always choose the formulæ of gases so that they shall represent the molar weight of the gas. For example, the molar weight of hydrogen is 2, since it is found by experiment that 2 grams of hydrogen occupy 22.4 litres at N.T.P. Similarly the molar weight of chlorine is 71, and that of hydrochloric acid 36.5. To represent hydrogen gas we therefore use the formula H_2, which indicates 2 grams, and not the simpler formula H, which indicates only 1 gram. Chlorine gas is similarly represented by the formula Cl_2 and hydrochloric acid gas by the formula HCl, since these formulæ stand for 71 grams and 36.5 grams respectively.

Using molar or molecular formulæ, we represent the combination of hydrogen and chlorine to form hydrochloric acid by the following equation:—

H_2	+	Cl_2	=	$2HCl$
22.4 l		22.4 l		2×22.4 l
1 vol.		1 vol.		2 vols.

and not by the simpler equation—

$$H + Cl = HCl$$

since the former, in addition to yielding information as to the quantities by weight which enter into the reaction, also gives us directly the correct proportions by volume, as for each molecular formula we may substitute the volume of 22.4 l, at N.T.P.

Similarly, if we write the molecular equation

C	+	O_2	=	CO_2
		22.4 l		22.4 l

we see at once that the volume of carbon dioxide produced is equal to the volume of oxygen consumed.

We find, further, that by the use of molecular formulæ we are enabled at once to pass from the weights of gases to their volumes and conversely. This is a great practical advantage, because we, in general, measure the volumes of gases and not their weights, so that it is very important, if we are to compare the weights of solids and gases occurring in a reaction, that we should be able to pass freely in the case of the latter from weight to volume and from volume to weight.

It must be remembered, however, in making this passage, that the volume of 22.4 litres holds good for 0° and 760 mm. only. If the actual volumes considered are measured under other conditions of temperature and pressure, they must be reduced to the normal conditions before the passage from volumes to weights can be made.

Suppose we have to solve the following question:—What volume of carbon dioxide at N.T.P. can be produced by heating 20 grams of calcium carbonate to redness? We first of all write the equation for the action, using molecular formulæ for the gases, and then note alongside the substances whose weights are required, the weight in grams represented by the formulæ, and alongside the gaseous substances 22.4 litres for each molecular formula of the gases, thus—

$CaCO_3$	=	CaO	+	CO_2
100 g		[56 g]		[44 g]
—		—		22.4 litres

We at once see from this equation that 100 grams of calcium carbonate give 22.4 litres of carbon dioxide at N.T.P., and therefore that 20 grams give 4.48 litres under these conditions.

Again, we may be required to solve a question like the following:—How much calcium carbonate must be heated in order to give one litre of carbon dioxide measured at 20°C. and 770 mm.? We first of all reduce this volume to N.T.P. as follows:—

$$\frac{770 \times 1}{293} = \frac{760x}{273}$$

$$x = 0.94$$

From the above equation 22.4 l are yielded by 100 g, so that 0.94 l will be yielded by

$$\frac{100 \times 0.94}{22.4} = 4.2 \text{ g.}$$

For purposes of calculation the student will do well at first always to write down the equations for the actions involved, each formula being accompanied by the weight in grams which it expresses, and each molecular formula of a gas by the corresponding volume in litres. Thus, for example, he should write—

H_2	+	Cl_2	=	$2HCl$
2 g		71 g		73 g
22.4 l		22.4 l		2 × 22.4 l at N.T.P.

This will enable him to solve any question with regard to the weights and volumes of the gases entering into this reaction.

CHAPTER XIII

GASEOUS MIXTURES

ALL gases are capable of mixing with each other naturally—*i.e.* of **diffusing** into each other. If a bottle containing ammonia, or any other gas which is recognisable by the smell, is carefully opened, then even although the air is free from mechanical disturbance the smell of the ammonia will very soon be perceptible at a considerable distance from the bottle, showing that the ammonia gas must have diffused into the gases of the atmosphere.

The process of gaseous diffusion may also be rendered visible by choosing a coloured gas and a colourless gas for the experiment. If a small bulb containing liquid bromine is crushed at the bottom of a tall cylinder, the liquid bromine on escaping is partially converted into bromine vapour—*i.e.* bromine gas, which is easily recognised by its reddish-brown colour. If the cylinder is left to itself, the bromine vapour will be found to rise gradually, the tint throughout the cylinder not becoming uniform until several hours have elapsed. Now, bromine vapour is bulk for bulk over five times heavier than air, and the action of gravity would tend to keep the heavy vapour at the bottom of the cylinder, yet the bromine moves upwards at a considerable rate. If the cylinder is originally filled with hydrogen instead of with air, the rate of diffusion can be seen to be very much greater than in the former instance, notwithstanding the fact that bromine is eighty times heavier than an equal bulk of hydrogen. The gravitational action against diffusion in this second case is much greater than in the first, yet the diffusion proceeds at a greater rate. We have, however, been looking at the process of diffusion only from the point of view of the coloured bromine gas, but this gas alone is not responsible for the whole of the diffusion or mixing process. The air in one case and the

hydrogen in the other really play the principal part in the mixing. It is found that the lighter a gas is the faster it diffuses. Now hydrogen is $14\frac{1}{2}$ times lighter than air. It diffuses, therefore, more rapidly than air, and the process of mixing of hydrogen and bromine is consequently more rapid than the mixing of air and bromine.

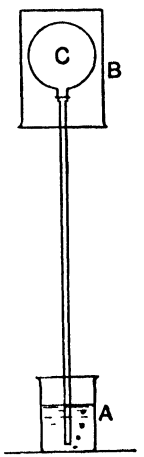


Fig. 21.—Diffusion of Gases.

The bulb *C*, of porous earthenware, has a long glass tube fastened into its neck by means of a cork. The end of this tube dips under water in the beaker *A*, and over the bulb a beaker *B*, filled with hydrogen, is inverted. Since hydrogen diffuses much faster than air, it enters *C* through the pores more rapidly than the air can pass out through them. Gas thus accumulates inside the bulb and escapes through the water in *A*.

The relation between the density of a gas and the rate at which it diffuses may be stated quite definitely. *The speed of diffusion of a gas has been found to be inversely proportional to the square root of its density.* Oxygen is sixteen times as heavy as hydrogen. These gases will therefore have speeds of diffusion proportional to—

$$\frac{1}{\sqrt{16}} : \frac{1}{\sqrt{1}} \quad \text{or} \quad \tfrac{1}{4} : 1$$

Collection of Gases. — These considerations are of importance when we come to deal with practical methods for collecting and manipulating gases. If a gas is heavier than air, it may be collected by *downward displacement* in the manner shown in the figure. The gas is delivered at the bottom of the jar, and since diffusion is a comparatively slow process, it there forms a layer heavier than the air, the surface of this layer gradually rising as more gas is delivered, and displacing the air with which the jar was originally filled. If the heavy gas is delivered slowly there is little mechanical disturbance, so that the gas and air can only mix by diffusion. It is possible in this way, then, to collect a sample of a heavy gas which will contain very little air.

If the heavy gas were delivered at the top of the cylinder

it would, in virtue of its greater weight, tend to fall to the bottom of the cylinder; we should therefore have a current of the heavy gas proceeding downwards and the lighter air coming upwards. This would involve considerable disturbance, so that the two gases would mingle not only by diffusion but by actual mechanical mixing.

When the gas which it is desired to collect is lighter than air, it may be collected by *upward displacement*, as shown in the figure. The jar in which the gas is to be collected is inverted so that the open mouth is downwards. The delivery tube ends at the upper portion of the jar. The light gas as it is delivered forms a layer at the upper end of the jar, which gradually increases in size, forcing the heavier air downwards. There are thus no conflicting currents of the two gases, and, consequently, no mechanical mixing. Any process of mixing that goes on must be due to the natural diffusion of the gases.

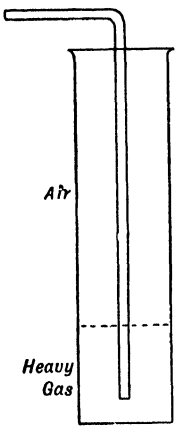


Fig. 22.—Collection by Downward Displacement.

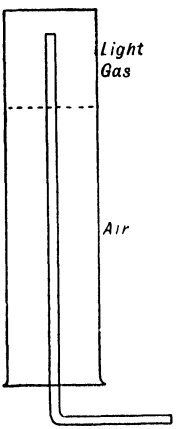


Fig. 23.—Collection by Upward Displacement.

The dotted lines in the figures show the surface of separation of the gases.

It has just been said that air is about 14.5 times as heavy as hydrogen — *i.e.* about 29 grams of air can be contained in 22.4 litres at N.T.P. Any gas, then, whose molecular weight is greater than 29, is heavier than air, and can be collected by downward displacement; any gas whose molecular weight is less than 29, is lighter than air, and can be collected by upward displacement. Examples of the former class are CO_2, HCl, N_2O, O_2, the corresponding weights being 44, 36.5, 44, 32: examples of the second class are H_2, NH_3, CH_4, with the weights, 2, 17, 16 respectively.

In the above methods, the gases which it is desired to collect are made to displace the air with which the vessels are

originally filled. Another very common method of collecting gases is to collect them over a liquid. This method resembles the method of collection by upward displacement; only the vessel is originally filled, not with air, but with a suitable liquid. The resemblance of collection by upward displacement depends, of course, on the fact that all gases are much lighter than liquids. In selecting a liquid for the purpose, it is evident that one must be chosen in which the gas is insoluble, or only slightly soluble, for otherwise the gas which it is desired to collect would dissolve in the liquid, and be lost as gas. The liquid, usually water, is contained in a comparatively shallow vessel, in which the collecting jars, also filled with the liquid, are immersed mouth downwards. The end of the tube which delivers the gas is brought immediately beneath the mouth of the jar in which the gas is to be collected. The gas bubbles up through the liquid in the jar, displacing it and forcing it downwards, and the process can be continued till all the liquid is displaced (see fig. 27, p. 86).

Partial Volume and Partial Pressure. — When we are dealing with a mixture of gases we can consider the mixture from two points of view. In the first place, it should be noted that gases, when mixed, do not (for ordinary purposes) influence each other's pressure or each other's volume. We can consider, therefore, that the total volume of the gas mixture is the sum of the volumes of the separate gases it contains. Thus we say that, roughly speaking, air is a mixture containing one volume of oxygen, and four volumes of nitrogen. This means that if the air were separated into its components, the nitrogen would occupy four-fifths of the original volume, and the oxygen would occupy one-fifth, provided all measurements were made under the same conditions of temperature and pressure. These volumes may be called the **partial volumes** of the components, so that we can say that the total volume of a gas is equal to the sum of the partial volumes of its components.

The other way of considering a mixture of two gases is to look at it from the point of view of their pressures. We can suppose the mixture to be separated into its two component gases, each component occupying a volume equal to the original volume of the mixture. Thus, we can suppose the

nitrogen and the oxygen of air to be separated from each other, and each to occupy the whole volume occupied by the air from which they were obtained. Now, if we consider that at the pressure of the original air oxygen occupies only one-fifth of the original volume of the air, then if it is expanded so as to occupy a volume equal to the whole volume occupied by the air, its pressure, by Boyle's law, will be reduced to one-fifth of the original pressure. Similarly, if the nitrogen is expanded so as to occupy, not four-fifths of the original volume, but a volume equal to the total original volume, then its pressure will be reduced to four-fifths of the original pressure. We can therefore say that the total pressure of the air is composed of the pressure of oxygen, which is equal to one-fifth of the total, and of the pressure of nitrogen, which is equal to four-fifths of the total. These pressures are called the **partial pressures** of the components, and we may state in general that the total pressure of a mixture of gases is equal to the sum of the partial pressures of its components.

When we are dealing with the solubility of a mixture of gases, we find that each gas dissolves independently of the presence of the other gases, and we may state this in the following form, which is usually known as **Dalton's law of partial pressures**:—*Each gas in a mixture dissolves according to its own partial pressure.* For example, we may investigate the solubility of air in water, supposing that it consists of a mixture of oxygen and nitrogen, which for rough purposes of calculation we may represent by the proportions of $\frac{1}{5}$ to $\frac{4}{5}$. The absorption coefficient of oxygen in water at 0°C. is 0.04; the absorption coefficient of nitrogen at the same temperature is 0.02. Now, if we suppose the pressure of the atmosphere to be at its average value, then the quantity of oxygen which will be dissolved by one volume of water will amount to $0.04 \times \frac{1}{5} = 0.008$, this volume being measured at one atmosphere pressure. Similarly, a quantity of nitrogen dissolved by one volume of water will be $0.02 \times \frac{4}{5} = 0.016$, this volume being again measured at one atmosphere pressure. Measuring by volumes, then, the quantity of oxygen dissolved by the given quantity of water is equal to $\frac{1}{2}$ the volume of the dissolved nitrogen, instead of being $\frac{1}{4}$ of the volume, as it was in the original mixture.

CHAPTER XIV

THE KINETIC THEORY OF GASES—MOLECULES AND ATOMS

FROM what has been stated in previous chapters it appears that gases obey certain general laws, which in the case of liquids and solids do not exist. This similarity in behaviour of all gases would naturally lead to the idea that all gases must have a similar structure. The kinetic theory of gases assumes that every gas consists of similar particles which are in continual movement in all directions in straight lines, from which they are deflected by collisions with each other or with the walls of the containing vessels. This spontaneous movement of the gas particles, or **gas molecules**, accounts in the first place for the diffusion of one gas into another, or its movement into a vacuum. The pressure of a gas on this theory is caused by the impacts of the molecules on the solid or liquid surfaces in contact with it, and may be increased by augmenting the number of molecules in a given volume; or, if the volume is kept constant, by increasing their average speed, which may be done by raising the temperature. Thus, diminished volume or increased temperature is accompanied by increased pressure, in accordance with the laws of Boyle and of Gay Lussac.

When we compare the number of molecules present in equal volumes of two different gases under like conditions of temperature and pressure, we assume according to the theory that these numbers are equal. For example, a litre of hydrogen at N.T.P. will contain the same number of molecules as a litre of oxygen at N.T.P. But since a litre of oxygen weighs sixteen times as much as a litre of hydrogen under like conditions, it follows that each molecule of oxygen weighs sixteen times as much as each molecule of hydrogen. It follows, in other words, that the weights of the molecules of different gases are proportional to their densities. Being thus proportional to the gas densities, the weights of the

molecules are also proportional to the molar weights (or gram molecular weights), and are indeed represented by the same numbers. In this way 2 is both the molar and molecular weight of hydrogen, 32 the molar and molecular weight of oxygen, etc. We thus see that the kinetic theory of gases gives results in accordance with Avogadro's principle.

The question now arises: Is the molecule of hydrogen—*i.e.* the smallest particle of hydrogen which exists in the elements as gas—identical with the smallest particle of hydrogen found in the molecules of other gases containing hydrogen? Plainly this is not so. If the molecular weight of hydrogen is 2, that of hydrochloric acid is 36.5, these numbers being in the ratios of the densities of the two gases. But 36.5 parts of hydrochloric acid contain only 1 part of hydrogen. The quantity of hydrogen, therefore, in the molecule of hydrochloric acid is only half the quantity of hydrogen in the molecule of hydrogen gas. The molecule of hydrogen is consequently not the smallest particle of hydrogen capable of existence in the molecules of gaseous compounds of hydrogen. If we now consider all the gaseous compounds of hydrogen we find that the quantities of hydrogen which their molecules contain are all multiples of half the quantity contained in the molecule of gaseous hydrogen. The half-molecule of hydrogen, therefore, is the minimum quantity of hydrogen which apparently exists in gaseous molecules containing this element, and is called the **atom** of hydrogen. For every other element analogous reasoning leads to the assumption of a similar minimum quantity, or atom, for that element.

All molecules may be regarded as being built up of atoms of the various elements. If the molecule is that of an element, the atoms of which it consists are of the same kind; if it is that of a compound, the atoms are of different kinds. Sometimes the molecule of an element consists of a single atom. This is the case with argon and with mercury vapour.

If we now regard the molecular formula-weights of gases as representing the relative weights of the various gaseous molecules, the weights represented by the various elementary symbols contained in the formula may be regarded as the relative weights of the atoms of the elements, or **atomic**

weights. The list of atomic weights given at the end of the book may therefore be regarded not merely as a system of combining weights but as the relative weights of the ultimate particles or atoms of the various elements.

The actual weights of these atoms is almost inconceivably small. The atom of hydrogen, for example, is of such minute proportions that a million times a million hydrogen atoms would only weigh about the thousand-millionth part of a milligram.

According to modern theory, the atom is not a changeless, indivisible unit, but a more or less complex structure of electrical nature, consisting essentially of a positively charged nucleus, around which circulate particles of negative electricity, or electrons, much as satellites revolve round a planet.

CHAPTER XV

THE ATMOSPHERE

It has already been stated that air is a mixture consisting chiefly of nitrogen and oxygen. In view of what we have learned concerning the behaviour of a mixture of gases, we can give the composition of the air either in terms of the partial volumes, or of the partial pressures. The first method is that usually adopted in giving the composition of a mixture of gases; but, as we have seen, it is sometimes convenient to adopt the second method in considering some of the properties of such mixtures. The average composition by volume of what we term purified air is—

Nitrogen,	N_2	78.2	volumes per cent.
Oxygen,	O_2	21.0	,, ,,
Argon,	A	0.8	,, ,,
		100.0	

The partial pressures of these gases are represented by the same numbers. If we wish to know the composition of the air by weight, we can easily calculate it from the molecular weights of the component gases, and the proportions in which these gases occur in the mixture. The calculation is performed as follows:—

78.2×28	=	2190	=	75.7 per cent
21.0×32	=	672	=	23.2 ,,
0.8×40	=	32	=	1.1 ,,
		2894		100.0

The argon in the atmosphere was only discovered in 1894, although the quantity of the gas in the air must be estimated in billions of tons. The reason why chemists were so long in detecting its presence is that, like nitrogen, it is a very

inert gas, and takes no part in those chemical actions in which atmospheric air is one of the reacting substances. It was lost sight of in the very much larger quantity of nitrogen, and was only detected by the slightly greater weight of "atmospheric nitrogen" (that is, the mixture of nitrogen and argon), when compared with the weight of pure nitrogen prepared from a chemical compound.

That the composition of the air should be practically constant is no proof of the chemical union of its components, for, as we have seen, gases mix with each other very readily, and the atmosphere is being perpetually disturbed by air currents in the form of wind.

It may be shown in many different ways that the nitrogen and oxygen in the air are not in chemical combination. In the first place, the quantities of nitrogen and oxygen in the air are not related in any simple way to the combining weights of these elements. In the second place, if pure oxygen and nitrogen in the requisite proportions are simply mixed, no sign of any chemical action can be detected, and yet the mixture has all the properties of ordinary purified air. That air is a mixture of oxygen and nitrogen can also be proved by considering the manner in which it dissolves in water.

We have seen that if air consists of a mixture of oxygen and nitrogen, in the proportions of $\frac{1}{5}$ to $\frac{4}{5}$, these proportions should be altered when the gases dissolve in water, owing to their different solubilities, and that, if we recovered the dissolved gases from the water, their proportions should then be $\frac{1}{3}$ oxygen to $\frac{2}{3}$ nitrogen (p. 76). The dissolved air can readily be expelled by boiling the water, for at the boiling point neither nitrogen nor oxygen is appreciably soluble in water. The gases thus evolved can be collected, and the composition of the gaseous mixture can be ascertained. When this experiment is performed, it is found that the dissolved air is much richer in oxygen than air before being dissolved in water, and that the proportions are very nearly those required by the above calculation. If the air had been a compound of oxygen and nitrogen, it would have been a single gas having its own single absorption coefficient, and the composition of the gas expelled from the water by boiling would have been exactly the same as the composition of the gas before it was dissolved.

If we wish to ascertain experimentally the quantity of oxygen in the air, one of the following methods may be employed :—

Oxygen being the active constituent of the atmosphere, may be made to combine with many other substances, the nitrogen and the argon, which together constitute what is still frequently called "atmospheric nitrogen," being unaffected. It is easy, then, to choose some substance which will combine with the oxygen and leave the atmospheric nitrogen behind. One such substance is phosphorus. If we leave a stick of yellow phosphorus exposed to a small quantity of moist air, the phosphorus combines slowly with the oxygen at the ordinary temperature, and after a period of a few hours all the oxygen will have been removed and converted into oxides of phosphorus, which dissolve in water. By measuring the original volume of the mixture, and then measuring the volume of the atmospheric nitrogen which remains after the oxygen has been removed, making due allowance for temperature, pressure, and the presence of moisture, the composition of the mixture by volume is at once ascertained.

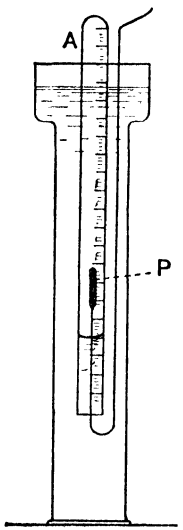


Fig. 24.—Proportion of Oxygen in Air.

A measured quantity of air in a graduated tube *A* is exposed over water to the action of a piece of yellow phosphorus *P*, fused to the end of a bent wire. When the action is complete the volume of residual gas is measured.

A more exact method may be applied to the dry mixture. We have seen that copper when heated in oxygen combines with the oxygen to form copper oxide. In a specially constructed apparatus, a measured volume of dry air may be brought into contact with copper wire which is heated to redness by means of an electric current passing through it. The copper, when it is heated, takes up all the oxygen in the air, and leaves the atmospheric nitrogen behind. A measurement of the volume of this atmospheric nitrogen gives, by subtraction from the original volume, the volume of oxygen which has been removed, and thus the volumetric composition of the purified dry air is ascertained.

Atmospheric air, besides containing these permanent constituents, also contains considerable quantities of other gases. The gas which exists in greatest quantity, although this quantity is liable to great variation, is **water-vapour**. It can be easily understood that water-vapour occurs to a large extent in the atmosphere, if we consider that nearly three-fourths of the earth's surface is covered by water, with which the atmosphere is in constant contact. This water evaporates, and consequently we find that the air is always more or less moist.

At each temperature air is capable of taking up a definite amount of moisture. Sometimes the full amount of moisture is found in the air, and the air is then said to be *saturated* with moisture. This occurs in fog or mist, or during a heavy rain. As a rule, however, the air is only about two-thirds saturated, and the average amount of moisture contained in the air at the mean temperature of the atmosphere is about 1.4 volumes per cent.

Carbon dioxide is also invariably present in the atmosphere, and although the proportions in which it is found do not vary so much as in the case of the atmospheric moisture, yet they are not so constant as the proportion of the permanent gases nitrogen, oxygen, and argon. In country air, and in the air over the ocean, the proportion of carbon dioxide is about 3 volumes in 10,000 volumes of air. This proportion does not fluctuate very much in such regions, but in towns the proportion of carbon dioxide in the air is considerably higher, the air in the streets containing usually about 4 volumes of carbon dioxide in 10,000. The larger amount of carbon dioxide in towns arises from the respiration of living beings in these places, and from the amount of carbon consumed as fuel. In inhabited rooms, especially in ill-ventilated rooms in which gas is burnt, the proportion of carbon dioxide frequently rises to 10 volumes in 10,000, and in crowded apartments occasionally reaches as much as 50 volumes in 10,000. Carbon dioxide is not in itself a poisonous gas, but its presence in the air in excessive quantity indicates insufficient ventilation.

The quantity of carbon dioxide present in air may be estimated in various ways. The methods, however, chiefly depend upon the absorption of the carbon dioxide by a

liquid such as lime water, or baryta water. The absorption takes place according to the equations—

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$
$$Ba(OH)_2 + CO_2 = BaCO_3 + H_2O$$

the calcium or barium carbonate formed being insoluble. If we know the concentration and amount of the calcium or barium hydroxide solution originally taken, and ascertain its concentration after it has been brought into contact with a measured volume of air, then by finding what the diminution in strength is, we can tell how much carbon dioxide the air originally contained.

Air can be freed from moisture and from carbon dioxide by passing it in succession through tubes containing concentrated sulphuric acid, to remove water, and soda-lime, to remove carbon dioxide. When we speak of *purified air*, we usually mean air which has been treated in this fashion.

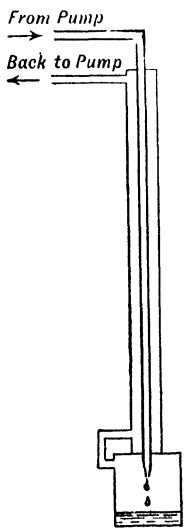


Fig. 25.

Recent observations have shown that besides the gases previously mentioned, ordinary atmospheric air contains a great many other gases which are present only in very small quantity. Thus, in the air have been found minute amounts of ammonia, hydrocarbons, hydrogen, helium, and other gases of a similar nature.

Liquid Air.—If air is sufficiently cooled it may be obtained in the liquid state at the ordinary atmospheric pressure. The reduction of temperature required, however, is very great, and is effected on the large scale by mechanical means. In one type of apparatus the air, freed from moisture and carbon dioxide, is compressed by means of a pump to a pressure of about two hundred atmospheres. It is then allowed to expand through a small orifice, its pressure being thereby reduced to one atmosphere. In the process of expansion its temperature falls about 50°. This cooled air then passes backwards through a heat-interchanger, the object of which is to cool the next portion of air which reaches the orifice, at the expense of the air which was first cooled by

expansion. The principle of the interchanger is shown in fig. 25.

The cooled air returns after expansion by a path which surrounds the pipe through which the fresh portion of compressed air is arriving. If the double piping is narrow and in the shape of a long coil, an almost perfect exchange of heat is effected. The second portion of air then begins its expansion at a lower temperature than the first portion and is consequently cooled to a lower temperature still. Thus the temperature progressively falls, and at last sinks to a point ($-193°$) at which the air begins to liquefy.

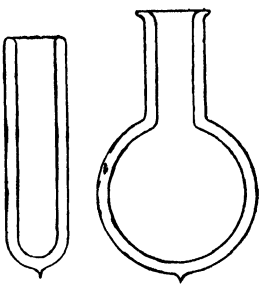


Fig. 26.—Vacuum Flasks.

Liquid air is a clear liquid of approximately the same density as water. It may be preserved for a considerable time in double-walled glass vessels, the space between the walls of which is highly evacuated. If the vessels are silvered the liquid air evaporates still more slowly. Such evacuated vessels prevent exchange of heat with the exterior, and are commonly employed under the name of Dewar tubes or vacuum flasks, as non-conducting vessels (Fig 26). In a good vacuum flask the air slowly evaporates at the surface without any appearance of boiling. Since liquid air remains at a temperature of about $-190°$ (its boiling point) it can be used to investigate the properties of bodies under the influence of extreme cold. Thus india-rubber plunged in liquid air becomes brittle and may be broken with a hammer. Mercury freezes to a hard solid. Lead from being a soft metal becomes hard and elastic. Carbon dioxide, ammonia, sulphur dioxide and many other gases solidify when passed into a tube cooled with liquid air.

The chief technical use of liquid air is in the preparation of oxygen.

CHAPTER XVI

OXYGEN

Oxygen is prepared in the laboratory from some compound containing it. On the large scale it is prepared from the atmosphere. When mercuric oxide is heated to a temperature approaching redness, it splits up into metallic mercury and oxygen, which by means of suitable apparatus can be collected in the pure state. The method is of historical interest, as oxygen was first isolated by the use of this reaction, the equation for which is—

$$2HgO = 2Hg + O_2$$

The usual substance employed in the laboratory for the generation of oxygen is potassium chlorate. When heated

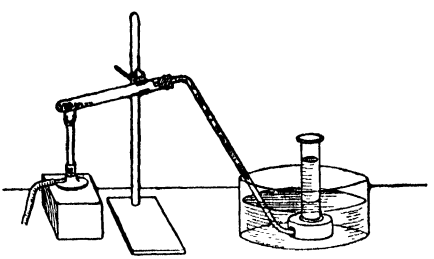


Fig. 27.—Preparation of Oxygen from Mercuric Oxide.

The oxide is heated in a test-tube and the oxygen gas given off collected over water.

in a hard glass tube to a temperature somewhat below a red heat, potassium chlorate fuses and evolves oxygen, the equation for the complete action being—

$$\underset{\text{Potassium chlorate}}{2KClO_3} = \underset{\text{Potassium chloride}}{2KCl} + 3O_2$$

This same reaction may be carried out at a much lower temperature by mixing a little manganese dioxide MnO_2 with the potassium chlorate. The manganese dioxide is not permanently changed at the temperature which is used to decompose the chlorate, but it acts upon the chlorate in some way so

as to make the evolution of oxygen take place much more rapidly and at a much lower temperature. A substance which acts in this way—*i.e.* a substance which facilitates a chemical action without itself undergoing any permanent change—is called a **catalytic agent** or **catalyst**. It should be noted that the oxygen prepared from potassium chlorate is not so pure when manganese dioxide is mixed with the chlorate, as when the chlorate is used alone.

Many other substances besides potassium chlorate give up oxygen when heated. Thus potassium permanganate decomposes readily as follows:—

$$\underset{\text{Potassium permanganate}}{2KMnO_4} = \underset{\text{Potassium manganate}}{K_2MnO_4} + \underset{\text{Manganese dioxide}}{MnO_2} + O_2$$

Manganese dioxide, when heated to a high temperature, gives up a third of its oxygen, according to the equation—

$$3MnO_2 = Mn_3O_4 + O_2$$

Red lead in a similar way decomposes as follows:—

$$\underset{\text{Red lead}}{2Pb_3O_4} = \underset{\text{Litharge}}{6PbO} + O_2$$

Oxygen may also be prepared by the action of water on fused sodium peroxide, the equation being—

$$2Na_2O_2 + 2H_2O = 4NaOH + O_2$$

The preparation of oxygen from the atmosphere on a commercial scale is now effected by the rectification of liquid air, advantage being taken of the fact that the boiling point of nitrogen (-195°) is considerably lower than that of oxygen (-182°). The evaporation of the liquid air is conducted through a rectifying apparatus similar in principle to that used in separating two liquids of different boiling points, such as alcohol and water. Oxygen of 99.5 per cent. can readily be obtained in this way and is put on the market compressed to about 200 atmospheres in steel cylinders.

Oxygen prepared by any of these methods is a gas which is somewhat heavier than air. Being colourless, it is invisible, and it possesses neither smell nor taste. It cannot be compressed to a liquid at the ordinary temperature, but when sufficiently cooled it liquefies and produces a pale blue liquid. It is, as we have seen, only very slightly soluble in water, and

in this connection it may be noted that solubility in water and compressibility to the liquid form usually go hand-in-hand. That is, gases which can be compressed to liquids at the ordinary temperature are usually soluble in water, whilst gases which are not compressible to liquids at the ordinary temperature are usually but very slightly soluble in water.

All combustions which take place in air also take place in oxygen, the vigour of the chemical action and the brilliancy of the combustion being greatly enhanced when pure oxygen is used. Thus, a piece of sulphur or phosphorus will burn with much greater brilliancy in pure oxygen than in air; and a piece of iron wire, which, when heated to redness, soon becomes cold in air, will produce showers of sparks when introduced into a jar of oxygen, the combustion going on until the metal is almost entirely converted into oxide. The common test for oxygen is its action on a splinter of wood, the flame of which has been extinguished so as only to leave a tip of glowing carbon. When this is introduced into a vessel of oxygen, the combustion of the carbon increases so greatly in vigour that the splinter again bursts into flame.

Mixtures containing free oxygen in sufficient quantity will always support combustion, and the vigour of the combustion will be in general dependent on the amount of oxygen they contain. Some gaseous *compounds* of oxygen also support combustion, but the vigour of combustion in them is regulated, not only by the proportion of oxygen contained in them, but also by the ease with which the oxygen can part from the element with which it is combined. Examples of this will be seen when we consider oxides of nitrogen. It should be noted that respiration cannot be supported except by free oxygen. That is, a mixture of oxygen and nitrogen will support the respiration of animals, whilst a compound of oxygen and nitrogen will not, although it may easily support the ordinary processes of high temperature combustion.

Ozone

A gas exists which differs in many ways from ordinary oxygen, and yet contains nothing but the element oxygen. This gas is known as ozone, and is said to be an *allotropic modification* of oxygen.

It is produced from ordinary oxygen under the influence of electric excitation. When an electric machine is being worked, a peculiar smell is perceptible in its neighbourhood. This smell is due to ozone, which is produced from the oxygen of the air in the neighbourhood of the electric spark. Ozone may be produced in much larger quantity from oxygen by passing the oxygen through a space which is subjected to rapid alternation of electric charges, a tube devised for this purpose being shown in the figure. The rapid change in the electric charge is brought about by means of an induction coil, the terminals of which become alternately positive and negative, the rate of alternation being many hundred times a minute.

It is impossible by means of such a piece of apparatus to convert the whole of any given amount of oxygen into ozone,

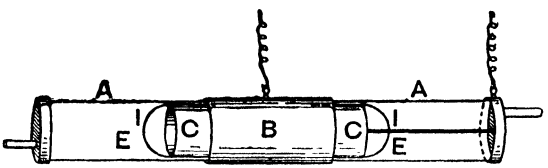


Fig. 28.—Preparation of Ozone.

Oxygen is passed through the narrow space between the outer glass tube *A A* and the inner glass tube *I I*, the metallic conductor *B* outside the outer glass tube and the metallic conductor *C C* inside the inner glass tube are connected with the opposite poles of an induction coil. Under the influence of the high tension between the conductors a so-called silent discharge passes through the oxygen and converts a portion of it into ozone.

about one-tenth of the total oxygen being as much as can be converted into ozone under favourable conditions.

Ozone is a colourless gas which is about twice as soluble in water as ordinary oxygen, and more readily condensible to the liquid state. It differs from oxygen in having a peculiar odour by means of which it can be recognised even in traces. The liquid produced from it has a deep blue colour.

The chemical properties of ozone are also very different from those of ordinary oxygen, although the difference is rather one of degree than of kind. Ozone is a much more powerful oxidising agent than ordinary oxygen. Thus, at the ordinary temperature ozone will oxidise potassium iodide with liberation of iodine, a reaction which is very commonly used as a test for ozone, free iodine being

readily visible from its colour, and still more so if starch is added, blue "iodide of starch" being then produced. A solution of a lead salt such as lead acetate is also oxidised by ozone at the ordinary temperature, although it is quite unaffected by oxygen. The lead salt is oxidised to lead peroxide, PbO_2, the change being evident by the production of the brown colour of this compound. Indigo solution, which retains its deep blue colour indefinitely in presence of ordinary oxygen, is very soon oxidised by ozone, the blue colour disappearing entirely. India-rubber is rapidly attacked by ozone, and mercury becomes foul and loses its characteristic property of forming a meniscus when it remains for any length of time in an atmosphere containing ozone.

If we ask for an explanation of the difference in properties that exists between ozone and ordinary oxygen, we find that it is connected with a difference in the molecular weights of the two gases. When a measured volume of ordinary oxygen is partly converted into ozone, it is found that during conversion a contraction in volume takes place, although the weight of the gas remains the same. A given volume of ozone must, therefore, be heavier than an equal bulk of oxygen—that is, a greater weight of ozone can be contained at normal temperature and pressure in 22.4 litres than is the case with ordinary oxygen. The molecular weight of ozone must, therefore, be greater than that of ordinary oxygen.

It is not difficult to find by how much the molecular weight of ozone is greater than that of oxygen. Ozone is entirely absorbed by oil of turpentine, whilst oxygen is quite unaffected by this liquid. If we note the contraction which takes place during partial conversion of a given volume of oxygen into ozone, and then note the further contraction which occurs when the ozone thus formed is absorbed by oil of turpentine, we find that the second contraction is exactly double the first contraction. If we call the original contraction one volume, then the second contraction is equal to two volumes, and the total contraction equal to three volumes. Now, the second contraction is equal to the volume of ozone produced, and the total contraction is the volume of the ordinary oxygen which disappeared. As there was no loss of weight in the experiment, it is evident then that three volumes of oxygen weigh as much as two volumes of ozone under the same conditions of

temperature and pressure. Put in another way, ozone is volume for volume half as heavy again as oxygen, and therefore, according to Avogadro's principle, p. 66, its molecular weight must be half as great again as that of ordinary oxygen, which is 32. The molecular weight of ozone is, therefore, 48, and its molecular formula O_3. Evidence has been recently obtained that a proportion of a compound with the molecular formula O_4 may also exist in ozone.

When ozone is heated, it is reconverted into ordinary oxygen. The equation for the conversion of oxygen into ozone, and for the reconversion of ozone into oxygen, is as follows:—

$$3O_2 \rightleftharpoons 2O_3$$

When ozone acts as an oxidising agent it is usually only the *extra* oxygen which affects the oxidation, ordinary oxygen being produced. Thus the equation which expresses the action of ozone on potassium iodide is as follows:—

$$2KI + O_3 + H_2O = 2KOH + O_2 + I_2$$

Potassium iodide Ozone Water Potassium hydroxide Oxygen Iodine

Here the extra oxygen of the ozone disappears, and an equal volume of ordinary oxygen is generated.

Ozone exists in minute quantity in the air, the amount even in the upper regions of the atmosphere not exceeding one volume in 400,000 of air. It is now prepared on a large scale for the purpose of sterilising public water supplies, and of purifying or at least deodorising air. When employed for the latter purpose it may only be mixed with the air in minute proportions as its continued inhalation in larger quantities produces poisonous effects.

CHAPTER XVII

WATER

We must carefully distinguish between the chemical substance water H_2O, and the various kinds of water that occur in nature —*e.g.* fresh water, salt water, or mineral water. No natural water is the pure chemical compound. This is on account of the solvent power of water, which, in the form of liquid, is capable of dissolving at least traces of most substances with which it comes into contact. Gaseous water and solid water—*i.e.* water-vapour and ice—do not act as solvents in the same way. If we wish, therefore, to obtain pure water from a natural water containing dissolved material, the easiest method is to convert it either into water-vapour or into ice, and then liquefy these substances in vessels on which the liquid water has no solvent action.

The purest liquid water that we find in nature is condensed water-vapour in the form of rain. Even rain water, however, contains substances in the state of solution, for rain in falling through the air dissolves at the very least some of the gases which constitute the atmosphere, and since the atmosphere is never free from dust, the dust particles are also carried down in some quantity with the rain. Rain water collected in towns is, of course, far from pure, a great deal of soot and other materials being carried down with it.

If the rain water falls on the ground and permeates the soil it dissolves some of the constituents of the soil. Consequently, we find that lakes, rivers, and springs (the water in all of which is ultimately derived from rain water which has been in contact with the earth's crust) all contain considerable quantities of dissolved substances. The nature of the dissolved substances and the quantities of them in any given water will, of course, depend upon the nature of the rocks with which the water has been in contact.

Waters from springs, which contain either very large quantities of dissolved substances or else unusual substances which are easily recognised by the smell or taste, are called **mineral waters.** The **salt water** which occurs in such enormous quantities in the ocean contains, of course, common salt in solution; but besides common salt a great many other substances are present. On the average sea water contains between 3 and 4 per cent. of dissolved salts. The water of salt lakes, such as the Dead Sea, contains even more dissolved material, the Dead Sea holding over 20 per cent. of salts. The ordinary **tap water** of town supplies is usually lake water or river water, and does not in general contain much dissolved solid, the quantity not being more than about one-hundredth of a per cent.

Two of the commonest substances in ordinary water supplies are *calcium hydrogen carbonate* $CaH_2(CO_3)_2$, and *calcium sulphate* $CaSO_4$. If a water contains much of these substances it is said to be a **hard water**; if it contains little of these substances it is said to be a **soft water.** Hard waters are unsuitable for washing purposes on account of the amount of soap they render useless before a lather is formed. Soap is a mixture of the sodium salts of various acids of which the calcium salts are insoluble. When, therefore, we bring the soap into contact with the water containing dissolved calcium salts, double decomposition takes place, sodium hydrogen carbonate and sodium sulphate being produced on the one hand, and the insoluble calcium salts of fatty acids on the other. The insoluble calcium salts fall out of the solution, whilst the sodium sulphate and sodium hydrogen carbonate remain dissolved. These, however, are quite valueless as cleansing agents, and so more soap must be added until all the calcium salts are precipitated. The degree of hardness of water (usually stated in parts of calcium carbonate per 100,000) is generally ascertained by finding how much of a standard soap solution the water will use up before it produces a permanent lather—Clarke's **soap test.**

The hardness produced by calcium hydrogen carbonate differs from the hardness produced by calcium sulphate. The former is called **temporary hardness**, the latter **permanent hardness.** These names are applied on account of the hardness caused by the calcium hydrogen carbonate

disappearing on boiling, while the hardness caused by the calcium sulphate persists after the water has been boiled. The action which results in the disappearance of the temporary hardness on boiling is the following:—

$$CaH_2(CO_3)_2 = \underline{CaCO_3} + H_2O + \uparrow CO_2$$

The carbon dioxide escapes as gas, and the normal calcium carbonate falls out as solid. If the water considered has much calcium hydrogen carbonate in solution, it deposits a fur or crust on the interior of the vessel in which the hard water has been boiled. This crust is usually very hard, and is a poor conductor of heat, so that much more fuel is required to boil water in a vessel which has been thus encrusted than to boil water in a clean metal vessel. This renders such water unsuitable for steam-raising purposes.

If we wish to estimate both temporary and permanent hardness by the soap test, we first of all take a sample of the water and estimate its total hardness. Then we boil a sample and estimate the hardness which remains after boiling. The difference between the total and permanent hardness gives the hardness which has disappeared—that is, the temporary hardness.

Rain water, since it contains little or no dissolved solid, is very frequently used for washing purposes, where the other natural waters are hard. Hard water, however, may be softened in various ways. For washing purposes the common substance to employ is washing soda or sodium carbonate. When a little of this is added to the hard water, the following reactions take place:—

$$Na_2CO_3 + CaH_2(CO_3)_2 = 2NaHCO_3 + \underline{CaCO_3}$$

$$Na_2CO_3 + CaSO_4 = Na_2SO_4 + \underline{CaCO_3}$$

Calcium carbonate is precipitated and nothing but sodium salts are left in the water, and these in no way impair the cleansing power of soap. Another substance which may be used for softening water is calcium hydroxide. When this is added to a solution of calcium hydrogen carbonate, normal

insoluble calcium carbonate is produced according to the equation—

$$Ca(OH)_2 + CaH_2(CO_3)_2 = \underline{2CaCO_3} + 2H_2O$$

and thus the water loses its temporary hardness.

The **pure chemical substance H_2O** is colourless when viewed in a thin layer, but is seen to be greenish blue when a thick layer is traversed by a beam of light. It is without odour, but possesses a somewhat mawkish taste. The purest water we employ in the laboratory is **distilled water**—*i.e.* condensed steam,—and for all practical purposes this distilled water may be treated as pure water. It is a standard substance for many purposes, because it can be easily prepared in a state nearly approaching purity, and can be obtained in unlimited amount. Thus, the zero point on the centigrade thermometer is fixed at the temperature at which pure water freezes, and similarly 100° on the same thermometer is fixed as the temperature at which pure water boils under a pressure of 760 mm. Pure water is also taken as the standard of specific gravity, the specific gravities of all other substances being practically referred to water under specified conditions as unity.

Water is a substance distinguished for its **solvent power**, and it is by far the commonest solvent we employ. Nearly all the substances we use in the chemical laboratory are dissolved in water if they are at all soluble. The reason for this has already been given on p. 9. Water is distinguished also by its power of ionising salts, acids, and bases, dissolved in it (see Chapter XXIII.). No other common solvent possesses this ionising power to anything like the same degree.

Water has very different solvent properties according to the substances with which we bring it in contact, and also according to the temperature at which it acts on these substances (p. 15). It should be noted that the substances which we usually speak of as being **insoluble** are in reality slightly soluble in water. The slight solubility may not be of importance in the chemical laboratory, but it is sometimes of great importance in the phenomena of nature. Thus, as we have seen, water will take up from the atmosphere about 0.8 per cent. of its own volume of oxygen, or if we measure by weight instead of by volume, about 0.001 per cent. of its own weight

of oxygen. This quantity is very small, but it is on this small amount of oxygen that fish and other animals which inhabit the water have to depend for their respiration. Rocks, too, which we should call insoluble in water, are in reality gradually dissolved away by water when the water acts over great lengths of time. Glass is a substance which we commonly employ to contain water and aqueous liquids, and we usually state it to be insoluble in water. It is easy to show, however, that water when boiled in glass vessels attacks them and dissolves up recognisable quantities. The so-called insoluble precipitates are by no means insoluble in water; thus, the following substances, which are generally treated as insoluble substances, dissolve in water to the extents given below :—

Substance	Milligrams dissolved by 1 litre of water at 18°.
Silver chloride	1.7
Mercurous chloride	3.1
Barium sulphate	2.6
Lead sulphate	46
Calcium carbonate	13

Many substances when they separate out from solution in water, separate out with what is called **water of crystallisation.** This water of crystallisation is combined with the substance in some way which we do not altogether understand, and is in no sense liquid water. Ordinary washing soda, for example, contains water of crystallisation, and if we wish to represent the amount of the water of crystallisation, we can do so by means of the formula $Na_2CO_3,10H_2O$. The sodium carbonate and the water of crystallisation, are contained in washing soda in perfectly definite proportions, and so it is with other substances of a similar nature. Substances which contain water of crystallisation are called **hydrates**, and we can indicate the number of formula-weights of water combined with one formula-weight of substance by means of the Greek numerals. Thus, *washing soda* $Na_2CO_3,10H_2O$ is called a decahydrate of sodium carbonate; *blue vitriol*, $CuSO_4,5H_2O$ is called a pentahydrate of copper sulphate; *Glauber's salt* $Na_2SO_4,10H_2O$ is a decahydrate of sodium sulphate, and

so on. These hydrates part with their water when heated. Very frequently the water comes off at 100°C., but occasionally the water may remain combined with the substance at a much higher temperature than this. Thus, if we heat blue vitriol $CuSO_4,5H_2O$, four of the five formula-weights of water are easily driven off by heat, while the fifth formula-weight of water is not driven off until the temperature is raised to a much higher point. When substances are without water of crystallisation they are said to be **anhydrous.**

Some hydrates lose their water of crystallisation when exposed to the air at the ordinary temperature. This may be observed with a clean crystal of washing soda. The surface of the crystal is at first bright and uniform, but soon becomes covered on exposure to the air with a white powder, especially at the angles of the crystal. This white powder is a hydrate of sodium carbonate, which contains less water than the washing soda, and is formed from the washing soda by loss of water to the air. Substances which behave in this way are called **efflorescent,** and the crust that appears on the surface is called an efflorescence.

Other substances behave in exactly the opposite way. An anhydrous substance or a lower hydrate may absorb moisture from the air to form a higher hydrate. Such **hygroscopic** substances may be used as drying agents.

The crystals of calcium chloride hexahydrate, which have the formula $CaCl_2,6H_2O$, continue to absorb water from the air, and finally pass into solution in the water which they have absorbed. Substances of this kind are said to be **deliquescent.** The tendency of anhydrous calcium chloride to absorb water is so great that it is very frequently employed to dry gases and liquids, which do not themselves act upon the calcium chloride. The calcium chloride absorbs the water in these moist gases or liquids, and becomes first of all a hydrate of calcium chloride, and then, if sufficient water is present, a concentrated solution of calcium chloride. It should be noted that all deliquescent substances are very soluble in water. A substance which is insoluble in water or only moderately soluble in water can never be deliquescent in ordinary air.

The hydrates have very often different colours from the anhydrous substances, and use is made of this fact in the

preparation of *sympathetic inks*. A dilute solution of cobalt chloride $CoCl_2$ has a pale pink colour, and when used as ink dries up on the paper to a practically colourless hydrate. When this hydrate is heated, however, by holding the paper before the fire, the water of crystallisation is driven off and the anhydrous chloride which remains is plainly evident from its deep blue colour. When the paper is allowed to cool, the blue anhydrous salt again absorbs moisture from the air and the writing disappears.

The chemical properties of water will be frequently referred to in succeeding chapters.

CHAPTER XVIII

HYDROGEN

WATER is directly or indirectly almost the only source of hydrogen and its compounds. Water can be split up into its elements—namely, hydrogen and oxygen—directly by means of the electric current. In order, however, to make water conduct electricity, sulphuric acid must be added to it in small quantity before the current can be passed. Oxygen appears at the positive pole, and hydrogen appears at the negative pole, the two being in the proportions necessary to form water. By weight these proportions are roughly, 1 part of hydrogen to 8 parts of oxygen; by volume they are 2 measures of hydrogen to 1 measure of oxygen (fig. 17).

Hydrogen can also be liberated from water by acting upon the water with various substances which are capable of removing oxygen. Thus, if the metal sodium is thrown into water a vigorous action at once takes place, with production of sodium hydroxide and hydrogen, according to the equation—

$$2Na + 2H_2O = 2NaOH + H_2$$

Other metals, such as zinc, iron, and aluminium have no action upon water at the ordinary temperature; but if they are raised to a red heat, and if steam is then passed over them, they decompose the steam with formation of an oxide of the metal and hydrogen gas, the equations being—

$$Fe + H_2O = FeO + H_2$$
$$Zn + H_2O = ZnO + H_2$$
$$2Al + 3H_2O = Al_2O_3 + 3H_2$$

Some metals, such as mercury, silver, and gold, are incapable of decomposing water at any temperature (p. 155).

It frequently happens that two metals which cannot decompose water singly can decompose water when in contact

with it together. Thus neither mercury nor aluminium can decompose water at the ordinary temperature. Yet, if aluminium is coated with mercury, the *aluminium-mercury couple*, as it is called, can decompose water easily at the ordinary temperature, and very rapidly at the boiling point, aluminium hydroxide being produced. The explanation of this is that a difference of electric state is set up between the two metals, which is sufficient to decompose the water. Similarly, zinc when coated with copper can decompose water with production of zinc hydroxide, although metallic zinc alone has no action on water below a red heat.

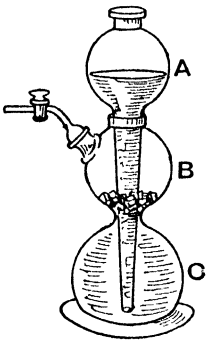


Fig. 29—Kipp Machine.

This piece of apparatus is used to obtain an automatically regulated supply of gas, produced by the interaction of a liquid and a solid—*e.g.* hydrogen from sulphuric acid and zinc. There is no connection between *A* and *B* except through *C*. When the tap is opened the acid falls in *A* and rises in *C* until it comes in contact with the zinc in *B*. If the chemical action thus induced supplies more gas than can escape through the tap, the acid is forced downwards away from the zinc, so that less gas is generated. In this way the apparatus is self-regulating.

The ordinary method of preparing hydrogen in the laboratory is by the action of hydrochloric or dilute sulphuric acid on a metal, the metal usually chosen being zinc, and a Kipp machine (fig. 29) being commonly used as the generator.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

Hydrogen prepared by any of these methods is a colourless and inodorous gas. Frequently, however, the crude gas has a distinctly unpleasant smell, which is not that of hydrogen, but of some impurity derived from the materials used in its production. Hydrogen is singular in many respects. It is the lightest gas known, and one of the most difficult to condense to a liquid, an extremely low degree of temperature being necessary to effect liquefaction. The temperature of boiling hydrogen is -253°, that is, only 20° above the absolute zero of temperature. At this temperature practically all other gases are condensed to solids. In accordance with this very low boiling point, we find that the gas is very slightly soluble in water, the solubility being approximately the same as that of nitrogen—namely, 0.02.

Hydrogen has the smallest combining weight of any of the

elements, and all the other combining weights are for ordinary purposes referred to it as unity. If we weigh the amount of hydrogen which occupies 22.4 litres at normal temperature and pressure we find that it is two grams. The molecular weight is therefore 2 and the molecular formula H_2

Since hydrogen is the lightest of all gases, the densities of other gases are very frequently referred to the density of hydrogen under the same conditions as unity. It therefore follows that the molecular weights of gases or vapours are equal to double their densities when these densities are referred to hydrogen, for the density of hydrogen is chosen equal to 1 whilst its molecular weight is equal to 2. *To get the molecular weight of any gas, then, we have simply to multiply its density referred to hydrogen by* 2.

Hydrogen is a combustible gas which burns in air or oxygen with a non-luminous flame, the only product of the combustion being water, which is formed according to the equation—

$$\underset{2\text{ vols.}}{2H_2} + \underset{1\text{ vol.}}{O_2} = 2H_2O$$

A mixture of hydrogen and oxygen in the above proportions by volume explodes with great violence when a light is applied to it, and is often called a *detonating mixture*. It can be made with the components in the proper proportions by the electrolysis of acidulated water.

Hydrogen is often employed as a deoxidising or reducing agent, inasmuch as it is capable of removing oxygen from many oxygen compounds when these are heated in a stream of hydrogen gas. For example, copper oxide when heated is converted by hydrogen into metallic copper—

$$CuO + H_2 = Cu + H_2O$$

Coal-gas contains 40 to 50 per cent. by volume of hydrogen, which gives out a great deal of heat when burned, but no light. On account of this amount of hydrogen which it contains, coal-gas can sometimes be used in the laboratory as a gaseous reducing agent. Thus, if it is passed over heated lead oxide, the oxygen will be removed by the hydrogen, and metallic lead will be left.

Hydrogen peroxide, H_2O_2

Water is not the only substance formed by the union of oxygen and hydrogen, although when these two elements combine directly, water is the sole product. There is another compound of hydrogen and oxygen—hydrogen peroxide, which for a given amount of hydrogen contains twice as much oxygen as water. Hydrogen peroxide has quite different properties from water, being in its nature a very weak acid, and also a powerful oxidising agent.

Salts of hydrogen peroxide can easily be prepared. Thus if we heat metallic sodium in air, it burns to produce sodium peroxide Na_2O_2, which is the sodium salt of hydrogen peroxide. When therefore we treat this sodium salt of the weak acid, hydrogen peroxide, with a stronger acid, the stronger acid turns out the hydrogen peroxide and takes the base. Thus, sodium peroxide and sulphuric acid give in aqueous solution, sodium sulphate and hydrogen peroxide—

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2$$

Barium peroxide is a similar salt of hydrogen peroxide. When mixed with water, in which it is only slightly soluble, and treated with an equivalent quantity of sulphuric acid, insoluble barium sulphate is produced, and hydrogen peroxide passes into solution. The barium peroxide may also be decomposed by means of a current of carbon dioxide according to the following equation:—

$$\underset{\text{Barium peroxide}}{BaO_2} + CO_2 + H_2O = \underline{BaCO_3} + \underset{\text{Hydrogen peroxide}}{H_2O_2}$$

The barium carbonate is insoluble, and may be separated from the solution of hydrogen peroxide.

The solution of hydrogen peroxide prepared in any of these ways decomposes, on heating, into water and oxygen, which comes off in the form of bubbles of gas, the equation for the decomposition being—

$$2H_2O_2 = 2H_2O + O_2$$

At the ordinary temperature, hydrogen peroxide in solution is moderately stable, especially when the solution is dilute and faintly acid. If the solution is kept over concentrated

sulphuric acid in a vessel which has been exhausted of air, the water of the solution evaporates, and is absorbed by the sulphuric acid, leaving behind a syrupy residue of pure hydrogen peroxide, which is almost half as heavy again as water. Pure hydrogen peroxide is stable if the temperature remains in the neighbourhood of the freezing point, but on a warm day it decomposes with evolution of bubbles of oxygen, and at the boiling point it evolves oxygen with explosive violence. Some substances, such as silver, cause it to evolve oxygen very vigorously at the ordinary temperature by mere contact, the substances themselves apparently remaining unchanged.

When hydrogen peroxide is brought into contact with silver oxide, the following action occurs:—

$$\underset{\text{Silver oxide}}{Ag_2O} + H_2O_2 = \underset{\text{Silver}}{2Ag} + O_2 + H_2O$$

Here the hydrogen peroxide apparently behaves as a deoxidising agent so far as the silver oxide is concerned. With powerful oxidising agents it often presents this character.

When a few drops of potassium bichromate solution, acidified with acetic acid, are added to a solution of hydrogen peroxide, an intense blue colour is produced. This blue colour is attributed to perchromic acid, and its production can be made use of as a test both for hydrogen peroxide and for chromates. The hydrogen peroxide in this reaction behaves as an oxidising agent, giving up oxygen to the bichromate, and being itself transformed into water.

Hydrogen peroxide therefore possesses both oxidising and deoxidising properties, either of which may be developed according to circumstances.

CHAPTER XIX

CARBON

ALL living substances contain the element carbon, which is also a constituent of a great number of minerals, chiefly carbonates.

The element carbon itself is found in nature in a more or less pure condition. It exists in two crystalline modifications: first, the comparatively rare and precious **diamond**; second, the much more common and less costly **graphite**. These two varieties of carbon when pure contain nothing but the element carbon, yet they have absolutely different physical properties, although their chemical properties are practically speaking identical. Diamond is the hardest substance known; graphite, which is commonly called *plumbago* or *black lead*, is so soft that it is used as a lubricant and in the manufacture of writing pencils—*i.e.* it is so soft as to be abraded by paper and leave a track of black particles behind. Diamond is colourless and transparent; graphite is black and opaque. Graphite is now manufactured artificially: diamond has never been prepared except as microscopic crystals.

When either of these substances is heated in oxygen it burns to form carbon dioxide, and a given weight of either substance will, if pure, yield a quantity of carbon dioxide in the proportion expressed by the equation—

$$C + O_2 = CO_2$$

This experiment shows that the two substances, although differing so greatly in their physical properties, are chemically identical.

There are many varieties of artificially prepared carbon, all more or less impure. **Lamp-black** is one of these, and is simply condensed smoke. Certain substances, like oil of turpentine and acetylene, burn with a very smoky flame when an insufficient supply of air is used in the combustion. The smoke produced consists of small particles of unburnt carbon,

and may be made to deposit on the walls of a chamber or on sheets, which, when scraped, give carbon in the form of loose powder known as lamp-black. Lamp-black is chiefly used in the production of printers' ink, and as an ingredient of certain pigments.

Another form of carbon which is extensively used is **charcoal**. This charcoal is by no means so pure a form of carbon as lamp-black, but it is produced in much greater quantities. It is made by heating wood to such a temperature that most of the organic substances which form the wood are decomposed and driven off as gases, a residue of impure carbon remaining behind.

The production of charcoal was formerly carried out entirely by piling up billets of wood, covering the pile with turf, and setting fire to the wood at the bottom of the pile, the air supply being carefully regulated. Part of the wood burned in the defective supply of air, and the whole of the mass was heated by this partial combustion of the wood to such a temperature that charcoal was left behind. The kind of charcoal obtained depended on the temperature to which the wood was heated. All charcoal is more or less porous and light, as it retains the original form of the wood, although most of the material of the wood has been removed in the form of gas. If the charcoal burning is conducted at a high temperature, the charcoal is comparatively dense and contains very little of other substances than carbon and the incombustible salts forming the ash of the wood; whilst, if the temperature is low, the charcoal still contains considerable proportion of carbon compounds as well as carbon itself. Nowadays a great deal of wood charcoal is prepared by heating the wood in retorts, air being excluded from the process altogether. The wood is decomposed by the rise of temperature as before, but instead of the gases and vapours derived from the wood being allowed to burn, they are carefully collected and a variety of useful products are derived from them.

On account of its porous nature and the very large internal surface which it presents, charcoal has the power of condensing large amounts of gases. Thus, if a piece of dry charcoal is introduced into a cylinder of ammonia contained over mercury, the ammonia will be absorbed by the charcoal and the mercury will rise in the cylinder to take its place. Similarly, charcoal,

especially **bone-charcoal** prepared by heating bones, will absorb colouring matters from solutions, so that it finds a considerable application as a decolorising and deodorising agent. The chief use of wood charcoal is as a smokeless fuel and as an ingredient of gunpowder.

Coal is a natural product rich in carbon which occurs in enormous quantities. Coal is formed by the decomposition of vegetable matter in a special way. When wood decays in absence of air it loses a portion of its carbon and proportionately more of its hydrogen and other gaseous elements, so that the residue contains more carbon than the original wood. The following table gives roughly the percentage of carbon in dry wood, and of some kinds of vegetable matter which have undergone partial decay:—

	Carbon
Dry wood	50 per cent.
Peat	60 ,,
Brown coal	70 ,,
Cannel coal	85 ,,
Newcastle coal	90 ,,
Anthracite	95 ,,

When this kind of decay has gone on for a very long time coal is the result, and coal contains amounts of carbon varying from 80 to nearly 100 per cent. In anthracite coal most of the carbon is present as the free element. In other coals the quantity of free carbon may be comparatively small, the coal consisting chiefly of complex compounds of carbon with hydrogen, oxygen and nitrogen.

Coal finds its main use as fuel and in the production of coal gas, but it is also used as a chemical agent in many reducing processes of which we have already had examples.

A form of carbon much used by electricians is what is known as **gas carbon**. This is a hard substance which is formed on the walls of retorts in which coal is heated for the manufacture of coal gas, and is a good conductor of electricity. To form the carbons for electric lighting or for electrodes this gas carbon is ground to powder and then moulded with tar into the proper form and strongly heated. Graphite, which is now produced artificially, is also a good conductor of electricity.

Coke is an impure form of carbon produced in gas retorts

or in coke ovens. It is formed by heating coal to a very high temperature, the volatile gases which come off from the retorts being partially condensed to coal tar and partially used for illuminating purposes as coal gas. The coke, which contains a portion of the original carbon and a large quantity of ash, remains in the retort, and is used chiefly as fuel. It burns with difficulty, but produces a clear, smokeless fire.

It has already been noted that carbon burns without flame, because it cannot be converted into gas at the temperature which can be generated by its own combustion. Indeed, carbon cannot even be melted by the temperature of its own combustion, and can only be melted in the most intense heat of the electric arc.

Oxides of Carbon

Carbon forms two oxides, carbon monoxide CO and carbon dioxide CO_2. Although carbon monoxide may probably be formed in small quantity in the direct combustion of carbon when the supply of oxygen is defective, the greater part of the carbon which combines with oxygen is directly converted into carbon dioxide.

Carbon dioxide, CO_2, is not only evolved in the processes of combustion, respiration, and fermentation, but is also emitted in large quantities from volcanoes, so that it is a constant constituent of the atmosphere. It is a gas which is already fully supplied with oxygen, and will not burn in the air. The oxygen which it contains, however, is held in firm union by the carbon, so that it does not act readily as an oxidising agent or a supporter of combustion. If a lighted taper or other substance is plunged into a jar filled with the gas it is at once extinguished. Carbon dioxide, as we can calculate from its formula-weight, is considerably heavier than air, and is generally collected by downward displacement. It can be poured from one vessel to another like a liquid. A simple test for its presence is the turbidity which it produces in coming into contact with lime-water or baryta water.

The ordinary mode of producing carbon dioxide in the laboratory is to treat calcium carbonate, usually in the form of marble, with hydrochloric acid. Decomposition occurs according to the equation—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

and the carbon dioxide, being the only gaseous product, is ob-

tained nearly pure. A Kipp machine (fig. 30) is frequently used in the laboratory for the production of carbon dioxide in this way. It has already been stated that the volumetric composition of carbon dioxide may be determined by means of the apparatus referred to in fig. 18. The gravimetric composition of the gas may be ascertained by burning a known weight of carbon (most easily in the form of pure dry sugar charcoal) in a current of oxygen, and absorbing the carbon dioxide produced in alkali, which readily unites with the gas to form a carbonate. The apparatus employed is indicated in the figure.

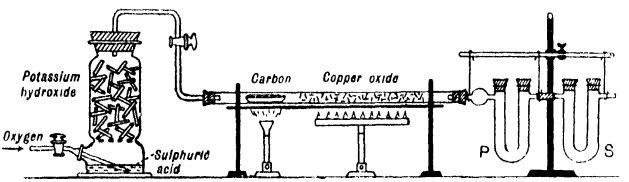


Fig. 30.

A tube of hard glass or porcelain is heated in a gas furnace to a dull red heat. A current of pure oxygen, freed from moisture by sulphuric acid and from carbon dioxide by solid caustic potash, is passed in at one end and comes into contact with the carbon contained in a porcelain boat. Beyond this there is a column of heated copper oxide for the purpose of oxidising any carbon monoxide which might be produced if the supply of oxygen were defective. Its action may be represented by the equation—

$$CuO + CO = Cu + CO_2$$

The gases on leaving the combustion tube pass first through the tube P, containing anhydrous calcium chloride, which removes any trace of moisture they may contain, and then through the tube S, which is charged for three-fourths of its length with soda-lime, followed in the remaining fourth by dry calcium chloride. The soda-lime (a dry granular mixture of calcium oxide and sodium or potassium hydroxide) absorbs, if fresh, the whole of the carbon dioxide. The loss in weight of the porcelain boat and its contents during the combustion gives the weight of carbon consumed: the corresponding

increase in weight of the soda-lime tube gives the weight of carbon dioxide produced. The difference between these two weights gives the weight of oxygen used to oxidise the carbon.

Thus if 0.2400 grams of carbon gave 0.8800 grams of carbon dioxide, the difference of 0.6400 grams represents oxygen which is combined in carbon dioxide with 0.2400 grams of carbon.

The combustion method described is practically that used to ascertain the percentage of carbon present in carbon compounds, more particularly those containing hydrogen. If the calcium chloride tube is also weighed before and after the combustion its increase in weight, due to absorption of water, affords the necessary information for determining the percentage of hydrogen in the compound.

Carbon dioxide is a gas which can be compressed to a liquid if sufficient pressure is employed, and liquid carbon dioxide is supplied in steel cylinders under a pressure of about fifty atmospheres. When the liquid is allowed to escape from such a cylinder it partly evaporates and is partly converted into solid "carbonic acid snow." When prepared on the large scale, carbon dioxide is either made from some form of calcium carbonate, by treatment with acid or by heat alone, or else it is obtained as a by-product in the process of fermentation.

Corresponding to the comparatively easy compressibility to a liquid, we have moderate solubility of carbon dioxide in water. At the ordinary temperature water can dissolve about its own volume of carbon dioxide. Some of this carbon dioxide remains unchanged in the water, but some of it unites with the water and becomes carbonic acid, according to the equation—

$$\underset{\text{Carbonic anhydride}}{CO_2} + H_2O \rightleftarrows \underset{\text{Carbonic acid}}{H_2CO_3}$$

Effervescing beverages are aqueous liquids charged with carbon dioxide under pressure. They usually contain about five times as much carbon dioxide as the liquid would be capable of dissolving at one atmosphere pressure. In order that the liquid may retain this quantity of carbon dioxide, the pressure within the bottle must be equal to about five atmospheres. When the bottle is uncorked the pressure over the liquid is at once reduced to one atmosphere. Under these conditions the liquid can only retain in the dis-

solved state about one-fifth of the amount it originally contained, and the remaining four-fifths escape from the liquid in the form of bubbles. The water of some natural springs is slightly charged with carbon dioxide, which has been dissolved under considerable pressure at a distance below the earth's surface.

Rain in falling through the atmosphere absorbs some carbon dioxide, which, when dissolved by the water, is partially converted into carbonic acid. The carbonic acid thus formed enables the water to dissolve many substances which it would not otherwise attack. In particular, it enables the water to dissolve the insoluble normal carbonates. Thus calcium carbonate, which is practically insoluble in pure water, dissolves to a much more considerable extent in water containing carbonic acid. In this solution, however, it does not exist as the original normal calcium carbonate, but is converted by the carbonic acid into the soluble acid carbonate, in accordance with the equation—

$$CaCO_3 + H_2CO_3 = CaH_2(CO_3)_2$$

this acid carbonate conferring *temporary hardness* on the water (p. 93). The carbonic acid of the air therefore plays a great part in the disintegration of rocks, particularly those consisting of carbonates.

Carbon dioxide is not in the ordinary sense a poisonous gas, but when mixed with air in the proportion of one to ten it may cause death by suffocation, chiefly on account of its preventing the carbon dioxide brought by the blood to the lungs from escaping freely into the air, and thus the corresponding volume of fresh air from taking its place. The *choke-damp* in mines which produces suffocation is chiefly due to the presence of carbon dioxide.

Carbon monoxide, CO, differs greatly in its properties, both physical and chemical, from carbon dioxide. It is formed, by the combustion of carbon in a defective supply of oxygen, chiefly by the action of carbon dioxide on excess of heated carbon, the equation being—

$$C + CO_2 = 2CO$$

It may be prepared most readily in the laboratory by the action of concentrated sulphuric acid on formic acid or a

formate. The action on formic acid consists essentially in the abstraction of water, and may be represented by the equation—

$$\underset{\text{Formic acid}}{H_2CO_2} = H_2O + \underset{\text{Carbon monoxide}}{CO}$$

As it is not fully saturated with oxygen it burns in air with a blue flame to produce carbon dioxide, and can act as a deoxidising agent, for example in the following action :—

$$CO + CuO = Cu + CO_2$$

It is a gas which is slightly lighter than air, as its formula weight indicates, and cannot therefore be collected by down-

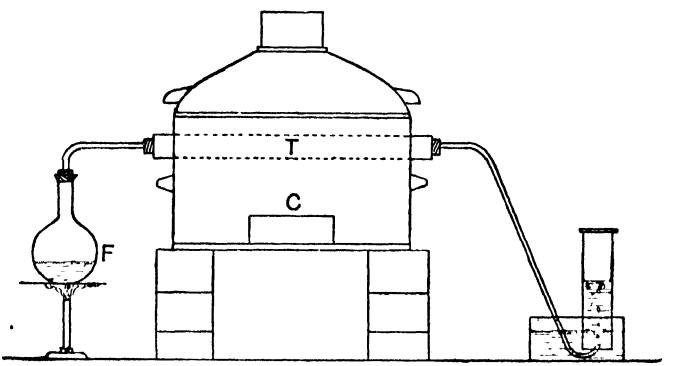


Fig. 31.—Preparation of "Water-gas" and Carbon Monoxide.

Steam is generated by boiling water in the flask *F*, and is passed over pieces of charcoal contained in the iron tube *T*, which is heated to bright redness in the charcoal furnace *C*. The gas, which is collected over water, consists of carbon monoxide and hydrogen. If carbon dioxide is delivered into the tube instead of steam, the gas which issues is nearly pure carbon monoxide.

ward displacement. Unlike carbon dioxide, it is not easily liquefied, no pressure, however great, being capable of reducing it to the liquid state at the ordinary temperature. Corresponding to this, it is only very slightly soluble in water.

When breathed, even in small quantity, it acts as a powerful poison, combining with the hæmoglobin of the blood, and preventing it from absorbing oxygen in the lungs. Carbon monoxide is the poisonous gas contained in the fumes from a bright charcoal fire, and it is also to its presence that the poisonous character of coal gas is due.

When air is passed over white-hot carbon, the oxygen is all

consumed by the carbon and converted into carbon monoxide, the nitrogen of the air not being attacked. This mixture of carbon monoxide and nitrogen is called *producer gas*, or *generator gas*, and is much used as a gaseous fuel.

Another kind of gaseous fuel may be obtained by passing steam over red-hot carbon. The carbon combines with the oxygen of the water to form carbon monoxide, and the hydrogen of the water is liberated.

$$H_2O + C = CO + H_2$$

A mixture of gases thus obtained is usually called *water gas*, and contains nitrogen, carbon monoxide, and hydrogen. The last two gases are both combustible, so that water gas can either be used as a gaseous fuel, or, when enriched by naphtha or other suitable substance, as an illuminating gas.

Mond gas is produced by the joint action of steam and air on heated coal-slack. It contains about half its volume of nitrogen, the other half being a mixture of hydrogen, carbon monoxide, and carbon dioxide. It is extensively used as a fuel for gas-engines.

Hydrocarbons

The compounds which contain only carbon and hydrogen are called **hydrocarbons**. Whilst carbon only forms two compounds with oxygen, it forms hundreds of compounds with hydrogen. We shall only consider here a few of the simplest gaseous hydrocarbons.

Methane or **marsh gas, CH_4,** contains the largest proportion of hydrogen of any hydrocarbon. When vegetable matter decays beneath the water of a marsh, methane is produced, and rises in bubbles to the surface, whence the name *marsh gas*. It cannot be formed by the direct union of carbon and hydrogen; indeed, these two elements can only be made to unite under exceptional circumstances. It can be made, however, indirectly, and is a product of the decomposition by heat of a great many organic substances. It is one of the chief constituents of coal gas, prepared by heating coal to a high temperature in closed retorts. An average sample of coal gas contains about one-third of its volume of marsh gas. The gas which issues from the earth's crust in enormous quantities in the neighbourhood of oil wells consists chiefly of marsh gas; and it is also

found enclosed in fissures in coal seams, so that when these enclosures are broken into by miners, the marsh gas escapes into the mine, and there forms a combustible mixture with the air in the mine. It is known for this reason as *fire-damp*. Coal-mine explosions are mostly due to the ignition of this explosive mixture.

In the laboratory it may be prepared by heating a mixture of dry sodium acetate and caustic soda:

$$\underset{\text{Sodium acetate}}{NaC_2H_3O_2} + NaOH = \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Methane}}{CH_4}$$

It is also evolved when aluminium carbide is treated with water:

$$\underset{\substack{\text{Aluminium}\\\text{carbide}}}{Al_4C_3} + 12H_2O = \underset{\substack{\text{Aluminium}\\\text{hydroxide}}}{4Al(OH)_3} + \underset{\text{Methane}}{3CH_4}$$

Like all hydrocarbons, it burns readily in air, the complete combustion being expressed by the equation—

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = CO_2 + 2H_2O$$

If methane and oxygen are taken in these proportions by volume, the mixture is violently explosive, especially when in large quantities.

Methane burns in air with a flame which is only slightly luminous. It is not poisonous, is incompressible to a liquid at the ordinary temperature, and corresponding to this, is only slightly soluble in water.

Ethylene, C_2H_4, is formed along with methane during the dry distillation of coal, although not in anything like the same proportion. It burns with a brightly luminous flame, and is one of the *illuminating* agents present in coal gas.

It may be prepared in the pure state by the action of concentrated sulphuric acid on alcohol. If these substances are warmed together in a flask, a brisk reaction takes place, whereby alcohol loses water, according to the equation—

$$\underset{\text{Alcohol}}{C_2H_6O} = \underset{\text{Ethylene}}{C_2H_4} + \underset{\text{Water}}{H_2O}$$

ethylene gas being produced. The ethylene which comes off is mixed with sulphur dioxide as well as traces of alcohol vapour. It may be freed from these impurities by passing

the gas first through strong caustic soda solution, and then through water. The sulphur dioxide is converted by the caustic soda into sodium sulphite, and the alcohol is retained by the water. This impurity may be avoided by the use of syrupy phosphoric acid instead of sulphuric acid. On the large scale ethylene is prepared by passing alcohol vapour over alumina Al_2O_3 heated to 360°. The heated alumina acts as a catalytic agent and accelerates the decomposition of the alcohol into ethylene and water.

Ethylene is, like methane, a colourless combustible gas, the equation for its complete combustion being—

$$\underset{\text{1 vol.}}{C_2H_4} + \underset{\text{3 vols.}}{3O_2} = 2CO_2 + 2H_2O$$

It has a faint, pleasant odour, can be compressed to liquid at the ordinary temperature, and is much more soluble in water than marsh gas.

Ethylene is what chemists call an **unsaturated** substance, a term which is usually applied to such carbon compounds as can combine directly with chlorine or bromine. If ethylene gas is led through a tube containing bromine, the two substances unite, according to the equation—

$$\underset{\text{Ethylene}}{C_2H_4} + Br_2 = \underset{\text{Ethylene dibromide}}{C_2H_4Br_2}$$

with formation of *ethylene dibromide*, which is a heavy, colourless, fragrant oil. Similarly, if ethylene and chlorine gas are brought together in equal volumes, they unite, with production of *ethylene dichloride*, the equation being—

$$\underset{\text{1 vol.}}{C_2H_4} + \underset{\text{1 vol.}}{Cl_2} = \underset{\text{Ethylene dichloride}}{C_2H_4Cl_2}$$

This reaction was observed long ago by certain chemists in Holland, and ethylene dichloride was for that reason called oil of Dutch chemists, and the ethylene which produced it is still frequently known under the name of *olefiant gas—i.e.* oil-producing gas.

Acetylene, C_2H_2, is a hydrocarbon which is of great practical importance. It is formed in small quantity when coal gas burns in a defective supply of air, and is probably produced in the interior of all hydrocarbon flames, being afterwards burned to carbon dioxide and water, when it reaches the more

plentiful oxygen supply in the external flame. It has long been known for the extremely luminous character of the flame which it produces when burnt in air, and now that a process has been found for its manufacture in large quantity it is extensively used as an illuminant.

When quicklime is raised to the intense heat of an electric furnace along with carbon, usually in the form of coal-slack, the following action takes place:—

$$\underset{\text{Calcium oxide}}{CaO} + \underset{\text{Carbon}}{3C} = \underset{\text{Calcium carbide}}{CaC_2} + \underset{\text{Carbon monoxide}}{CO}$$

the products being carbon monoxide, which comes off as gas, and **calcium carbide**, which remains in the furnace, in the form of a hard grey crystalline mass. When treated with water, calcium carbide is at once decomposed with production of calcium hydroxide and acetylene—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$

It is therefore an easy matter to prepare acetylene gas from calcium carbide, and all acetylene generators are merely appliances to produce an automatically regulated supply of acetylene gas by the interaction of calcium carbide and water.

The equation for the combustion of acetylene is as follows:—

$$\underset{\text{2 vols.}}{2C_2H_2} + \underset{\text{5 vols.}}{5O_2} = 4CO_2 + 2H_2O$$

If acetylene and oxygen are mixed together in these proportions, and a light is applied, the mixture explodes with great violence, usually shattering the vessel in which it is contained. The oxygen-acetylene blowpipe flame has a temperature considerably higher than the oxyhydrogen flame, and is used for cutting metals by fusing them at the point where the flame is applied, excess of oxygen being commonly employed to oxidise the metal at the same time.

Acetylene, like ethylene, is produced in the distillation of coal, although only in small quantity, and helps to give coal gas its illuminating power. Like ethylene, it is an unsaturated substance, combining directly with chlorine and bromine to form oily liquids.

When pure, acetylene has a smell which is not at all unpleasant, and closely resembles that of ethylene. Impure acetylene, on the other hand, especially that derived from

calcium carbide, has an obnoxious smell, and very poisonous properties. Both the unpleasant smell and the poisonous character of this commercial acetylene may be got rid of by suitable methods of purification.

Acetylene can easily be distinguished from the preceding hydrocarbons by its action on a solution of silver nitrate to which ammonia has been added. Pure acetylene when bubbled through the ammoniacal solution produces a white precipitate, while ethylene and marsh gas do not affect the solution at all. The precipitate is an insoluble substance called *silver acetylide*. Crude commercial acetylene, instead of producing a white precipitate, produces a dark precipitate owing to the presence of impurities, such as sulphuretted hydrogen and phosphine, which produce black compounds with silver salts.

CHAPTER XX

NITROGEN

NITROGEN, as we have seen, forms the bulk of the atmosphere. It is an extremely inactive substance, and as an element only enters into few chemical actions, although many of its compounds are extremely active. It has already been said that what was formerly known as atmospheric nitrogen is not pure nitrogen, but a mixture containing about 1 per cent. of argon together with much smaller quantities of other inert gases.

Pure nitrogen may be prepared from compounds of nitrogen. Thus, if any of the oxides of nitrogen is passed over heated copper, the copper decomposes these oxides, retaining the oxygen and liberating nitrogen.

$$\underset{\text{Nitric oxide}}{2NO} + 2Cu = 2CuO + N_2$$

$$\underset{\text{Nitrous oxide}}{N_2O} + Cu = CuO + N_2$$

This method may be used in the laboratory, but if only a small quantity of nitrogen is required, the following may be substituted. *Ammonium nitrite* when gently heated splits up according to the following equation:—

$$\underset{\text{Ammonium nitrite}}{NH_4NO_2} = 2H_2O + N_2$$

It is not necessary to prepare ammonium nitrite, which is not a common salt, specially for this purpose, since the action takes place equally well if we heat a solution containing potassium nitrite and an ammonium salt—*e.g.* ammonium sulphate. Potassium sulphate and ammonium nitrite will be formed by double decomposition, and the ammonium nitrite

will be at once decomposed on heating, so that the whole action is represented by the equation—

$$\underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + \underset{\text{Potassium nitrite}}{2KNO_2} = \underset{\text{Potassium sulphate}}{K_2SO_4} + 4H_2O + 2N_2$$

The nitrogen may be removed from the atmospheric mixture of nitrogen and argon by either of the following methods:—If excess of oxygen is added to the mixture, and a series of powerful electric sparks passed through the moist gases, the nitrogen, oxygen, and water react so as to produce nitric acid, which can be absorbed by means of a base. The process is a comparatively slow one, but if carried on for a sufficiently long time, all the nitrogen may be made to disappear, a mixture of argon and oxygen remaining behind. The oxygen may easily be removed by means of metallic copper, and so **argon** may be obtained. The other method is to pass the mixture of nitrogen and argon over heated metallic magnesium. Magnesium under these circumstances combines slowly with the nitrogen to produce a substance known as magnesium nitride, N_2Mg_3. The nitrogen can thus be all absorbed, the less active argon being unattacked.

The first of the above methods is now used commercially to produce nitrates from atmospheric nitrogen. Another process in which atmospheric nitrogen is used on a large scale is the production of calcium cyanamide $CaCN_2$, a valuable nitrogenous manure, by passing nitrogen over heated calcium carbide.

$$CaC_2 + N_2 = CaCN_2 + C$$

The nitrogen used for this or similar purposes, where the presence of much oxygen is undesirable, is prepared by the rectification of liquid air (compare p. 85), which thus serves as a source both of commercial oxgyen and of commercial nitrogen.

Nitrogen is one of the least soluble of gases, and is in general characterised by negative properties.

Ammonia, NH_3

Nitrogen forms several compounds with hydrogen, of which ammonia is by far the most important. The elements can

only be made to unite directly in small quantity, but ammonia, when once formed, is a stable substance. Notwithstanding the difficulty experienced in making nitrogen and hydrogen unite directly, the process is now used for the technical preparation of ammonia, high pressures and a catalyst being used to facilitate the process.

In the distillation of coal to produce coal-gas, much of the nitrogen contained in the coal comes off with hydrogen in the form of ammonia, which is for the most part converted at the gas-works into ammonium sulphate. From this, or any other ammonium salt, ammonia may readily be prepared by mixing it with lime and heating, the action which takes place being as follows :—

$$CaO + (NH_4)_2SO_4 = CaSO_4 + 2NH_3 + H_2O$$

The ammonia may be dried by passing over a layer of quicklime, which absorbs any water vapour it may contain.

Ammonia is a gas which is easily detected by its characteristic smell. It is considerably lighter than air, and may be collected by upward displacement. It is excessively soluble in water, and can be liquefied by pressure at the ordinary temperature of the atmosphere. The solution in water contains a large proportion of ammonium hydroxide, formed according to the equation—

$$NH_3 + H_2O \rightleftarrows NH_4OH$$

All the ammonia may be expelled from solution in water by continued boiling.

Ammonia burns readily in an atmosphere of oxygen—

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

but not in air unless heat is supplied to keep the action going (p. 10), or unless a catalyst is employed.

When a succession of electric sparks is passed through ammonia gas it is gradually decomposed into its elements, and if the residual gas is analysed, the volumetric composition of the ammonia is completely determined. One volume of ammonia gas gives two volumes of a mixture of nydrogen and nitrogen, containing one-fourth of its volume of nitrogen, as may be ascertained by removing the hydrogen as water

to produce nitric acid. On heating the pentoxide decomposes with violence into nitrogen peroxide and oxygen—

$$2N_2O_5 = 2N_2O_4 + O_2$$

Nitrogen peroxide, NO_2 or N_2O_4

Nitrogen peroxide is frequently produced when we heat the nitrates of the heavy metals. The substance generally employed in the laboratory is lead nitrate, which on heating decomposes according to the equation—

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2$$

a mixture of nitrogen peroxide and oxygen coming off. The nitrogen peroxide may be condensed to a light brown liquid, by passing it through a tube immersed in a freezing mixture of ice and salt.

Nitrogen peroxide can also be easily produced by the direct union of nitric oxide and oxygen, in accordance with the equation—

$$\underset{\text{Nitric oxide}}{2NO} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Nitrogen peroxide}}{2NO_2}$$

This union takes place at the ordinary temperature, and is rendered evident by the fact that nitric oxide and oxygen are both colourless gases, whilst nitrogen peroxide is a reddish-brown gas.

If nitrogen peroxide is heated, the colour may be seen to darken until the gas becomes practically opaque. On cooling again, the colour falls off to its original tint. These colour changes are connected with the following action :—

$$\underset{\text{1 vol.}}{N_2O_4} \rightleftarrows \underset{\text{2 vols.}}{2NO_2}$$

This action is a reversible action, decomposition taking place on heating, and recombination taking place on cooling. A decomposition of this kind is called a **dissociation,** the essential character of dissociation being *reversibility* and the *production of a larger volume of gas* by the decomposition.

At ordinary temperatures, nitrogen peroxide consists partly of the gas NO_2, and partly of the gas N_2O_4, the proportions of these two substances which are present being variable with the temperature, the NO_2 increasing in amount as the tempera-

ture is raised. The N_2O_4 has a somewhat pale reddish-brown colour, while the NO_2 has a very deep and almost opaque brown colour. Not only does the proportion of the two kinds of molecules NO_2 and N_2O_4 change with temperature, it also changes with volume. As the volume which the gas occupies increases, the amount of NO_2 increases—*i.e.* the degree of dissociation increases. The statement is perfectly general for all cases of true dissociation—namely, that the degree of dissociation is increased by increasing the volume of the gas, or, in other words, by diminishing the pressure.

Nitrogen peroxide at once dissolves in water, but it does not dissolve as such, water decomposing it with formation of other compounds of nitrogen. If the water is cold, the action takes place as follows:—

$$2NO_2 + H_2O = \underset{\text{Nitric acid}}{HNO_3} + \underset{\text{Nitrous acid}}{HNO_2}$$

At a higher temperature, nitric oxide is produced, owing to the decomposition of nitrous acid, thus:

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

By means of the preceding reactions nitrites and nitrates are now extensively prepared on a technical scale from nitric oxide, which is produced electrically from the nitrogen and oxygen of the atmosphere (p. 125). The nitric oxide combining with excess of oxygen and water produces nitric and nitrous acids, which on combination with bases yield nitrates and nitrites.

Nitrogen trioxide, N_2O_3

This oxide of nitrogen is very unstable. It can easily be prepared by mixing nitrogen peroxide with nitric oxide, the partial combination which takes place being represented by the equation—

$$\underset{\text{Nitrogen peroxide}}{NO_2} + \underset{\text{Nitric oxide}}{NO} \rightleftarrows \underset{\text{Nitrogen trioxide}}{N_2O_3}$$

If the oxides be taken in the proper proportions, and the gases liquefied by means of a freezing mixture, the liquid obtained differs altogether in colour from the brown nitrogen peroxide, being of a deep greenish-blue. This liquid consists, of the substance N_2O_3, but when it is converted into a gas

the nitrogen trioxide, unless absolutely dry, dissociates largely into nitric oxide and nitrogen peroxide. Nitrogen trioxide is most conveniently prepared by heating nitric acid with arsenious oxide (white arsenic), which decomposes the nitric acid with formation of nitrogen trioxide.

$$\underset{\text{Nitric acid}}{2HNO_3} + \underset{\text{Arsenious oxide}}{As_2O_3} + \underset{\text{Water}}{2H_2O} = \underset{\text{Arsenic acid}}{2H_3AsO_4} + \underset{\text{Nitrogen trioxide}}{N_2O_3}$$

When nitrogen trioxide is dissolved in cold water, it yields a bluish liquid which contains nitrous acid.

$$\underset{\text{Nitrogen trioxide}}{N_2O_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Nitrous acid}}{2HNO_2}$$

Nitrogen trioxide would thus seem to be the anhydride of nitrous acid, which has not been obtained in the pure state.

Nitrous acid and the Nitrites

Nitrous acid, HNO_2, cannot be prepared in the pure state owing to the ease with which it decomposes, the equation being—

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

Thus when a nitrite solution is warmed with dilute acid, brown fumes are produced owing to the liberation and decomposition of nitrous acid, and subsequent union of the nitric oxide with atmospheric oxygen.

When nitrates of most medals are heated, we find that the residue consists of an oxide of the metal. If potassium or sodium nitrate, however, is moderately heated, the residue consists of potassium or sodium *nitrite*, the decomposition taking place according to the equations—

$$2KNO_3 = 2KNO_2 + O_2$$
$$2NaNO_3 = 2NaNO_2 + O_2$$

These nitrites are solid substances, like the nitrates. They can easily be distinguished from nitrates by the production of brown fumes on warming with dilute sulphuric acid. Nitrates give no brown fumes under similiar conditions.

Nitric oxide, NO

Nitric oxide is one of the commonest products of the action of nitric acid on a metal. Thus, when lead, copper, or silver

is attacked by nitric acid, nitric oxide is produced, according to the equations—

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O$$
$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$
$$3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$$

In the laboratory, it is generally produced by the action of slightly diluted nitric acid on copper turnings. A convenient apparatus for the production of nitric oxide on the small scale from these materials is shown in fig. 32.

When a succession of electric sparks is passed through a mixture of oxygen and nitrogen such as atmospheric air, a portion of these gases at the high temperature of the spark combine to form nitric oxide—

$$N_2 + O_2 \rightleftarrows 2NO$$

This action is made use of on the large scale for the technical production of nitric oxide, prepared for subsequent conversion into nitrites or nitrates. Instead of electric sparks, a steady high-tension arc-discharge is used to heat the gases, and although only a very small percentage of the nitrogen present is converted into nitric oxide, the yield is sufficiently great to permit of profitable working.

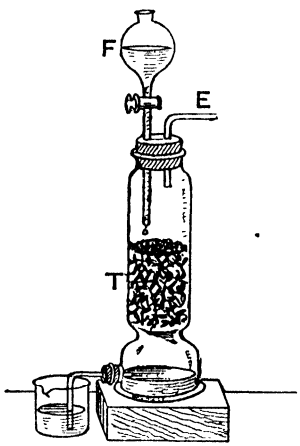


Fig. 32.—Preparation of Nitric Oxide

Copper turnings are contained in the upper part of the tower *T*, and nitric acid, slightly diluted with water, drops on them from the tap-funnel *F*. The nitric oxide escapes through the delivery tube *E*.

Nitric oxide is a colourless gas which is incompressible to a liquid at the ordinary temperature, and is only very slightly soluble in water. As soon as it comes into contact with oxygen or air, it combines with the oxygen, according to the equation—

$$2NO + O_2 = 2NO_2$$

and forms red fumes of nitrogen peroxide. It will not support the combustion of a taper, but if burning phosphorus is brought into contact with it, the phosphorus continues to

burn, decomposing the nitric oxide by combining with the oxygen and liberating the nitrogen.

$$4P + 10NO = 2P_2O_5 + 5N_2$$

Nitric oxide gives a characteristic dark brown coloration with a solution of ferrous sulphate, the production of which is a convenient means for detecting the presence of nitric acid, or of a nitrate, in solution.

The solution suspected to contain a nitrate is mixed with a little ferrous sulphate solution, and this mixed solution is poured carefully down the side of a test tube, which contains a little concentrated sulphuric acid, care being taken that the two liquids are not allowed to mix. If a nitrate is present, a brown ring is produced at the surface of contact of the two liquids. The nitric acid formed at the surface from the nitrate and concentrated sulphuric acid is converted by the ferrous sulphate into nitric oxide, which dissolves in the excess of the ferrous sulphate with production of the brown compound. The equation may be written as follows:—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

As this brown compound is easily destroyed by heat, the sulphuric acid must not be allowed to mix in bulk with the aqueous solution, for then so much heat would be evolved as to destroy the brown ring and thus render the test useless.

Since nitrites liberate nitric oxide on acidification with sulphuric acid, they give the brown ring test even more readily than nitrates.

Nitrous oxide, N_2O

We have seen that when ammonium nitrite is heated it decomposes into water and nitrogen, according to the equation—

$$NH_4NO_2 = N_2 + 2H_2O$$

Now ammonium nitr*ate* contains more oxygen than ammonium nitr*ite*, and when heated decomposes in a similar manner, with production, however, not of nitrogen, but of nitrogen monoxide or nitrous oxide.

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{Nitrous oxide}}{N_2O} + 2H_2O$$

Nitrous oxide, like nitric oxide, is a colourless gas. It possesses a faint sweetish smell and taste, and is moderately soluble in cold water.

It may also be prepared by heating a mixture of ammonium sulphate and potassium nitrate, the action which takes place being represented by the equation–

$$(NH_4)_2SO_4 + 2KNO_3 = 2N_2O + 4H_2O + K_2SO_4$$

A little nitric oxide and nitrogen peroxide are formed at the same time. These, however, can easily be removed by passing the gas through ferrous sulphate solution. Since

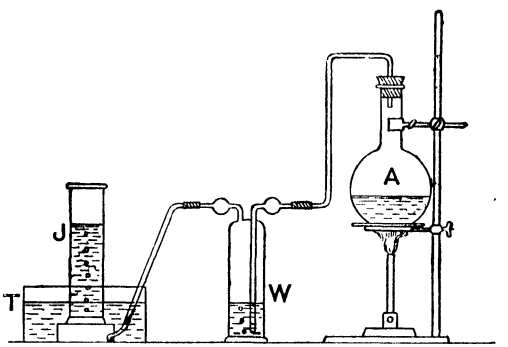


Fig. 33.—Preparation of Nitrous Oxide

The gas produced in the flask *A* is washed by bubbling through ferrous sulphate solution contained in the wash-bottle *W*, and collected over warm water.

the gas is soluble in cold water, it is usually collected over warm water, in which it is much less soluble.

Nitrous oxide is sometimes known by the name of *laughing gas*. When inhaled it produces a sense of exhilaration and hysterical laughter, which is afterwards succeeded by complete insensibility. Nitrous oxide is therefore used as an anæsthetic for the smaller operations of dentistry and the like. Corresponding to its solubility in water, we find that it can be compressed to a liquid at the ordinary temperature, and it is usually supplied to dentists in this form, the liquid being contained in small steel bottles.

Nitrous oxide can easily be distinguished from nitric oxide owing to the fact that it does not combine with oxygen to produce the red nitrogen peroxide, and that it is a vigorous

supporter of combustion. When a lighted taper is introduced into a jar of nitrous oxide it burns with increased brilliancy, and when a glowing splinter of wood is brought into contact with the gas it bursts into flame just as if it had been placed in a jar of oxygen.

Nitrous oxide is thus a better supporter of combustion than nitric oxide, although it contains proportionately less oxygen, and either of these gases is a better supporter of combustion than nitrogen peroxide, which contains more oxygen still. We therefore see that the power of supporting combustion depends, in the case of a compound, not so much on the quantity of oxygen it contains, but on the ease with which it parts with its oxygen. Nitrous oxide, which has a comparatively small amount of oxygen, parts with this oxygen very readily, and is thus a good supporter of combustion.

It is necessary, however, that the substance which is to burn in the nitrous oxide should be at such a temperature as to decompose the nitrous oxide and abstract the oxygen from the nitrogen. If we take some sulphur which is only burning feebly, and place it in a jar of nitrous oxide, the sulphur will be extinguished. If, on the other hand, the sulphur is burning brightly before it is placed in the nitrous oxide, it will now burn more brightly than ever. We have thus the facts that feebly burning sulphur is extinguished by nitrous oxide, and brightly burning sulphur burns in the nitrous oxide with increased brilliancy. In the first case, the temperature of the burning sulphur is not sufficient to enable it to abstract oxygen from the nitrous oxide, and in the second case the temperature is sufficiently high to effect this decomposition, and the proportion of oxygen which is thus produced is greater than the proportion of oxygen in air, and thus the brilliancy of the combustion is increased.

CHAPTER XXI

POSITIVE AND NEGATIVE RADICALS

In order to deal in a simple way with many actions in which acids, bases, and salts take part, it is convenient to conceive these substances to be composed each of two parts—namely, a **positive radical** and a **negative radical.** By radical we mean an element or group of elements in definite proportions which occurs in a number of similar compounds; thus all the sodium salts contain the simple radical Na, all the calcium salts contain the simple radical Ca, and all the ammonium salts contain the compound radical NH_4. Similarly, all chlorides contain the simple chloride radical Cl, and all nitrates the compound radical NO_3. Positive radicals are so called because they can under certain circumstances unite with and carry charges of positive electricity. Negative radicals in a similar manner can unite with and carry charges of negative electricity.

TABLE OF COMMON RADICALS AND IONS

	Positive Radicals. (Cations.)		Monad	Negative Radicals. (Anions.)		
	$H^{\cdot}$	Hydrogen		OH'	Hydroxide	
Metallic Radicals	$Na^{\cdot}$	Sodium		Cl'	Chloride	Salt Radicals
	$K^{\cdot}$	Potassium		Br'	Bromide	
	$NH_4^{\cdot}$	Ammonium		I'	Iodide	
	$Ag^{\cdot}$	Silver		ClO_3'	Chlorate	
	$Hg^{\cdot}$	Mercurous		NO_3'	Nitrate	
				HS'	Hydrosulphide	
			Dyad			
	$Hg^{\cdot\cdot}$	Mercuric		SO_4''	Sulphate	
	$Ca^{\cdot\cdot}$	Calcium		S_2O_3''	Thiosulphate	
	$Ba^{\cdot\cdot}$	Barium		SO_3''	Sulphite	
	$Mg^{\cdot\cdot}$	Magnesium		S''	Sulphide	
	$Zn^{\cdot\cdot}$	Zinc		$[O''$	Oxide]	
	$Cu^{\cdot\cdot}$	Copper		CO_3''	Carbonate	
	$Pb^{\cdot\cdot}$	Lead				
	$Sn^{\cdot\cdot}$	Stannous				
	$Fe^{\cdot\cdot}$	Ferrous				
			Triad			
	$Fe^{\cdot\cdot\cdot}$	Ferric		PO_4'''	Orthophosphate	
	$Al^{\cdot\cdot\cdot}$	Aluminium				

The table on the preceding page gives a list of the common positive and negative radicals. The symbols of the radicals are to be interpreted in the usual way; thus Na stands for 23 parts by weight of sodium; Cl stands for 35.5 parts by weight of chlorine; NH_4 stands for 14 parts of nitrogen combined with 4 parts of hydrogen. The dots and dashes attached to the symbols indicate the amounts of electricity with which the quantities expressed by the symbols may be associated. Each dot stands for an electro-chemical unit, or **faraday**, of positive electricity, each dash for an equal charge of negative electricity.

The symbol Ca··, then, indicates that, as compared with the symbol Na·, 40 parts of the calcium radical are charged with twice as much positive electricity as 23 parts of the sodium radical. Again, comparing the symbols Na· and Cl′, we see that 23 parts of the sodium radical are charged with just as much positive electricity as would neutralise the negative electricity carried by 35.5 parts of the chloride radical.

A consideration of the electrical charges associated with each radical gives us some notion of how these radicals might be expected to combine with each other. It is a fundamental electrical fact that charges of the same kind repel each other—that is, positive repels positive, and negative repels negative; whilst charges of opposite kinds attract each other—that is, positive attracts negative. We should therefore expect to find that radicals charged with positive electricity combine, not with other radicals charged with positive electricity, but with radicals charged with negative electricity; and similarly, that radicals charged with negative electricity combine, not with other negatively charged radicals, but with the oppositely charged positive radicals. This indication is in accordance with fact. Acids, bases, and salts are all composed of positive radicals combined with negative radicals.

We know that acids, bases, and salts are under ordinary circumstances electrically neutral—that is, they have, on the whole, neither a charge of positive electricity nor a charge of negative electricity. The charges of positive and negative electricity, therefore, which they are capable of assuming, must be such as will exactly neutralise each other. Now, we have expressed the unit charge by a dot if the electricity is positive, and by a dash if the electricity is negative. In the formulæ each dot is thus capable of exactly neutralising each

dash. If the substance expressed by a combination of symbols, then, is to be electrically neutral, the formulæ must contain *equal numbers of dots and dashes.*

This equivalence in the number of dots and dashes contained in the formula for an acid, base, or salt gives us an easy means of writing chemically correct formulæ for these substances. Thus, if we are asked what is the formula of a salt containing the sodium radical and the chloride radical, we can say at once that it must be $Na{\cdot}Cl'$, because each sodium radical has one positive charge, and each chloride radical one negative charge, so that they must be associated in equal numbers in order to make an electrically neutral compound. Again, if we are required to give the formula of a salt containing calcium as the positive radical, and chloride as the negative radical, we must write $Ca{\cdot\cdot}Cl_2'$. In order to balance the two positive charges on the calcium radical, we must have two chloride radicals each associated with one negative charge. Other examples of a similar nature will be given in the course of the chapter.

Salts receive names which indicate the positive and negative radicals they contain. Thus the chemical name of common salt $Na{\cdot}Cl'$ is *sodium chloride*, the chemical name of saltpetre or nitre $K{\cdot}NO_3'$, is *potassium nitrate*, the chemical name for calc-spar, etc., $Ca{\cdot\cdot}CO_3''$ is *calcium carbonate*, and so on. In naming the salt the positive radical is placed first and the negative radical second.

Adopting this system, we are enabled at once to write the correct formula for a salt as soon as its systematic chemical name is given. We are required, for example, to write the formula of *zinc nitrate*. We know that the positive radical of this salt is zinc $Zn{\cdot\cdot}$, and that the negative radical is nitrate NO_3'. In order that the number of dashes on the negative portion shall be equal to the two dots on the zinc radical, we must take two of the nitrate radicals, and so we write the formula of zinc nitrate as follows:—$Zn{\cdot\cdot}(NO_3')_2$. Again, we may be asked to write the formula of *potassium carbonate*. This salt contains the potassium radical $K{\cdot}$ combined with the carbonate radical CO_3'', and to get equivalence of the dots and dashes we must take two potassium radicals for one carbonate radical. We thus obtain the formula $K{\cdot}_2CO_3''$ for potassium carbonate.

If it is desired to write the formula of *calcium phosphate*, we

first of all take the calcium radical $Ca^{\cdot\cdot}$ with its two dots, and the phosphate radical $PO_4^{'''}$ with its three dashes. To get the number of dots and dashes to correspond, we have to take three calcium radicals and two phosphate radicals. This gives us 3×2 positive charges for the three calcium radicals, and 2×3 negative charges for the two phosphate radicals, the six positive charges thus balancing the six negative charges. The formula then is $Ca^{\cdot\cdot}{}_3(PO_4^{'''})_2$.

It will be observed that in the table we have grouped the radicals according to the number of unit charges associated with them. Radicals with one unit charge are called univalent or *monad* radicals; radicals with two unit charges are called bivalent or *dyad* radicals; radicals with three unit charges are called trivalent or *triad* radicals. The monad radicals are all equivalent to one another, the dyad radicals are also equivalent amongst themselves, and so likewise are the triad radicals. In each class, therefore, we have equivalence; and if the positive and the negative radicals in a salt belong to the same class, they combine in equal numbers. If the positive and negative radicals belong to different classes, then we have the following rules, of which examples have just been given. Two monad radicals combine with one dyad radical; three monad radicals combine with one triad radical; and three dyad radicals combine with two triad radicals. The beginner is strongly advised to write the formula for all possible combinations of positive and negative radicals, so as to gain expertness in writing correct formulæ for acids, bases, and salts. He should at first make use of the table, but in doing so should endeavour to get the names, symbols, and the electric charges expressed by the dots and dashes firmly fixed in his memory, so that he may be able to write, without consulting the table, the correct formula for any salt whose systematic name is given to him.

It will be seen that in the table the *hydrogen radical* has been separated from the other positive radicals, and that the *hydroxide radical* has been separated from the other negative radicals. This is on account of the peculiar character of compounds containing hydrogen as the positive radical on the one hand, and hydroxide as the negative radical on the other. Compounds which contain only hydrogen as the positive radical are **acids**; compounds which contain only

hydroxide as the negative radical are **bases**. All other combinations of positive and negative radicals are **salts**. When the two peculiar radicals, hydrogen and hydroxide, are combined together we get a substance which, although common, has chemically speaking very peculiar properties, namely, **water**.

According to our system, a substance having the formula HCl should be called hydrogen chloride, and a substance having the formula H_2SO_4, hydrogen sulphate. These names are sometimes employed, and similarly other compounds having hydrogen as the positive radical are referred to as hydrogen salts; but as a rule an older system is adhered to, and hydrogen salts according to it are called *acids*. Thus, instead of hydrogen chloride we say hydrochloric acid, instead of hydrogen sulphate we say sulphuric acid. There is a definite mode of connecting the names of the various acids with the names of the salts derived from them. If the name of the negative radical ends in **ite** the name of the acid ends in **ous**. If the name of the negative radical ends in **ate** the name of the acid ends in **ic**. Finally, if the name of the salt radical ends in **ide** the name of the corresponding acid begins with **hydro** and ends with **ic**. We have thus the following correspondence :—

Acid	Salt
——————**ous**	——————**ite**
——————**ic**	——————**ate**
Hydro——**ic**	——————**ide**

Corresponding to the sulph*ates* we have sulphur*ic* acid; corresponding to the sulph*ites* we have sulphur*ous* acid; corresponding to the sulph*ides* we have *hydro*sulphur*ic* acid. Chlor*ides* are derived from *hydro*chlor*ic* acid, brom*ides* from *hydro*brom*ic* acid, iod*ides* from *hydr*iod*ic* acid. Exceptions to this rule of correspondence sometimes occur, but they are not very frequent.

Occasionally we find that one and the same metal occurs in the form of two different metallic radicals. Thus mercury is the sole constituent of the *mercurous* radical $Hg^{\cdot}$ and of the *mercuric* radical $Hg^{\cdot\cdot}$. The salts derived from these different radicals have entirely different properties, and, as we see, are called by different names. In such cases one of the names ends in **ous**, the

other ends in **ic**. In giving these terminations to the different radicals the following rule is always observed:—The radical with the smallest number of dots receives the termination **ous**, the radical with the greatest number of dots receives the termination **ic**. This is exemplified in the case of mercury, and we see the same thing in the case of iron. The ferr**ous** radical $Fe^{\cdot\cdot}$ has two dots associated with it, the ferr**ic** radical $Fe^{\cdot\cdot\cdot}$ has three dots.

The positive radicals may be subdivided into the radical hydrogen and the **metallic radicals** which constitute all the other positive radicals. Similarly, the negative radicals may be divided into the hydroxide radical and all the other negative radicals, which are classed together as **salt radicals**. Thus we may define acids, bases, salts, and water according to their radicals as follows:—

Hydrogen radical, Hydroxide radical . .	**Water**
Hydrogen radical, Salt radical . . .	**Acid**
Metallic radical, Hydroxide radical . .	**Base**
Metallic radical, Salt radical . . .	**Salt**

We sometimes find that the positive portion of a salt does not consist of one radical only, but of various radicals combined with the same negative portion. Thus we can have the salt *sodium potassium sulphate* $Na{\cdot}K{\cdot}SO_4''$, which contains as the positive portion both sodium and potassium radicals. Such a salt is called a **mixed salt**, and the systematic name is given by mentioning the two positive radicals first and then the negative radical. Another instance is found in *magnesium ammonium phosphate* $Mg^{\cdot\cdot}NH_4{\cdot}PO_4'''$. In such mixed salts the rule about dots and dashes holds good, as may be seen by reference to the formulæ. Salts of the opposite type, with one metallic radical and two or more salt radicals, are not common.

When the positive portion of a compound consists partly of the hydrogen radical, the compound is said to be an **acid salt**. As an example we may take the common *bisulphate of soda*, which has the formula $Na{\cdot}H{\cdot}SO_4''$, and is named according to our systematic method *sodium hydrogen sulphate*.

The phosphates show many instances of mixed salts and acid salts. We have already seen the mixed salt magnesium ammonium phosphate $Mg^{\cdot\cdot}NH_4{\cdot}PO_4'''$. The ordinary sodium phosphate is, in reality, an acid salt; its formula is $Na{\cdot}_2H{\cdot}PO_4'''$,

and its systematic name *disodium hydrogen phosphate.* Another salt exists which has the formula $Na{\cdot}H{\cdot}_2PO_4'''$, which can be distinguished from the previous one by naming it *sodium dihyrogen phosphate.* We may even have a salt which is at once a mixed salt and an acid salt—thus, *sodium ammonium hydrogen phosphate* $Na{\cdot}NH_4{\cdot}H{\cdot}PO_4'''$.

When a compound consists of one metallic radical combined with two or more negative radicals, one of which is the hydroxide radical, it is said to be a **basic salt.** Thus we have the *basic mercuric nitrate* $Hg''(OH')(NO_3')$, one of the negative radicals in which is the hydroxide group, and the other the nitrate group.

Salts of the ordinary type, which consist of metallic radicals only combined with salt radicals only, are said to be **normal salts.**

From a consideration of the formulæ, it is evident that acid salts are intermediate in composition between the acid and the normal salt of the acid. Sodium hydrogen sulphate $Na{\cdot}H{\cdot}SO_4''$ is evidently intermediate between normal sodium sulphate $Na{\cdot}_2SO_4''$ and sulphuric acid $H{\cdot}_2SO_4''$. These acid salts are only found when the acid has two or more hydrogen radicals in its formula. When this is the case, the hydrogen may be replaced by a metallic radical in successive steps. For instance, phosphoric acid, with the formula $H{\cdot}_3PO_4'''$, has three hydrogen radicals, which can be replaced in three successive stages by metallic radicals, such as the sodium radical, with production of the two acid salts $Na{\cdot}H{\cdot}_2PO_4'''$, $Na{\cdot}_2H{\cdot}PO_4'''$, and the normal salt $Na{\cdot}_3PO_4'''$.

Acids which have only one hydrogen radical in the formula are said to be **monobasic;** acids with two hydrogen radicals are **dibasic;** acids with three hydrogen radicals are **tribasic.** Thus hydrochloric and nitric acids are monobasic; sulphuric acid is dibasic; and phosphoric acid tribasic.

It must not be supposed that salts which are in this formal sense acid salts, have always the properties of acids. It is true that sodium hydrogen sulphate is a strongly acid substance, being sour to the taste, and its solution at once turning blue litmus red, but this is not invariably the case. The ordinary sodium phosphate $Na{\cdot}_2H{\cdot}PO_4'''$, although formally an acid salt, is not acid to litmus; in fact, it has a slightly alkaline reaction. We must then carefully distinguish between the

classification of salts in a purely formal way into acid, normal, and basic salts; and the classification of the same substances according to their action on an indicator like litmus. A formally acid salt may be acid, neutral, or even alkaline to litmus; and, similarly, a normal salt may be acid, alkaline, or neutral to litmus. When we are dealing with strong bases, such as sodium hydroxide, potassium hydroxide, or calcium hydroxide, and with strong acids such as hydrochloric, nitric, or sulphuric acids, the two modes of classification coincide: normal salts are then neutral to litmus, and acid salts are acid to litmus. But when salts formed from strong bases and weak acids, or weak bases and strong acids, are in question, then the two classifications do not coincide. Normal salts formed from a strong acid and a weak base frequently give solutions which are acid to litmus—*e.g.* copper sulphate $CuSO_4$. Normal salts which are formed from a strong base and a weak acid frequently give solutions which are alkaline to litmus—*e.g.* sodium carbonate Na_2CO_3.

CHAPTER XXII

DOUBLE DECOMPOSITION

A VERY frequent type of chemical action occurs in aqueous solution by positive and negative radicals changing places. In this way what we call a **double decomposition** is brought about, and already in the phenomenon of neutralisation we have had examples of this kind of action. When we write the equations for the neutralisation of some of the simple acids by some of the simple bases, indicating the positive and negative radicals, we find that the neutralisation consists in the hydrogen radical of the acid combining with the hydroxyl radical of the base to form water.

$$\begin{array}{rcrcrcl}
Na{\cdot}OH' & + & H{\cdot}Cl' & = & Na{\cdot}Cl' & + & H{\cdot}OH' \\
2K{\cdot}OH' & + & H{\cdot}_2SO_4'' & = & K{\cdot}_2SO_4'' & + & 2H{\cdot}OH' \\
Ca{\cdot\cdot}(OH')_2 & + & 2H{\cdot}NO_3' & = & Ca{\cdot\cdot}(NO_3')_2 & + & 2H{\cdot}OH' \\
Al{\cdot\cdot}(OH')_3 & + & 3H{\cdot}Cl' & = & Al{\cdot\cdot\cdot}Cl_3' & + & 3H{\cdot}OH' \\
3NH_4{\cdot}OH' & + & H{\cdot}_3PO_4''' & = & (NH_4{\cdot})_3PO_4''' & + & 3H{\cdot}OH'
\end{array}$$

The hydrogen radical of the acid changes places with the metallic radical of the base, and the salt radical of the acid changes places with the hydroxide radical or hydroxyl of the base. The positive and negative radicals, therefore, merely change partners, and in every instance of neutralisation it will be seen that water is an essential product.

Now, by writing down the formulæ of any two salts, and interchanging their positive and negative radicals, we obtain an equation which is chemically a possible equation, but which may or may not express an actual chemical reaction. There are some rules, however, which we can use for our guidance in determining which of these double decompositions actually take place and which do not. It can be said that, without exception, if one of the positive radicals is hydrogen, and if one of the negative radicals is hydroxyl, a double

decomposition will undoubtedly take place, the hydrogen and the hydroxyl combining to form water. Similarly, there are other pairs of positive and negative radicals which, when brought together, always combine with each other, and thus bring about double decomposition between salts. In general, when by interchange of the radicals of two soluble salts there is possibility of formation of an **insoluble** salt, then a double decomposition will take place. It is therefore of the utmost importance that the student should know which salts are soluble in water, and which salts are insoluble in water; for on this knowledge depends his power of predicting whether a possible double decomposition between salts will take place or not. The following general statements, then, regarding solubility will be found to be of use:—

All normal *nitrates*, *acetates*, and *chlorates* are **soluble** in water.

All *potassium*, *sodium*, and *ammonium* salts are **soluble** in water.

All normal *chlorides* **are soluble,** except HgCl, CuCl, AgCl, **and** $PbCl_2$.

All normal *sulphates* **are soluble except** $BaSO_4$, $SrSO_4$, $PbSO_4$, Hg_2SO_4, **and** $CaSO_4$.

The ordinary *acids* are **soluble.**

All normal *phosphates* and *carbonates* are **insoluble** except those of potassium, sodium, and ammonium.

All *hydroxides* are **insoluble** except those of sodium, potassium, and ammonium, which are freely soluble, and those of calcium, strontium, and barium, which are sparingly soluble.

If we consider the equation—

$Na\cdot Cl'$	+	$K\cdot NO_3'$	=	$K\cdot Cl'$	+	$Na\cdot NO_3'$
Sodium chloride		Potassium nitrate		Potassium chloride		Sodium nitrate

we find that all the substances concerned in it are soluble, and the above rule about insoluble substances does not therefore apply. *It must not be supposed, however, that because the rule does not apply the reaction cannot take place.* When the rule is not applicable, we are simply not in a position to tell whether the reaction can occur or not.

If we now consider the equation—

$$\underset{\text{Zinc sulphate}}{Zn^{\cdot\cdot}SO_4''} + \underset{\text{Barium nitrate}}{Ba^{\cdot\cdot}(NO_3')_2} = \underset{\text{Zinc nitrate}}{Zn^{\cdot\cdot}(NO_3')_2} + \underline{\underset{\text{Barium sulphate}}{Ba^{\cdot\cdot}SO_4''}}$$

we can say that the action, according to the above rule, will occur, because one of the products of the reaction is insoluble—that is, the substances on the left of the equation by interchange of radicals can produce the insoluble barium sulphate. The action will therefore take place.

Again, if we ask: Will zinc nitrate and sodium phosphate enter into double decomposition? we can say that they will, for zinc nitrate and sodium phosphate are soluble salts, but by interchange of radicals can produce sodium nitrate which is soluble and zinc phosphate which is insoluble.

$$3Zn^{\cdot\cdot}(NO_3')_2 + 2Na_3{\cdot}PO_4''' = \underset{\text{Zinc phosphate}}{Zn^{\cdot\cdot}{}_3(PO_4''')_2} + 6Na{\cdot}NO_3$$

Suppose now we ask: Will barium sulphate and sodium chloride enter into double decomposition to produce barium chloride and sodium sulphate? It is evident that they will not, for here we should have an insoluble and a soluble substance reacting together to produce two soluble substances, a reaction which in view of the above rule is impossible, for these soluble substances would themselves interact to produce sodium chloride and the insoluble barium sulphate.

We can therefore reverse the rule, and say that an insoluble and a soluble salt will not react to produce two soluble salts.

Take now the following case:—

$$Na{\cdot}{}_2CO_3'' + \underline{Ba^{\cdot\cdot}SO_4''} = Na{\cdot}{}_2SO_4'' + \underline{Ba^{\cdot\cdot}CO_3''}$$

On one side we have the insoluble salt barium sulphate, on the other side we have the insoluble salt barium carbonate. The conditions for the application of the rule are therefore not fulfilled, and we cannot say whether the action will take place or not.

It must be understood that the above rule applies only to *salts*, and not to reactions involving *acids*. For example, if we consider the reaction—

$$\underline{Zn^{\cdot\cdot}{}_3(PO_4''')_2} + 6HCl = 3Zn^{\cdot\cdot}Cl_2'' + 2H{\cdot}{}_3PO_4'''$$

we should say, if the rule were applicable to this case, that

the zinc phosphate would not react with the hydrochloric acid to produce zinc chloride and phosphoric acid; but as a matter of fact, these substances do interact, and the zinc phosphate dissolves up entirely when treated with hydrochloric acid. When an acid, therefore, takes part in a double decomposition, we must be prepared for exceptions to the rule given above.

The **displacement of one acid from its salts by another acid**, of which the above reaction is an example, is of great importance. If we treat a solution of sodium chloride with nitric acid, some of the hydrochloric acid is displaced by the nitric acid, according to the equation—

$$Na\cdot Cl' + H\cdot NO_3' = Na\cdot NO_3' + H\cdot Cl'$$

Here we have the same kind of interchange of radicals as before; the hydrogen radical, which was originally connected with the chloride radical, being now combined with the nitrate radical. This reaction is a balanced action, for if we add hydrochloric acid to a solution of a nitrate, the following interchange occurs:—

$$H\cdot Cl' + Na\cdot NO_3' = Na\cdot Cl' + H\cdot NO_3'$$

Here the nitric acid is displaced from its salt by the hydrochloric acid.

This kind of reaction between one acid and the salt of another acid is quite general in aqueous solutions, and in every case the action is a balanced one when all the substances are soluble. *Any acid is capable of displacing to a greater or less extent any other acid from its salts*, and we can conveniently define the inherent strength of an acid by the extent to which it will turn out other acids from solutions of their salts. It must be clearly understood, however, that the two acids must compete against each other under conditions equally favourable to both. If one of the acids is removed from the sphere of reaction, then the other acid is of course favoured, for the first acid after its removal from the sphere of reaction is no longer in a position to compete with the other acid. Now, substances may be removed from the sphere of reaction in two ways. First, they may separate out as insoluble precipitates; and, second, they may separate out as gases. As most of the common acids are freely soluble

in water, the second mode of removal of the acids is of greater practical importance than the first in determining the conditions for the displacement of one acid by another.

If we heat a non-volatile acid together with salt of another acid, which is itself volatile, then the second will pass off as vapour as soon as it is formed, and the result will be that the non-volatile acid, if taken in sufficient quantity, will eventually displace all the volatile acid from its salt. Thus, when concentrated sulphuric acid is warmed with sodium chloride, it displaces some of the hydrochloric acid from the chloride, and the hydrochloric acid being in the form of a gas at the temperature of the experiment, is removed from the sphere of action as soon as formed; so that if the action of the sulphuric acid on the sodium chloride is sufficiently prolonged, all the hydrochloric acid will be expelled, according to the equations—

$$NaCl + H_2SO_4 = \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + HCl\uparrow$$

$$NaCl + NaHSO_4 = \underset{\text{Normal sodium sulphate}}{Na_2SO_4} + HCl\uparrow$$

The expulsion here takes place in two stages. The temperature necessary for the first stage is comparatively low, the temperature necessary for the second stage is much higher; but in each case the hydrochloric acid is much more volatile than the sulphuric acid, and is consequently expelled as gas, this fact being conveniently indicated by the arrow attached to the formula.

In the above instance the sulphuric acid and the hydrochloric acid are not competing on equal terms, because the hydrochloric acid cannot remain in the sphere of reaction. Suppose, now, we add sulphuric acid to a *dilute solution* of sodium chloride at the ordinary temperature. In that case, neither the sulphuric acid nor the hydrochloric acid is volatile, and the hydrochloric acid produced remains in the solution and consequently continues to compete against the sulphuric acid. When we consider the extent to which the sulphuric

acid displaces the hydrochloric acid under such conditions, we find that the sulphuric acid, instead of being inherently stronger than the hydrochloric acid, as is generally supposed, is in reality considerably weaker.

The expulsion of nitric acid from a nitrate by means of sulphuric acid is similar. At the temperature at which the reaction is conducted, the nitric acid is volatile, and the sulphuric acid is not. The consequence is, that if sufficient sulphuric acid is employed, all the nitric acid is expelled, according to the equation—

$$Na{\cdot}NO_3' + {\cdot}H{\cdot}_2SO_4'' = \underset{\text{Sodium hydrogen sulphate}}{Na{\cdot}H{\cdot}SO_4''} + H{\cdot}NO_3'$$

When the two acids are made to compete against each other in aqueous solution, under conditions equally favourable to both, it is found that the nitric acid is considerably stronger than the sulphuric acid.

When the strength of the acids is measured in this way, by finding to what extent they displace each other in aqueous solution, it appears that hydrochloric and nitric acids are about equally strong, that sulphuric acid is somewhat weaker than these, and that phosphoric acid is weaker still. *Acetic acid* (the acid in vinegar) is so weak in comparison with these others, that nearly all of it is displaced from its salts by them. Thus:

$$\underset{\text{Sodium acetate}}{Na{\cdot}C_2H_3O_2'} + \underset{\text{Hydrochloric acid}}{H{\cdot}Cl'} = \underset{\text{Sodium chloride}}{Na{\cdot}Cl'} + \underset{\text{Acetic acid}}{H{\cdot}C_2H_3O_2'}$$

Acetic acid may be taken as a typical weak acid, the acid properties of which still remain quite pronounced. For example, acetic acid, although weak, has still a very sour taste, and at once reddens litmus.

Carbonic acid $H{\cdot}_2CO_3''$ is a very much weaker acid than acetic acid. Its solutions have no sour taste, and are just capable of reddening litmus. *Sulphuretted hydrogen*, or hydrosulphuric acid, $H{\cdot}_2S''$, is another acid of much the same strength as carbonic acid. These two acids are also similar in another respect—namely, they are not very soluble in water, and are easily expelled from aqueous solution by heating, the

carbonic acid breaking up at the same time into carbon dioxide and water, according to the equation—

$$H_2CO_3'' = H_2O + CO_2$$

When solutions of the carbonates are treated with hydrochloric, or even with acetic acid, the carbonates are converted into chlorides or acetates almost completely, according to the equations—

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$
$$K_2CO_3 + 2H{\cdot}C_2H_3O_2' = 2\,K{\cdot}C_2H_3O_2' + H_2O + CO_2$$

These reactions are favoured not only by the inherent weakness of the carbonic acid, but also by its tendency to split up into water and carbon dioxide, which passes off as gas. Similarly, if a soluble sulphide is treated with hydrochloric, nitric, sulphuric, or acetic acid, sulphuretted hydrogen is at once produced, on account both of its inherent weakness, and on account of its being a gas which is incapable of remaining to any great extent in solution.

$$Na_2S + 2H{\cdot}C_2H_3O_2' = 2Na{\cdot}C_2H_3O_2' + \nearrow H_2S$$

When solid insoluble carbonates are treated with any strong acid, they split up with evolution of carbon dioxide. For example, if calcium carbonate is treated with hydrochloric acid, though the calcium carbonate is in the dense form of marble, it is at once decomposed, according to the equation—

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + \nearrow CO_2$$

Even acetic acid is a sufficiently strong acid to decompose solid carbonates in this way.

Some insoluble sulphides can be similarly decomposed by strong acids. For example, ferrous sulphide, FeS, although insoluble in water, is easily attacked by moderately dilute hydrochloric acid, with evolution of sulphuretted hydrogen, according to the equation—

FeS	$+ 2HCl =$	$FeCl_2$	$+$	$\nearrow H_2S$
Ferrous sulphide		Ferrous chloride		Sulphuretted hydrogen

This action is usually made use of in the laboratory to prepare

sulphuretted hydrogen gas. Some insoluble sulphides, however, resist decomposition by acid. For example, mercuric sulphide HgS, and arsenious sulphide As_2S_3, are scarcely attacked by a solution of hydrochloric acid, and very little sulphuretted hydrogen is expelled from them.

The displacement of bases by each other from their salts is subject to the same rules as those we have just seen regarding acids. If two bases compete with each other under fair conditions, their strength can be measured by the extent to which they can displace each other. Thus it is found that potassium hydroxide and sodium hydroxide are almost equally strong. If one of the bases is removed as soon as it is formed, then, of course, the competition does not take place under fair conditions, and so one base may throw out another base from its salts, although the second is as strong as the first. Thus, if we add a concentrated solution of potassium hydroxide to a concentrated solution of calcium chloride, calcium hydroxide will be produced according to the equation—

$$\underset{\text{Potassium hydroxide}}{2KOH} + \underset{\text{Calcium chloride}}{CaCl_2} = \underset{\text{Potassium chloride}}{2KCl} + \underset{\text{Calcium hydroxide}}{Ca(OH)_2}$$

Now, this calcium hydroxide is only sparingly soluble in water, and consequently soon begins to separate out. The portion which is separated out as solid has practically left the sphere of the reaction, and so it is possible by means of potassium hydroxide to displace a very large proportion of calcium hydroxide from its salts, if the solutions are concentrated. If enough water is present, however, to dissolve all the calcium hydroxide which would be produced—that is, if we work with dilute solutions, then it is found that calcium hydroxide is almost as strong a base as the potassium hydroxide.

As most of the hydroxides are insoluble or sparingly soluble in water, sodium or potassium hydroxide, which are soluble, can in general displace them from their salts. The following are examples of such reactions :—

$$ZnSO_4 + 2NaOH = Na_2SO_4 + \underset{\text{Zinc hydroxide}}{Zn(OH)_2}$$

$$CuCl_2 + 2KOH = 2KCl + \underset{\text{Cupric hydroxide}}{Cu(OH)_2}$$

Ammonium hydroxide is a base which bears much the same

relation, so far as strength is concerned, to potassium or sodium hydroxide, that acetic acid does to nitric or hydrochloric acid. Consequently, if we add caustic soda to a solution of an ammonium salt, even though all the ammonium hydroxide remains in solution, a very large proportion of it will be displaced from its salt. If the solution is boiled, the ammonium hydroxide splits up into water and ammonia gas, which leaves the solution, so that, both on account of its inherent weakness, and of its volatility, ammonium hydroxide can always be displaced from ammonium salts by heating the solutions with caustic alkalies.

$$(NH_4)_2SO_4 + 2NaOH = Na_2SO_4 + 2NH_4OH$$

$$NH_4OH = \underset{\text{Ammonia}}{\uparrow NH_3} + H_2O$$

CHAPTER XXIII

SOLUTIONS

Molecular Weights—Ionisation—Hydrolysis

WHEN a substance is dissolved in water it may or may not undergo a change of a chemical nature. The inert gas argon has never been made to enter into any kind of chemical action whatever, so that when argon is dissolved in water there can be no action of a chemical nature between the solvent and the dissolved body. On the other hand, when a gas like carbon dioxide is dissolved in water, chemical action certainly takes place, part at least of the carbon dioxide uniting with water to form carbonic acid. Again, many substances, when crystallised from their aqueous solutions, separate out combined with water as hydrates, and it is therefore only reasonable to assume that in the solution itself some kind of combination with water had also taken place. Occasionally, the existence of chemical combination with a solvent is made evident by great heat evolution when the solvent and dissolved body are mixed, a good instance being afforded by the mixing of sulphuric acid and water. Some kind of action then may frequently be assumed between water and the substances dissolved in it, although such action is not a necessary condition for solution to take place.

In the case of dilute solutions of substances there is an analogy between the condition of the substance in such a solution and the condition of the same substance in the gaseous state. At the ordinary temperature water dissolves about its own volume of carbon dioxide. The concentration of the carbon dioxide then in the state of gas and in the state of solution is much the same, if we set aside for the moment the chemical action between the carbon dioxide and water. Since there is this analogy in the distribution of the particles of the substance in the gaseous and in the dissolved state, it is

not unreasonable to look for methods of determining the molecular weight of the dissolved substance since such a determination can be made for gases. A method suitable for this purpose is found in measurements of the freezing-points of water and of aqueous solutions.

Molecular Weight in Solution.— It has long been known that the freezing-point of aqueous solutions is lower than the freezing-point of pure water, and with dilute solutions the difference between the freezing-point and that of pure water, in other words, the *depression of the freezing-point* by the dissolved substance, is nearly proportional to the concentration of the solution. For example, a two-per-cent. solution of sugar freezes very nearly twice as far below the freezing-point of water as a one-per-cent. solution.

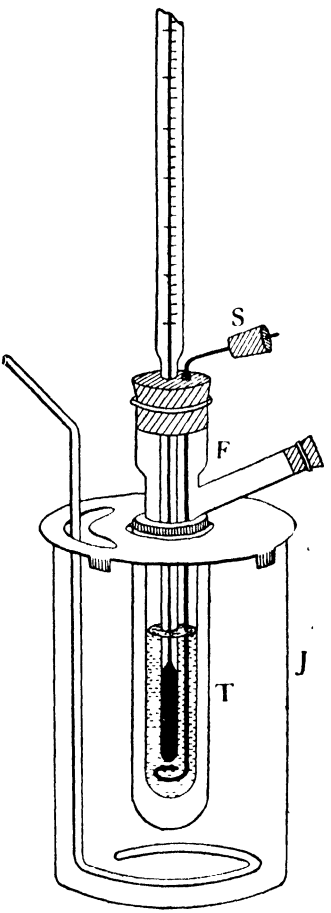


Fig. 34

When aqueous solutions of different substances are compared, it is found in general that those solutions which contain in them amounts of the dissolved substances which are proportional to their molar or molecular weights have the same freezing-point. Experiment shows that solutions of various substances which contain one gram molecule of each substance dissolved in a kilogram of water have all approximately a freezing-point of − 1.86°C.—that is, the depression of the freezing-point for these molecular-normal solutions is 1.86. We may say then that if a solution of an unknown substance shows a freezing-point depression of 1.86 we may conclude that it contains one molar weight

in a litre of water, so that if we analyse the solution to ascertain the amount of dissolved substance we can say that the number of grams dissolved in a litre of water gives, at least approximately, the molecular weight of the substance.

This method of determining molecular weights by the freezing-point is frequently spoken of as **Raoult's method**, and is practically carried out in the apparatus sketched in fig. 34. The tube F contains the liquid, the freezing-point of which is to be determined, and through the cork closing the upper portion there passes a thermometer and also a stirrer S. The apparatus is surrounded by a freezing mixture of ice, salt and water in the wide jar J, having a temperature of about $-5°$ to $-10°$.

To perform the experiment a weighed portion of water is placed in F and the apparatus arranged as in the figure. The water gradually cools until its temperature falls below the freezing-point. After a time ice begins to separate, and the liquid in the tube is vigorously stirred in order to get good contact between ice and water. The thermometer then registers the freezing-point of water.

A weighed quantity of the substance to be dissolved is then introduced, if a solid, in the form of a pellet through the side tube. The cooling is continued. When more ice has separated the liquid is briskly stirred and the thermometer again read off. The new temperature is the freezing-point of the solution, and the difference between it and the freezing-point of pure water is the lowering or depression of the freezing-point. From this and the concentration of the solution the molecular weight may be calculated as in the following example.

A solution containing 17.8 g. of water and 0.1834 g. of hydrogen peroxide gave a freezing-point depression of 0.571°. What is the molar weight of hydrogen peroxide in the solution? The quantity of hydrogen peroxide in 1000 grams of water would be

$$\frac{1000 \times 0.1834}{17.8} = 10.31$$

This quantity gives a depression of 0.571; the quantity which gives a depression of 1.86 is

$$\frac{10.31 \times 1.86}{0.571} \quad 33.6 \text{ g}$$

The molecular weight of hydrogen peroxide is thus approximately 33.6, which corresponds to the formula H_2O_2 and not to the simpler formula HO.

Other methods of determining molecular weights of dissolved substances are also employed. Such methods for dissolved substances are of great importance, because they enable us to ascertain the molecular weights of substances which cannot be obtained in the gaseous state. Thus in the above example we are able to determine the molecular weight of hydrogen peroxide from its solutions, the determination by the vapour density method being impossible, since hydrogen peroxide cannot be vaporised without decomposition.

Colloidal Solutions.—Some aqueous solutions have practically the same freezing-point as pure water, even although they are of considerable concentration. For example, a solution of gelatine or of albumen in water has a freezing-point almost identical with that of water itself. This would point to albumen, gelatine and similar substances having a very high molecular weight, much above those of ordinary substances which dissolve in water, since for a given concentration of solution the depression is inversely proportional to the molecular weight. Solutions of this kind are called **colloidal** solutions, and their properties differ in many ways from those of ordinary solutions. The dissolved particles in them are supposed not to be simple molecules as in ordinary solutions, but large aggregates of molecules which in some cases may be detected by optical methods, although to the naked eye the solutions may be quite clear and pass without residue through ordinary filtering materials. Instances of such colloidal solutions will be met with in subsequent chapters.

Conducting Solutions.—When hydrochloric acid gas is liquefied by pressure, the liquid obtained is a very poor conductor of electricity. Pure distilled water is also a poor electrical conductor. Yet when these two poorly conducting liquids are mixed, the aqueous solution of hydrochloric acid so obtained conducts electricity very readily. It may be said in general that aqueous solutions of salts, strong bases and strong acids, if sufficiently concentrated, are excellent conductors of electricity. On the other hand, solutions of weak

bases (such as ammonia) and of weak acids (such as carbonic acid) are poor conductors of electricity.

Ionisation.—If the freezing-point of a solution which conducts electricity well is determined, it is found that the depression is much greater than would be observed with a corresponding solution which did not conduct electricity. It has been stated, for example, that the freezing-point depression of molecular normal solutions is 1.86. The molecular normal solution of hydrochloric acid, however, is found to have a depression of about 3.5, which is almost double the normal value. This anomalous behaviour of conducting solutions may be accounted for by the assumption that a kind of decomposition takes place in them which on the one hand gives them the power of conducting electricity, whilst on the other it increases the number of molecules in solution, thus diminishing the average molecular weight, and giving an abnormally large depression of the freezing-point.

This decomposition is termed **electrolytic dissociation** or **ionisation**, and is conceived as follows. When an acid, base or salt, is dissolved in water it is split up to some extent into its positive radical and its negative radical, the decomposition being reversible. For example, we may write for hydrochloric acid the equation—

$$HCl \rightleftharpoons H^{\cdot} + Cl'$$

The extent to which this splitting up or dissociation occurs varies greatly in different cases; the dissociation is most marked for salts, strong acids and strong bases, and only takes place to a very slight extent in the case of weak acids and weak bases.

The free positive and negative charged radicals thus produced are called **ions**, and a consideration of the electrical properties of the solutions shows that the ions are charged with quantities of positive and negative electricity in accordance with the dots and dashes attached to the radicals in the table given on p. 129.

The existence in solution of these freely moving particles charged with positive and negative electricity enables the solution to conduct electricity, and the extent to which a solution will act as a conductor depends on the number of these charged particles, and also, on the rate at which the

particles move. As in gaseous dissociation, dilution—*i.e.* increase of volume—favours dissociation (p. 123); so that though a concentrated solution of hydrochloric acid has only a small proportion of the dissolved substance in the state of ions, the same solution when largely diluted with water may contain practically all the hydrochloric acid in the ionised condition. The extent of ionisation in a given solution is not greatly affected by changes of temperature within the ordinary range.

Salt-hydrolysis.—Not only has water this power of converting salts into their ions; it has also the power of partially decomposing many salts into the acid and base from which they are derived by neutralisation. It has already been pointed out (p. 136) that only normal salts derived from strong bases and strong acids are neutral to indicators when they are dissolved in water. A salt derived from a strong base with a weak acid has an alkaline reaction. Thus, sodium carbonate, which is derived from the strong base, sodium hydroxide NaOH, and the weak acid, carbonic acid H_2CO_3, is alkaline to litmus and many other indicators. The same is observed with a solution of sodium sulphide, derived from sodium hydroxide and the weak acid sulphuretted hydrogen. On the other hand, salts such as copper sulphate, ferric chloride, and aluminium sulphate (or alum), which are derived from strong acids and the weak bases $Cu(OH)_2$, $Fe(OH)_3$, $Al(OH)_3$, give aqueous solutions which have always an acid reaction to ordinary indicators. The reason why these solutions are alkaline or acid is that they actually contain free alkali and free acid repectively, produced by the action of the solvent water on the normal salt. This action of water on a normal salt, with production of free acid or free base, is usually termed **salt-hydrolysis**, and must be clearly distinguished from ionisation, or the action of water to produce positive and negative ions. For example, the ionisation equation for potassium cyanide is

$$KCN \rightleftarrows K^{\cdot} + CN'$$

whereas the salt-hydrolysis equation is

$$\underset{\text{Potassium cyanide}}{KCN} + H_2O \rightleftarrows KOH + \underset{\text{Hydrocyanic acid}}{HCN}$$

It will be observed that salt-hydrolysis is the opposite of neutralisation, and that salts which are hydrolysed are those in which the neutralisation of acid and base is incomplete.

In the case of sodium carbonate, the action of the water may be represented by the reversible equation—

$$Na_2CO_3 + H_2O \rightleftarrows NaHCO_3 + NaOH$$

It must be understood that in most cases of this kind the hydrolysis only proceeds to a small extent. In a weak solution of sodium carbonate only about 1 per cent. of the total dissolved salt is thus split up into sodium hydroxide and the bicarbonate. The sodium hydroxide is strongly alkaline in its action, and sodium hydrogen carbonate practically neutral, so that the solution on the whole has an alkaline reaction.

The hydrolysing action in the case of ferric chloride may be represented as follows:—

$$FeCl_3 + 3H_2O \rightleftarrows Fe(OH)_3 + 3HCl$$

This action also goes on to a very small extent, but the hydrochloric acid produced is a strong acid, and the ferric hydroxide produced is a very weak base, so that the solution on the whole has a distinctly acid reaction.

Ferric hydroxide is what we ordinarily call an insoluble substance. In the above case, however, it does not fall out of the solution, but remains suspended in the solution in such a state that it cannot be detected, even by the aid of a microscope, although its presence in the undissolved state may be rendered evident by proper optical means. Here the base is in a state of colloidal solution (p. 149).

CHAPTER XXIV

DISPLACEMENT OF RADICALS

THE simple radicals can all exist in the free state as elements as well as in the charged state of ions in solution. The compound radicals are, as a rule, incapable of independent existence except as charged ions. We find that the tendency of the elements to assume the form of electrically charged radicals varies very much, some elements having a great tendency to become charged with electricity and to pass into solution as ions, whilst other elements have little or no tendency in that direction. If we take a piece of metallic iron and immerse it in a solution of copper sulphate, the iron passes into solution and metallic copper is precipitated, the chemical action being expressed by the equation—

$$\underset{\text{Iron}}{Fe} + \underset{\text{Copper sulphate}}{Cu^{\cdot\cdot}SO_4''} = \underset{\text{Ferrous sulphate}}{Fe^{\cdot\cdot}SO_4''} + \underset{\text{Copper}}{Cu}$$

The iron has here displaced the copper from the solution of copper salt. In other words, the iron has assumed the form of a charged radical, whilst the copper has lost its electric charge and become metallic copper. We can, therefore, infer that iron has a greater tendency to assume an electric charge in solution than copper has. Similarly, if we immerse a strip of copper in a solution of mercuric salt, say mercuric nitrate, the copper immediately becomes coated with a grey film of metallic mercury, and the originally colourless solution assumes a blue colour, showing that a copper salt is now in solution. The action which has actually taken place is as follows:—

$$\underset{\text{Copper}}{Cu} + \underset{\text{Mercuric nitrate}}{Hg^{\cdot\cdot}(NO_3')_2} = \underset{\text{Copper nitrate}}{Cu^{\cdot\cdot}(NO_3')_2} + \underset{\text{Mercury}}{Hg}$$

The mercuric radical has lost its charge and become metallic

mercury, whilst the metallic copper has taken up the charge originally on the mercury, and become the copper radical.

Considering the various metals from the point of view that they have each a perfectly definite tendency to assume electrical charges, we find that if we bring them into intimate contact with solutions of one another's salts, they displace each other in a perfectly definite order, the metal with the greater tendency to unite with electricity passing into solution as a charged ion, and the metal with the smaller tendency to unite with electricity being thrown out of solution as the uncharged metal. The order in which some of the commoner metals replace each other from solutions of their salts in this way is given in the following list:—

Electro-chemical List

Magnesium
Aluminium
Zinc
Iron
Tin
Lead
(Hydrogen)
Copper
Mercury
Silver
Gold

The metal magnesium, which heads this short list, has the greatest tendency to unite with positive electricity, and displaces all the other metals from their salt solutions. It should be noted that by salt solutions we generally understand either chlorides or sulphates, in order that complications which sometimes arise in connection with other negative radicals may be avoided. In general, we may say that any metal which occurs on this list will displace from their salt solutions the metals which follow it in the list, but will not displace the metals which precede it, being rather displaced from its own solution by these metals. We can tell at once, therefore, from an inspection of this table, that metallic iron will probably turn out copper from copper sulphate, but that it will not turn out zinc from zinc sulphate. Aluminium often shows exceptional behaviour.

Hydrogen, which has a peculiar position in the list of positive radicals, has a definite position in this electro-chemical

list. It is readily displaced from hydrogen salts—that is, the acids such as hydrogen chloride (hydrochloric acid), or hydrogen sulphate (sulphuric acid)—by means of metals which precede it in the list, and cannot be displaced from these acids by the metals which follow it in the list. But on account of its being a nearly insoluble gas it cannot very readily be brought into contact with aqueous solutions, and so does not easily displace the metals which occur below and near it in the list. If hydrogen, however, is bubbled through a solution of gold chloride, hydrochloric acid is formed and metallic gold separates.

We can thus see at once from the table that a metal such as zinc or iron will be acted upon by hydrochloric or dilute sulphuric acid with evolution of hydrogen, and that a metal like copper or mercury will not be attacked by these acids. In the first case, the iron and zinc have a greater tendency to assume electrical charges and become positive radicals than the hydrogen has, and, in the second case, the hydrogen has a greater tendency to remain combined with positive electricity than either the copper or the mercury, and consequently will not be displaced from its solutions by these metals.

In connection with this we may consider the action of the various metals on water. Some metals are capable of attacking water at the ordinary temperature; sodium, for example, at once liberates hydrogen from water according to the equation—

$$\underset{\text{Sodium}}{2Na} + \underset{\text{Water}}{2HOH} = \underset{\text{Sodium hydroxide}}{2NaOH} + \underset{\text{Hydrogen}}{H_2}$$

Magnesium acts very slowly. The other metals preceding hydrogen in the list do not attack water at the ordinary temperature, but if they are heated with water to a sufficiently high degree, the water is attacked with formation of a metallic oxide or hydroxide and liberation of hydrogen—*e.g.*

$$\underset{\text{Aluminium}}{2Al} + 3H_2O = \underset{\text{Aluminium oxide}}{Al_2O_3} + \underset{\text{Hydrogen}}{3H_2}$$

$$2Al + 6H_2O = \underset{\text{Aluminium hydroxide}}{2Al(OH)_3} + 3H_2$$

None of the metals which follow hydrogen in the list are capable of attacking water at any temperature.

When we consider that any substance found in the earth's crust is now, or has been at some period, in contact with water at a high temperature, we see that we cannot expect the metals which precede hydrogen in the list to occur in the free state in nature, whilst we may very reasonably expect that the metals which follow hydrogen in the list should be found in nature in the metallic state. This is actually the case : sodium, magnesium, aluminium, and zinc are never found as metals, but always in a state of combination with oxygen, or sometimes with sulphur. Iron only occurs in nature in minute quantities in some rocks, or else in meteorites, which, properly speaking, are not a part of the earth's crust at all.

On the other hand, copper, mercury, silver, and gold, are found in considerable quantities in the metallic state, although (with the exception of gold) they are also found combined with oxygen and with sulphur.

The chief elements which can exist as negative ions in solution are chlorine, bromine, and iodine, which form the negative radicals of chlorides, bromides, and iodides. Just as we can arrange the positive elements, so we can arrange these three negative elements in the order in which they can displace each other. The list is as follows :—

Chlorine
Bromine
Iodine

Chlorine is capable of displacing bromine from bromides and iodine from iodides ; bromine is capable of displacing iodine from iodides, but not chlorine from chlorides. Iodine is incapable of displacing either bromine from bromides or chlorine from chlorides. The equations representing the various actions which can occur in the case of the sodium salts are as follows :—

$$Cl_2 + 2Na{\cdot}Br' = 2Na{\cdot}Cl' + Br_2$$
$$Br_2 + 2Na{\cdot}I' = 2Na{\cdot}Br' + I_2$$
$$Cl_2 + 2Na{\cdot}I' = 2Na{\cdot}Cl' + I_2$$

Chlorine, bromine, and iodine are all capable of displacing sulphur from soluble sulphides or hydrosulphides, the re-

actions being represented as follows in the case of hydrogen sulphide :—

Cl_2 Chlorine	+	H_2S Sulphuretted hydrogen	=	$2HCl$ Hydrochloric acid	+	S Sulphur
Br_2 Bromine	+	H_2S	=	$2HBr$ Hydrobromic acid	+	S
I_2 Iodine	+	H_2S	=	$2HI$ Hydriodic acid	+	S

Chlorine is also capable of replacing oxygen to some extent from solutions of oxides or hydroxides, although in most cases the displacement is complicated by the occurrence of other actions (Chapter XXVIII.).

CHAPTER XXV

ELECTROLYSIS

It has been stated in Chapter XXIII. that the sodium chloride in an ordinary solution of salt is split up to a very considerable extent into electrically charged ions. If the solution is very dilute, the decomposition into ions is almost complete. We have now to consider the electrical properties of such a solution. Since the solution, as a whole, is electrically neutral—*i.e.* is neither positively nor negatively charged—the amount of positive electricity carried by the sodium ion must be exactly equal to the amount of negative electricity carried by the chloride ion. Let us now introduce into the solution two conductors, one charged with positive and the other with negative electricity. Since opposite electricities attract, the positive radical will be attracted to the negatively charged conductor, and the negative radical will be attracted to the positively charged conductor.

Now, we can charge conductors by connecting them with the opposite terminals of an electric battery. At one terminal there is always a charge of positive electricity; at the other terminal there is always a charge of negative electricity, and electrical conductors attached to these terminals assume similar charges, which are maintained by the action of the battery. If, then, into a solution of common salt we dip conductors connected with the terminals of a galvanic battery, the positive ion will travel towards the negative terminal, and the negative ion will travel towards the positive terminal. There will thus, on the whole, be separation of the positive radical of the salt from the negative radical.

We may now ask what is likely to happen when the charged negative radical actually comes in contact with the positively charged conductor. The opposite charges neutralise each other; the negative radical thus loses its charge and becomes electrically neutral. Now, when any radical loses its charge of electricity its chemical properties are profoundly modified.

So long as the chloride radical in an aqueous solution of sodium chloride retains its negative charge and exists as chloride ion, it has certain well-marked properties, use of which is made in the general tests employed for detecting soluble chlorides. As soon as it loses its charge and ceases to be a negative ion it assumes altogether different properties: two of the uncharged radicals unite to form the free element chlorine, which we represent by the formula Cl_2.

$$\underset{\text{Chloride ion}}{2Cl'} = \underset{\text{Chlorine}}{Cl_2}$$

This chlorine is a greenish-yellow gas, only moderately soluble in water, and possessed of a pungent, suffocating smell, by means of which it is easily recognised. It differs altogether, therefore, from the chloride ion, which is colourless and inodorous.

When the sodium radical which exists in the solution of sodium chloride as a positive ion loses its charge on coming into contact with the negatively charged electrode, it becomes ordinary metallic sodium. Now, as we have seen in the preceding chapter, metallic sodium cannot exist in contact with water. It immediately reacts with water, according to the equation—

$$2Na + 2H_2O = 2NaOH + H_2$$

caustic soda being produced in the solution, and hydrogen liberated as gas.

When, therefore, we decompose a solution of sodium chloride by means of a current of electricity, chlorine gas is produced at one of the terminals and hydrogen gas at the other, the liberation of hydrogen being accompanied by the formation of caustic soda.

The process of separating the positive and negative ions from each other, and discharging them by means of an electric current, is called **electrolysis**. The conductors connected with the two terminals of the electric battery are called the **electrodes**, that connected with the zinc end of an ordinary cell being called the **negative electrode** or **cathode**, that connected with the other terminal of the battery being termed the **positive electrode** or **anode**. The negative ion, which moves towards the positive electrode or anode, is called the **anion**. The positive ion, which moves towards the negative

electrode or cathode, is called the **cation.** The solution which is decomposed is called the electrolyte, but this term is sometimes applied also to the substance dissolved in the water of the electrolytic solution.

It is possible, by passing an electric current through an aqueous solution of an electrolyte, to separate the anion from the kation, and to make them lose their charges. Sometimes the discharged anion or cation may be liberated as the element—for example, in the case of chlorine being evolved by the discharge of the chloride ion. Sometimes, however,

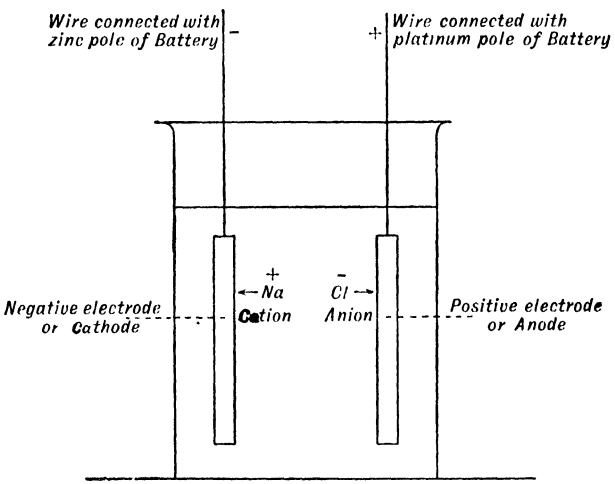


Fig. 35.—Diagrammatic Representation of the Electrolysis of a Solution of Sodium Chloride

as in the case of potassium, the discharged ion is not capable of existing as such under the conditions in which the electrolysis takes place. The discharged ion may then, as frequently happens, attack the water of the electrolyte. For example, if we electrolyse a solution of potassium sulphate the discharged potassium at once attacks the water, according to the equation—

$$2K + 2H_2O = \underset{\text{Potassium hydroxide}}{2KOH} + \underset{\text{Hydrogen}}{H_2}$$

with formation of potassium hydroxide and hydrogen The

discharged sulphate radical is altogether incapable of independent existence, and it also attacks the water, according to the equation—

$$2SO_4 + 2H_2O = \underset{\text{Sulphuric acid}}{2H_2SO_4} + \underset{\text{Oxygen}}{O_2}$$

with formation of sulphuric acid and oxygen.

If we only pay attention to the gases which are evolved during the electrolysis of potassium sulphate, we find that they are oxygen and hydrogen in the proportions necessary to form water. It would therefore appear as if the electric current merely decomposed the water in which the potassium sulphate was dissolved. If, however, we attend to all the chemical changes which have taken place during the action, we find that potassium hydroxide has been produced at the cathode and sulphuric acid at the anode, as may be readily shown by adding a little litmus to the solution. Potassium sulphate before electrolysis is neutral, and on the passage of a current the purple litmus will be observed to become blue at the cathode and red at the anode.

When a solution of an acid is electrolysed, the discharged hydrogen usually comes off at the cathode as hydrogen gas. Thus, a solution of sulphuric acid gives hydrogen at the cathode and oxygen at the anode, produced by the action of the discharged sulphate ions, according to the preceding equation. Here it will be observed that sulphuric acid is reproduced at the anode, so that the only chemical change observed is that hydrogen is evolved at the cathode and oxygen at the anode, the total action being again apparently a mere decomposition of water by the electric current. A closer investigation, however, shows that this is not the only action which takes place. If the anode and cathode compartments are separated by a porous material which permits free passage to the current, but does not permit mechanical mixing of the solutions in the two compartments, it will be found that after a current has been passed for some time sulphuric acid will have been transferred from the cathode to the anode. Thus the electrolysis is not the mere decomposition of water, but a reaction in which the sulphuric acid dissolved in the water plays a part.

Similarly, when a solution of sodium hydroxide is electrolysed

the total action is decomposition of water, and transference of sodium hydroxide from the anode to the cathode, the separate actions being—

$$\text{At anode} \quad . \quad . \quad . \quad 4OH = 2H_2O + \underset{\text{Oxygen}}{O_2}$$

$$\text{At kathode} \quad 2Na + 2H_2O = \underset{\text{Sodium hydroxide}}{2NaOH} + \underset{\text{Hydrogen}}{H_2}$$

When a solution of hydrochloric acid is electrolysed under proper conditions, hydrogen appears at the cathode and chlorine at the anode, so that the total action is apparently decomposition of the hydrochloric acid. If the hydrochloric acid solution which is electrolysed is dilute, another action takes place at the anode. Some of the discharged chloride ion, instead of coming off as chlorine gas, attacks the water of the electrolyte, with formation of hydrochloric acid and oxygen, in accordance with the equation—

$$4Cl + 2H_2O = \underset{\text{Hydrochloric acid}}{4HCl} + \underset{\text{Oxygen}}{O_2}$$

We may therefore have two actions going on round the anode at one and the same time, the result being production of both chlorine gas and oxygen gas in varying proportions, according to the conditions under which the electrolysis is conducted.

In what has preceded, it has been assumed that the material of the electrodes is not attacked by the discharged ions. Most metallic conductors may be used as cathodes, because a discharged cation very seldom attacks them. It is much more difficult to get an anode which is not attacked. On a small scale, the anode generally employed is platinum, which is not attacked readily by any discharged anion. On the manufacturing scale, the anode almost invariably employed is a form of carbon which conducts electricity, being practically the same as the carbons used in arc-lamps (Chapter XIX.).

If we electrolyse a solution of sulphuric acid between copper electrodes, hydrogen comes off at the copper cathode as usual. When the sulphate ion, however, is discharged at the anode it does not attack the water of the electrolyte, as it would were a platinum anode employed, but rather attacks the copper of

the anode, the action being one of simple union, as expressed by the equation—

$$SO_4 + Cu = \underset{\text{Copper sulphate}}{CuSO_4}$$

The copper anode thus dissolves up, and copper sulphate is formed in the solution.

Suppose now we consider the electrolysis of a solution of copper sulphate between two copper electrodes. As we have just seen, the copper anode is attacked by the discharged sulphate ions with production of copper sulphate. On the other hand, the discharged cation is capable of existence as metallic copper and is deposited as such on the cathode No gas is evolved during this electrolysis, and the whole action seems to be a transference of copper from the anode to the cathode, the copper anode diminishing in weight, and the copper cathode increasing.

Such processes of electrolysis as the above are carried out on the large scale in the electrolytic refining of metals like copper, and in the electro-deposition of metals—that is, the process usually known as electro-plating. The aim of electro-plating is to protect a metallic object by covering it with a thin coating of a valuable metal, such as silver or gold, which is more capable of resisting ordinary atmospheric influences. The valuable metal, say silver, is taken as the anode, and the object formed of metal to be silver-plated, say copper, as the kathode, the solution employed being some salt of silver. When a current is passed through the solution, the silver dissolves up and is deposited on the copper object, the conditions of electrolysis being so chosen that the deposit adheres closely to the cathode in the form of a fine continuous film. The copper is then said to be silver-plated.

When the same electric current is passed in succession through a series of solutions, say of sulphuric acid, copper sulphate, sodium hydroxide, and hydrochloric acid, it is found that at all the electrodes where hydrogen is evolved (*i.e.* in the sulphuric acid, sodium hydroxide, and hydrochloric acid solutions), the quantity of hydrogen produced is exactly the same. In the solution of copper sulphate, where no hydrogen is evolved, the quantity of copper deposited is exactly equivalent to the quantity of hydrogen appearing

at the other cathodes. For every gram of hydrogen liberated by a given current, 31.5 grams of copper are deposited. A reference to the table of atomic weights and of positive radicals will show that these proportions are equivalent proportions. This equivalence finds a representation in the dots affixed to the symbols of the positive radicals. A given current will neutralise the same quantity of positive electricity in any part of the circuit. The quantity of positive electricity, therefore, which is neutralised at the various cathodes is in every case the same. But, since a given quantity of positive electricity is always associated with the same quantity of hydrogen, it is evident, therefore, that at the cathodes equal quantities of hydrogen will be evolved. Further, since 63 grams of copper, according to our table, are associated with the same amount of positive electricity as 2 grams of hydrogen, the current which will neutralise the positive electricity of one gram of hydrogen, will serve to neutralise the positive electricity of 31.5 grams of copper.

What holds good here for the substances produced at the cathode also holds good for the substances produced at the anode. The amount of oxygen evolved at the anode in the sulphuric acid, copper sulphate, and sodium hydroxide solutions, is exactly the same in the three cases.

Not only is this so, but the substances produced at the cathode are exactly equivalent to the substances produced at the anode. Thus, the hydrogen liberated at the cathode in the sulphuric acid, or caustic soda, is exactly in the proportions necessary to combine with the oxygen which is liberated by the same current at the anode.

In the case of the hydrochloric acid solution, both chlorine and oxygen may be liberated at the anode. Here the amount of chlorine which is produced is not equivalent to the hydrogen which is simultaneously produced at the cathode, nor is the amount of oxygen equivalent to this amount of hydrogen, but the oxygen and chlorine together are exactly equivalent to the hydrogen which is liberated by the same current. That is, if the chlorine is made to combine with hydrogen to produce hydrochloric acid, then there will be just enough hydrogen over to combine with the oxygen for the production of water.

Equivalence of the products at the anode and cathode holds good for the substances produced in the solution as well

as for the gases evolved. When sodium sulphate is electrolysed, sodium hydroxide is formed at the cathode, and sulphuric acid at the anode. Now, these two substances are formed by the same current in exactly equivalent proportions. The sodium hydroxide produced at the cathode is in precisely the right proportion for neutralising the sulphuric acid produced at the anode.

These facts regarding the chemical equivalence of the various substances produced at the electrodes on electrolysis were first experimentally ascertained by Faraday, who also showed that a given amount of electricity passed through a circuit always liberated the same amount of a given material, *e.g.* hydrogen, from an electrolyte, no matter what the substance dissolved in the water might have been, provided, of course, that hydrogen was the only gas produced at the cathode.

These facts are generally known under the name of **Faraday's laws of electrolysis**, and it will be seen that our system of symbolisation is in accordance with them. Chemically equivalent quantities—that is, quantities which can either combine with each other, or which can combine with the same quantity of other substances—are, according to our system, charged with equal amounts of electricity as expressed by the dots and dashes.

The idea that the positive and negative radicals of salts are to a great extent independent of each other in aqueous solution affords a ready explanation of the ease with which double decomposition in aqueous solution can take place between these substances. The double decompositions, examples of which have been given in the preceding chapter, take place practically instantaneously. On the other hand, reactions in aqueous solutions which are not merely recombinations of positive and negative radicals take place comparatively slowly.

CHAPTER XXVI

OXIDATION AND REDUCTION

SOMETIMES we observe what we may call a competition for oxygen. For example, if we burn a substance like turpentine, which contains the elements carbon and hydrogen, the flame produced by the combustion is of a very smoky character, so that if a cold substance is held near it soot will at once be deposited. This soot consists of small particles of carbon. When the turpentine burns, therefore, the hydrogen which it contains is oxidised in preference to the carbon. Here we have carbon and hydrogen competing, as it were, for a limited amount of oxygen within the hot region of the flame, and in the competition the hydrogen prevails, the whole of it burning to form water, while only a portion of the carbon burns to form carbon dioxide, the rest being liberated in the unburnt state.

There is another sense in which two substances can compete for oxygen. If we take one substance which is already oxidised, and heat it in contact with another substance which is not oxidised, but is capable of oxidation, then in some instances the second substance will take away the oxygen from the first. An example may be found in the reaction between lead oxide and hydrogen. If a current of hydrogen gas is led over heated lead oxide, the following reaction occurs:—

PbO	+	H_2	=	Pb	+	H_2O
Lead monoxide		Hydrogen		Lead		Water

Here the hydrogen has taken away the oxygen from the lead, and is oxidised to water. The lead oxide is said to have been *deoxidised* or *reduced* to metallic lead, and the process is generally spoken of as one of **reduction**. Lead oxide may be similarly reduced by means of carbon. If we heat a mixture of lead oxide and charcoal, the carbon of the

charcoal removes the oxygen from the lead oxide and reduces it to metallic lead, according to the equations—

PbO	+	C	=	Pb	+	CO
Lead monoxide		Carbon		Lead		Carbon monoxide
$2PbO$	+	C	=	$2Pb$	+	CO_2
						Carbon dioxide

The carbon is itself oxidised to carbon monoxide or carbon dioxide.

Instances of similar actions are given below, the equations representing the reduction of certain metallic oxides to metals by means of hydrogen and of carbon—

FeO	+	H_2	=	Fe	+	H_2O
Ferrous oxide		Hydrogen		Iron		Water
SnO_2	+	$2C$	=	Sn	+	$2CO$
Stannic oxide		Carbon		Tin		Carbon monoxide
CuO	+	H_2	=	Cu	+	H_2O
Cupric oxide		Hydrogen		Copper		Water

In what has preceded we have met with another case of reduction. When red-hot carbon acts on carbon dioxide, the following action occurs :—

C	+	CO_2	=	$2CO$
Carbon		Carbon dioxide		Carbon monoxide

Here carbon is oxidised to carbon monoxide, and carbon dioxide is reduced to the same product.

Carbon monoxide, being capable of still further oxidation, can reduce certain other oxides. Thus, if a current of carbon monoxide is led over heated oxide of copper, it removes oxygen from the copper oxide, which it thus reduces to metallic copper, and is itself oxidised to carbon dioxide, the equation being—

CO	+	CuO	=	CO_2	+	Cu
Carbon monoxide		Copper oxide		Carbon dioxide		Copper

One metal is sometimes capable of removing oxygen from another. If we mix, for example, finely divided aluminium

with ferric oxide, and start the reaction by heating a portion of the mixture to a very high temperature, the aluminium abstracts oxygen from the ferric oxide and reduces it to metallic iron, in accordance with the equation—

$$\underset{\text{Ferric oxide}}{Fe_2O_3} + \underset{\text{Aluminium}}{2Al} = \underset{\text{Iron}}{2Fe} + \underset{\text{Aluminium oxide}}{Al_2O_3}$$

So much heat is given out in this reaction that the temperature of the mass is raised to a very bright white heat, and a mixture of the above kind has come into use under the name of *thermit* as a means of producing extremely high temperatures.

It will be seen from these instances that reduction and oxidation go hand-in-hand. When one substance is reduced another substance is oxidised. If in the action

$$FeO + H_2 = Fe + H_2O$$

we consider only the ferrous oxide, then we say that the action is a reducing action, for the ferrous oxide is reduced to metallic iron. But if we consider the same reaction from the point of view of the hydrogen, then we must call it an oxidising action, because the hydrogen combines with oxygen and is oxidised to water.

Similarly, in the equation—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

the ferric oxide is reduced to metallic iron, and so the action is in this sense a reduction; but, at the same time, the aluminium is oxidised to aluminium oxide, and so the action must also be considered an oxidation.

A substance which is capable of reducing an oxide is usually called a **reducing agent**. Thus, in the above examples hydrogen, carbon, aluminium, and carbon monoxide act as reducing agents. The reducing agents which are most extensively employed on the large scale, chiefly in the reduction of metals from their oxides, are carbon and carbon monoxide. These are used in preference to others on account of their cheapness. Impure carbon can be obtained in any quantity in the form of coal, or, if greater purity is desired, of charcoal; and carbon monoxide can be obtained

simply by the combustion of these in a defective supply of air.

The terms oxidation and reduction are sometimes used in a wider sense than that given to them in the above instances. Oxidation does not necessarily mean actual union with oxygen of the element which is said to be oxidised. Thus, it is customary to speak of sulphuretted hydrogen when it is converted into sulphur as being *oxidised* to sulphur. This action occurs when a solution of sulphuretted hydrogen is exposed to air, the equation being—

$$2H_2S + O_2 = 2H_2O + 2S$$

Now, there is no oxygen in sulphur, and the term oxidation, when used with respect to the sulphur, here implies that hydrogen has been removed from it, and not that oxygen has been added. We very often find the term oxidation used in this sense to mean *removal of hydrogen*, on account of the fact that oxygen itself can frequently remove hydrogen from hydrogen compounds, so that addition of oxygen and removal of hydrogen are in a certain sense actions of the same type.

Any substance **which is capable of adding oxygen to other substances, or of removing hydrogen from them, is said to** be an **oxidising agent.** If we bring chlorine into contact with sulphuretted hydrogen, sulphur is liberated.

$$Cl_2 + H_2S = 2HCl + S$$

The chlorine, by removing hydrogen, has acted as oxygen acts, and is therefore said to be an oxidising agent. Although, as we see from the equation, no oxygen is involved at all, yet the action may be spoken of as one of oxidation and reduction, the sulphuretted hydrogen being oxidised to sulphur, and the chlorine reduced to hydrochloric acid. Reduction, therefore, may not only mean removal of oxygen, it may also mean *addition of hydrogen*, as in the above instance.

Oxidising and reducing agents are frequently employed in the laboratory in the liquid or dissolved form. The **chief oxidising agents** which are used in this way are nitric acid, chlorine, hypochlorites, and bromine. **Nitric acid,** when

dilute, does not part with its oxygen very readily at the ordinary temperature, but when some substances are boiled with it, it gives up part of its oxygen, and is converted into less highly oxidised compounds of nitrogen, usually oxides of nitrogen. **Chlorine** is an oxidising agent even at the ordinary temperature, and its solution is employed in the laboratory under the name of *chlorine water*. A similar solution of **bromine**, called *bromine water*, is also employed: it is a somewhat less powerful oxidising agent than chlorine. **Sodium hypochlorite** NaClO, and **bleaching powder** solution (which contains calcium hypochlorite $Ca(ClO)_2$) are occasionally used, either with or without addition of acid. In presence of acid these hypochlorites are more powerful oxidising agents than when the solution is alkaline or neutral.

The following is a ready test for an oxidising substance. *Potassium iodide* solution, when oxidised, yields iodine, which can be easily recognised by its brown colour or by the deep blue coloration which it imparts to starch solution. Papers impregnated with potassium iodide and starch are, in consequence, sometimes used in the laboratory as test papers for oxidising gases. The action of potassium iodide solution with some of the above oxidising agents may be seen from the following equations:—

$$2KI + Cl_2 = 2KCl + I_2$$

$$2KI + Br_2 = 2KBr + I_2$$

$$2KI + NaClO + H_2O = 2KOH + NaCl + I_2$$

Potassium nitrate, KNO_3, and **potassium chlorate**, $KClO_3$, part readily with their oxygen when heated, and so are often used as oxidising agents in the solid or fused state. **Sodium peroxide**, Na_2O_2, is another substance of the same kind which is now extensively used.

The following are the **chief reducing agents** employed in the laboratory:—**Sulphuretted hydrogen**, either as a gas or in solution; a solution of **sulphur dioxide**; a solution of **stannous chloride**, $SnCl_2$; a solution of **sodium hydrosulphite**, $Na_2S_2O_4$; and reducing mixtures which yield what is called **nascent hydrogen**. Nascent hydrogen has, properly speaking, no existence. It is supposed to be hydrogen in the state of formation from the interaction of two substances—

i.e. hydrogen before it has become ordinary hydrogen gas. Thus zinc and sulphuric acid, which can act together so as to produce hydrogen, are capable of jointly reducing certain substances. Such a reduction is said to be due to *nascent* hydrogen, although hydrogen is not necessarily formed at all if the oxidising agent is present.

The reducing action of such substances can be most easily shown by means of *potassium permanganate*, $KMnO_4$, a solution of which possesses an intense purple colour. When a reducing agent acts upon it in acid solution, it parts with a portion of its oxygen, and the colour disappears.

When sulphuretted hydrogen acts as a reducing agent, free sulphur is produced; when sulphur dioxide acts as a reducing agent, it is oxidised to sulphuric acid; stannous chloride is oxidised to stannic chloride; and nascent hydrogen is oxidised to water.

The formation of these substances is shown in the following equations, in which the symbol (O) indicates oxygen derived from the substance which is reduced, and not free oxygen gas:—

$$\underset{\text{Sulphuretted hydrogen}}{H_2S} + (O) = H_2O + \underset{\text{Sulphur}}{S}$$

$$\underset{\text{Sulphur dioxide}}{SO_2} + H_2O + (O) = \underset{\text{Sulphuric acid}}{H_2SO_4}$$

$$\underset{\text{Stannous chloride}}{SnCl_2} + 2HCl + (O) = \underset{\text{Stannic chloride}}{SnCl_4} + H_2O$$

$$\underset{\text{"Nascent hydrogen"}}{2(H)} + (O) = H_2O$$

$$Zn + H_2SO_4 + (O) = H_2O + ZnSO_4$$

It is not always easy to find the **stage of oxidation** of an element in a given compound by direct reference to the formula of the compound. If we compare the compounds SO_2 and SO_3, it is plain that the sulphur in the latter is more highly oxidised than in the former, and the same may be said with respect to the acids corresponding to these anhydrides H_2SO_3 and H_2SO_4. If we are asked, however, to say whether the sulphur in potassium sulphate K_2SO_4, or in potassium persulphate $K_2S_2O_8$, is in the higher stage of

oxidation, it is impossible to answer the question by a direct inspection of the formulæ. The proportion of oxygen to sulphur is the same in both compounds, but the proportion of potassium in the two compounds is different. In such a case, the comparison may most readily be made by first of all referring these salts to the acids from which they are derived, and then by subtraction of water, referring these acids to the corresponding acidic oxides. These acidic oxides contain only oxygen besides the element considered, and so it is an easy matter to tell which is the more highly oxidised—that is, which contains the greater proportion of oxygen. Thus we have—

K_2SO_4	H_2SO_4	SO_3 *or* S_2O_6
$K_2S_2O_8$	$H_2S_2O_8$	S_2O_7

The sulphur in the persulphate is therefore more highly oxidised than the sulphur in the sulphate.

If we wish to determine the degree of oxidation of a metallic radical, we proceed in a similar way. Thus, if we ask whether the iron in ferric chloride $FeCl_3$, or in ferrous sulphate $FeSO_4$, is in the higher stage of oxidation, we cannot say off-hand by inspection of the formulæ. It is true that in ferric chloride no oxygen is present at all, and that in ferrous sulphate there is a considerable amount of oxygen, but it does not follow from this that the iron in ferrous sulphate is more highly oxidised than the iron in ferric chloride. What we must do is to refer the positive radical to the corresponding basic oxide. Ferric chloride may be prepared by neutralising the base ferric hydroxide $Fe(OH)_3$, ferrous sulphate may be prepared by neutralising the base ferrous hydroxide $Fe(OH)_2$. If now we subtract the elements of water from these two hydroxides, we are left with the oxide Fe_2O_3 in the case of the ferric chloride, and the oxide FeO in the case of the ferrous sulphate. There is obviously a greater proportion of oxygen in Fe_2O_3 than in FeO, so we may say that the iron in ferric chloride is more highly oxidised than the iron in ferrous sulphate, although in ferric chloride there is no oxygen at all. That this conclusion is general may be demonstrated by the fact that any of the oxidising agents just mentioned is capable of converting a ferrous salt into a ferric salt, and that any of the

reducing agents mentioned above is capable of converting a ferric salt into a ferrous salt.

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + 2HCl + (O) = \underset{\text{Ferric chloride}}{2FeCl_3} + H_2O$$

$$\underset{\text{Ferrous chloride}}{2FeCl_2} + Cl_2 = \underset{\text{Ferric chloride}}{2FeCl_3}$$

$$\underset{\text{Ferrous sulphate}}{2FeSO_4} + H_2SO_4 + (O) = \underset{\text{Ferric sulphate}}{Fe_2(SO_4)_3} + H_2O$$

$$\underset{\text{Ferric chloride}}{FeCl_3} + \underset{\text{Nascent hydrogen}}{(H)} = \underset{\text{Ferrous chloride}}{FeCl_2} + HCl$$

$$\underset{\text{Ferric sulphate}}{Fe_2(SO_4)_3} + 2H_2O + SO_2 = \underset{\text{Ferrous sulphate}}{2FeSO_4} + 2H_2SO_4$$

$$\underset{\text{Ferric chloride}}{2FeCl_3} + H_2S = \underset{\text{Ferrous chloride}}{2FeCl_2} + 2HCl + S$$

$$\underset{\text{Ferric chloride}}{2FeCl_3} + SnCl_2 = \underset{\text{Ferrous chloride}}{2FeCl_2} + SnCl_4$$

In the case of a positive radical, it is easy to tell at once its stage of oxidation by counting the number of dots attached to the symbol. The ferrous radical $Fe^{\cdot\cdot}$ has only two dots, the ferric radical $Fe^{\cdot\cdot\cdot}$ has three. The ferric radical is in a higher stage of oxidation than the ferrous radical, because each dot represents capacity for combining with negative radicals, and these negative radicals may be hydroxyl or oxygen. The degree of oxidation of a positive radical, therefore, corresponds with the number of dots which are attached to its formula.

In the case of mercury we have two sets of salts, the mercurous salts containing the mercurous radical $Hg^{\cdot}$, and the mercuric salts containing the mercuric radical $Hg^{\cdot\cdot}$. Now the mercuric radical has two dots, where the mercurous radical has only one. We can therefore say at once that the salts containing the mercuric radical have the mercury in a higher stage of oxidation than the salts containing the mercurous radical, and can be formed from the mercurous salts by treatment with oxidising agents.

When a metal passes into the state of a metallic radical, it assumes a charge of electricity which is represented by one

or more dots. Thus, when zinc is dissolved in sulphuric acid, according to the equation—

$$Zn + H_2^{\cdot}SO_4'' = H_2 + Zn^{\cdot\cdot}SO_4''$$

and becomes the positively charged zinc radical, it may be said to be oxidised. This can be shown by the fact that zinc and sulphuric acid can act as a reducing mixture, whereas zinc sulphate, which contains the zinc radical, is entirely without reducing properties. It may be asked, seeing that the zinc has been oxidised by the sulphuric acid: What has been reduced? The answer is that the hydrogen radical has been reduced. The hydrogen radical has lost its charge of electricity and has become uncharged hydrogen gas. In the above sense, therefore, it has been reduced.

The same thing may be seen by referring the zinc and hydrogen in zinc sulphate and sulphuric acid back to the oxides representing their stage of oxidation. If we do this, we find that the zinc in zinc sulphate corresponds to the oxide ZnO, and the hydrogen in the sulphuric acid to the oxide H_2O. So far as oxidation and reduction are concerned, therefore, the solution of zinc in sulphuric acid with production of zinc sulphate and hydrogen corresponds to the action—

$$Zn + H_2O = ZnO + H_2$$

an action which may be made to take place by passing steam over heated zinc.

The student will no doubt have observed that so long as he was concerned merely with the displacement and rearrangement of radicals, the equations to express the reactions were extremely simple, and could be solved numerically with very little trouble. On the other hand, equations representing actions of oxidation and reduction are often somewhat complex, and not to be solved by simple inspection. For example, if we proceeded by a process of trial and error to solve the equation—

$$?\,Cu + ?\,HNO_3 = ?\,Cu(NO_3)_2 + ?\,NO + ?\,H_2O$$

we might make a great many trials before we found the proportions $3Cu$ and $8HNO_3$, which satisfy this equation numerically. It is always easy, however, by systematic procedure to

arrive at the correct numerical solution even with equations much more complicated than that given above. The actual method adopted may be varied to suit particular cases, but the essential feature is to split up the total reaction into a series of simpler reactions, the equations for which may be arrived at by inspection, and then to combine these so as to give the equation for the complex reaction.

One part of the action of nitric acid on copper consists in oxidation of the copper, and reduction of the nitric acid. We may begin, then, by writing an equation to express the reduction of the nitric acid to nitric oxide, and so ascertain the proportion of oxygen available for oxidising the copper.

The equation to express the decomposition of nitric acid into water, nitric oxide, and oxygen is as follows :—

$$? HNO_3 = ? H_2O + ? NO + ? O$$

It is evident that the solution of this equation is

$$2HNO_3 = H_2O + 2NO + 3O$$

The quantity of oxygen represented by 3O is not given off as such, but goes to oxidise copper to the stage of oxidation in which it is contained in copper nitrate. Referring back to the basic oxide from which copper nitrate is derived, we find that this stage of oxidation is represented by the formula CuO. Each Cu which passes into CuO requires O, therefore to use up all the oxygen available from the nitric acid we must take 3Cu, and then arrive at the equation—

$$3Cu + 3O = 3CuO$$

Now, all this copper oxide must be converted into copper nitrate, which can easily be done by acting on the copper oxide with nitric acid. No oxidation or reduction being involved in this process, we arrive at once at the solution—

$$3CuO + 6HNO_3 = 3Cu(NO_3)_2 + 3H_2O$$

If we now add these three equations together, we get—

$$3Cu + 3O + 3CuO + 8HNO_3 = 3Cu(NO_3)_2 + 3CuO + 4H_2O + 2NO + 3O$$

or, if we strike out terms which are common to both sides,

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

This last equation is the correct equation for the action of nitric acid on copper with formation of the substances copper nitrate, nitric oxide, and water.

Suppose we have to solve the equation—

$$?\,Zn + ?\,HNO_3 = ?\,Zn(NO_3)_2 + ?\,N_2O + ?\,H_2O$$

we may proceed in exactly the same way as before. First of all, we find out how much oxygen is available for oxidation when nitric acid is reduced to nitrous oxide. This quantity is given by the equation—

$$2HNO_3 = H_2O + N_2O + 4O$$

Now, zinc in zinc nitrate is in the stage of oxidation corresponding to the oxide ZnO. To use up all the oxygen available from the nitric acid we must therefore write—

$$4Zn + 4O = 4ZnO$$

and to convert the amount of zinc oxide thus obtained into zinc nitrate we must write—

$$4ZnO + 8HNO_3 = 4Zn(NO_3)_2 + 4H_2O$$

Adding these three equations together right and left, and striking out members common to both sides, we get the solution—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O$$

for the action of zinc on nitric acid, with formation of nitrous oxide as the reduction product of nitric acid.

Under certain conditions nitric acid acts upon zinc with production of ammonium nitrate.

$$?\,Zn + ?\,HNO_3 = ?\,Zn(NO_3)_2 + ?\,NH_4NO_3 + ?\,H_2O$$

The student might find this equation somewhat complicated to solve, but having arrived at the solution of the equation which represents the formation of nitrous oxide, he can easily deduce the equation representing the formation of ammonium

nitrate by finding out in what way nitrous oxide and ammonium nitrate are related to each other. If we write the formula of ammonium nitrate $N_2H_4O_3$, and deduct from this the formula of nitrous oxide N_2O, we find there remains as residue H_4O_2, or $2H_2O$. We can therefore write the equation—

$$N_2O + 2H_2O = NH_4NO_3$$

This equation represents a purely imaginary reaction (the reversed equation, however, being true), but since this reaction cuts out in the final result, it is permissible to make use of it. If we now add the two equations- -

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$$
$$N_2O + 2H_2O = NH_4NO_3$$

and cut out the terms common to both sides, we arrive at the equation—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$$

The student is advised to practise this mode of dissecting complicated reactions into simpler reactions (as far as possible into those with which he is familiar), and then building up the complicated equation by means of the equations for these simpler reactions.

CHAPTER XXVII

EXAMPLES OF CHEMICAL TRANSFORMATION

By applying the general rules which have been given in the previous chapters concerning acids, bases, and salts, the student is in a position to solve many practical questions regarding the conversion of one compound into another.

For example, if he is asked how he might prepare zinc chloride from zinc hydroxide, he can at once say that zinc hydroxide, being a base, can be converted into any salt of zinc by treatment with the corresponding acid; so that for the conversion of zinc hydroxide into zinc chloride, the hydroxide has merely to be dissolved in the requisite amount of hydrochloric acid.

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

If, again, he is asked how metallic zinc may be converted into zinc chloride, he knows, from the electro-chemical list on p. 154, that zinc is capable of displacing hydrogen from acids, so that if metallic zinc is treated with hydrochloric acid, zinc chloride will be formed, and hydrogen evolved according to the equation—

$$Zn + 2HCl = ZnCl_2 + H_2$$

If he is asked to convert zinc chloride into zinc sulphate, he knows that sulphuric acid, being less volatile than hydrochloric acid, can drive out the latter from its salts on heating. Thus, to convert zinc chloride into zinc sulphate it is merely necessary to heat the chloride with sulphuric acid, when reaction will occur as follows:—

$$ZnCl_2 + H_2SO_4 = ZnSO_4 + 2HCl$$

hydrochloric acid being expelled as a gas.

Suppose, however, he is required to convert zinc sulphate into zinc chloride. This cannot be done by heating zinc sulphate with hydrochloric acid, for the hydrochloric acid, being more volatile, is expelled on heating, the zinc sulphate remaining behind unchanged. Some other method must therefore be adopted, and the student might, for example, make use of his knowledge of the solubility of the various salts. Zinc sulphate and zinc chloride, according to the rules given on page 68, are both soluble in water. Now, by interchange of radicals it is possible in aqueous solution to convert zinc sulphate into zinc chloride, provided a salt be selected which will give an insoluble compound with the negative radical of zinc sulphate. This salt must, of course, contain the chloride radical in order to give zinc chloride. The problem, therefore, resolves itself into finding a radical whose chloride is soluble and whose sulphate is insoluble. If the student refers to the table on p. 138, he finds that barium fulfils these conditions. By adding, therefore, a solution of barium chloride to a solution of zinc sulphate interchange of radicals takes place, with formation of insoluble barium sulphate and soluble zinc chloride, the equation being—

$$ZnSO_4 + BaCl_2 = \underline{BaSO_4} + ZnCl_2$$

The insoluole barium sulphate may be filtered off, and if the substances were taken in the proportions indicated by the equation, the solution will contain nothing but zinc chloride. This type of reaction is quite general. We can convert any soluble sulphate into the corresponding soluble chloride by the addition of barium chloride to the solution of the sulphate.

If the chloride which is required from the soluble sulphate is itself insoluble, we get it at once by double decomposition with any soluble chloride. Thus, if we have to convert silver sulphate, which is soluble, into silver chloride, which is insoluble, we have merely to add to the silver sulphate solution a solution of any soluble chloride, say sodium chloride, and we at once get silver chloride precipitated in accordance with the equation—

$$Ag_2SO_4 + 2NaCl = \underline{2AgCl} + Na_2SO_4$$

This silver chloride may be filtered off from the soluble sodium

sulphate produced at the same time, and thus obtained free from the other salts.

Besides this mode of precipitation by means of a suitable salt, there is another very important method by means of which soluble sulphates may be converted into soluble chlorides. This method is the one which is most generally used, not only in this case, but in most similar cases. The method is to carry out the reaction in two stages. We know that all carbonates except the alkaline carbonates are insoluble in water. We can therefore convert any soluble sulphate into the insoluble carbonate which corresponds to it by adding to the sulphate solution a solution of alkaline carbonate. Thus, we can precipitate zinc carbonate from a solution of zinc sulphate by the addition of sodium carbonate.

$$ZnSO_4 + Na_2CO_3 = \underline{ZnCO_3} + Na_2SO_4$$

It should be noted in this connection that basic carbonates are very frequently precipitated by sodium carbonate instead of the normal carbonates. The precipitate which is actually obtained by the addition of sodium carbonate to a solution of zinc sulphate, is not the normal carbonate, as represented by the above equation, but a basic carbonate which is, like the normal carbonate, insoluble.

Now, we know that all carbonates are decomposed by acids, with evolution of carbon dioxide. Thus, when we treat zinc carbonate with hydrochloric acid, reaction takes place according to the equation—

$$ZnCO_3 + 2HCl = ZnCl_2 + H_2O + \nearrow CO_2$$

zinc chloride being produced, and carbon dioxide escaping from the solution as gas. Consequently, by treating a solution of zinc sulphate with sodium carbonate, filtering off the basic zinc carbonate produced by the decomposition, and then dissolving the latter in hydrochloric acid, we can convert zinc sulphate into zinc chloride.

The hydroxides, like the carbonates, are nearly all insoluble in water. We can therefore precipitate hydroxides by means of sodium hydroxide, instead of carbonates by means of sodium carbonate. Thus, if we add the requisite amount of sodium

hydroxide to a solution of zinc sulphate, reaction takes place as follows :—

$$ZnSO_4 + 2NaOH = \underline{Zn(OH)_2} + Na_2SO_4$$

The zinc hydroxide thus produced may be filtered off and separated from the sodium sulphate, and then dissolved in hydrochloric acid, again with production of zinc chloride.

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

Since hydroxides and carbonates are soluble in acids with equal readiness, it does not in the least matter whether the carbonate which is precipitated by sodium carbonate is the normal or the basic carbonate, which is intermediate between the hydroxide and the normal salt; for in either case, on treatment with acid the corresponding salt will be formed, the only difference being in the amounts of water and of carbon dioxide produced at the same time.

It sometimes happens that the metallic radical considered has no insoluble compounds with salt radicals. Thus, if the problem before the student is to convert sodium nitrate into sodium chloride, no precipitation method in the above sense is available, because all the compounds of sodium with salt radicals are soluble, and all the compounds of the nitrate radical with metallic radicals are soluble. We cannot, therefore, add to a dilute solution of sodium nitrate any salt which will precipitate either the sodium or the nitrate radical—that is, we cannot bring about double decomposition by the production of an insoluble substance. Even in such cases, however, a precipitation method may be used if we deal with concentrated solutions and properly selected temperatures. Thus it is possible, by bringing sodium nitrate and potassium chloride together in presence of only a little hot water, to get double decomposition to occur, according to the equation—

$$NaNO_3 + KCl = NaCl + KNO_3$$

sodium chloride falling out of the solution. As will be seen in the chapter on potassium, this method is actually adopted, not for the conversion of sodium nitrate into sodium chloride, but for the production of potassium nitrate.

Another method, in this case an indirect one, might be

adopted to convert sodium nitrate into sodium chloride. If the sodium nitrate is subjected to electrolysis, sodium hydroxide is formed at the kathode. The solution of sodium hydroxide thus obtained could be neutralised by means of hydrochloric acid, and thus sodium chloride would be produced.

If the problem before the student is to convert metallic copper into copper chloride $CuCl_2$, he might adopt several methods, all more or less indirect, since it is impossible to obtain copper chloride directly from metallic copper by the action of hydrochloric acid alone. One method would be to heat the metallic copper in air, so as to obtain copper oxide CuO. This oxide being basic, dissolves in hydrochloric acid, with formation of copper chloride according to the equation—

$$CuO + 2HCl = CuCl_2 + H_2O$$

Again, although copper is not soluble in dilute hydrochloric acid, it is soluble in hot concentrated sulphuric acid, copper sulphate being produced in accordance with the equation—

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

This copper sulphate could then be converted into copper chloride by any of the methods already given for the conversion of zinc sulphate into zinc chloride. Thus it might be precipitated by means of sodium carbonate, and the basic carbonate so obtained dissolved in hydrochloric acid.

Instead of sulphuric acid, nitric acid might be employed as the solvent for metallic copper, the action then being—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O$$

The copper nitrate produced in this way could either be converted into chloride in the same way as the sulphate, or it might be subjected to heat, when it decomposes as follows:—

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2$$

with formation of copper oxide, which could then be dissolved in hydrochloric acid, as in the preceding instance.

When the substance to be dealt with is insoluble in acids, there is often considerable difficulty in converting it into soluble compounds containing the same metallic radical. For example,

barium sulphate is not only insoluble in water, but also in the common acids. If it is desired, then, to convert barium sulphate into barium chloride, we cannot employ any of the precipitation methods, since the barium sulphate which occurs on the left of the equation is itself the least soluble of all the substances likely to be involved. Some other means must therefore be adopted to bring the barium sulphate into a soluble form. A common method adopted is to reduce barium sulphate at a red heat by means of carbon. Reaction occurs according to the equations—

$$\underset{\text{Barium sulphate}}{BaSO_4} + 4C = \underset{\text{Barium sulphide}}{BaS} + 4CO$$

$$BaSO_4 + 2C = BaS + 2CO_2$$

with production of barium sulphide. This barium sulphide is soluble in acids, and may be easily converted into barium chloride by the action of hydrochloric acid—

$$BaS + 2HCl = BaCl_2 + H_2S$$

the sulphuretted hydrogen produced at the same time escaping as gas.

Silver chloride is another example of a substance which is insoluble in both water and acids. It also can be brought into a soluble form indirectly through a process of reduction. When the insoluble silver chloride is brought into contact with zinc and acidulated water, the zinc displaces the silver from its compound in accordance with the list given on page 154, metallic silver and zinc chloride being produced.

$$2AgCl + Zn = ZnCl_2 + 2Ag$$

The metallic silver obtained in this way may then be converted into silver nitrate by dissolving it in nitric acid, and from this soluble compound any of the other silver salts may be prepared. A similar method for obtaining metallic silver from the insoluble silver sulphide is given in the chapter on silver.

CHAPTER XXVIII

CHLORINE

COMMON salt, or *sodium chloride*, NaCl, is the universal source of chlorine and all its compounds. This substance occurs not only in enormous quantity in sea water, from which it may be obtained by evaporation, but also in brine springs and as solid *rock salt.*

Chlorine is now obtained from sodium chloride on the manufacturing scale by *electrolytic decomposition.* The negative radical of the chloride travels to the positive electrode, which consists of carbon, and is there discharged with formation of free chlorine.

$$\underset{\text{Chloride radical}}{2Cl} = \underset{\text{Chlorine gas}}{Cl_2}$$

Another manufacturing process for the production of chlorine, which can also be used in the laboratory, is the dehydrogenisation of hydrochloric acid. This acid when treated with many oxidising agents loses hydrogen in the form of water, the chlorine being at the same time liberated as gas. The oxidising agent most commonly employed is manganese dioxide, and the action may be represented by the equation—

$$\underset{\text{Manganese dioxide}}{MnO_2} + 4HCl = \underset{\text{Manganese chloride}}{MnCl_2} + 2H_2O + \underset{\text{Chlorine}}{Cl_2}$$

In the laboratory the black manganese dioxide is warmed in a flask with a moderately concentrated solution of hydrochloric acid, and the chlorine gas, which is evolved in a steady stream, may be dried by passing through concentrated sulphuric acid. The gas is generally collected by downward displacement, since it is somewhat soluble in water and readily attacks mercury.

Instead of using hydrochloric acid, we may substitute a

mixture of sodium chloride and concentrated sulphuric acid which is capable of producing it. The action is then represented by the equation—

$$\underset{\text{Manganese dioxide}}{MnO_2} + 2NaCl + 2H_2SO_4 = \underset{\text{Manganese sulphate}}{MnSO_4} + Na_2SO_4 + 2H_2O + \underset{\text{Chlorine}}{Cl_2}$$

Chlorine is a greenish yellow gas, with a pungent suffocating odour, by means of which it may be easily recognised. It is moderately soluble in water, the solution being termed *chlorine water*, and can be condensed to a liquid at the ordinary temperature by means of pressure. Its molecular weight is 71, so that the gas is nearly two and a half times as heavy as air under the same conditions.

Chlorine is a very active element, readily attacking metals with formation of metallic chlorides, and uniting directly with such non-metals as hydrogen, sulphur, and phosphorus. Thus phosphorus, if brought into a jar of chlorine, takes fire spontaneously with production of the chlorides of phosphorus. Chlorine has a special attraction for hydrogen, not only uniting with it directly, but even removing it from compounds in which it is a constituent, hydrochloric acid being in each case produced by the union. Thus chlorine comes to be used as a dehydrogenising (or oxidising) agent, its practical application being mostly for bleaching or for disinfecting. On account of its gaseous nature and insupportable odour, chlorine is very seldom used in the free state, but is at once converted into *bleaching powder*, from which chlorine can at any time be readily obtained, and which possesses both the bleaching and disinfecting properties of the element itself.

The dehydrogenising action of chlorine may readily be seen by placing a piece of filter paper saturated with turpentine in a vessel filled with chlorine. Turpentine is a compound of carbon and hydrogen, and from it chlorine abstracts the hydrogen with such vigour that the liquid bursts into flame, with formation of a dense black smoke consisting of particles of carbon, on which chlorine has no action. For the same reason, if a taper or a jet of coal-gas is burnt in a jar of chlorine, the flame produced is exceedingly smoky owing to the separation of carbon.

The bleaching properties of chlorine may be seen by adding

a little chlorine water to ink, or a solution of indigo, the colour of these substances being at once discharged.

Hydrochloric acid, HCl

Hydrochloric acid is prepared both in the laboratory and on the large scale by heating common salt with strong sulphuric acid. The first action, which occurs without special heating, is the production of hydrochloric acid and acid sodium sulphate.

$$NaCl + H_2SO_4 = HCl + NaHSO_4$$

The hydrochloric acid is a gas, and so escapes; the acid sodium sulphate is a solid, and remains behind. If more salt is now added and the temperature raised, a second action takes place—viz.

$$NaCl + NaHSO_4 = HCl + Na_2SO_4$$

more hydrochloric acid and normal sodium sulphate being produced. These two actions may both be expressed in one equation, derived from the preceding equations by adding their corresponding sides together, and eliminating terms common to both sides. The equation for the whole action is then—

$$2NaCl + H_2SO_4 = 2HCl + Na_2SO_4$$

As a rule, in the laboratory the action is not pushed beyond the first stage.

Hydrochloric acid is very seldom used in the form of gas. It is almost invariably dissolved in water, in which it is excessively soluble. What is known as strong or concentrated hydrochloric acid is an aqueous solution containing about one-third of its weight of the pure acid. The commercial solution is sometimes known under the old names of *spirit of salt*, or *muriatic acid*, derived from the Latin, *muria*, brine.

Hydrochloric acid is a colourless gas with a very pungent odour, quite distinct, however, from that of chlorine. Its molecular weight is 36.5, corresponding to the formula HCl, so that the gas is considerably heavier than air, and may be collected by downward displacement. It is very soluble in water, one volume of which under ordinary conditions dis-

solves nearly 500 volumes of the gas. From this solution hydrochloric acid (unlike ammonia, p. 119) cannot be expelled by boiling, as after a time the hydrochloric acid and water boil off together in constant proportions until all the liquid has disappeared. When brought into contact with air, it fumes strongly, the white fumes consisting of small particles of liquid solution of hydrochloric acid produced by the condensation of the gas with the moisture of the air. The gas may be liquefied at the ordinary temperature by the application of pressure.

As has already been indicated, hydrochloric acid may be produced by the direct union of hydrogen and chlorine. These gases can be mixed and kept for an indefinite time in the dark without undergoing alteration, but if the mixture is exposed to light, a slow union goes on with production of hydrochloric acid, according to the equation—

$$\underset{\text{1 vol.}}{H_2} + \underset{\text{1 vol.}}{Cl_2} = \underset{\text{2 vols.}}{2HCl}$$

Should the hydrogen and chlorine be present in the mixture in exactly the proportions required for the reaction—*i.e.* in equal volumes—exposure to a bright light will cause the union to take place so rapidly as to be explosive. Direct sunlight or the light from burning magnesium ribbon is usually sufficient to determine the explosive combination of the two gases. In all cases the sudden combination may be brought about by applying a lighted taper directly to the mixture.

Many metals when heated in an atmosphere of hydrochloric acid are converted into chlorides, hydrogen being liberated at the same time. Ferrous chloride, for example, may be prepared in this way, the action taking place according to the equation—

$$\underset{\text{Iron}}{Fe} + \underset{\text{2 vols.}}{2HCl} = \underset{\text{Ferrous chloride}}{FeCl_2} + \underset{\text{1 vol.}}{H_2}$$

The volume of hydrogen liberated is always equal to half the volume of the hydrochloric acid gas which has been decomposed. It may be said in general, that the metals which are acted on by dilute hydrochloric acid solution, also decompose the gas, either at the ordinary temperature or when heated.

Hydrochloric acid, being a strong acid, readily attacks most

basic oxides or hydroxides, with formation of a metallic chloride and water, thus—

$$ZnO + 2HCl = ZnCl_2 + H_2O$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O$$

In one point hydrochloric acid differs from the other strong common mineral acids, nitric and sulphuric acids,—it never acts as an oxidising agent. We therefore find that its action on metals is more restricted than the action of these other acids: it closely resembles the action of *dilute* sulphuric acid, which likewise possesses no oxidising properties.

Oxides of Chlorine

Chlorine monoxide, Cl_2O.—Chlorine and oxygen will not, under any circumstances, combine directly. They may be made to unite, however, if the oxygen is previously combined with some other element. In this way chlorine monoxide may be formed by passing a current of chlorine through a long tube containing dry mercuric oxide. The chlorine unites with the mercury and with the oxygen simultaneously, forming mercuric chloride and chlorine monoxide, thus—

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O$$

If the mercuric oxide is in excess, a compound $HgO,HgCl_2$ intermediate between the oxide and chloride is produced *—

$$2HgO + 2Cl_2 = \underset{\text{Basic mercuric chloride}}{HgO,HgCl_2} + Cl_2O$$

Chlorine monoxide is a dense yellow gas at the ordinary temperature, which even on gentle heating decomposes into its elements with explosive violence. Care must therefore be taken in its preparation.

* According to the definition given on p. 135, basic mercuric chloride should have the formula $Hg(OH)Cl$ or $Hg(OH)_2,HgCl_2$, and be intermediate in composition between the base $Hg(OH)_2$ and the normal salt $HgCl_2$. The name basic salt is frequently given, however, to compounds intermediate between the *basic oxide* and the normal salt. Thus the compound Hg_2OCl_2, or $HgO,HgCl_2$ is termed basic mercuric chloride.

It dissolves readily in water, forming a solution of hypochlorous acid HClO, and is therefore frequently termed hypochlorous anhydride.

$$\underset{\text{Chlorine monoxide}}{Cl_2O} + H_2O = \underset{\text{Hypochlorous acid}}{2HClO}$$

Chlorine peroxide, ClO_2.—This substance resembles chlorine monoxide in many ways, and is more frequently met with, since its production from a chlorate and strong sulphuric acid is generally employed as a test for chlorates. Its formation from potassium chlorate is represented by the following equation :—

$$3\underset{\text{Potassium chlorate}}{KClO_3} + H_2SO_4 = \underset{\text{Potassium perchlorate}}{KClO_4} + K_2SO_4 + 2\underset{\text{Chlorine peroxide}}{ClO_2} + H_2O$$

The gas has a bright yellow colour, not greenish yellow like chlorine, and a characteristic odour, which renders it easy of detection. At a temperature considerably below the boiling point of water, it decomposes explosively into its elements. At the ordinary temperature, combustible substances like sulphur catch fire when brought into contact with it.

Chlorine heptoxide, Cl_2O_7, is the anhydride of perchloric acid, $HClO_4$, from which it may be prepared by dehydration with phosphorus pentoxide.

$$2HClO_4 + P_2O_5 = 2HPO_3 + Cl_2O_7$$

It is a colourless liquid which explodes violently on percussion.

Action of Chlorine on Alkalies

When chlorine is led into a cold solution of caustic soda, caustic potash, or calcium hydroxide, it forms with these substances bleaching solutions which contain the **chloride** and the **hypochlorite** of the metal.

$$2NaOH + Cl_2 = \underset{\text{Chloride}}{NaCl} + \underset{\text{Hypochlorite}}{NaOCl} + H_2O$$
$$2KOH + Cl_2 = KCl + KOCl + H_2O$$
$$2Ca(OH)_2 + 2Cl_2 = CaCl_2 + Ca(OCl)_2 + 2H_2O$$

The bleaching action of the solutions prepared in this way is due to the *hypochlorites*, the chlorides of the alkalies having no bleaching properties.

If the alkaline solution is hot instead of cold, the solution obtained by the action of chlorine does not bleach, and contains **chlorate** instead of hypochlorite. The equations representing this type of action are as follows:—

$$6NaOH + 3Cl_2 = 5NaCl + NaClO_3 + 3H_2O$$
$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$
$$6Ca(OH)_2 + 6Cl_2 = \underset{\text{Chloride}}{5CaCl_2} + \underset{\text{Chlorate}}{Ca(ClO_3)_2} + 6H_2O$$

The production of chlorate instead of hypochlorite at the higher temperature depends on the fact that when a solution of a hypochlorite is boiled it becomes converted into a mixture of chloride and chlorate, thus—

$$\underset{\text{Hypochlorite}}{3NaOCl} = \underset{\text{Chloride}}{2NaCl} + \underset{\text{Chlorate}}{NaClO_3}$$

If chlorine is permitted to act on slightly moist solid calcium hydroxide, a very important substance is produced—namely, **bleaching powder.** This substance is, as it were, intermediate between calcium chloride and calcium hypochlorite, and when dissolved in water gives a bleaching solution which contains both of these salts. The actions may be represented by the equations—

$$Ca(OH)_2 + Cl_2 = \underset{\text{Bleaching powder.}}{CaOCl_2} + H_2O$$
$$\underset{\text{Bleaching powder}}{2CaOCl_2} = \underset{\text{Chloride}}{CaCl_2} + \underset{\text{Hypochlorite}}{Ca(OCl)_2}$$

Bleaching powder, however, does not consist entirely of a compound $CaOCl_2$, as a portion of the solid calcium hydroxide is always unattacked by the chlorine. Thus, when bleaching powder is treated with water so as to form a bleaching solution, a quantity of the sparingly soluble calcium hydroxide remains undissolved.

The action of chlorine on ammonia differs entirely from its action on other alkalies. In this case no hypochlorite or chlorate is permanently formed, the ammonia being decomposed with liberation of nitrogen. This action occurs whether the ammonia is present in the gaseous state or in aqueous solution, and may be represented by the equation—

$$2NH_3 + 3Cl_2 = N_2 + 6HCl$$

If the ammonia is present in excess, the hydrochloric acid is,

of course, converted into ammonium chloride. If the chloride is present in excess, the highly explosive nitrogen trichloride may be formed, thus—

$$NH_3 + 3Cl_2 = \underset{\text{Nitrogen trichloride}}{NCl_3} + 3HCl$$

The action of chlorine on the basic mercuric oxide has already been alluded to on p. 188.

Bleaching Action of Chlorine and Hypochlorites

That the bleaching action of chlorine is a process of oxidation and not of direct dehydrogenisation (compare p. 169) may be illustrated by the following experiment:—If a piece of carefully dried red calico is placed in a jar of dry chlorine, there is scarcely any bleaching action; but if the experiment is repeated with a piece of moist calico, the bleaching action is almost instantaneous. The chlorine, therefore, in absence of water, is unable to destroy the colouring matter by its own dehydrogenising action.

If water is present it is attacked by chlorine according to the following equation:—

$$Cl_2 + H_2O \rightleftarrows HCl + HClO$$

hypochlorous acid being produced in minute quantity. Since hypochlorous acid is a powerful bleaching agent it at once exercises its action on the colouring matter, oxidising and decolourising it, whilst it is itself converted into hydrochloric acid. A further quantity of hypochlorous acid is then generated by the chlorine and water, and is in turn used up, and so the bleaching process continues.

The bleaching solutions, which contain both chloride and hypochlorite, are not themselves powerful bleaching agents like hypochlorous acid, or chlorine and water, since they do not so readily part with oxygen. If these solutions are acidified, however, hypochlorous acid is liberated, and this at once acts as a bleaching agent. Carbon dioxide, although the

anhydride of a very weak acid, is still strong enough to liberate hypochlorous acid with ease from a hypochlorite, so that if the substance to be bleached is soaked in a bleaching solution and exposed to the air, the carbonic acid present in small quantities in the atmosphere will slowly liberate hypochlorous acid and effect the bleaching action.

When a strong acid is added to a bleaching solution, hydrochloric acid is set free along with hypochlorous acid. But we have already seen that these two acids cannot exist together in quantity, since they react to form water and chlorine. We therefore get chlorine as a product when a bleaching solution is strongly acidified. Weak acids such as boric acid or carbonic acid only liberate hypochlorous acid. The smell of bleaching powder and of bleaching solutions in general is due to hypochlorous acid, liberated in small quantity from the hypochlorite by the action of atmospheric carbonic acid.

The bleaching solution from bleaching powder in no way differs, so far as its bleaching properties are concerned, from the other bleaching solutions, since it behaves precisely as a mixture of calcium chloride and calcium hypochlorite. The yarn or other substance to be bleached is generally freed from resin, grease, etc., by boiling in a weak alkaline bath of washing soda, and then dipped successively into weak solutions of bleaching powder, sulphuric acid, and carbonate. The sulphuric acid acts on the hypochlorite, liberating hypochlorous acid and chlorine, which then perform the work of bleaching.

The reason why bleaching powder is used so extensively in place of the bleaching solutions lies in the fact of its being a solid, which can be kept for a long time without much alteration. It can, therefore, be conveniently stored and transported, which is not the case with bleaching solutions.

Chlorates and Perchlorates

Chlorates do not occur in nature, but, as we have seen, are prepared by the action of chlorine on alkaline solutions in the

heat. The chlorate which is most frequently used is **potassium chlorate**, $KClO_3$. This substance might be made directly from caustic potash and chlorine, according to the equation—

$$6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$$

but on the large scale this mode of preparation is needlessly expensive, on account of the quantity of comparatively dear potassium hydroxide which is converted into the comparatively cheap potassium chloride. The inexpensive alkali, calcium hydroxide, is therefore substituted for potassium hydroxide, so that calcium chlorate and calcium chloride are produced by the action of the chlorine; and then a strong solution of the calcium chlorate is mixed with a strong solution of potassium chloride. On cooling, the sparingly soluble potassium chlorate separates out of the solution, the chemical action being—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3$$

It is chiefly on account of the ease with which potassium chlorate can be purified by crystallisation that it is prepared on a large scale in preference to other chlorates.

Chlorates, like nitrates, part readily with their oxygen when heated, and are consequently used as sources of oxygen in the production of fireworks, compositions for the tips of matches, etc. Such mixtures consist essentially of a combustible substance (*e.g.* sulphur, sugar, charcoal), and an oxidising substance (*e.g.* nitrate or chlorate). When the mixture is heated to a certain temperature, chemical action begins, the combustible substances being oxidised by the nitrate or chlorate.

In neutral aqueous solution chlorates, like nitrates, do not behave as strong oxidising agents, but, on the addition of acid, the oxidising properties become apparent. This is due to the formation of the strongly oxidising chloric acid itself, and also of chlorine peroxide and free chlorine. Thus, when sulphuric acid is added to a chlorate, chlorine peroxide is produced, according to the equation—

$$3KClO_3 + H_2SO_4 = KClO_4 + K_2SO_4 + 2ClO_2 + H_2O$$

Hydrochloric acid generates by its action on a chlorate a

mixture of chlorine and its peroxide, formerly thought to be one substance, and called "euchlorine." Here two independent actions take place together—viz.

$$\underset{\text{Chlorate}}{KClO_3} + 6HCl = \underset{\text{Chloride}}{KCl} + 3H_2O + \underset{\text{Chlorine}}{3Cl_2}$$

$$\underset{\text{Chlorate}}{5KClO_3} + 6HCl = \underset{\text{Chloride}}{5KCl} + 3H_2O + \underset{\substack{\text{Chlorine}\\\text{peroxide}}}{6ClO_2}$$

We may, if we choose, combine these two equations by adding them together, and obtain the simple equation—

$$2KClO_3 + 4HCl = 2KCl + 2H_2O + Cl_2 + 2ClO_2$$

It must be remembered, however, that this particular equation states that the two gases are produced in the proportion of two molecular weights (or volumes) of peroxide to one molecular weight (or volume) of chlorine, which is by no means in general the case; so that, on the whole, it is better to consider the two actions separately.

Another similar instance of two independent actions proceeding simultaneously is to be found in the decomposition of potassium chlorate by heat. This action may proceed as follows, the chlorate decomposing simply into chloride and oxygen, thus—

$$2KClO_3 = 2KCl + 3O_2;$$

or a portion of the chlorate may be oxidised to perchlorate at the expense of another portion which is reduced to chloride, thus—

$$\underset{\text{Chlorate}}{4KClO_3} = \underset{\text{Perchlorate}}{3KClO_4} + \underset{\text{Chloride}}{KCl}$$

These two equations may again be combined by addition into the simple equation—

$$2KClO_3 = KClO_4 + KCl + O_2$$

which expresses the case where one formula-weight each of chloride and perchlorate is formed — a special case of the

general action. On further heating, the perchlorate decomposes into chloride and oxygen, thus—

$$KClO_4 = KCl + 2O_2;$$

so that if the chlorate is heated to a sufficiently high temperature, chloride and oxygen are the only products.

Most chlorates, when heated, decompose like potassium chlorate, but some give off chlorine as well as oxygen.

All the chlorates and perchlorates are soluble in water, the potassium salts being amongst the most sparingly soluble.

Chloric acid, $HClO_3$, **and perchloric acid,** $HClO_4$, are both liquid substances, and very strong oxidisers. When pure they oxidise organic matter with explosive violence. Moderately concentrated solutions of perchloric acid are, however, quite safe, and are used to precipitate potassium from solutions of potassium salts, potassium perchlorate being very sparingly soluble in solutions of perchloric acid.

Nitrogen trichloride

Chlorine will not combine directly with nitrogen, but will do so when it has the opportunity of combining with hydrogen simultaneously. Thus it has already been stated that nitrogen trichloride is formed by the action of chlorine on ammonia. The best method of preparing nitrogen trichloride, however, is by the action of chlorine on a saturated solution of ammonium chloride. The chlorine is gradually absorbed, and oily drops of nitrogen chloride appear in the liquid. The formation of the chloride proceeds according to the equation—

$$\underset{\text{Ammonium chloride}}{NH_4Cl} + 3Cl_2 = \underset{\text{Nitrogen trichloride}}{NCl_3} + 4HCl$$

Nitrogen trichloride must be prepared in very small quantities at a time, as it is a most violent explosive, decomposing into its elements on the slightest provocation.

CHAPTER XXIX

FLUORINE, BROMINE AND IODINE

FLUORINE

FLUORINE is the most active element known, and can only be separated with difficulty from the compounds which contain it. The chief of these compounds are hydrofluoric acid and the fluorides.

Hydrofluoric Acid

The fluorides are fairly abundant in nature, the most common mineral fluoride being calcium fluoride CaF_2, which is known as *fluorite* or *fluorspar*. This mineral has a comparatively low melting-point, and is used as a flux in certain furnace operations, an application from which the name fluorspar is derived. When warmed with concentrated sulphuric acid it is decomposed like the corresponding chloride, calcium sulphate and the hydrogen compound of the halogen being formed, thus—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

Since hydrofluoric acid attacks glass, its preparation is generally carried out in metal retorts, which in the laboratory are either of cast-iron or lead. The acid is evolved as a gas, which, however, can be condensed in an ice-cooled vessel to a colourless liquid which boils at 20°. In this respect hydrofluoric acid differs from hydrochloric acid, which requires a considerable lowering of temperature to convert it into liquid. Like the other halogen acids, hydrofluoric acid is very soluble in water. The solution is generally kept in gutta-percha bottles, since, like the vapour, it readily attacks glass.

Hydrofluoric acid is a much weaker acid than hydrochloric acid and the other halogen acids, and it differs from them also in readily forming acid salts, such as potassium hydrogen fluoride, which may be written either KF, HF, or, more properly, KHF_2. In this and similar compounds hydrofluoric acid apparently behaves as a dibasic acid, and its formula is therefore sometimes written H_2F_2, from which the acid salt KHF_2 and a normal salt K_2F_2 may be derived. That there is some justification for this view is shown by the vapour density

which, at temperatures slightly above the boiling-point of the liquid acid, corresponds to the formula H_2F_2. At higher temperatures, however, the vapour density corresponds to the formula HF. We are here dealing with a case of dissociation like that of nitrogen peroxide, and may write the following equation to express it:—

$$H_2F_2 \rightleftarrows 2HF$$

With regard to their solubility, the fluorides often differ greatly from the corresponding chlorides. Thus calcium fluoride is insoluble in water, whereas calcium chloride is very soluble; again silver fluoride is freely soluble in water, whilst silver chloride is quite insoluble.

The most important application of hydrofluoric acid is in the etching of glass. Hydrofluoric acid differs entirely from hydrochloric acid by readily attacking silica and the silicates at the ordinary temperature, the equation representing the action being—

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

The silicon fluoride thus formed is a gas at the ordinary temperature which is readily decomposed by water. Consequently if glass, which is a mixture of silicates, is brought into contact with either gaseous hydrofluoric acid or its solution in water, the material of the glass is attacked and eaten away by the acid. For the purpose of etching lines in glass, the glass is covered with a continuous coating of wax. Lines are then traced with a fine point on the wax, the substance of the glass being thereby exposed. When the whole is now subjected to the action of hydrofluoric acid, only the exposed portions of the glass are etched, the rest of the surface being protected by the wax coating.

Fluorine.—Owing to its extreme activity fluorine does not occur in nature, and the oxidising agents which easily separate chlorine from hydrochloric acid are quite incapable of liberating fluorine from hydrofluoric acid. The only practical method for liberating fluorine is by means of electrolysis. Since, however, fluorine immediately attacks water with liberation of oxygen, an aqueous solution cannot be used. The best solution to electrolyse is made by dissolving potassium fluoride in anhydrous liquid hydrofluoric acid. When the current passes, hydrogen is liberated at the cathode and fluorine at the anode. The electrodes are made

of platinum, and the electrolytical vessel may be either of platinum or copper. The electrolysis is conducted at a temperature of about $-20°$ in order to lessen the activity of fluorine by cooling. Fluorine is a pale yellow gas which condenses at the temperature of liquid air to a clear yellow fluid. Even at low temperatures it combines explosively with hydrogen in the dark, and it briskly attacks nearly all the other elements with formation of fluorides. Fluorine differs from chlorine in forming neither oxides nor oxygen acids.

BROMINE

The chief sources of bromine are the bromides contained in the salt deposits of Stassfurt, in Prussia. These deposits are worked up systematically for the potassium salts which they contain, the bromine being derived from the liquors out of which the potassium salts have crystallised. It may also be prepared from the mother-liquors obtained in the crystallisation of sodium chloride from sea-water or brine, in which it exists in small quantities in the form of bromides.

Bromine can be liberated from a bromide by treatment with manganese dioxide and sulphuric acid, thus—

$$2NaBr + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + Br_2$$

It may also be set free by passing chlorine into a bromide solution, in the manner expressed by the following equation :—

$$2NaBr + Cl_2 = 2NaCl + Br_2$$

These equations hold good for any metallic bromide, magnesium bromide being that mostly dealt with in the actual manufacture. If the solutions are kept near the boiling point, the bromine distils off as vapour, which may be condensed to a liquid.

At the ordinary temperature bromine is a dark, almost black, liquid, which has a strong, irritating odour, resembling that of chlorine. It is a very volatile substance, boiling at about 60°, and giving off a reddish brown vapour even at the ordinary temperature. When shaken up with water, it only partially dissolves, the bulk of the liquid separating out as an oily layer on the bottom of the vessel. The solution has a colour similar to that of bromine vapour, and is known as *bromine water*. Bulk for bulk, bromine is about three times as heavy as water.

In chemical properties, bromine resembles chlorine very closely, attacking in general those substances which are attacked by chlorine. Thus it unites readily with most metals, and also with non-metallic elements like sulphur or phosphorus. It does not combine with hydrogen so readily as chlorine does; indeed, a mixture of bromine vapour and hydrogen may be exposed to sunlight, or brought in contact with a lighted taper without combination occurring. The union does take place, however, if the mixed gases are passed through a red-hot tube. Although its power of combination with hydrogen is thus feebler than is the case with chlorine, bromine can yet be used as a dehydrogenising and bleaching agent. Its action on alkalies is precisely the same as that of chlorine. If the alkaline solution is cold, a **hypobromite** is produced, if hot, a **bromate.**

$$2NaOH + Br_2 = \underset{\text{Bromide}}{NaBr} + \underset{\text{Hypobromite}}{NaOBr} + H_2O$$

$$6NaOH + 3Br_2 = \underset{\text{Bromide}}{5NaBr} + \underset{\text{Bromate}}{NaBrO_3} + 3H_2O$$

The hypobromites are bleaching agents in the same way as the hypochlorites. The bromates, too, resemble the chlorates very closely. There is this difference between them, however. The bromates on heating give no perbromate, but pass directly into bromide and oxygen, thus—

$$2KBrO_3 = 2KBr + 3O_2$$

Perbromic acid and perbromates are, in fact, unknown; and so, likewise, are oxides of bromine.

Hydrobromic acid

When sulphuric acid acts on a bromide, hydrobromic acid is produced, just as hydrochloric acid is produced from a chloride under similar circumstances.

$$NaBr + H_2SO_4 = NaHSO_4 + HBr$$

A further action, however, here takes place, for the strong sulphuric acid acts on the hydrobromic acid to some extent as an oxidising agent, liberating bromine, thus—

$$\underset{\text{Hydrobromic Acid}}{2HBr} + H_2SO_4 = \underset{\text{Bromine}}{Br_2} + SO_2 + 2H_2O$$

No such action occurs with hydrochloric acid, as the sulphuric acid is unable to dissolve the union between the hydrogen and the chlorine, whilst, owing to the hydrogen and bromine being less firmly combined, it succeeds in effecting the decomposition of hydrobromic acid. If we take a non-oxidising acid instead of sulphuric acid, we can liberate the hydrobromic acid from a bromide without decomposing it. Thus, phosphoric acid and a bromide give a phosphate and hydrobromic acid—

$$2NaBr + H_3PO_4 = Na_2HPO_4 + 2HBr$$

Gaseous hydrobromic acid, however, is most conveniently

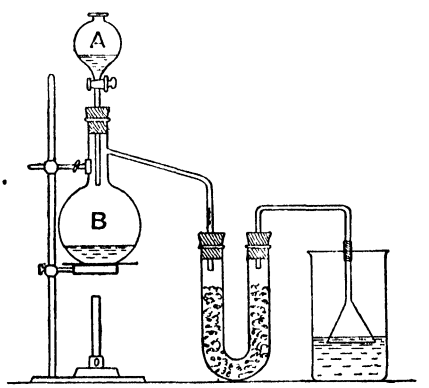


Fig. 36.—Preparation of Hydrobromic Acid.

Bromine is run from the tap-funnel *A* into a mixture of red phosphorus and water contained in the flask *B*. The hydrobromic acid gas which is formed is freed from bromine by a mixture of broken glass and red phosphorus in the U tube. If it is wished to dissolve the hydrobromic acid in water, it may be done as shown in the figure, a filter funnel just dipping beneath the surface of the water being used as a delivery tube.

prepared from bromine. When bromine is brought into contact with phosphorus, a very vigorous action occurs, a bromide of phosphorus being produced. This bromide of phosphorus, if brought into contact with a little water, is at once decomposed in accordance with the following equation :—

$$\underset{\text{Phosphorus tribromide}}{PBr_3} + 3H_2O = \underset{\text{Hydrobromic acid}}{3HBr} + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

The phosphorous acid is non-volatile, and so the hydrobromic

acid comes off alone. In order to make hydrobromic acid, it is not necessary to prepare phosphorus tribromide specially. A quantity of red phosphorus is mixed with a little water, and bromine is added drop by drop from a tap-funnel. Action at once ensues, and hydrobromic acid comes off steadily. The total action may be represented by the equation—

$$P + 3Br + 3H_2O = 3HBr + H_3PO_3$$

The hydrobromic acid may be freed from a little bromine vapour which passes over with it by passing it through a tube containing red phosphorus.

The acid thus prepared is very like hydrochloric acid. It is a colourless gas which is extremely soluble in water, and fumes strongly in air. It is much heavier than hydrochloric acid, as its high molecular weight shows. The aqueous solution is scarcely to be distinguished from hydrochloric acid by its behaviour towards metallic oxides or metals, but the two can easily be discriminated from each other by means of chlorine. Chlorine has, of course, no action on hydrochloric acid, but it immediately decomposes hydrobromic acid with liberation of bromine, which can be recognised by its reddish brown colour. The same test may be applied to all bromides, the solutions of which, on addition of chlorine water, yield bromine.

The bromides in other respects closely resemble the corresponding chlorides. Thus silver bromide, like silver chloride, is insoluble in water and acids; and in general it may be said that whatever the solubility of the chloride of a metal may be, the solubility of the bromide of the same metal will closely approximate to it.

IODINE

The chief sources of iodine are certain species of seaweed, and the mother liquors derived from the crystallisation of Chili saltpetre. The seaweed is dried, and either burned in shallow pits, or better, distilled. The residue in either case contains iodine in the form of iodide. The iodide is extracted with water, and is either precipitated by passing chlorine into the liquors, or distilled off as vapour by treating the liquor with manganese dioxide and sulphuric acid, the actions which take

place being exactly analogous to those occurring in the libera tion of bromine from bromides.

$$2NaI + Cl_2 = 2NaCl + I_2$$

$$2NaI + MnO_2 + 2H_2SO_4 = MnSO_4 + Na_2SO_4 + 2H_2O + I_2$$

In the mother liquors obtained from the crystallisation of crude Chili saltpetre (sodium nitrate), iodine is contained in the form of *sodium iodate*. This is an oxidising substance, which yields iodine as its first reduction product (compare the oxidation of iodine to iodic acid by means of nitric acid, p. 203). In practice the iodine is obtained by adding a mixture of sodium sulphite and sodium hydrogen sulphite to the iodate liquors. These substances are oxidised to sulphate, and the iodate is reduced to iodine, thus—

$$\underset{\text{Iodate}}{2NaIO_3} + \underset{\text{Sulphite}}{3Na_2SO_3} + 2NaHSO_3 = \underset{\text{Sulphate}}{5Na_2SO_4} + \underset{\text{Iodine}}{I_2} + H_2O$$

Excess of sulphite must be avoided, for otherwise the iodine would be further reduced to iodide. The iodine separates out as a dark precipitate, which is pressed free from liquor and purified by sublimation.

Iodine is a dark solid which is very sparingly soluble in water, but freely soluble in an aqueous solution of potassium iodide, the solution being brown in colour. When heated, it melts at a temperature not much above 100°, and sends off, even at that temperature, a fine violet-coloured vapour. This vapour is very characteristic of the substance, and when cooled condenses in shining black scales. Iodine is usually met with in this latter form, since it is almost invariably purified by sublimation. Iodine is much more soluble in carbon disulphide than it is in water, so that if the brown aqueous solution is shaken up with a little of the disulphide, which does not itself mix with water, the iodine leaves the water and dissolves in the disulphide, the solution produced being of a violet colour resembling that of iodine vapour.

Iodine acts chemically in much the same way as chlorine and bromine, combining directly with many metals and non-metals to form iodides. It will only combine partially with hydrogen, however, when the two elements are brought

together at a high temperature. It is much more readily oxidised than either chlorine or bromine. Thus, whilst these substances are not attacked by concentrated nitric acid, iodine when boiled with nitric acid is oxidised to **iodic acid**, the nitric acid being reduced principally to nitrogen peroxide, in accordance with the equation—

$$5HNO_3 + \underset{\text{Iodine}}{I} = \underset{\text{Iodic acid}}{HIO_3} + 5NO_2 + 2H_2O$$

The action of iodine on alkaline solutions is similar to that of chlorine and bromine. When the alkaline solutions are cold, iodide and hypoiodite are produced; when the solutions are hot, iodide and iodate. It must be remarked, however, that the hypoiodites are extremely unstable, and pass very soon into iodates. Iodine itself has little bleaching action, but the hypoiodite solutions are powerful bleaching agents.

The most characteristic test for iodine is the deep blue colour which even a trace of it will produce when brought into contact with starch solution. The blue substance is frequently called "iodide of starch," but there is no evidence in support of its being a true chemical compound—it behaves rather as if it were starch dyed with iodine. When the solution is warmed, the colour disappears, but reappears when the solution is cooled. This reaction is largely made use of as an indirect test for oxidising agents (compare pp. 91, 170). Almost any oxidising agent will liberate iodine from an iodide, so if a moist paper impregnated with potassium iodide and starch is brought into contact with an oxidising substance, it speedily assumes a blue colour owing to the production of the "iodide of starch."

Hydriodic acid

Hydriodic acid is generally prepared from iodine, phosphorus, and water, by a reaction similar to that employed in the preparation of hydrobromic acid. The equation is—

$$P + 3I + 3H_2O = 3HI + H_3PO_3$$

Like hydrochloric and hydrobromic acids, hydriodic acid is a heavy colourless gas which fumes strongly in moist air, and is

extremely soluble in water. When heated to a temperature approaching a red heat, the gas is partially decomposed into hydrogen and iodine, thus—

$$2HI \rightleftarrows H_2 + I_2$$

This action is a reversible one, for when the elements are mixed at a similar temperature, partial combination results. Hydrobromic and hydrochloric acids are not thus decomposed by heat.

When a strong solution of hydriodic acid is exposed to air, it rapidly darkens owing to liberation of iodine, the oxygen of the air combining with some of the hydrogen of the hydriodic acid to form water. Here again it is evident that iodine parts with hydrogen much more readily than either bromine or chlorine. Owing to this circumstance, hydriodic acid solution is sometimes used as a reducing or hydrogenising agent. Thus, if we mix a solution of iodic acid with a solution of hydriodic acid, iodine is formed, not only by the reduction of the iodic acid, but also by the oxidation of the hydriodic acid, the hydrogen and oxygen of the original acids uniting to form water.

$$\underset{\text{Iodic acid}}{HIO_3} + \underset{\text{Hydriodic acid}}{5HI} = \underset{\text{Water}}{3H_2O} + \underset{\text{Iodine}}{3I_2}$$

Concentrated sulphuric acid is also reduced by hydriodic acid, with production of sulphurous acid and iodine—

$$H_2SO_4 + 2HI = 2H_2O + SO_2 + I_2$$

For this reason concentrated sulphuric acid cannot be used to prepare hydriodic acid from an iodide. It should be remembered that dilute sulphuric acid does not act as an oxidising agent, and in consequence it does not liberate iodine from hydriodic acid; indeed, the action expressed by the above equation is reversed when much water is present—*i.e.* sulphurous acid and iodine produce sulphuric acid and hydriodic acid, thus—

$$2H_2O + SO_2 + I_2 = H_2SO_4 + 2HI$$

The iodides bear a general resemblance to the chlorides and bromides, but differ from them in many points. Thus, while it may be said that if the chloride and bromide of a metal are

insoluble, the iodide is also insoluble, the converse statement is not true; for there are many insoluble iodides corresponding to soluble bromides and chlorides. Again, where the bromides and chlorides are colourless, the iodides are frequently coloured. For example, mercuric chloride and mercuric bromide are colourless and soluble, whilst mercuric iodide has a brilliant scarlet colour and is insoluble in water

Comparison of the Halogen Elements

Fluorine, chlorine, bromine, and iodine form the natural family of the **halogens.** Fluorine diverges more from the last three elements than they do from each other, and will not, in the first instance, be considered. The resemblance of the three other elements is apparent from the formulæ of their corresponding compounds, to which similar names have been given, as may be seen in the subjoined table—

Chlorine . . Cl_2	Bromine . . Br_2	Iodine . . I_2
Hydrochloric acid HCl	Hydrobromic acid HBr	Hydriodic acid HI
Sodium chloride NaCl	Sodium bromide NaBr	Sodium iodide NaI
Chloric acid . $HClO_3$	Bromic acid . $HBrO_3$	Iodic acid . HIO_3
Sodium chlorate $NaClO_3$	Sodium bromate . $NaBrO_3$	Sodium iodate . $NaIO_3$
Perchloric acid $HClO_4$		Periodic acid HIO_4

Not only are these compounds similar in their formulæ—they are also similar in their properties. The halogen elements, therefore, may be substituted for each other without any great change in the properties of the resulting compounds.

Bromides and iodides occur in nature as well as chlorides, but in very much smaller quantity, so that the compounds of bromine and iodine are comparatively rare and expensive. Sea water, for instance, contains at least fifty times as much chlorine in the form of chloride as it does bromine in the form of bromide. Only mere traces of iodine exist in sea water, but this quantity is available for the production of iodine owing to the fact that certain seaweeds absorb and concentrate these iodine compounds, which are afterwards found as iodides in the ash produced when the seaweed is burnt.

When we compare the halogen elements with each other, we

often find a distinct gradation of properties, bromine being usually intermediate between chlorine and iodine. Thus we have the series of combining weights F = 19, Cl = 35·5, Br = 80, I = 127. Again, at the ordinary temperature fluorine is an uncondensable gas, chlorine a condensable gas, bromine a liquid, and iodine a solid. Comparing the depth of colour of the vapours, we find that fluorine has least colour, and iodine most, with chlorine and bromine intermediate. With respect to chemical activity, too, the same gradation appears. Fluorine combines with hydrogen explosively, chlorine with great readiness, bromine less readily, and iodine only partially at a high temperature. Conversely hydriodic acid and iodides are easily oxidised with liberation of iodine, hydrobromic acid and bromides require more powerful oxidising agents, hydrochloric acid and chlorides more powerful oxidising agents still, to effect the liberation of the halogen, whilst fluorine cannot be liberated by oxidation at all. Bromine liberates iodine from iodides, but not chlorine from chlorides, being thus intermediate. Fluorine expels all the other halogens briskly.

When we compare the oxygen compounds of the halogens, however, we find that fluorine and bromine no longer resemble chlorine and iodine. Thus, whilst both chlorine and iodine have oxides, no oxides of fluorine or bromine exist; and again, although we know both perchlorates and periodates, no perbromates have ever been prepared, and oxygen salts of fluorine are unknown.

CHAPTER XXX

SULPHUR

SULPHUR is an element which occurs in the uncombined state in many volcanic districts, particularly in Sicily, from which the bulk of the European supply is derived. The native

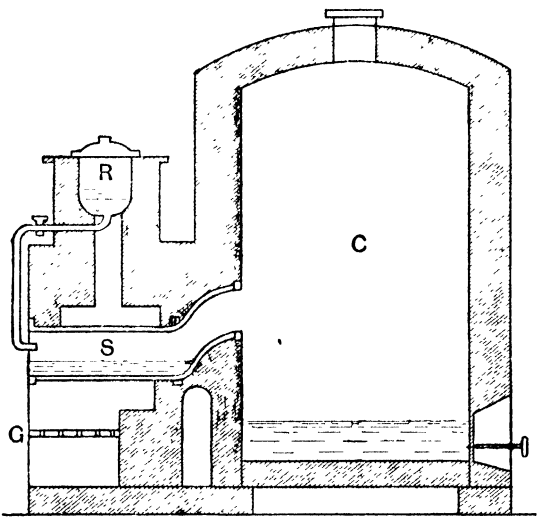


Fig. 37.—Distillation of Sulphur.

Sulphur in the retort *S* is boiled by means of a fire in the grate *G*. The heat from this fire serves to keep sulphur melted in the reservoir *R*, from which the retort can be replenished. The sulphur vapour passes into the condensing chamber *C*, and ultimately forms a liquid layer on its floor.

sulphur can easily be purified by distillation, since it melts at a comparatively low temperature, and boils below a red heat.

In America the sulphur deposits of Louisiana are so pure that the sulphur, melted underground by means of superheated water and brought to the surface in the liquid state, need not be subjected to any refining process.

In the combined state sulphur chiefly occurs along with

metals in the form of metallic sulphides, or along with metals and oxygen in the form of metallic sulphates. Some of the sulphides—for example, *iron pyrites* FeS_2, and *copper pyrites* $CuFeS_2$—part with a portion of their sulphur when heated in closed vessels, commercial sulphur being frequently obtained in this way.

The sulphur vapour produced by the distillation of crude native sulphur is usually condensed in large brickwork chambers. At the beginning of the distillation, the walls of the chamber are cold, and the sulphur condenses on them in the form of a pale yellow powder which is known as *flowers of sulphur*. As the operation proceeds the walls become hot, and the sulphur condenses not as a solid but as a liquid, which collects on the floor of the chamber and is drawn off into cylindrical moulds, where it solidifies on cooling to form the ordinary *roll sulphur*.

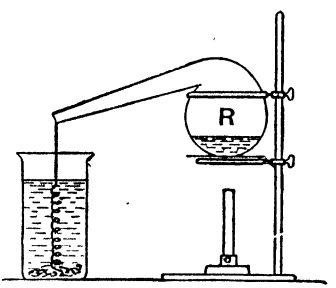


Fig. 38.—Formation of Plastic Sulphur.

Sulphur is distilled from the retort *R*. The vapour condenses in the beak of the retort and flows into cold water, the sudden chilling causing it to assume the form of stringy masses of non-crystalline plastic sulphur, which slowly become brittle and pass into the ordinary form.

When sulphur is heated to a temperature a little above that of boiling water, it melts to an amber-coloured fluid, which on further heating becomes darker in colour, and finally boils with production of a deep reddish-brown vapour at about 450°. Different varieties of sulphur may be obtained by cooling the heated liquid, according to the method by which the cooling is effected. If the sulphur is cooled suddenly by being poured into cold water, it forms a soft stringy material which is known as *plastic sulphur*. If a quantity of it is allowed to cool slowly in a covered vessel until a crust forms on the surface, and if the portion which is still liquid is now poured off through a hole broken in the crust, the interior of the vessel will be seen to be filled with transparent brownish-yellow needles of *monoclinic sulphur*, which on standing gradually lose their transparency and pass into lemon-yellow *rhombic sulphur*.

Rhombic and monoclinic sulphur are crystalline; plastic

sulphur is amorphous. Both of the crystalline modifications are soluble in carbon disulphide, whilst the amorphous sulphur is not. Roll sulphur when freshly cast consists chiefly of monoclinic sulphur, but this variety slowly passes into rhombic sulphur.

Flowers of sulphur are partially crystalline and partially amorphous, so that on treatment with carbon disulphide a portion dissolves and a portion remains unaffected. When a solution of sulphur in carbon disulphide is allowed to evaporate, transparent amber-coloured crystals of the rhombic variety are deposited.

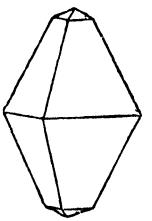


Fig. 39.—Crystal of Rhombic Sulphur.

Sulphur, then, exists in various allotropic modifications just as carbon does, some of these being crystalline and some amorphous. The two elements differ from each other, however, in this respect, that whilst both the crystalline varieties of carbon (graphite and diamond) can be kept for an indefinite period, only the rhombic variety of sulphur is permanent at the ordinary temperature.

Sulphur may also be thrown out of solution in the form of a yellow or white precipitate. Thus, if chlorine water is added to a solution of sulphuretted hydrogen, the liquid at once becomes milky by the precipitation of sulphur.

$$Cl_2 + H_2S = 2HCl + S$$

Sulphur precipitated from calcium penta-sulphide by the action of an acid

$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$$

is white and very finely divided, and is used in medicine under the name of *milk of sulphur*.

Sulphur combines readily with many elements. For example, it burns in air with a blue flame, forming the oxide SO_2; and when heated with metals such as iron, zinc, and copper, it unites with them to form sulphides. It is attacked by chlorine, bromine, and iodine, and at a white heat combines with carbon to produce carbon disulphide CS_2. Many oxidising agents attack it. Thus, when heated with concentrated nitric acid, it is converted into sulphuric acid, and

at a sufficiently high temperature it is oxidised by solid substances such as potassium nitrate, or potassium chlorate. On this account it is used as an ingredient of gunpowder and of many pyrotechnic mixtures. When such mixtures are fired, the nitrate or chlorate suddenly parts with its oxygen to the sulphur, the action being occasionally so rapid as to be accompanied by an explosive evolution of gas.

Oxides of Sulphur

Sulphur dioxide, SO_2.—This substance is produced when sulphur burns in air or in oxygen. It is gaseous under ordinary circumstances, and possesses the familiar smell of burning sulphur, by means of which property it is most easily recognised. The most convenient mode of preparation of sulphur dioxide in the laboratory is by the action of a metal, usually copper, on warm concentrated sulphuric acid, thus—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

At the temperature of a good freezing mixture of ice and salt, the gas condenses to a colourless liquid. The same liquefaction can also be brought about at the ordinary temperature by the application of about two atmospheres pressure. Corresponding to this easy condensability, the gas is moderately soluble in water, one volume of water dissolving about 40 volumes of the gas under ordinary conditions. The aqueous solution of the gas contains sulphurous acid formed according to the equation—

$$\underset{\text{Sulphurous anhydride}}{SO_2} + H_2O \rightleftarrows \underset{\text{Sulphurous acid}}{H_2SO_3}$$

Sulphur dioxide is chiefly prepared for the manufacture of sulphuric acid, but it also finds extensive use as a bleaching agent and as a disinfectant.

Sulphurous acid, H_2SO_3, has not been obtained in the pure state, since it breaks up very readily again into its anhydride and water. It is a dibasic acid, and the salts formed by its neutralisation are called **sulphites**. Thus the formula of normal sodium sulphite is Na_2SO_3. When any sulphite is warmed with hydrochloric or sulphuric acid it is decomposed with evolution of sulphur dioxide. For example, sodium sulphite and hydrochloric acid react according to the equation—

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$

Sulphur trioxide, SO_3.—Although sulphurous acid and the sulphites tend to take up oxygen from the atmosphere under ordinary conditions, and become thereby converted into sulphuric acid and sulphates—

$$2H_2SO_3 + O_2 = 2H_2SO_4$$
$$2Na_2SO_3 + O_2 = 2Na_2SO_4$$

gaseous sulphur dioxide only unites directly with oxygen under exceptional circumstances. The two gases may be heated together alone without union taking place, but it has been found that various apparently inert bodies act as catalysts and promote the union without being themselves affected. Thus, if we pass a mixture of the gases through a tube containing heated ferric oxide or finely divided platinum, combination takes place according to the equation—

$$2SO_2 + O_2 = 2SO_3$$

Sulphur trioxide thus produced is a gas at the temperature of the reaction, but it readily condenses, not to a liquid, but to fibrous silky masses, which fume strongly in air, uniting with the moisture in it to form sulphuric acid.

Sulphuric acid

Sulphuric acid, H_2SO_4, is the acid which is most extensively prepared on the commercial scale, most other acids being obtained from salts by its aid. The hydrogen which it contains is derived from water, the oxygen partly from water and partly from the atmosphere, and the sulphur either from native sulphur or from a metallic sulphide such as pyrites.

The first stage in the manufacture of sulphuric acid is the production of sulphur dioxide, which is then made to unite with water and oxygen thus—

$$2SO_2 + O_2 + 2H_2O = 2H_2SO_4$$

In the *contact process* sulphur trioxide is prepared catalytically from sulphur dioxide and oxygen in the manner indicated in the preceding section, and is then absorbed by concentrated sulphuric acid to produce fuming sulphuric acid, sufficient water being subsequently added to produce sulphuric acid of the desired concentration.

SO_3	+	H_2O	=	H_2SO_4
Sulphur trioxide		Water		Sulphuric acid

A very large quantity of sulphuric acid, however, is still produced by the *chamber process* which has been in use for over a century. In this process nitric oxide NO acts as carrier of oxygen from the air to the sulphur dioxide, instead of the platinum or ferric oxide previously mentioned. The operation is conducted in large leaden chambers, which are supplied with air, steam, sulphur dioxide, and small quantities of oxides of nitrogen to make up for unavoidable loss. The actions which go on are most simply represented by the equations, which do not, however, express the actual and somewhat complicated processes which occur in the lead chambers—

$$\underset{\text{Nitric oxide}}{2NO} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Nitrogen peroxide}}{2NO_2}$$

$$\underset{\text{Nitrogen peroxide}}{NO_2} + \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Nitric oxide}}{NO}$$

The nitric oxide is oxidised by the oxygen of the air to nitrogen peroxide, which then reacts with sulphur dioxide and steam to form sulphuric acid, nitric oxide being at the same time regenerated. The regenerated nitric oxide can again take up oxygen, and start the whole process afresh. Thus it merely plays the part of a bearer of oxygen, and in theory a very small quantity would suffice to effect the combination of an unlimited amount of sulphur dioxide, oxygen, and water; but in practice a slight loss is unavoidable, so that fresh quantities of nitric oxide must be supplied from nitre.

The *chamber acid* produced in this way contains only about 70% of sulphuric acid, the rest being almost entirely water, which must be driven off by heating in vessels of silica or iron containing a high percentage of silicon. The crude commercial acid prepared from pyrites contains considerable amounts of various impurities, especially oxides of nitrogen, lead sulphate, and arsenic compounds. It is frequently purified by re-distillation.

The concentrated distilled acid contains 98.3% of pure sulphuric acid, and 1.7% of water. It boils at 330°, is nearly twice as heavy as water, bulk for bulk, and is quite

colourless. On account of its comparatively high boiling point, it can drive out more volatile acids from their salts on heating, and is thus used in the preparation of hydrochloric, nitric, and other acids. Its most remarkable property is the avidity with which it absorbs water. Not only does it eagerly take up water-vapour from the air and other moist gases, but it even removes the elements of unformed water from many compounds, thus breaking them up and destroying them. For example, many organic compounds, which contain hydrogen and oxygen in combination with carbon, are blackened and charred by concentrated sulphuric acid. The charring consists in the removal of the hydrogen and oxygen as water, a black residue of carbon being left. Although no definite compound appears to be formed, the mixing of concentrated sulphuric acid with liquid water develops so much heat as often to convert a large proportion of the water into steam.

Sulphuric acid dissolves sulphur trioxide to form what is known as *oleum* or *fuming sulphuric acid.* The definite compound $H_2S_2O_7$, formed by the union of H_2SO_4 with SO_3, is termed *pyrosulphuric acid.*

Sulphates—Sulphuric acid is a *dibasic acid* and forms acid salts, such as $NaHSO_4$, sodium hydrogen sulphate, as well as normal salts, such as ordinary sodium sulphate, Na_2SO_4. Some of the most common sulphates are—

Gypsum . . .	$CaSO_4,2H_2O$
Epsom salt	$MgSO_4,7H_2O$
White vitriol	$ZnSO_4,7H_2O$
Green vitriol	$FeSO_4,7H_2O$
Blue vitriol	$CuSO_4,5H_2O$

Many of the sulphates are decomposed by heat, sulphur dioxide and oxygen being evolved, and metallic oxide left behind. Thus copper sulphate decomposes according to the following equation :—

$2CuSO_4$	=	$2CuO$	+	$2SO_2$	+	O_2
Copper sulphate		Copper oxide		Sulphur dioxide		Oxygen

Ferrous sulphate or green vitriol when heated yields, amongst other products, sulphuric acid, which was first prepared in this way, and from its source and oily appearance received the name of *oil of vitriol.*

Sulphuric acid as an oxidising agent.—When sulphuric

acid is raised to a red heat, as may be done for example by throwing the acid on red-hot bricks, it is decomposed in much the same way as copper sulphate, thus—

$$\underset{\text{Sulphuric acid}}{2H_2SO_4} = \underset{\text{Water}}{2H_2O} + \underset{\text{Sulphur dioxide}}{2SO_2} + \underset{\text{Oxygen}}{O_2}$$

If a substance capable of uniting with the oxygen is also present, the decomposition is effected at a much lower temperature, so that concentrated sulphuric acid frequently behaves as an oxidising agent, being reduced in the action to sulphurous acid, or to sulphur dioxide and water. Thus, if pure sulphuric acid is warmed with carbon, sulphur, or a metal such as zinc or copper, it oxidises these substances according to the following equations :—

$$\underset{\text{Carbon}}{C} + 2H_2SO_4 = \underset{\text{Carbon dioxide}}{CO_2} + 2SO_2 + 2H_2O$$

$$\underset{\text{Sulphur}}{S} + 2H_2SO_4 = \underset{\text{Sulphur dioxide}}{SO_2} + 2SO_2 + 2H_2O$$

$$\underset{\text{Zinc}}{Zn} + 2H_2SO_4 = \underset{\text{Zinc sulphate}}{ZnSO_4} + SO_2 + 2H_2O$$

$$\underset{\text{Copper}}{Cu} + 2H_2SO_4 = \underset{\text{Copper sulphate}}{CuSO_4} + SO_2 + 2H_2O$$

As has already been stated, the action of concentrated sulphuric acid on copper is used in the laboratory for the preparation of sulphur dioxide.

It is only if the sulphuric acid is pure or mixed with a *small* quantity of water that it acts in this way as an oxidising agent; dilute sulphuric acid has no oxidising properties. Thus, dilute sulphuric acid leaves carbon, sulphur, and copper quite unaffected; and although it does act on zinc, no sulphur dioxide is produced, hydrogen being evolved in its stead.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

In dilute solution the tendency is rather for sulphurous acid and sulphites to pass into sulphuric acid and sulphates (p. 171). A solution of sodium sulphite, for example, absorbs oxygen from the air, and is gradually converted into sodium sulphate—

$$\underset{\text{Sodium sulphite}}{2Na_2SO_3} + O_2 = \underset{\text{Sodium sulphate}}{2Na_2SO_4}$$

Similarly, sulphurous acid can often be employed as a reducing agent (p. 170).

A good example of the effect of water in determining the relative stability of the two oxygen acids of sulphur is afforded by the reversible action (p. 202)—

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Hydriodic acid}}{2HI} \rightleftarrows \underset{\text{Water}}{2H_2O} + \underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Iodine}}{I_2}$$

If little or no water is present, the sulphuric acid acts as an oxidising or dehydrogenising agent, removing hydrogen from the hydriodic acid and being itself converted into sulphur dioxide. If much water is present, this reaction does not occur; on the contrary, sulphur dioxide and iodine regenerate sulphuric acid and hydriodic acid.

Thiosulphates

Just as sodium sulphite unites with oxygen to form sodium sulphate, so also does it unite with sulphur when a solution of it is boiled with that substance. The product of the action is called sodium thiosulphate, and its formation may be represented by the equation—

$$\underset{\text{Sodium sulphite}}{Na_2SO_3} + \underset{\text{Sulphur}}{S} = \underset{\text{Sodium thiosulphate}}{Na_2S_2O_3}$$

The prefix *thio* is used to indicate substitution of sulphur for oxygen, and a reference to the formulæ will show that sodium thiosulphate is related to sodium sulphate by the replacement of one-fourth of its oxygen by an equivalent amount of sulphur.

The **thiosulphuric acid** from which the thiosulphates are derived is a dibasic acid, which, however, cannot be obtained in the pure state, owing to its tendency to decompose according to the equation—

$$\underset{\text{Thiosulphuric acid}}{H_2S_2O_3} = \underset{\text{Sulphurous acid}}{H_2SO_3} + \underset{\text{Sulphur}}{S}$$

Thus, if hydrochloric acid is added to a solution of sodium thiosulphate, the solution speedily becomes milky owing to the separation of sulphur, and the smell of sulphur dioxide is perceptible, these substances being formed by the decomposition of the thiosulphuric acid originally liberated.

Sodium thiosulphate is largely used in photography under

the name of "hypo," derived from the name *hyposulphite of soda*, which was formerly applied to this compound. Its employment in photography depends on the property that its solutions readily dissolve many silver salts which are insoluble in water. Thus silver bromide dissolves in hypo solution with production of sodium bromide and sodium silver thiosulphate, which are both soluble in water. Note that this is an apparent exception to the rule given on p. 139.

$AgBr$	+	$Na_2S_2O_3$	=	$NaBr$	+	$NaAgS_2O_3$
Silver bromide		Sodium thiosulphate		Sodium bromide		Sodium silver thiosulphate

Hydrosulphites

Sodium hydrosulphite, $Na_2S_2O_4$, is formed by the electrolytic reduction of sodium hydrogen sulphite—

$$2NaHSO_3 + 2(H) = Na_2S_2O_4 + 2H_2O$$

The dry salt is fairly stable in air, but when moist it is reoxidised to sulphite. Its alkaline solution readily absorbs oxygen from gaseous mixtures, such as atmospheric air, and is on this account employed in gas analysis. The solutions also act as powerful reducing agents and have a considerable technical application. They may readily be distinguished from sulphites by their power of reducing indigo solution and thus discharging its colour.

Sulphuretted hydrogen

When iron filings and flowers of sulphur are heated together, they unite to form a sulphide of iron, which is different from the iron pyrites found as a mineral. It contains, for a given amount of iron, only half as much sulphur as pyrites, and is known as ferrous sulphide, its formula being FeS. This substance is the usual source of sulphuretted hydrogen in the laboratory, for when treated with dilute hydrochloric or sulphuric acid, it decomposes as follows :—

FeS	+	H_2SO_4	=	H_2S	+	$FeSO_4$
Ferrous sulphide		Sulphuric acid		Hydrogen sulphide		Ferrous sulphate

The hydrogen sulphide, or sulphuretted hydrogen, thus pre-

pared, is not quite pure, being usually mixed with a little hydrogen derived from a small quantity of metallic iron which the ferrous sulphide contains, but this impurity as a rule is of no moment.

Hydrogen sulphide is easily recognisable by its unpleasant odour, which resembles that of rotten eggs. It is a colourless gas, somewhat heavier than air, is moderately soluble in water (p. 112), and is condensable to a liquid at the ordinary temperature. In a plentiful supply of air it burns with formation of water and sulphur dioxide: if the supply of air is defective, the hydrogen burns in preference to the sulphur. The following equations represent the complete and partial combustion of hydrogen sulphide:—

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$
$$2H_2S + O_2 = 2H_2O + 2S$$

A solution of hydrogen sulphide on exposure to the air rapidly becomes turbid, owing to the deposition of sulphur caused by partial oxidation, the equation for the action being the last one of the preceding pair.

Sulphuretted hydrogen is a weak acid, like carbonic acid, which it also resembles in being dibasic. The normal sulphide of sodium has the formula Na_2S, but in addition to this, there is a sulphide NaHS, which is called sodium hydrogen sulphide, or *sodium hydrosulphide*. The solutions of these sulphides, like those of the corresponding carbonates, have an alkaline reaction, due to their partial hydrolysis by water, with liberation of sodium hydroxide (p. 151).

All the metallic sulphides, except those of the alkali metals, are insoluble in water. Some, however, are hydrolysed by water with formation of soluble products. Thus, calcium sulphide on being brought into contact with water slowly splits up according to the following equation:—

$$\underset{\text{Calcium sulphide}}{2CaS} + \underset{\text{Water}}{2H_2O} = \underset{\text{Calcium hydroxide}}{Ca(HO)_2} + \underset{\text{Calcium hydrosulphide}}{Ca(HS)_2}$$

the hydrosulphide being easily soluble, and the hydroxide sparingly soluble in water.

On account of the insolubility of the majority of metallic sulphides, and on account of the characteristic colours which many

of them possess, sulphuretted hydrogen is a valuable reagent in the laboratory for identifying the metallic radicals in salts. For example, if we add sulphuretted hydrogen to solutions of the sulphates of copper, zinc, and cadmium, we obtain precipitates of the corresponding sulphides, in accordance with the equations—

$$\begin{aligned} CuSO_4 &+ H_2S = CuS + H_2SO_4 \\ ZnSO_4 &+ H_2S = ZnS + H_2SO_4 \\ CdSO_4 &+ H_2S = CdS + H_2SO_4 \end{aligned}$$

Of these, copper sulphide is black, zinc sulphide white, and cadmium sulphide yellow. The different solubility of the sulphides in dilute acid, too, affords a valuable means of separating the metallic radicals into well-defined groups. Thus, zinc sulphide dissolves in very dilute hydrochloric acid, whilst copper and cadmium sulphides are practically unaffected by an acid of the same concentration. It must be borne in mind that, in such a case, the sulphide does not dissolve as such in the acid, but is decomposed by it, with formation of a soluble salt and sulphuretted hydrogen—

$$\underset{\text{Zinc sulphide}}{ZnS} + 2HCl = \underset{\text{Zinc chloride}}{ZnCl_2} + H_2S$$

The presence of a very small amount of hydrochloric acid will thus prevent the precipitation of zinc sulphide from a zinc salt by means of sulphuretted hydrogen, but will not interfere with the precipitation of copper or cadmium sulphides under the same conditions, thus affording a method of separating zinc from copper and cadmium.

When heated in air, or *roasted*, many of the metallic sulphides are converted into sulphates, though this action is also usually accompanied by the formation of oxides. For example, lead sulphide on being roasted at a high temperature is oxidised as follows:—

$$\underset{\text{Lead sulphide}}{PbS} + 2O_2 = \underset{\text{Lead sulphate}}{PbSO_4}$$

$$\underset{\text{Lead sulphide}}{2PbS} + 3O_2 = \underset{\text{Lead oxide}}{2PbO} + \underset{\text{Sulphur dioxide}}{2SO_2}$$

Both these actions are made use of in the extraction of lead from the sulphide, which is its chief ore.

On the other hand, the metallic sulphates can usually be

converted into the corresponding sulphides by heating them with carbon at a red heat, thus—

$$\underset{\text{Barium sulphate}}{BaSO_4} + 4C = \underset{\text{Barium sulphide}}{BaS} + 4CO$$

Chlorides of Sulphur

The ordinary chloride of sulphur, which is largely used in vulcanising rubber, has the formula S_2Cl_2, and is usually called the monochloride, to distinguish it from the others, which have proportionately more chlorine. It is prepared by the direct union of the elements, chlorine being passed into a vessel containing gently heated sulphur. The chloride is formed according to the equation—

$$2S + Cl_2 = S_2Cl_2$$

and distils over at the temperature of the operation.

It is a yellow liquid with a peculiar unpleasant odour, and boils at a temperature somewhat above the boiling point of water. It sinks in water and is slowly decomposed by it, forming hydrochloric acid, sulphurous acid, and sulphur, thus—

$$2S_2Cl_2 + 3H_2O = 4HCl + H_2SO_3 + 3S$$

The other chlorides, SCl_2 and SCl_4, are unstable and of no practical utility.

Carbon disulphide

Carbon disulphide (or carbon *bi*sulphide, as it is still usually called) differs from the metallic sulphides as much as carbon dioxide differs from the metallic oxides. It is formed by the direct union of sulphur vapour and carbon (in the form of charcoal or coke) at a bright red heat, thus—

$$\underset{\text{Carbon}}{C} + \underset{\text{Sulphur}}{2S} = \underset{\text{Carbon disulphide}}{CS_2}$$

Carbon disulphide is a volatile liquid (boiling-point 46°) which will not mix with water, and on which water floats, on account of the higher specific gravity of the disulphide. When perfectly pure it has a pleasant smell resembling that of chloroform, but on standing it rapidly acquires a very offensive odour, by means of which it is easily recognised. It is chiefly useful as a solvent for some substances which do not dissolve in water—*e.g.* fats, oils, sulphur, phosphorus.

It burns readily in oxygen or air with a blue flame, the carbon becoming carbon dioxide, and the sulphur, sulphur dioxide—

$$CS_2 + 3O_2 = CO_2 + 2SO_2$$

In a deficient supply of oxygen, the carbon burns in preference to the sulphur.

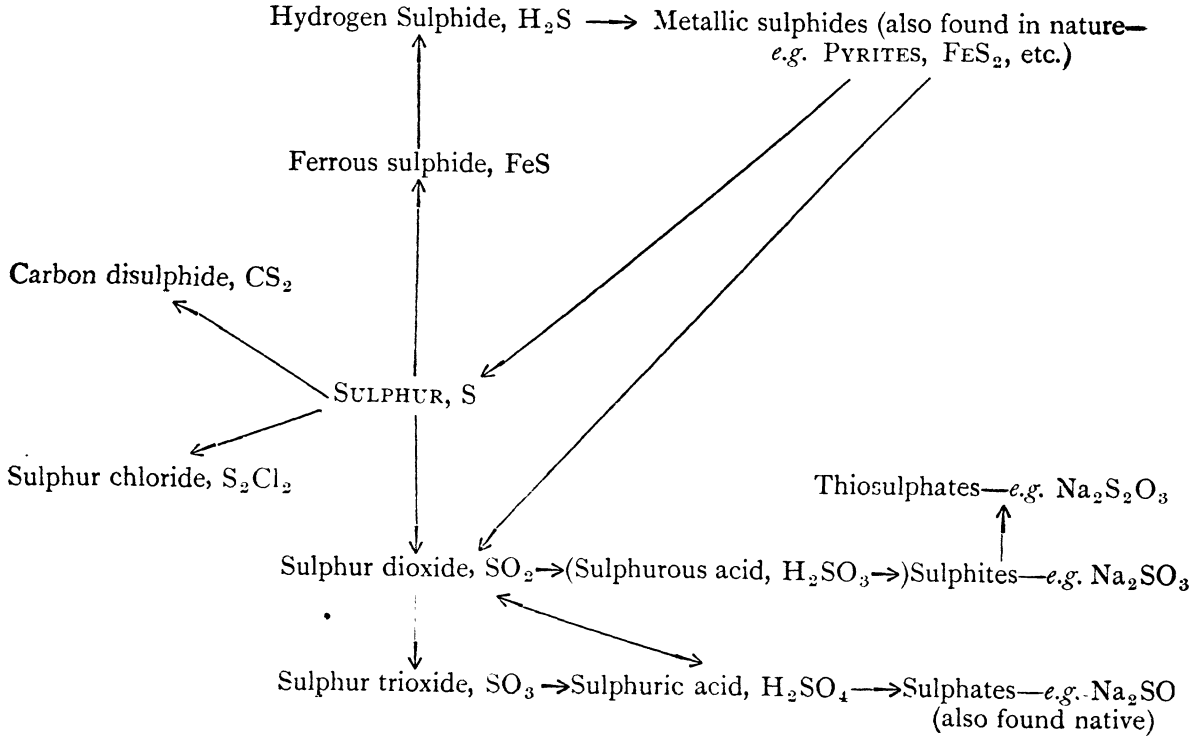
Comparison of Sulphur and Oxygen

Although widely divergent in their physical properties, oxygen and sulphur exhibit so many points of analogy in their compounds that chemists are in the habit of classifying them along with each other in the same natural family of elements. It must be admitted, however, that the resemblance between the corresponding compounds is mostly a resemblance in formulæ and not in properties, differing therefore in character from the resemblance between the halogen elements. From the following table it is evident that sulphur is capable of taking the place of oxygen, but the compounds thus produced are often very dissimilar in physical and chemical characters:—

Oxygen compounds		Sulphur compounds	
H_2O	Water	H_2S	Sulphuretted hydrogen
NaOH	Sodium hydroxide	NaSH	Sodium hydrosulphide
CaO	Calcium oxide	CaS	Calcium sulphide
Na_2SO_4	Sodium sulphate	$Na_2S_2O_3$	Sodium thiosulphate
CO_2	Carbon dioxide	CS_2	Carbon disulphide

Whilst water is a neutral odourless liquid, sulphuretted hydrogen is an acid offensive gas. Sodium hydroxide is a very powerful alkali: sodium hydrosulphide has scarcely any alkaline properties. Carbon dioxide is a gas under ordinary conditions: carbon disulphide is a heavy liquid, and so on. We have here, then, a *formal* resemblance between oxygen and sulphur, but little *real* resemblance in properties. It is important that the student should note this point, for much of chemical classification is based on resemblances which are more formal than real.

The following scheme indicates by means of arrows how the various compounds of sulphur are usually derived from each other, and the student is strongly recommended to draw up for himself similar tables in greater detail for this and other elements:—


Hydrogen Sulphide, H_2S → Metallic sulphides (also found in nature—*e.g.* PYRITES, FeS_2, etc.)
Ferrous sulphide, FeS
Carbon disulphide, CS_2
SULPHUR, S
Sulphur chloride, S_2Cl_2
Thiosulphates—*e.g.* $Na_2S_2O_3$
Sulphur dioxide, SO_2 →(Sulphurous acid, H_2SO_3 →)Sulphites—*e.g.* Na_2SO_3
Sulphur trioxide, SO_3 →Sulphuric acid, H_2SO_4 →Sulphates—*e.g.* Na_2SO
(also found native)

CHAPTER XXXI

PHOSPHORUS

PHOSPHORUS always occurs in nature in the oxidised state as phosphate, and practically the only source of phosphorus compounds is *calcium phosphate* $Ca_3(PO_4)_2$. This substance is found nearly pure in certain minerals, and can be prepared in quantity from bones, which in the dry state contain fully half their weight of calcium phosphate, and when burned in air leave behind *bone-ash* consisting chiefly of this compound.

In order to prepare phosphorus, calcium phosphate is heated in an electric furnace together with silica (in the form of sand) and charcoal. At the high temperature of the furnace, the carbon reduces the phosphate to phosphorus, and the silica, being an acid anhydride, unites with the calcium oxide to form calcium silicate. The action may be represented thus—

$$\underset{\text{Calcium phosphate}}{Ca_3(PO_4)_2} + 3SiO_2 + 5C = 2P + 3CaSiO_3 + 5CO$$

Silica — Carbon — Phosphorus — Calcium silicate

Or calcium phosphate may first be converted into phosphoric acid by the action of sulphuric acid. The metaphosphoric acid, on heating with charcoal in retorts contained in an ordinary furnace, is reduced by the carbon, with production of phosphorus, carbon monoxide, and hydrogen.

$$2HPO_3 + 6C = 6CO + H_2 + 2P$$

The phosphorus in either case distils over in the form of vapour, and is condensed in cold water. It is then melted under warm water and cast into sticks. When quite pure, phosphorus is perfectly colourless and transparent, but as actually obtained it generally possesses a yellow colour, and is known as yellow phosphorus. At the ordinary temperature **yellow phosphorus** is a soft waxy substance which can be scratched by the nail or cut with a knife. It melts at 44°, and if exposed to air at that temperature, invariably takes fire. The heat developed by friction in cutting it at the ordinary temperature is often sufficient to inflame it, so that it should

always be cut under water. It is customary indeed to keep phosphorus permanently under water, so as to avoid the liability to accident from its easy inflammability.

Yellow phosphorus has a characteristic smell, and is seen to glow in the dark when exposed to moist air. It is soluble in carbon disulphide, and is deposited in the crystalline state when the solvent is allowed to evaporate slowly.

Yellow phosphorus even at the ordinary temperature slowly combines with the oxygen of the air, and may be used for removing oxygen from a mixture of gases (compare p. 82). When the phosphorus exposes a large surface to the atmosphere, the oxidation may proceed so rapidly as to raise the temperature to the ignition point of phosphorus, which then bursts into flame. Such a large surface may be secured by allowing a little of the solution in carbon disulphide to evaporate on a piece of filter paper, a small quantity of phosphorus being thus spread over a great space.

Ordinary matches in this country were formerly tipped with a mixture of phosphorus, potassium chlorate, and glue. The use of yellow phosphorus in the manufacture of matches is now forbidden owing to its poisonous nature, and a sulphide of phosphorus which has a low ignition temperature has been substituted for it. The end of the splint is first of all dipped in melted paraffin wax, and then into a paste made of the above substances together with a small quantity of fine sand, and vermilion as a colouring matter. When the match is rubbed on a rough surface, the friction, which is increased by the presence of the sand, is sufficient to raise the temperature of the composition to a point at which the phosphorus sulphide takes fire, most of the oxygen being supplied by the potassium chlorate. The flame of the phosphorus compound under these conditions is not capable of igniting wood directly. It will, however, ignite paraffin, which in its turn is able to ignite the wood. The glue is present merely to hold the composition together, and fix it to the splint, playing no essential part in the chemical action.

There is another variety of phosphorus, **red phosphorus**, which differs greatly in its properties from yellow phosphorus. Although this variety is sometimes called *amorphous* phosphorus, it is in reality crystalline. It may be prepared by heating phosphorus in absence of air to a temperature of about 240°. If a very small quantity of iodine is added to

the liquid phosphorus, the conversion occurs at a temperature of about 200°.

Red phosphorus differs from yellow phosphorus, not only in its crystalline form and physical properties, but also greatly in chemical activity. It has no smell and no poisonous action, it does not glow in the dark, it is insoluble in carbon disulphide, and does not ignite in the air until warmed to a temperature exceeding 200°.

On account of its non-poisonous properties and smaller liability to ignition, red phosphorus is used in the manufacture of **safety matches**, or rather of the surface on which the safety matches are struck. The tip of the safety match resembles that of an ordinary match, with the exception that the combustible substance in it is not phosphorus, but antimony sulphide, Sb_2S_3. When drawn along the striking surface, which contains amorphous phosphorus, a little of the phosphorus ignites at the point of contact, where it comes into contact with the potassium chlorate in the head of the match. The combustion, however, is not transmitted to the rest of the amorphous phosphorus on the prepared surface, but to the mixture on the match head, which contains both the combustible sulphide and the chlorate to supply the necessary oxygen.

Red phosphorus is thus much less active chemically than yellow phosphorus, yet the difference is only one of degree. The two substances enter into exactly the same combinations, but the yellow phosphorus does so with greater readiness, and at a lower temperature.

Besides combining with oxygen and the halogens, phosphorus combines with some metals to form *phosphides*, which are in many respects analogous to the sulphides.

Phosphorus in the state of vapour has a density corresponding to the molecular formula P_4.

Oxides of Phosphorus

The two chief oxides of phosphorus are the trioxide and the pentoxide. When phosphorus burns in the air or in oxygen, dense white fumes are produced, which consist of a mixture of

these two oxides, the latter predominating. Their formation is represented by the equations—

$$4P + 3O_2 = \underset{\text{Phosphorus trioxide}}{2P_2O_3}$$

$$4P + 5O_2 = \underset{\text{Phosphorus pentoxide.}}{2P_2O_5}$$

Phosphorus trioxide, P_2O_3.—In order to obtain this oxide, the phosphorus is burned in a defective supply of air, and the fumes passed through a glass tube containing a plug of glass wool. This serves to stop the solid pentoxide, but permits the trioxide to pass on into a condensing vessel. The trioxide is liquid on a warm day, solid on a cold day. Its vapour has a density corresponding to the molecular formula P_4O_6, although its name is derived from the simpler formula P_2O_3. It unites slowly with cold water to form phosphorous acid, for which reason it is sometimes called *phosphorous anhydride*. The equation representing this action is—

$$\underset{\text{Phosphorus trioxide}}{P_2O_3} + 3H_2O = \underset{\text{Phosphorous acid.}}{2H_3PO_3}$$

When warmed in oxygen, the trioxide burns to form pentoxide—

$$\underset{\text{Trioxide}}{P_2O_3} + O_2 = \underset{\text{Pentoxide}}{P_2O_5}$$

Phosphorus pentoxide, P_2O_5.—When the supply of air or oxygen in which phosphorus burns is plentiful, the pentoxide is produced. This substance is usually met with as a white powder, which possesses a great attraction for moisture. If exposed to the air it deliquesces to form a syrupy mass, and if thrown into water it dissolves with a hissing noise, owing to the heat produced by its combination with the water. The action which takes place is represented by the following equation :—

$$\underset{\text{Phosphorus pentoxide}}{P_2O_5} + H_2O = \underset{\text{Metaphosphoric acid.}}{2HPO_3}$$

Since the substance produced by its union with water is a variety of phosphoric acid, phosphorus pentoxide is frequently called *phosphoric anhydride*. Phosphoric anhydride is largely employed in the laboratory for drying gases, etc., when it is essential

to get rid of the last traces of moisture. Not only, however, will it remove water actually present in a mixture—it will, like sulphuric acid, remove the elements of water from a compound; it will even remove the elements of water from sulphuric acid itself, thus—

$$\underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Phosphoric anhydride}}{P_2O_5} = \underset{\text{Sulphuric anhydride}}{SO_3} + \underset{\text{Metaphosphoric acid}}{2HPO_3}$$

Phosphoric anhydride is, in fact, one of the most powerful dehydrating agents with which we are acquainted.

Phosphorus and the Halogens

Yellow phosphorus when brought into contact with the halogens at the ordinary temperature, unites with them spontaneously, evolving heat, and forming a phosphorus chloride, bromide, or iodide. Red phosphorus is also readily attacked by bromine and chlorine at the ordinary temperature, but requires to be slightly warmed before it unites with iodine.

Phosphorus trichloride, PCl_3.—This substance, formed according to the equation—

$$2P + 3Cl_2 = 2PCl_3$$

is a fuming liquid, which boils at a temperature lower than the boiling point of water. When poured into water it is rapidly decomposed with formation of hydrochloric acid and phosphorous acid—

$$\underset{\text{Phosphorus trichloride}}{PCl_3} + 3H_2O = 3HCl + \underset{\text{Phosphorous acid.}}{H_3PO_3}$$

Phosphorus pentachloride, PCl_5.—When excess of chlorine is used, or when the trichloride is exposed to the action of chlorine, the pentachloride of phosphorus is produced—

$$\begin{array}{lcl} 2P + 5Cl_2 & = & 2PCl_5 \\ PCl_3 + Cl_2 & \rightleftarrows & PCl_5 \end{array}$$

Unlike the trichloride, the pentachloride is a yellow crystalline solid. When converted into vapour the pentachloride dissociates into trichloride and chlorine, which recombine when the vapour is cooled. The action expressed by the second of the above pair of equations is thus reversible.

The action of water on the pentachloride is vigorous, and similar in character to the action on the trichloride, ordinary phosphoric acid being formed instead of phosphorous acid—

$$\underset{\text{Phosphorus pentachloride}}{PCl_5} + 4H_2O = 5HCl + \underset{\text{Phosphoric acid.}}{H_3PO_4}$$

If only a small quantity of water is used in the decomposition, **phosphorus oxychloride**, a liquid substance containing both oxygen and chlorine, is produced, thus—

$$\underset{\text{Phosphorus pentachloride}}{PCl_5} + H_2O = 2HCl + \underset{\text{Phosphorus oxychloride.}}{POCl_3}$$

This oxychloride on further treatment with water is converted into phosphoric acid.

Bromides of phosphorus.—There are two bromides of phosphorus, the tribromide, PBr_3, and the pentabromide, PBr_5, which resemble the chlorides very closely, both in physical and chemical properties. When acted upon by water they produce phosphorous and phosphoric acids respectively, together with hydrobromic acid, which here appears in place of hydrochloric acid—

$$\underset{\text{Tribromide}}{PBr_3} + 3H_2O = 3HBr + \underset{\text{Phosphorous acid}}{H_3PO_3}$$

$$\underset{\text{Pentabromide}}{PBr_5} + 4H_2O = 5HBr + \underset{\text{Phosphoric acid}}{H_3PO_4}$$

These actions are used in the preparation of gaseous hydrobromic acid.

Iodides of phosphorus.—The chief iodide of phosphorus has the formula PI_2 or P_2I_4. It is a reddish solid which is decomposed by water with formation of red phosphorus, phosphorous acid, and hydriodic acid, for the preparation of which it is mostly employed (p. 203).

Oxygen Acids of Phosphorus

Phosphorus forms a series of oxygen acids, the chief of which are noted below, together with their formulæ and the names of their salts—

Acid		Salt
Phosphoric acid . .	H_3PO_4	Phosphate
Phosphorous acid . .	H_3PO_3	Phosphite
Hypophosphorous acid .	H_3PO_2	Hypophosphite

By far the most important of these is the most highly oxidised —namely, phosphoric acid.

Phosphoric acid.—An impure phosphoric acid is prepared from the natural calcium phosphate, or from bone ash, by decomposing these substances with sulphuric acid, in accordance with the equation—

$$\underset{\text{Calcium phosphate}}{Ca_3(PO_4)_2} + 3H_2SO_4 = \underset{\text{Phosphoric acid}}{2H_3PO_4} + \underset{\text{Calcium sulphate}}{3CaSO_4}$$

As calcium sulphate is insoluble it may be separated from the phosphoric acid, which remains in solution. To obtain pure phosphoric acid, phosphorus is oxidised by boiling with nitric acid, thus—

$$\underset{\text{Phosphorus}}{3P} + \underset{\text{Nitric acid}}{5HNO_3} + 2H_2O = \underset{\text{Phosphoric acid}}{3H_3PO_4} + \underset{\text{Nitric oxide}}{5NO}$$

The excess of nitric acid is driven off by evaporation, the heating being usually continued until the **orthophosphoric acid** (ordinary or *tribasic* phosphoric acid) is converted into **metaphosphoric acid** (glacial phosphoric acid) by loss of water.

$$\underset{\text{Orthophosphoric acid}}{H_3PO_4} = \underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O$$

Glacial phosphoric acid is a glassy mass which is often cast into the form of sticks. If metaphosphoric acid is dissolved in water and the solution boiled, it is reconverted into orthophosphoric acid—

$$\underset{\text{Metaphosphoric acid}}{HPO_3} + H_2O = \underset{\text{Orthophosphoric acid}}{H_3PO_4}$$

which may be crystallised out of the solution.

The solution obtained by dissolving phosphorus pentoxide in water is a solution of metaphosphoric acid, which may similarly be converted into orthophosphoric acid by boiling.

If orthophosphoric acid is gently heated, an acid can be obtained from it which is different from the original acid and also from metaphosphoric acid. This acid is called **pyrophosphoric acid**, and its formation may be represented by the equation—

$$\underset{\text{Orthophosphoric acid}}{2H_3PO_4} = \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7} + H_2O$$

Pyrophosphoric acid on further heating loses water and is converted into metaphosphoric acid—

$$\underset{\text{Pyrophosphoric acid}}{H_4P_2O_7} = \underset{\text{Metaphosphoric acid}}{2HPO_3} + H_2O$$

Conversely, pyrophosphoric acid is formed as an intermediate product when orthophosphoric acid is produced from metaphosphoric acid by heating with water. The equations are the reverse of those given above—namely,

$$2HPO_3 + H_2O = H_4P_2O_7$$
$$H_4P_2O_7 + H_2O = 2H_3PO_4$$

Pyrophosphoric acid is thus exactly intermediate between orthophosphoric acid and metaphosphoric acid, being converted into the former by the addition of one formula weight of water, and into the latter by the removal of one formula weight of water.

The relations of these acids are perhaps rendered most clearly evident if we consider them as consisting of water and phosphoric anhydride in different proportions. Thus we have

P_2O_5	Phosphoric anhydride
P_2O_5, H_2O or $2HPO_3$.	Metaphosphoric acid
P_2O_5, $2H_2O$ or $H_4P_2O_7$.	Pyrophosphoric acid
P_2O_5, $3H_2O$ or $2H_3PO_4$.	Orthophosphoric acid

There are two points to be noted in connection with this mode of viewing the phosphoric acids. If phosphoric anhydride, metaphosphoric, or pyrophosphoric acids are left in contact with water for a sufficient length of time, they will eventually be converted into orthophosphoric acid—*i.e.* into that form which has the maximum amount of water in its composition. On the other hand, if water is driven off from any of the phosphoric acids by heating, the ultimate product is metaphosphoric acid, and not phosphoric anhydride as we might expect. It is impossible by heating to procure phosphoric anhydride from any of the phosphoric acids.

Each of the phosphoric acids has its own salts, but, like the corresponding acids themselves, the meta and pyrophosphates pass into orthophosphates when left for a long time in contact with water, or, more rapidly, when boiled with water.

Orthophosphoric acid is a *tribasic acid*, and therefore forms three sets of salts—namely, normal salts and two sets of acid salts. We are thus acquainted with three orthophosphates of sodium—normal sodium orthophosphate, Na_3PO_4; disodium hydrogen orthophosphate, Na_2HPO_4; and sodium dihydrogen orthophosphate, NaH_2PO_4. The normal salt yields a strongly alkaline solution, the second or mon-acid salt yields a feebly alkaline solution, and the third or di-acid salt yields an acid solution. The common phosphate of soda is the mon-acid salt, Na_2HPO_4.

The action of heat on the various orthophosphates is of interest. If the base or basic oxide from which the phosphates are derived is capable of resisting heat, as sodium hydroxide is, for instance, the following rules hold good. The normal phosphate is unaffected by heat, the mon-acid phosphate is converted into a pyrophosphate, and the di-acid phosphate is converted into a metaphosphate. The equations for the sodium salts are as follows:—

$$\underset{\text{Mon-acid salt}}{2Na_2HPO_4} = \underset{\text{Pyrophosphate}}{Na_4P_2O_7} + H_2O$$

$$\underset{\text{Di-acid salt}}{NaH_2PO_4} = \underset{\text{Metaphosphate}}{NaPO_3} + H_2O$$

All the normal orthophosphates, except those of the alkalies, are practically insoluble in water. Bone ash and natural calcium phosphate are extensively used as manure to supply phosphorus to plants, without which they do not thrive. On account of its insolubility, the calcium phosphate in this form acts but slowly, so that "soluble phosphate" is often employed in its stead. This *soluble phosphate* or *superphosphate* is the di-acid calcium phosphate which, like most acid salts, is soluble in water. It is prepared from the normal phosphate by treating it with sulphuric acid, the quantities being chosen in accordance with the equation—

$$\underset{\text{Normal phosphate}}{Ca_3(PO_4)_2} + 2H_2SO_4 = \underset{\text{Soluble phosphate}}{CaH_4(PO_4)_2} + 2CaSO_4$$

The calcium sulphate being insoluble can easily be separated from the solution of superphosphate if required.

The orthophosphates can readily be distinguished from the

meta and pyrophosphates by means of the colour of the silver salts. Solutions of orthophosphates yield, with silver nitrate, a bright yellow precipitate of normal silver orthophosphate: meta and pyrophosphates, under the same conditions, give white precipitates.

Phosphorous acid, H_3PO_3.—This acid may be prepared by dissolving the oxide P_4O_6 in water, or by the action of water on the trichloride—

$$\underset{\text{Trichloride}}{PCl_3} + 3H_2O = \underset{\text{Phosphorous acid}}{H_3PO_3} + 3HCl$$

The hydrochloric acid may be driven off by heat, the phosphorous acid being obtained in the crystalline form when the solution cools. Phosphorous acid when heated undergoes decomposition. A part of it is oxidised to phosphoric acid at the expense of another part which is reduced to phosphine, thus—

$$\underset{\text{Phosphorous acid}}{4H_3PO_3} = \underset{\text{Phosphoric acid}}{3H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

In solution, phosphorous acid acts as a reducing agent, taking up an atom of oxygen, and being converted into phosphoric acid.

The **phosphites** derived from phosphorous acid are also reducing agents.

Hypophosphorous acid, H_3PO_2.—When phosphorus is boiled with an alkali, it is partially oxidised to a salt of hypophosphorous acid, and partially hydrogenised to phosphine. Thus the action of a boiling solution of caustic soda on phosphorus is represented by the equation—

$$\underset{\text{Caustic soda}}{3NaOH} + \underset{\text{Phosphorus}}{4P} + 3H_2O = \underset{\text{Sodium hypophosphite}}{3NaH_2PO_2} + \underset{\text{Phosphine}}{PH_3}$$

A solution of barium hypophosphite may be formed in the same way by boiling phosphorus with barium hydroxide solution. If the requisite quantity of sulphuric acid is added, insoluble barium sulphate is produced, from which the solution of hypophosphorous acid may be separated by filtration—

$$\underset{\text{Barium hypophosphite}}{Ba(H_2PO_2)_2} + H_2SO_4 = \underset{\text{Hypophosphorous acid}}{2H_3PO_2} + BaSO_4$$

Hypophosphorous acid decomposes like phosphorous acid when heated, forming phosphoric acid and phosphine—

$$\underset{\text{Hypophosphorous acid}}{2H_3PO_2} = \underset{\text{Phosphoric acid}}{H_3PO_4} + \underset{\text{Phosphine}}{PH_3}$$

It also resembles phosphorous acid in being a powerful reducing agent, taking up oxygen to become phosphoric acid.

Although it has as much hydrogen as phosphoric acid in its formula, only one-third is replaceable by a metal —*i.e.* it is a monobasic acid, and forms only one series of salts. Sodium hypophosphite $Na{\cdot}H_2PO_2'$, is used in medicine.

Phosphine, PH_3

We have seen that when phosphorus is boiled with an alkaline solution, and when phosphorus or hypophosphorus acid is heated, the substance phosphine PH_3 is produced. This substance, which is often called *phosphuretted hydrogen*, resembles, in some respects, sulphuretted hydrogen. Thus when passed through solutions of many metallic salts, it forms precipitates of phosphides analogous to the sulphides; and just as sulphuretted hydrogen may be prepared by decomposing sulphides by means of acids, so phosphuretted hydrogen may be made by decomposing phosphides in a similar manner. Some phosphides, like some carbides, are even decomposable by water. For example, calcium phosphide when thrown into water decomposes with evolution of phosphine (compare the action of water on calcium carbide, p. 115)—

$$\underset{\text{Calcium phosphide}}{Ca_3P_2} + 6H_2O = 3Ca(OH)_2 + \underset{\text{Phosphine}}{2PH_3}$$

Phosphine is a gas which has an unpleasant odour, and is highly poisonous. It burns readily in air or oxygen with a brilliant flame, dense fumes of phosphorus pentoxide being produced.

When phosphine is prepared by any of the methods mentioned above, it is liable to contain small quantities of another compound of phosphorus and hydrogen — namely, P_2H_4, which is usually called *liquid phosphuretted hydrogen*. Now this compound is spontaneously inflammable—*i.e.* takes fire when brought into contact with air or oxygen, even at the ordinary temperature. It therefore inflames the gaseous phosphuretted hydrogen with which it is mixed, although this substance is not itself inflammable at the ordinary temperature. This may be proved by passing the gas prepared by any of the above methods through a layer of turpentine, which dissolves the vapour of the liquid phosphuretted hydrogen, and allows the gaseous phosphine to pass on. Before being washed with the turpentine the gas is spontaneously inflammable; after washing it is so no longer.

When the unpurified gas is made to bubble slowly through water, each bubble, when it rises to the surface and comes in contact with the air, takes fire, producing white fumes in the form of a vortex ring.

Phosphine unites with gaseous hydriodic acid to form a crystalline solid, called phosphonium iodide—

$$\underset{\text{Phosphine}}{PH_3} + HI = \underset{\text{Phosphonium iodide}}{PH_4I}$$

This action may be compared with the union of ammonia and hydriodic acid to form ammonium iodide—

$$\underset{\text{Ammonia}}{NH_3} + HI = \underset{\text{Ammonium iodide}}{NH_4I}$$

Phosphonium iodide, like ammonium iodide, is a true salt, so that phosphine acts in this respect as an anhydrous base, like ammonia. Just as ammonia may be liberated from ammonium iodide by treatment with caustic soda, so pure phosphine may be liberated from phosphonium iodide in like manner—

$$PH_4I + NaOH = NaI + H_2O + PH_3$$
$$NH_4I + NaOH = NaI + H_2O + NH_3$$

Although phosphine resembles ammonia in this respect, the analogy stops here. Phosphine is scarcely soluble in water

and does not turn red litmus blue; ammonia, on the other hand, is excessively soluble, yielding a strongly alkaline solution. Phosphine is easily inflammable: ammonia will not burn in air, unless heat is constantly supplied to enable the action to take place.

Comparison of Phosphorus with Nitrogen and Sulphur

Nitrogen and phosphorus are classed together in the same family of elements. The resemblance between them is, however, by no means close, and is generally confined to a practically formal similarity in the case of a few compounds. We have, in fact, here much the same kind of relation as we found between oxygen and sulphur. The following table shows the formal resemblance which exists:—

NH_3	Ammonia	PH_3	Phosphine
NH_4I	Ammonium iodide	PH_4I	Phosphonium iodide
NCl_3	Nitrogen trichloride	PCl_3	Phosphorus trichloride
N_2O_5	Nitrogen pentoxide	P_2O_5	Phosphorus pentoxide
HNO_3	Nitric acid	HPO_3	Metaphosphoric acid

The actual differences between ammonia and phosphine have already been insisted on. Nitrogen trichloride is not decomposed by water, and is one of the most explosive compounds with which we are acquainted. Phosphorus trichloride, on the other hand, has no tendency to explode, and is at once decomposed by water. Nitrogen pentoxide decomposes when heated into the peroxide and oxygen: phosphorus pentoxide will stand the highest temperatures without decomposing. Nitric acid is a powerful oxidising agent: phosphoric acid has no oxidising properties in any of its various forms. The elements themselves, too, differ as widely in their properties as any pair of elements. Nitrogen will combine directly with oxygen only under very exceptional circumstances, and will not combine directly with chlorine at all. Phosphorus, on the other hand, combines with both of these elements at the ordinary temperature. Owing to this comparative inertness of nitrogen it is found free in nature; phosphorus, on account of its activity, is always found in the combined state.

If, now, we compare phosphorus and sulphur together,

we find that although they belong to different groups of elements and show no similarity in the formulæ of their compounds, they yet closely resemble each other in many points of their actual behaviour. Thus they are both solids, comparatively easily fusible, and capable of existing in several modifications. They are both combustible, and unite readily with chlorine and the other halogens. Their hydrogen compounds are both gaseous and give precipitates of phosphides or sulphides with many metallic salts which on treatment with acids regenerate the original hydrogen compounds. Sulphuric anhydride, SO_3, as well as phosphoric anhydride, P_2O_5, has a great tendency to combine with water, a tendency not nearly so well developed in the lower oxides, sulphurous anhydride, SO_2, and phosphorous anhydride, P_2O_3. The chlorides, both of phosphorus and of sulphur, are decomposed by contact with water.

The points of difference which should perhaps be chiefly emphasised, are the feebly marked acid character of sulphuretted hydrogen as contrasted with the very feeble basic properties of phosphuretted hydrogen, of which we have evidence in the formation of phosphonium iodide, PH_4I. Sulphuric acid, again, can be easily reduced to sulphur dioxide when it is not mixed with water; whilst phosphoric acid cannot be reduced under any circumstances to form a lower oxide.

CHAPTER XXXII

ARSENIC—ANTIMONY—BISMUTH

ARSENIC

ARSENIC is an element which belongs to the same group as phosphorus, the formulæ of corresponding compounds being the same and the properties in many cases closely similar.

Arsenic does not occur in nature in the free state, but occurs in minerals either combined with oxygen, sulphur or the metals. Thus we have the oxide *arsenite* As_2O_3, the sulphides *realgar* As_2S_2 and *orpiment* As_2S_3, *arsenical iron* $FeAs_2$ and *arsenical pyrites* FeAsS. The last-named mineral is almost invariably contained in iron pyrites FeS_2, and when this is roasted for production of sulphur dioxide the arsenic is oxidised and volatilised as the trioxide As_2O_3. This oxide is the chief source of arsenic and its compounds, and is mostly produced as a by-product in the roasting of arsenical minerals, being found in the flue-dust deposited from the hot gases passing from the roasters.

The element arsenic may be obtained from the trioxide by reduction with charcoal. The two substances are heated together in a fireclay crucible provided with an iron cap. The reaction which takes place may be expressed by the equation—

$$As_2O_3 + 3C = 2As + 3CO$$

At the temperature of the reduction the arsenic exists as a vapour which, on coming into contact with the cold iron cap, condenses to a dark grey solid of metallic appearance. When heated in absence of air arsenic sublimes without production of a liquid. In presence of air it takes fire at a temperature of about 200° and burns with a bluish flame. Arsenic exists in several modifications, in this respect resembling phosphorus and sulphur.

Oxides of Arsenic

Arsenic trioxide As_2O_3 is sometimes known as *white arsenic*. As has already been stated, it occurs in flue-dust produced in metallurgical processes, from which it may be obtained and purified by a process of sublimation. When heated it sublimes at a temperature of little over 200° without melting. When the vapour is slowly condensed at a temperature slightly below that at which the compound vaporises, it is deposited in the form of a glassy amorphous substance which, on long exposure to the air at the ordinary temperature, gradually becomes opaque owing to the formation of the crystalline trioxide. The amorphous substance is considerably more soluble in water than the crystalline variety. When the vapour is rapidly cooled it condenses in the form of small shining octahedra which may be readily recognised under a good lens or a microscope. The vapour density of arsenic trioxide corresponds to the formula As_4O_6 at low temperatures and to the formula As_2O_3 at a white heat.

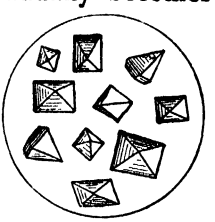


Fig. 40.

The solution of arsenic trioxide in water has a faintly acid reaction, from which it is concluded that the oxide combines with water to form an acid. This acid, **arsenious acid** H_3AsO_3, corresponds to phosphorous acid H_3PO_3, and gives rise to salts termed arsenites corresponding to the phosphites.

Arsenic trioxide dissolves much more readily in concentrated hydrochloric acid solution than it does in water. This increased solubility is, no doubt, due to the production of arsenic trichloride in the solution. It must therefore be conceded that arsenic trioxide in this respect shows some of the characters of a basic oxide, although it also readily reacts as an acidic oxide, dissolving in solutions of alkalies to form arsenites, and uniting with water to form arsenious acid. Oxides of this kind, which act as acidic oxides with regard to bases, and as basic oxides with regard to acids, are termed *amphoteric* oxides. It should be noted that the acids and bases derived from such oxides are always feeble.

Arsenic pentoxide As_2O_5 is the anhydride of the arsenic

acids just as phosphorus pentoxide P_2O_5 is the anhydride of the phosphoric acids. It cannot, however, be prepared like the phosphorus compounds by oxidation of the trioxide in air, but indirectly as follows. **Arsenic acid H_3AsO_4 is first** produced by warming the trioxide with nitric acid—

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$$

A syrupy solution is obtained from which crystals of arsenic acid deposit on cooling. These crystals when heated lose water in a manner analogous to orthophosphoric acid and give rise successively to pyroarsenic acid $H_4As_2O_7$, meta-arsenic acid $HAsO_3$ and ultimately to arsenic pentoxide As_2O_5. The last action,

$$2HAsO_3 = As_2O_5 + H_2O,$$

has nothing corresponding to it in the case of phosphorus. If the heating is prolonged at a higher temperature another action takes place which also has no analogue amongst the phosphorus compounds—namely, the decomposition of the pentoxide into trioxide and oxygen—

$$As_2O_5 = As_2O_3 + O_2$$

The arsenic acids give rise to arsenates of various types which correspond closely to the phosphates.

Arsenic and the Halogens

Arsenic combines with all the halogens, the trichloride being the most important of the compounds so produced. Unlike phosphorus, arsenic forms no pentachloride.

Arsenic trichloride $AsCl_3$ is most easily prepared by passing a current of chlorine over heated arsenic—

$$2As + 3Cl_2 = 2AsCl_3.$$

It is a colourless oily liquid which boils at 130° and emits dense white fumes when exposed to air. When brought into contact with a large amount of water it dissolves, and in the solutions are found arsenious acid and hydrochloric acid. The trichloride seems to be decomposed in much the same way as phosphorus trichloride, the decomposition in this case,

however, being only partial, so that it may be represented by the reversible equation—

$$AsCl_3 + 3H_2O \rightleftarrows 3HCl + H_3AsO_3$$

That the action is thus reversible is proved by the fact that arsenic trichloride may be produced by dissolving arsenic trioxide in concentrated hydrochloric acid.

Arsine, AsH_3

When arsenic is heated together with zinc in a closed crucible the mass melts and a substance named zinc arsenide Zn_3As_2 is produced. This substance may be decomposed by means of dilute sulphuric acid as follows :—

$$Zn_3As_2 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4$$

Arsine produced in this way is a gas of a disagreeable odour and very poisonous properties. It burns in air with a pale blue flame, producing water and arsenic trioxide, both the hydrogen and the arsenic being oxidised in the combustion. If a cold piece of porcelain, however, is held in the flame a black deposit of unoxidised arsenic is formed upon it, the hydrogen alone being burnt. If the gas is passed through a narrow tube heated by means of a Bunsen flame it is decomposed by the heat, according to the equation—

$$2AsH_3 = 3H_2 + 2As$$

and the arsenic is deposited on the cold portion of the tube as a black shining mirror.

Marsh's test for arsenic, which is excessively delicate, and is used in cases of suspected arsenic poisoning, depends upon the formation and decomposition of arsine. The solution suspected to contain arsenic is placed in a flask in which hydrogen is being generated by the action of zinc and dilute hydrochloric acid or sulphuric acid which have been proved to be free from arsenic by a previous blank experiment (fig. 41). The arsenic compound is reduced by the "nascent" hydrogen from the zinc and acid to arsine, which comes off

as gas along with hydrogen. If the mixed gases are now passed through a tube which is heated in front of the constriction S, the arsine is decomposed by heat and arsenic is deposited in the constricted part of the tube as a dark stain even although the total quantity of arsenic present may not exceed the thousandth part of a milligram. If the amount of arsenic dealt with is larger, the element produced as above may be converted into the trioxide by heating in presence of air and the characteristic octahedral crystals recognised under a microscope. With such quantities of arsenic a black deposit may generally be obtained on a piece of porcelain held in the jet of burning hydrogen from the generator.

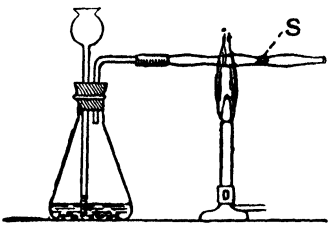


Fig. 41.

Reinsch's test.—A substance suspected to contain arsenic is mixed with a concentrated solution of hydrochloric acid, the action of which converts a portion at least of the arsenic compound into arsenic trichloride. A clean strip of metallic copper dipped into this solution becomes coated with a deposit of arsenic which is easily recognised by its dark colour. If the strip of copper is left for a long time in contact with the solution, practically all the arsenic is deposited on the copper, and thus arsenic may be detected in a solution which contains only a very small quantity of it. Once the arsenic is concentrated on the copper in this way it may be subjected to further transformation and its presence confirmed by other reactions

Sulphides of Arsenic

If sulphuretted hydrogen is passed into a solution of arsenic trichloride a bright yellow precipitate of **arsenic trisulphide** is produced—

$$2AsCl_3 + 3H_2S = As_2S_3 + 6HCl$$

This sulphide is insoluble in water and in dilute acids, but dissolves readily in solutions of the alkalies to form thio-arsenites, which have the same formula as the arsenites with the difference that a portion of the oxygen in these salts is

replaced by sulphur. Here we have evidence of a classification of sulphides analogous to that of oxides. Some sulphides, which we may call acidic sulphides, have properties analogous to the acidic oxides, reacting readily with bases and forming salts. Other sulphides have properties analogous to basic oxides, and react with acids to form salts.

If sulphuretted hydrogen is led into the colourless solution of arsenious acid, no precipitate is formed, but the solution assumes a bright yellow colour. Arsenious sulphide is formed as before, according to the equation—

$$2As(OH)_3 + 3H_2S = As_2S_3 + 3H_2O$$

The sulphide, however, remains in a state of colloidal solution. In this case the particles of the sulphide are so small that they cannot be detected by the naked eye, or by a microscope used in the ordinary way, and so small that they can easily pass through the pores of the finest filter paper. The addition of a small quantity of a good electrolyte, however, is sufficient to make these particles run together and fall out as a visible precipitate. Thus, if we add a few drops of a concentrated solution of hydrochloric acid, or sodium chloride, or calcium nitrate or any other highly ionised solution, immediate precipitation takes place. The hydrochloric acid formed from the solution of arsenic trichloride acts in this way, and so a definite precipitate is obtained when arsenic trichloride solution is brought into contact with sulphuretted hydrogen.

Besides arsenic trisulphide the disulphide, realgar, As_2S_2 is known, and also the pentasulphide As_2S_5. Arsenic pentasulphide is an acidic sulphide, readily dissolving in alkaline solutions to form thioarsenates.

ANTIMONY

The element antimony is chiefly found in nature as the mineral *antimonite* or *stibnite* Sb_2S_3, and is also found associated with arsenic in minerals. When the sulphide is heated with excess of iron the following reaction takes place :—

$$3Fe + Sb_2S_3 = 3FeS + 2Sb$$

Another method of preparation is to oxidise the sulphide by

heating in air, and to reduce the oxide thus produced by means of carbon:

$$Sb_2O_3 + 3C = 3CO + 2Sb$$

Antimony is a lustrous crystalline metal of a silvery grey colour which melts at a temperature of low redness. It does not tarnish or oxidise in air at ordinary temperatures, but when heated in air it burns with a bluish flame to form the trioxide Sb_2O_3. It is chiefly used in the production of low melting alloys, such as type metal and stereotype metal, in which it is associated with the other low melting metals, lead and tin.

The compounds of antimony resemble in many ways those of arsenic. Thus we have the hydride, **stibine** SbH_3, which may be formed from any soluble antimony compound as in Marsh's test (p. 239). Like arsine, it is decomposed by heat with production of metallic antimony, which when deposited on a piece of cold porcelain held in the flame from the Marsh's apparatus, or in the heated tube, closely resembles the corresponding deposit of arsenic. It may be distinguished from the arsenic deposit, however, by the action of a solution of bleaching powder, which readily dissolves the arsenic deposit and leaves the antimony deposit practically unaffected.

Antimony trioxide Sb_2O_3 differs from arsenic trioxide in being practically insoluble in water. It dissolves readily, however, in concentrated hydrochloric acid to form antimony trichloride $SbCl_3$. It is also readily soluble in solutions of the alkalies to form salts called antimonites, which correspond to the arsenites. The trioxide is thus, like arsenic trioxide, both acidic and basic. The basic characters, however, are much more developed than in the arsenic compound, and the acidic characters much less. Antimony trioxide may be regarded as a true basic oxide, for it not only gives rise to a chloride, but also to the sulphate $Sb_2(SO_4)_3$, and the nitrate $Sb(NO_3)_3$.

These salts of antimony are all decomposed by the action of water. If the trichloride is added to water, or if a solution of the trichloride in hydrochloric acid is largely diluted with water, nearly the whole of the antimony is precipitated in the form of the **oxychloride** SbOCl—

$$SbCl_3 + H_2O = SbOCl + 2HCl$$

This oxychloride may be redissolved in concentrated hydrochloric acid, being thereby reconverted into the trichloride, the equation for this action being the reverse of that just given. The group SbO which occurs in the oxychloride is also found in other compounds of antimony, and has received the name *antimonyl*. One of the commonest compounds of antimony which contains it is that known as **tartar emetic** or potassium antimonyl tartrate $K(SbO)C_4H_4O_6$, derived from tartaric acid $H{\cdot}_2C_4H_4O_6''$. This compound is soluble in water, and can be diluted without any precipitation occurring.

When metallic antimony is oxidised with concentrated nitric acid it is converted into the **pentoxide** Sb_2O_5, which does not dissolve in the acid. This is a purely acidic oxide entirely without basic properties, and gives rise to antimonic acid and the antimonates, which correspond to arsenic acid and the arsenates.

The two orange-yellow **sulphides** of antimony, Sb_2S_3 and Sb_2S_5, have acidic properties, and dissolve in alkaline solutions to form thioantimonites and thioantimonates respectively.

BISMUTH

This element is found in nature as the metal, as the oxide Bi_2O_3, and particularly as the sulphide Bi_2S_3. The metal is generally prepared from the sulphide by first oxidising it by heating in air and reducing the oxide so obtained by means of carbon. Bismuth is a crystalline metal of a deeper shade of grey than antimony, with a characteristic reddish tinge in addition. It melts at 270° and is almost exclusively used in the production of fusible alloys, some of which have melting-points below the temperature of boiling water—for example, *Rose's fusible metal*, which consists of 2 parts of bismuth, 1 of tin and 1 of lead, and melts at 94°. Bismuth oxidises slightly on the surface when exposed to air, and when heated in air it burns, producing the oxide Bi_2O_3.

Bismuth forms no compound with hydrogen, and only possesses basic oxides. The salts of bismuth are derived from the **trioxide** Bi_2O_3. Of these salts the chloride $BiCl_3$ and the nitrate $Bi(NO_3)_3$ are the most important. The nitrate may be readily formed by dissolving metallic bismuth in nitric acid and crystallising the solution.

These normal salts of bismuth are, like those of antimony, easily hydrolysed by water with production of insoluble basic salts. If a solution of bismuth chloride is diluted with water, practically the whole of the bismuth is taken out from solution in the form of the **oxychloride** BiOCl—

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

This oxychloride resembles that of antimony in being soluble in hydrochloric acid, but differs from it with regard to the action of tartaric acid, in which antimony oxychloride is easily soluble and bismuth oxychloride is not. The so-called "subnitrate of bismuth," which is extensively used in medicine, is a **basic nitrate** produced by adding boiling water to a concentrated solution of the normal nitrate. The decomposition is analogous to that of the chloride—

$$Bi(NO_3)_3 + H_2O \rightleftarrows BiO(NO_3) + 2HNO_3$$

Bismuth trisulphide Bi_2S_3 which is produced by adding sulphuretted hydrogen to the solution of a bismuth salt is readily distinguished from the sulphides of arsenic and antimony on account of its dark brown colour. Like the corresponding oxide, it has no acid properties, and consequently does not dissolve in solutions of the alkalies.

Oxides of bismuth having more oxygen than the trioxide Bi_2O_3 are known to exist. These oxides, however, are not salt-forming oxides, having neither acidic nor basic properties.

The Nitrogen Family of Elements

The nitrogen family of elements forms one of the best examples of a natural group and exhibits the gradual change in properties which are observed as we pass from one member to the next in the order of atomic weights. The following table gives the atomic weight, specific gravity and melting-point of the various elements constituting the group :—

	Atomic Weight	Specific Gravity	Melting-point
Nitrogen . .	14	1.0	-214°
Phosphorus. .	31	2.3	44°
Arsenic . .	75	5·7	480°
Antimony . .	120	6.6	629°
Bismuth . .	208	9.8	270°

The specific gravity given in the table is that of the densest modification when more than one exists. It will be observed that the melting-point of bismuth does not continue the regular rise shown by the other elements

The group is characterised as a whole by the elements in it acting in most of their compounds as triads or pentads. Thus we have throughout characteristic oxides of the formula E_2O_3 and E_2O_5, where E represents one atomic proportion of the various elements of the group. Other oxides than these exist in some cases—for example, N_2O, NO and NO_2. Such oxides, however, do not give rise to sets of salts, and are therefore less characteristic of the group than the salt-forming trioxides and pentoxides.

All the elements of the group, with the exception of bismuth, have trihydrides of the general formula EH_3, which are gaseous at the ordinary temperature. These hydrides exhibit considerable differences in their chemical properties. Ammonia, for example, combines readily with acids to form salts. Phosphine only combines with certain acids under special conditions; arsine and stibine do not combine with acids at all. Ammonia is the most stable of the hydrides, and the stability diminishes as the series is ascended in the order of atomic weights. Stibine SbH_3 decomposes slowly into its elements at the ordinary temperature, and in the case of bismuth the instability is so great that the compound has never been prepared.

In the series of trioxides we pass from the purely acidic oxide N_2O_3 to the purely basic oxide Bi_2O_3. The intermediate oxides As_2O_3 and Sb_2O_3 can act both as acidic and basic oxides, and it may be noted that as the series is ascended the acidic character diminishes, whilst the basic character increases. The pentoxides are throughout practically without basic properties, acting either as acidic oxides, or, in the case of bismuth, as a peroxide which is neither basic nor acidic.

From the consideration of these oxides it is evident that the transition from non-metal to metal is a gradual one. The extreme members of the family, nitrogen and bismuth, are respectively non-metallic and metallic in their properties. It is difficult to draw the line, however, between non-metal and metal when we come to the intermediate members of

the family. Phosphorus, like nitrogen, is undoubtedly a non-metal, both in its physical and chemical properties. Arsenic, on the other hand, has an appearance which might be described as metallic, and its trioxide shows a faint indication of basic properties. Antimony is distinctly a metal, both with regard to its physical characters and to the chemical properties of its trioxide. The majority of chemists now agree, in consideration of these facts, to classify arsenic with the non-metals and antimony with the metals. Yet, in view of the great similarity which exists between arsenic and antimony in their compounds, it must be conceded that the distinction between non-metal and metal is not a sharp one.

CHAPTER XXXIII

BORON AND SILICON

BORON

THE element boron occurs in nature in an oxidised state in the form of boric acid or borates which are derived from the acidic oxide B_2O_3. Boron may be prepared from this oxide by heating it with potassium or magnesium.

Boric Acid and Borates

In certain volcanic districts in Tuscany jets of steam issue from the ground and condense in part to form lagoons through which the jets make their way. The steam contains a small quantity of orthoboric acid, which is slightly volatile at the boiling-point of water. This acid dissolves in the water of the lagoons, which in the end become highly charged with it, and on evaporation yield orthoboric acid in the crystalline form. By systematic concentration of the water in the natural or artificial basins, the heat of the issuing steam being utilised to promote the evaporation, orthoboric acid is obtained from this source on a commercial scale.

Orthoboric acid, H_3BO_3, known commonly as *boric acid* or *boracic acid*, is only moderately soluble in cold water, but freely soluble in boiling water, from which it crystallises on cooling in soft pearly scales. When heated at 100° it is converted, by loss of water, into **metaboric acid** HBO_2. On further heating it loses more water to become **pyroboric acid** $H_2B_4O_7$, and finally the acid anhydride B_2O_3, which fuses to a clear liquid and sets on cooling to a transparent glass. The relationship of these various substances may be seen from the following formulæ: —

Orthoboric acid $3H_2O, B_2O_3$ . . .	H_3BO_3
Metaboric acid H_2O, B_2O_3 . . .	HBO_2
Pyroboric acid $H_2O, 2B_2O_3$ . . .	$H_2B_4O_7$

Boric acid has the characteristic property of imparting a green colour to flames, so that when a little boric acid is added to alcohol and a light is applied to the solution, the flame of the burning alcohol is tipped with green. Similarly, if the flame of a spirit lamp is held in the steam issuing from the boiling solution of boric acid it acquires a distinct greenish colour. This property of boric acid is useful in testing for the acid or its salts. Orthoboric acid has antiseptic properties, on account of which it is sometimes used as a preservative for foods and as a dressing for wounds.

The borates which occur in nature are not derived from orthoboric acid, but from acids which have lost more or less water. The native borates, which are generally those of calcium, are converted, for the most part, into sodium pyroborate, which crystallises with water to form the hydrate **borax** $Na_2B_4O_7$, $10H_2O$. Borax itself is found in an impure state in the mineral *tincal*, which occurs in India, Tibet and California in the beds of dried-up lakes. Borax is obtained from native calcium borate by boiling the mineral with sodium carbonate. Double decomposition takes place, calcium carbonate is precipitated, and sodium borate remains in solution. When the solution is evaporated crystals of borax separate out.

The solution of borax in water, notwithstanding the large proportion of acidic anhydride which the salt contains, is slightly alkaline to indicators, owing to the fact that boric acid is an excessively weak acid, so that its alkaline salts are extensively hydrolysed in solution. When borax is heated it loses its water of crystallisation and fuses to a clear mass, which, on cooling, is termed *borox glass*. This glass, on account of the large proportion of acidic oxide which it contains, is capable of combining with further quantities of basic oxide at a high temperature, and yielding glasses which are frequently brightly coloured. The formation of such coloured glasses in the form of borax beads is largely utilised in the laboratory in testing for basic oxides.

Boron Trichloride

Boron combines with the halogens to form compounds of the type BX_3. The chief of these is boron trichloride, BCl_3, which is generally prepared by the following method:—Boric

anhydride is intimately mixed with charcoal and the mixture ignited in a current of chlorine. The action which takes place may be represented by the following equation :—

$$B_2O_3 + 3C + 3Cl_2 = 2BCl_3 + 3CO$$

Boron trichloride comes off as a vapour, and may be condensed to a colourless liquid which is about half as heavy again as water and is very volatile, boiling at 18°. When boron trichloride is brought into contact with water it is decomposed with formation of boric acid and hydrochloric acid—

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl$$

SILICON

The element silicon is, after oxygen, the most abundant constituent of the earth's crust. It is not found in the elementary state in nature, but is always combined with oxygen either in the form of the acid anhydride silica SiO_2 or of the silicates derived from this anhydride. It is an element which belongs to the same family as carbon, the resemblance between the formulæ of corresponding compounds of carbon and silicon being evident in the following table :—

CH_4	CCl_4	$CHCl_3$	CO_2	C_2H_6
SiH_4	$SiCl_4$	$SiHCl_3$	SiO_2	Si_2H_6

Although the formulæ are thus analogous, the resemblance in properties between the corresponding compounds is seldom great.

Silicon and Silicon Carbide

The element silicon may be prepared by heating a mixture of powdered quartz, which consists entirely of silica, and metallic magnesium. A vigorous reaction takes place at a red heat, according to the equation—

$$2Mg + SiO_2 = 2MgO + Si$$

The magnesium oxide can be dissolved away by acid, leaving the silicon as a brown amorphous powder.

Commercial **crystalline silicon** is prepared by heating a mixture of coke and fine sand, which is an impure variety of silica, in an electric furnace to a high temperature. Reaction takes place according to the equation—

$$SiO_2 + 2C = Si + 2CO$$

The product has a dark silvery lustre, but contains a considerable amount of impurity. Silicon is not attacked by water or any acid, with the exception of hydrofluoric acid. It is attacked by alkalies, and at a high temperature unites with oxygen and with chlorine.

Carborundum.—If to the mixture of coke and sand used for the production of silicon a comparatively small quantity of sawdust and common salt are added, and if the mixture is fused in an electric resistance furnace at a higher temperature than that requisite for the production of silicon, reaction takes place with formation of silicon carbide, a compound of silicon with carbon. The equation representing the reaction is as follows:—

$$SiO_2 + 3C = \underset{\text{Silicon carbide}}{SiC} + 2CO$$

Silicon carbide or carborundum produced in this way is a crystalline solid, with a dark blue surface coloration. The pure substance, which may be obtained by the union of silicon and carbon in the electric furnace, is quite colourless. Carborundum is highly resistant to oxidation at high temperatures, and is one of the hardest substances known. It is therefore extensively used as a refractory material, and as an abrasive for grinding and polishing.

Silica, SiO_2

Silica occurs in enormous quantities in nature both in the crystalline and in the non-crystalline form. The chief crystalline variety of silica is *quartz*, which, in the form known as rock crystal, appears as a six-sided prism terminated by pyramidal faces. When pure, quartz is colourless; but coloured varieties—for example, amethyst, rose quartz and cairngorm—are frequently found. Sand and sandstone are impure varieties of quartz. Amorphous silica occurs as *opal*, which, however, contains, besides silica, a small amount of combined water. *Agate* and *flint* consist chiefly of amorphous silica intimately mixed with the crystalline variety.

Quartz is highly resistant to the action of acids but is slowly attacked by alkalies with formation of silicates. It withstands a high temperature without fusion, but in the oxyhydrogen flame or in the electric furnace it can be fused to a viscous

liquid. On cooling, this liquid sets to a clear solid glass, which differs from the original quartz in being amorphous and not crystalline. This *quartz glass* has a high temperature of fusion, and generally resists the action of chemical reagents well. It has besides a very small co-efficient of expansion, so that it may be heated or cooled suddenly without fear of cracking. Owing to these properties, it is largely used in laboratories and even in manufacturing operations as a substitute for platinum.

At high temperatures silica, acting as an acid anhydride, combines readily with bases to form silicates and will expel volatile acid anhydrides from salts containing them. Thus, if silica is fused with sodium carbonate at a bright red heat, bubbles of gas are seen to escape from the fused mass, the reaction which takes place being represented as follows:—

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$
$$2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2$$

Silicic Acids and Silicates

Silicic acid, like boric acid and carbonic acid, has very feebly acid properties. As in the case of boric acid the anhydride combines with more than one portion of water, so that we have, for example, the acid H_2O, SiO_2 or H_2SiO_3, **meta-silicic acid** and $2H_2O$, SiO_2 or H_4SiO_4, **ortho-silicic acid.**

When sodium silicate prepared by the fusion of silica with sodium carbonate is dissolved in water and the solution treated with a small quantity of hydrochloric acid, silicic acid separates out as a gelatinous mass. If, on the other hand, the solution of sodium silicate is poured into excess of dilute hydrochloric acid, no separation of silicic acid occurs, although in both instances sodium silicate is decomposed by hydrochloric acid according to the equation—

$$Na_4SiO_4 + 4HCl = 4NaCl + H_4SiO_4$$

The silicic acid which is formed in the second case remains in colloidal solution. It is still mixed with sodium chloride, which is in true solution, but it is possible to separate the two substances by the process known as dialysis.

The principle on which the process of **dialysis** is based is the following. Ordinary crystalline salts when dissolved in

water have the property of diffusing through a wet membrane, such as animal parchment or vegetable parchment paper, the membrane offering little resistance to ordinary diffusion. Substances like gelatine or glue, on the other hand, cannot pass through such a wet membrane. Graham therefore classified substances into *crystalloids* or *colloids*, according as they resembled the first or the second of these classes. Silicic acid gives colloidal solutions only, whereas sodium chloride is a typical crystalloid. If, therefore, we place the solution of these two substances on one side of the parchment membrane and pure water on the other, the sodium chloride will gradually diffuse through the membrane into the water while the silicic acid remains behind. Dialysis is commonly performed in the simple apparatus shown in fig. 42. A "sausage" of vegetable parchment contains the solution to be dialysed and is suspended in a vessel of pure water which is changed from time to time. A colloidal solution of silicic acid thus prepared sets to a jelly after a few days if it is sufficiently concentrated. When this jelly is dried by being kept over concentrated sulphuric acid, the residue which remains after all the water has evaporated has the formula H_2SiO_3, which is that of metasilicic acid. Orthosilicic acid H_4SiO_4, which is made by dehydrating the jelly to a less degree, loses water on standing in air.

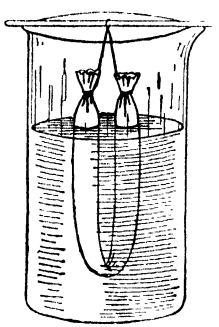


Fig. 42.

Once silicic acid has gelatinised it does not readily pass again into colloidal solution, and if dried at a temperature of 100° it is practically insoluble in water and in acids.

The **silicates** are found in nature in great variety, and may be regarded as derivatives of many different silicic acids which contain the anhydride and water in different proportions. Of these numerous acids, orthosilicic acid and metasilicic acid are two of the simplest. The only soluble silicates are those of the alkalies. The ammonium salt does not exist stably in solution, as silicic acid is too weak an acid to form a stable combination with the weak base ammonia. The silicates of sodium and potassium have a strongly alkaline reaction in

solution, owing to salt-hydrolysis with production of the strong alkali and a weak acid. Syrupy solutions of the silicates of the alkalies are sold under the name of *water glass.* These solutions are used in the preservation of buildings by filling up the pores of the stonework.

The natural silicates are practically insoluble in water. Those containing the alkaline oxides, calcium oxide, magnesium oxide and aluminium oxide in the basic portion are most numerous. Thus *lime felspar* has the composition CaO, Al_2O_3, $2SiO_2$; *kaolinite* or *china clay* is $2H_2O$, Al_2O_3, $2SiO_2$; *potash felspar* is K_2O, Al_2O_3, $6SiO_2$.

The silicates containing alkalies are liable to be attacked under the influence of the weather, and we find, for example, that potash felspar slowly loses its alkali and is converted into kaolinite.

Glass and Pottery

Glass is an amorphous mixture of silicates of potassium or sodium on the one hand and calcium or lead on the other. Thus soda lime glass, a variety of which ordinary soft glass tubing is made, may be prepared by heating together to a high temperature a mixture of sodium carbonate, calcium carbonate and fine white sand. The sodium carbonate fuses and is attacked by the silicate with expulsion of carbon dioxide. The calcium carbonate is similarly decomposed and finally a viscous mass of sodium calcium silicates is obtained, which, while soft, can be blown, rolled or moulded into any desired form, and sets on cooling to a hard clear glass. The hard Bohemian glass of which flasks, etc., are made contains potassium instead of sodium. It withstands the action of chemicals better than soft glass and requires a higher temperature to soften it. The lustrous flint glass, used for ornamental purposes, has a high refractive index and is a potash lead glass.

Pottery. — Bricks, earthenware, stoneware and porcelain contain as chief constituent anhydrous silicates of aluminium, derived from clay. Clays have the property of forming a plastic mass, when kneaded with water, which can be moulded into any desired shape. The plastic mass retains its shape on drying, and when fired at a red heat sinters together, and shrinks to a comparatively hard and porous mass. According to the purpose to which the material is to be put, the clay may

be used either in its natural condition or mixed with other siliceous substances such as flint, quartz and felspar. The porous material is frequently glazed by coating it with a silicate containing alkali, which fuses to a glass at the high temperature of the firing kiln and blocks up the superficial pores. The clays themselves are practically infusible at ordinary furnace temperatures.

Silicon and the Halogens

Silicon chloride $SiCl_4$ may be prepared by a method analogous to that adopted for boron trichloride. Finely divided silica is intimately mixed with charcoal and the mixture heated to bright redness in a current of chlorine. The following action then takes place :—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO$$

Silicon tetrachloride condenses as a colourless liquid which boils at 58° and fumes strongly in moist air, being decomposed by water with formation of silicic acid and hydrochloric acid—

$$SiCl_4 + 3H_2O = H_2SiO_3 + 4HCl$$

Silicon fluoride SiF_4 is prepared by heating a mixture of silica, calcium fluoride and sulphuric acid. The calcium fluoride and sulphuric acid generate hydrofluoric acid which attacks silica according to the equation—

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$

Silicon fluoride is a colourless gas which cannot be condensed by pressure at the ordinary temperature to the liquid state. When brought into contact with water, it decomposes with formation of silicic acid and an acid known as *fluosilicic acid* (or *hydrofluosilicic acid*). The equation representing this reaction may be written as follows :—

$$3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$$

The solution of fluosilicic acid may be separated from the silicic acid by filtration. When neutralised, it gives rise to well-defined fluosilicates, such as potassium fluosilicate K_2SiF_6.

CHAPTER XXXIV

THE PERIODIC CLASSIFICATION OF THE ELEMENTS

We have seen in the preceding sections that the elements may sometimes be grouped together in natural families, the members of which resemble one another more or less closely. The halogens afford an example of such a natural family, and we find another in the nitrogen, phosphorus, arsenic group. A general mode of classification of the elements in which this grouping into natural families is well brought out is that known as the periodic classification, in which the elements are arranged in the order of their atomic weights. The Table on p. 256 shows the elements thus arranged.

Beginning with the element helium (He = 4) the Table is read in rows from left to right. In the horizontal rows elements of the most diverse character are found, but in the vertical columns the elements are plainly related to each other with regard to their chemical properties, each column usually containing two natural families, which are distinguished from each other in the Table by the symbols being written to left and right of the atomic weights respectively.

For example, all the elements of the first column are inert gases like argon. In the first group of the second column we find the metals of the alkalies, including the rare elements rubidium and cæsium. The second group of the second column is constituted by the elements copper, silver and gold. In the third column we find the metals of the alkaline earths; in the sixth column the nitrogen group; in the eighth column the halogens, and so on.

It thus appears that as we run through the atomic weights in succession we come back periodically and in a regular way to elements of the same natural family, and hence the arrangement has been termed the periodic classification. The periodic character is specially well marked from the quantitative point of view when we consider the capacity of the elements to combine with oxygen. Taking the second

TABLE OF THE PERIODIC SYSTEM

The members of the same family of elements have their symbols arranged vertically

0	I	II	III	IV	V	VI	VII	VIII
He 4	Li 7	Gl 9	11 B	12 C	14 N	16 O	19 F	
Ne 20	Na 23	Mg 24.3	27 Al	28 Si	31 P	32 S	35.5 Cl	
Ar 39.9	K 39 63.6 Cu	Ca 40 65.3 Zn	Sc 44 70 Ga	Ti 48 72.5 Ge	V 51 75 As	Cr 52 79.2 Se	Mn 55 80 Br	Fe 56, Co 59, Ni 58.7
Kr 83	Rb 85.4 108 Ag	Sr 87.6 112.4 Cd	Y 89 115 In	Zr 90.6 119 Sn	Cb 93.5 120 Sb	Mo 96 127.5 Te	. 127 I	Ru 102, Rh 103, Pd 107
Xe 130	Cs 133 197 Au	Ba 137.4 200.6 Hg	La 139 204 Tl	Ce 140 * 207 Pb	Ta 181.5 208 Bi	W 184		Os 191, Ir 193, Pt 195
Nt 222.5	..	Ra 226.5	.	Th 232.5		U 238.5		

* In the gap between Cerium and Tantalum occur metals of the rare earths, which are not here classified.

horizontal row, for example, and considering the salt-forming oxides, we obtain the following series:—

$$Na_2O \quad MgO \quad Al_2O_3 \quad SiO_2 \quad P_2O_5 \quad SO_3 \quad Cl_2O_7;$$

or, referring the formulæ always to two atoms of the element—

$$Na_2O \quad Mg_2O_2 \quad Al_2O_3 \quad Si_2O_4 \quad P_2O_5 \quad S_2O_6 \quad Cl_2O_7$$

The *combining capacity* or *valence* of the elements with regard to oxygen thus increases with perfect regularity; and we find in general that the valence for oxygen is the same in any vertical column. In the first column the valence is zero, since the elements contained in it form no compounds. In the second column the valence is 1, and so on. With regard to compounds with other elements than oxygen there are similar regularities of valence, and it is not unusual to speak of the elements of the first column as being non-valent, those of the second as univalent or monad, those of the third as bivalent or dyad, etc. It will be observed that the chemical valence as here displayed coincides with the electrical valence (or capacity for combining with electricity) as given for the positive radicals in the Table on p. 129.

The periodic character of the elements with regard to any single property which can be numerically determined may be shown by means of a curve. Thus, if we plot the specific gravity of the solid elements against their atomic weights we obtain the curve of fig. 43. Here the curve plainly falls into waves or periods, similar elements occupying similar positions in the successive waves, which correspond to the horizontal sections of the Table on p. 256.

Certain irregularities in the periodic system are apparent. For example, hydrogen finds no suitable place in it; argon and potassium, tellurium and iodine must be interchanged in order to bring them into their proper position with regard to other elements of the same family, and it is now generally recognised that the position of an element in the periodic table is not governed entirely by the numerical value of its atomic weight.

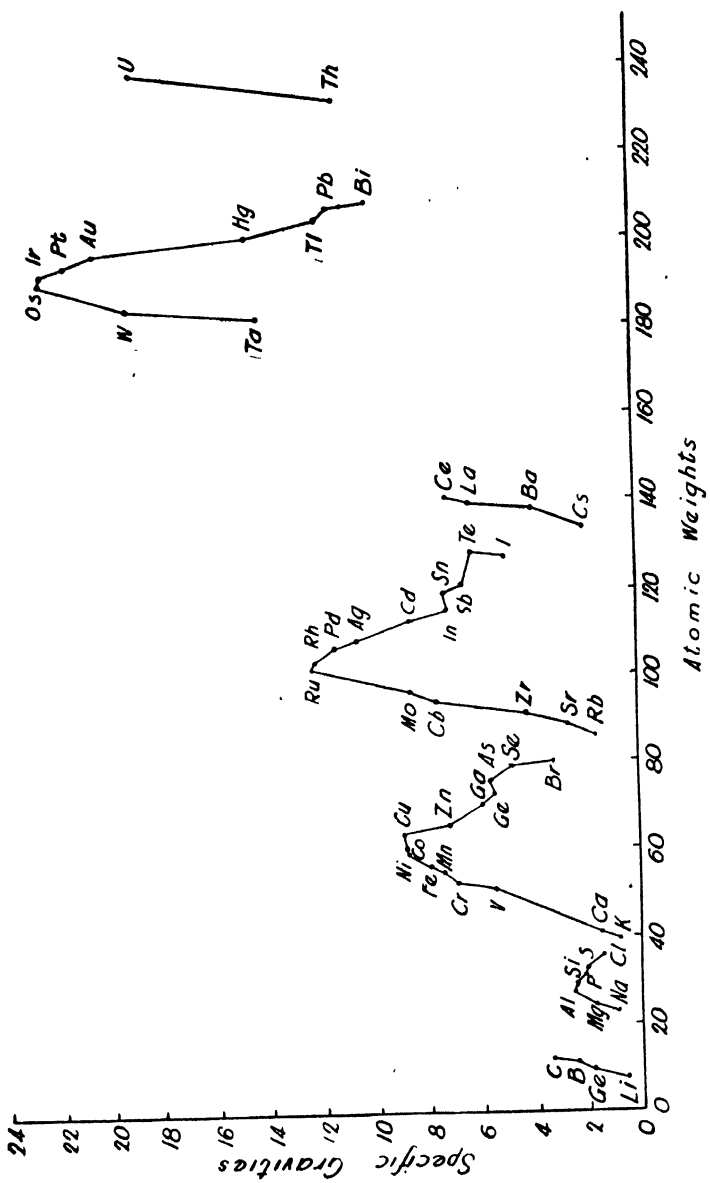

Specific Gravities
Atomic Weights
0
2
4
6
8
10
12
14
16
18
20
22
24
0
20
40
60
80
100
120
140
160
180
200
220
240
Li
Ge
B
C
Mg
Na
Al
Si
P
S
Cl
K
Ca
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Rb
Sr
Zr
Cb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Cs
Ba
La
Ce
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U

Fig. 43.

CHAPTER XXXV

SODIUM—POTASSIUM—AMMONIUM

SODIUM

PRACTICALLY all the sodium compounds are made from *sodium chloride*, which occurs abundantly in sea water, in brine springs, and in some places as solid *rock salt*. It has already been indicated that by electrolysing a solution of sodium chloride, both chlorine and sodium hydroxide may be produced. This electrolytic process is coming into extensive use as a source of sodium hydroxide, and of the sodium carbonates which are derived from sodium hydroxide by treatment with carbon dioxide, according to the equations—

$$NaOH + CO_2 = \underset{\text{Sodium hydrogen carbonate}}{NaHCO_3}$$

$$2NaOH + CO_2 = \underset{\text{Sodium carbonate}}{Na_2CO_3} + H_2O$$

There are two other methods still in use, however, for obtaining carbonates of sodium from sodium chloride. The oldest of these is called the **Leblanc process**, and the chemical actions involved are the following:—First, the sodium chloride is converted into sodium sulphate by the action of sulphuric acid, which, as we have already seen, occurs in the following two stages, the acid sulphate being first produced:—

$$NaCl + H_2SO_4 = \underset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + HCl$$

$$NaCl + NaHSO_4 = \underset{\text{Sodium sulphate}}{Na_2SO_4} + HCl$$

The normal sodium sulphate thus obtained is reduced by means of carbon at a high temperature with production of sodium sulphide.

$$Na_2SO_4 + 2C = Na_2S + 2CO_2$$

Limestone is added to the mixture of sulphate and carbon, so that at the same time we have the reaction—

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS$$

When the product of the reaction is treated with water, impure sodium carbonate is dissolved away from the calcium sulphide, and is then subjected to various processes of purification. The still somewhat impure sodium carbonate which has not been purified by crystallising, but merely by roasting, is called *soda ash.* When the sodium carbonate is recrystallised, it separates out as the decahydrate $Na_2CO_3,10H_2O$, which is familiarly known as *washing soda.*

Another process, by which sodium hydrogen carbonate is prepared, is also much employed. This is called the **ammonia soda process,** and is based on the following action:—When ammonium hydrogen carbonate and sodium chloride are brought together in concentrated solution, the following decomposition may take place:—

$$(NH_4)HCO_3 + NaCl = NaHCO_3 + NH_4Cl$$

In dilute solution all these salts would remain dissolved, but when very little water is present the least soluble of the four—namely, sodium hydrogen carbonate—falls out. In practice this action is brought about by taking strong brine, saturating it first with ammonia gas, and then leading carbon dioxide through it until the sodium hydrogen carbonate falls out.

Sodium hydrogen carbonate, $NaHCO_3$ usually called *bicarbonate of soda* or *baking soda,* decomposes when heated at a comparatively low temperature, according to the equation—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

so that the **normal carbonate,** Na_2CO_3, can easily be prepared from it. Normal sodium carbonate does not lose carbon dioxide even at a red heat.

Practically all sodium compounds are made either during the manufacture of the hydroxide and carbonates, or are prepared by the action of acids on the hydroxide or carbonates.

Thus **sodium sulphate,** Na_2SO_4, is produced in the Leblanc process in the commercial form known as *salt cake.*

When this is dissolved in water and the solution crystallised the decahydrate $Na_2SO_4,10H_2O$ separates out. This hydrate is known as *Glauber's salt.*

Sodium hydroxide or *caustic soda*, NaOH, can be made from the carbonate by treating its solution with calcium hydroxide, when double decomposition occurs, according to the equation—

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

The soluble sodium hydroxide is separated from the insoluble calcium carbonate and the solution is evaporated. In order that this reaction may take place, it is necessary that the solution should not be too concentrated, otherwise the reaction proceeds to a certain extent in the reverse direction—namely,

$$CaCO_3 + 2NaOH = Na_2CO_3 + Ca(OH)_2$$

On driving off the water from a solution of caustic soda, the sodium hydroxide does not separate out in the crystalline state, but remains fused as the temperature rises. The fused caustic soda is usually cast into sticks for laboratory purposes. Sodium hydroxide readily absorbs both moisture and carbon dioxide from the air, is excessively soluble in water, and very strongly alkaline. It is not decomposed by heat at any temperature.

Metallic sodium is prepared from sodium hydroxide either by electrolysis of the fused hydroxide, when the sodium travels to the cathode and is there separated as the fused metal, or by reduction at a high temperature by the carbon of iron carbide:

$$6NaOH + 2C = 2Na_2CO_3 + 3H_2 + 2Na$$

The metallic sodium is in the state of vapour, so that it comes off with the hydrogen and is condensed in iron tubes to a liquid, which afterwards solidifies.

Sodium, though a metal, is lighter than water and so soft that it can easily be cut with a knife. A freshly cut surface has a bright, silver-white appearance, but it immediately tarnishes on exposure to air, being attacked by the moisture and the carbon dioxide of the air. When thrown into water, even at the ordinary temperature, it at once attacks the water

with formation of sodium hydroxide and evolution of hydrogen, according to the equation—

$$2Na + 2H_2O = 2NaOH + H_2$$

The temperature of the reaction often rises so high that the hydrogen takes fire and burns with a yellow flame, due to the presence of sodium vapour. All sodium compounds when heated to a high temperature impart this characteristic yellow colour to a flame.

When sodium is heated in air it takes fire and burns with a bright yellow flame, not to form, as we might expect, the basic oxide Na_2O, but **sodium peroxide** Na_2O_2. As we have seen, this sodium peroxide is really a salt of the feeble acid hydrogen peroxide H_2O_2, which can be readily obtained from it by the action of dilute acids (p. 102). Sodium peroxide is now prepared on the commercial scale as a bleaching agent, and is much used for general oxidising purposes.

Sodium nitrate, $NaNO_3$, otherwise known as *Chili saltpetre*, occurs in quantity in the rainless districts of Chili and Peru. It is used, not as a source of sodium, but as a source of nitrates and nitric acid. It is much employed as a manure, being a convenient source of nitrogen for plants.

POTASSIUM

Potassium compounds were formerly prepared almost exclusively from wood ashes, which contain a large proportion of potassium carbonate, but nearly all potassium compounds have recently been derived from the salt deposits at Stassfurt, near Magdeburg, in Prussia. These deposits have been formed by the evaporation of sea water under peculiar conditions, the sodium chloride having apparently crystallised out first, and the other salts, which occur in smaller quantity in water, being then deposited separately. These salts are chiefly magnesium salts and potassium salts. Potassium chloride, as the mineral *sylvite*, is present in comparatively small quantity, the chief source of potassium compounds being a double chloride of potassium and magnesium called *carnallite*, which has the composition $KCl,MgCl_2,6H_2O$. As potassium chloride is less soluble than magnesium chloride, this salt by proper treatment with water may be made to yield crystals of potassium chloride.

Just as all the compounds of sodium are derived from sodium chloride, the corresponding compounds of potassium may be

produced by similar processes from potassium chloride, with the exception that potassium hydrogen carbonate cannot be produced from potassium chloride by a process analogous to the ammonia soda process.

When plants are burned, the ash which they leave behind contains a large proportion of potassium carbonate K_2CO_3. This substance does not exist as such in the plants, but is derived from the decomposition of potassium salts of complex organic acids, which are contained in them. These salts are necessary for all vegetable life, so that potassium salts must be present in the soil in which plants grow. On a natural soil, where the plants decay in the same place as that on which they develop, the potassium salts in the plants return to the soil. Where, however, a succession of crops is grown on the same soil and removed year after year, the land gets poorer and poorer in potassium salts, which must then be replaced by adding potassium in some form. A potassium compound, which is much used as a manure to supply potash to plants, is the Stassfurt mineral *kainite* $KCl,MgSO_4,3H_2O$.

Potassium carbonate, K_2CO_3, used to be derived almost entirely from wood ashes, and the name, *pot ashes*, being applied to the crude carbonate in a certain form, is the origin of the terms potash and potassium. Potassium carbonate is now chiefly made by a process analogous to the Le Blanc process for the manufacture of sodium carbonate. From it potassium hydrogen carbonate $KHCO_3$ can be prepared by the action of carbon dioxide, and potassium hydroxide KOH can be prepared by the action of calcium hydroxide.

Potassium nitrate, KNO_3, which is chiefly used in the production of gunpowder, is now mostly prepared by the double decomposition of potassium chloride and sodium nitrate. The sodium nitrate itself cannot be used in the manufacture of gunpowder, because it is slightly hygroscopic, so that in gunpowder it would attract moisture, and thus make the powder damp. Potassium nitrate is not hygroscopic, and gunpowder containing it remains quite dry when exposed to the air. The double decomposition between sodium nitrate and potassium chloride is carried out at a somewhat high temperature, the result being that sodium chloride, which is in these circumstances the least soluble salt, first falls out and leaves excess of

potassium nitrate in the solution. On cooling this potassium nitrate crystallises. Reference to the curves on p. 15 shows that whilst at a high temperature potassium nitrate is much more soluble than sodium chloride, at a low temperature this is not the case.

The metal **potassium** can be formed by the electrolysis of fused potassium hydroxide, but not so readily as sodium can be formed by the electrolysis of fused sodium hydroxide. Like sodium, it is a soft very light metal which immediately tarnishes in air and attacks water with great vigour, according to the equation—

$$2K + 2H_2O = 2KOH + H_2$$

The temperature of the reaction is so high that the hydrogen is inflamed, burning with the lavender flame characteristic of all potassium compounds.

The corresponding salts of potassium and sodium resemble each other in appearance and properties very closely, the principal difference between them being in their solubility. In nearly all cases potassium or sodium salts may be used indiscriminately for chemical purposes; although, as a matter of practice, sodium salts are usually preferred to potassium salts on account of their much smaller cost. Occasionally, of course, it happens that a slight difference in solubility, or attraction for moisture, may render it necessary to employ a potassium salt instead of a sodium salt. An instance of this has just been given in the case of gunpowder.

AMMONIUM

The resemblance between potassium salts and ammonium salts, except in their behaviour towards heat, is extremely close, much closer, in fact, than the resemblance of potassium salts to sodium salts. This resemblance exists in spite of the fact that the potassium salts contain a metal, and the ammonium salts contain no metal, but a compound radical or group NH_4, the constituents of which are gases in the free state.

It has already been stated that the source of ammonium compounds is ammonia derived from the distillation of coal for the purpose of producing coal gas. The ammonia gas is absorbed in water, in which it is extremely soluble, forming the *ammoniacal liquor* of the gas works, which, when distilled with

lime gives off ammonia gas in a purer form, which can then be reabsorbed by sulphuric acid, according to the equation—

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

The crude **ammonium sulphate**, $(NH_4)_2SO_4$, is heated to destroy some tarry material with which it is mixed, and then purified by crystallisation. It is extensively used as a manure for supplying nitrogen to the soil, in a form which plants can assimilate.

Ammonium carbonate is prepared by heating a mixture of ammonium sulphate and calcium carbonate in the form of chalk. When this mixture is heated, gases come off which condense again to form a white solid substance, which, however, is not pure normal ammonium carbonate $(NH_4)_2CO_3$, but a mixture of *ammonium hydrogen carbonate* $(NH_4)HCO_3$, and a substance called *ammonium carbamate* $(NH_4)CO_2NH_2$. This mixture behaves practically in aqueous solution as ammonium carbonate, and is generally known by that name.

Ammonium chloride, NH_4Cl, is prepared by absorbing ammonia gas from the ammoniacal liquor of the gasworks in hydrochloric acid instead of in sulphuric acid. These substances combine, according to the equation—

$$NH_3 + HCl = NH_4Cl$$

The ammonium chloride, or *sal ammoniac*, which is thus obtained, is first heated gently to destroy tarry material, and then purified by sublimation. When perfectly dry, ammonium chloride on heating passes into ammonium chloride vapour. When the ammonium chloride, however, is not absolutely dry, it dissociates on vaporisation into ammonia and hydrochloric acid. These gases, at the high temperature necessary for the sublimation, may exist side by side without combining. When the mixture is cooled, however, the gases recombine, with reproduction of ammonium chloride.

The **radical ammonium**, NH_4, has never been isolated, and it is doubtful if it has any existence apart from the negative radicals with which it is combined in salts.

Ammonium salts, like sodium and potassium salts, are all soluble in water, the actual solubilities resembling those of the corresponding potassium compounds rather than those of

the corresponding sodium compounds. When ammonium salts are heated, however, they undergo decompositions unlike any decomposition which can take place with similar potassium or sodium salts. The essence of this decomposition is that the ammonium radical splits up with production of ammonia gas, when the acid radical is a non-oxidising radical; and with production of nitrogen, or an oxide of nitrogen, when the acid radical is an oxidising radical. Thus, if we heat ammonium phosphate, we obtain ammonia gas and phosphoric acid, which remains as a non-volatile residue, the equation being—

$$\begin{aligned}(NH_4)_3PO_4 &= 3NH_3 + H_3PO_4 \\ &= 3NH_3 + H_2O + HPO_3\end{aligned}$$

The phosphate radical here has no oxidising power. When we heat ammonium nitrite or ammonium nitrate, on the other hand, which contain the oxidising nitrite and nitrate radicals, we obtain no ammonia gas, but in the first case nitrogen, and in the second case nitrogen monoxide, according to the equations—

$$\begin{aligned}NH_4NO_2 &= N_2 + 2H_2O \\ NH_4NO_3 &= N_2O + 2H_2O\end{aligned}$$

When the acid, as well as the ammonia, is volatile, both acid and ammonia come off together, and condense on cooling to form the original ammonium salt. An example of this has just been given in the case of ammonium chloride.

CHAPTER XXXVI

METALS OF THE ALKALINE EARTHS

CALCIUM

CALCIUM occurs in nature chiefly as *carbonate* $CaCO_3$, and to a smaller extent as *sulphate* $CaSO_4$ and *phosphate* $Ca_3(PO_4)_2$. An account of calcium carbonate has been given in the introductory chapter, and it need only be repeated here that calcium carbonate is chemically valuable on account of the ease with which it can be converted into the powerful basic **calcium oxide** CaO, which unites with water to give the powerful though not very soluble base **calcium hydroxide** $Ca(OH)_2$.

Calcium sulphate occurs in nature chiefly as the hydrate $CaSO_4,2H_2O$. Like the carbonate, this substance has various forms. When opaque it is known as *gypsum* and as *alabaster*, when transparent and distinctly crystalline like calc-spar it is known as *selenite*. When gypsum is heated to a temperature somewhat below 200° it parts with three-fourths of its water of crystallisation, and is converted into the lower hydrate $2CaSO_4,H_2O$. This hydrate has the property of taking up water again at the ordinary temperature to form the original gypsum. It is therefore much employed under the name of *plaster of Paris* for making plaster casts. It is ground to a fine powder, and then mixed with water to a stiff paste, which may be forced into moulds while it is still soft. It then gradually hardens and sets to a mass of what is practically gypsum, all the details of the mould being reproduced.

Calcium phosphate, $Ca_3(PO_4)_2$, is chiefly useful as a source of phosphoric acid and phosphorus (Chapter XXXI.), and not on account of the calcium which it contains.

Calcium chloride is the commonest soluble salt of calcium. It is obtained as a bye-product in many chemical manufactures, the calcium which it contains being derived originally from

limestone or chalk, and the chlorine which it contains being derived originally from sodium chloride. It may be readily prepared by dissolving calcium carbonate in hydrochloric acid, and crystallising the solution. The crystals which separate have the formula $CaCl_2,6H_2O$. These, when heated to a high temperature, lose their water of crystallisation, and yield anhydrous calcium chloride $CaCl_2$, which on account of the ease with which it absorbs moisture is much used as an agent for drying gases, and those liquids in which it is insoluble. When exposed to the air both the anhydrous calcium chloride and the hydrated chloride absorb moisture, and ultimately produce a solution of calcium chloride.

Calcium carbide, CaC_2, used in the production of acetylene, is prepared by heating lime and coal-slack to a very high temperature in the electric furnace—

$$CaO + 3C = CaC_2 + 3CO$$

Metallic calcium is now manufactured by the electrolysis of fused calcium chloride. It attacks water briskly at the ordinary temperature with liberation of hydrogen.

When metallic calcium is warmed in a current of dry hydrogen, it absorbs the gas and is converted into **calcium hydride** CaH_2, a solid which is decomposed on contact with water, yielding a large volume of hydrogen—

$$\underset{42\,\text{g.}}{CaH_2} + 2H_2O = Ca(OH)_2 + \underset{44.8\ \text{litres}}{2H_2}$$

On this account the substance has been used for the inflation of balloons and airships.

BARIUM

Barium is an element which closely resembles calcium, both in its mode of occurrence, and in its general chemical properties. Its compounds are not, however, nearly so widely distributed as those of calcium, and only occur in comparatively small quantities. It is found chiefly as the sulphate *heavy spar* $BaSO_4$, and as the carbonate *witherite* $BaCO_3$.

Most barium compounds are made from the natural sulphate. As this substance is almost perfectly insoluble in water, it must be converted into a soluble form before it can be transformed into other barium compounds (compare p. 183). The barium

sulphate is reduced by means of carbon at a high temperature, the equation being—

$$BaSO_4 + 4C = BaS + 4CO$$

The barium sulphide thus produced is soluble in water, and can be converted into other barium compounds by means of the appropriate acids.

Thus, if it is desired to prepare barium chloride, which is the soluble salt of barium mostly in use, the sulphide or the carbonate may be decomposed by hydrochloric acid, according to the equations—

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$$
$$BaS + 2HCl = BaCl_2 + H_2S$$

The **barium chloride** thereby produced may be crystallised out of the solution on evaporation in the form of the dihydrate $BaCl_2,2H_2O$, which is not nearly so soluble as calcium chloride, and is not deliquescent.

Barium hydroxide, $Ba(OH)_2$, may be prepared on the large scale by passing carbon dioxide and superheated steam over barium sulphide. Barium carbonate is probably first formed according to the equation—

$$BaS + H_2O + CO_2 = BaCO_3 + H_2S$$

and then decomposed by the superheated steam as follows:—

$$BaCO_3 + H_2O = Ba(OH)_2 + CO_2$$

the carbon dioxide being swept off in the current of steam. Barium hydroxide is more soluble in water than calcium hydroxide, and the saturated solution called *baryta water* is often used instead of lime-water in testing for, and in estimating, the amount of carbon dioxide in air. When it is brought into contact with carbon dioxide, barium carbonate is immediately formed, according to the equation—

$$Ba(OH)_2 + CO_2 = \underline{BaCO_3} + H_2O$$

and separates out as a precipitate.

Both barium hydroxide and barium carbonate resist the action of heat more strongly than the corresponding calcium compounds—that is, they may be heated to redness without

decomposition into barium oxide and water or carbon dioxide. If it is desired to prepare **barium oxide**, this is best done by heating the carbonate, not alone, but with carbon, when the following action takes places :—

$$BaCO_3 + C = BaO + 2CO$$

The carbon of the carbonate is here got rid of, not as carbon dioxide, as is the case with calcium, but as carbon monoxide. Barium oxide, like calcium oxide, combines very readily with water to form barium hydroxide. When heated in air it absorbs oxygen, with formation of **barium dioxide** BaO_2.

STRONTIUM

The metal strontium has an atomic weight intermediate between those of calcium and barium. Like them, it occurs in nature as the carbonate $SrCO_3$ *strontianite* and the sulphate $SrSO_4$ *celestine*. The properties of its compounds closely resemble those of the corresponding compounds of calcium and barium.

If we consider in what points calcium, strontium and barium resemble each other in their compounds, we find first of all that the compounds have similiar formulæ. Not only, however, is there this formal resemblance, but also a real resemblance in chemical properties. Thus the carbonates and the sulphates are nearly insoluble in water. The oxides unite very readily with carbon dioxide, and with water; but as has already been mentioned, the resulting carbonate and hydroxide are much less easily decomposed in the case of barium than in the case of calcium and strontium. The hydroxides are sparingly soluble in water, and the solutions which they form are strongly alkaline. To distinguish them from the metals of the alkalies which give freely soluble hydroxides, these elements are generally called metals of the alkaline earths.

MAGNESIUM

Magnesium is an element which occurs in the combined state on a very large scale in nature. Many of the natural silicates contain magnesium; for example, *talc*, *asbestos*, *serpentine* and *meerschaum*. Some of these are characterised

by being unctuous to the touch. Magnesium also occurs abundantly as magnesium carbonate, *magnesite*, $MgCO_3$, and more especially as the double carbonate of calcium and magnesium, *dolomite*, $CaCO_3,MgCO_3$. These minerals are insoluble or very sparingly soluble, but magnesium in the form of soluble salts, such as the chloride and sulphate, occurs in large quantities in sea water, and also in saline springs. Magnesium is associated with potassium in the minerals of the Stassfurt salt deposits, for example, *carnallite*, $KCl,MgCl_2,6H_2O$. The metal being comparatively readily acted on by water does not occur in nature.

Metallic magnesium is readily obtained by the electrolysis of a mixture of potassium and magnesium chlorides which may be obtained by driving off the water from carnallite. It burns in air to magnesium oxide with a brilliant bluish flame very rich in actinic rays, for which reason magnesium is largely used in flashlight photography.

Magnesium oxide, MgO, may be prepared by heating the carbonate, which decomposes much more easily than calcium carbonate into the basic oxide and carbon dioxide. The oxide, when brought into contact with water, unites with it somewhat slowly, yielding **magnesium hydroxide**, $Mg(OH)_2$, which is very sparingly soluble, but yields a solution which is alkaline to indicators.

The common soluble salts of magnesium are **magnesium chloride**, $MgCl_2,6H_2O$, and **magnesium sulphate** or *Epsom salts*, $MgSO_4,7H_2O$. These salts have a somewhat bitter taste to which the slight bitterness of sea water is due.

When sodium carbonate is added to a soluble salt of magnesium the white precipitate which is obtained does not consist of the normal carbonate, $MgCO_3$, but of a **basic carbonate** which has the composition $3MgCO_3,Mg(OH)_2,3H_2O$. This basic carbonate may be obtained in two forms known respectively as the light and heavy carbonates of magnesia, the first being prepared by precipitation in cold dilute solution, and the second by precipitation in hot concentrated solution. On heating, these carbonates give respectively a light and heavy variety of magnesium oxide or *calcined magnesia*. All of these substances are used in medicine.

Magnesium ammonium phosphate, $Mg(NH_4)PO_4,6H_2O$, has long been known as a sparingly soluble salt of magnesium,

the precipitation of which is useful in testing for magnesium and in removing it from solutions.

It will be seen from the above that magnesium compounds resemble those of calcium, strontium and barium to a considerable extent, but there are noteworthy points of difference amongst which the following may be mentioned. Although combining with water, magnesium oxide cannot be "slaked" by the addition of water as is the case with the alkaline earths proper. The carbonate which is precipitated by sodium carbonate is not the normal but a basic carbonate: in the case of calcium, strontium and barium, it is always the normal carbonate which is precipitated. The most striking difference perhaps is exhibited by the sulphates which are nearly insoluble in the case of the alkaline earths proper, but in the case of magnesium, easily soluble. In the above respects magnesium resembles zinc rather than the metals of the alkaline earths, although in other properties it is more nearly allied to the latter. There is thus a certain doubt as to whether magnesium should appear in the alkaline earth sub-group of the dyad elements in the period classification, or in the zinc sub-group.

RADIUM

The metal radium is undoubtedly a member of the alkaline earth sub-group, its compounds closely resembling those of barium in their ordinary properties. Radium compounds, however, differ from those of the other alkaline earths by emitting intensely active radiations, a brief account of which is given in Chapter XLV.

CHAPTER XXXVII

SILVER—COPPER—MERCURY

SILVER

SILVER is a metal which occurs in considerable quantity free in nature. It is generally found, however, not as the metal, but in combination with sulphur as *silver sulphide* Ag_2S.

The silver may be extracted from silver sulphide in many ways, of which the following is an example. The crushed silver ore is ground in mills with mercury and water, which contains a little salt in solution. The silver sulphide is slowly attacked by the mercury with formation of metallic silver and mercuric sulphide, according to the equation—

$$Ag_2S + Hg = HgS + 2Ag$$

Since a considerable excess of mercury is used, the silver which is liberated dissolves in the liquid quicksilver and forms what is called a silver amalgam (p. 279). The process is hence known as the *amalgamation process* for extracting silver. At the end of the reaction the mercury which contains the silver is run off from the other products and subjected to distillation in retorts. The mercury being volatile distils off, and metallic silver remains behind.

A large amount of silver is now extracted from argentiferous lead. A great many lead ores, which consist chiefly of lead sulphide, PbS, contain considerable quantities of silver sulphide, and in the process of getting lead from lead sulphide, the silver sulphide is at the same time converted into metallic silver, which dissolves in the lead. Several processes are in vogue for recovering this silver from the lead,

and an account of one of them will be given in the next chapter.

Silver is a white metal, very soft and very tough, so that it can be easily drawn into wire or beaten into foil. It is unaffected by any of the atmospheric gases, except by the sulphuretted hydrogen which is found in towns where coal is burned. This gas tarnishes a silver surface owing to the production of black silver sulphide.

Silver is so soft that it is practically impossible to employ it in the pure state for the production of ornaments or coins. In order to give it the requisite amount of hardness, it must be *alloyed* or mixed with some other metal, usually copper. The ordinary silver coinage of Great Britain consists of

Silver	92·5%
Copper	7·5%

Pure metallic silver does not readily combine with oxygen at any temperature (p. 52), nor can it be made to decompose water. Hydrochloric acid and dilute sulphuric acid are also practically without action on it. It is easily dissolved, however, by nitric acid and by concentrated sulphuric acid with formation of silver nitrate and silver sulphate respectively.

The chief soluble silver salt is **silver nitrate**, $AgNO_3$, which is also known under the name of *lunar caustic*. From it most of the other silver compounds are prepared by precipitation.

If we wish, for example, to prepare **silver oxide**, Ag_2O, we can do so by adding a solution of sodium hydroxide to a solution of silver nitrate. A brown precipitate falls out, which is sometimes said to be **silver hydroxide**. It is doubtful, however, if the brown substance is really the hydroxide. At all events, it very readily loses water and becomes converted into silver oxide, the equations representing these reactions being—

$$AgNO_3 + NaOH = AgOH + NaNO_3$$
$$2AgOH = Ag_2O + H_2O$$

The silver oxide thus prepared parts with its oxygen on

heating, and becomes metallic silver according to the equation—

$$2Ag_2O = 4Ag + O_2$$

When brought into contact with hydrogen peroxide (p. 103) it decomposes in a similar manner, the equation in this case being—

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2$$

The **halogen salts of silver**—namely, *silver chloride*, AgCl, *silver bromide*, AgBr, and *silver iodide*, AgI—are all insoluble in water, and are usually prepared by precipitating a solution of silver nitrate by means of sodium chloride, bromide, or iodide. Silver chloride is a pure white substance; the bromide and iodide are pale yellow in appearance. All of these halogen salts of silver are affected by light, assuming a dark violet tint when exposed to light for a sufficient length of time and being more easily reduced to metallic silver. Owing to their sensibility to light they are employed in photography, the sensitive substance in most photographic plates being silver bromide.

Although the soluble salts of silver are colourless, many of the insoluble compounds of silver are coloured. Thus silver oxide or hydroxide is brown, silver sulphide black, silver iodide yellow, silver phosphate yellow, silver arsenate brown, silver chromate crimson, and so on. On this account silver salts, which are mostly insoluble, are very often used in distinguishing the different salt radicals from each other.

COPPER

Metallic copper occurs free in nature in the neighbourhood of Lake Superior, but most of the copper found in commerce is produced either from *copper sulphide* Cu_2S, or from *copper pyrites* $CuFeS_2$, which is a double sulphide of copper and iron. The ordinary process adopted in this country for the extraction of copper from copper pyrites is a somewhat complicated

one, and cannot be described here. There is, however, a very simple wet process in use for extracting copper from poor ores. When moist copper sulphide is left in the air, the oxygen of the air converts the insoluble copper sulphide into soluble copper sulphate. This may then be dissolved out in water, and the solution may be made to yield metallic copper by the addition of scrap iron, according to the equation—

$$CuSO_4 + Fe = FeSO_4 + Cu$$

The precipitated copper is afterwards melted and refined.

Metallic copper in the pure or nearly pure state is used as a conductor of electricity. Copper, however, is mostly employed in the production of copper alloys. Thus *brass* contains about two-thirds copper and one-third zinc; *German silver* contains about two-thirds copper, the other components being zinc and nickel; *bronze* contains copper along with tin and sometimes zinc; our bronze coinage, for example, contains 95% of copper, with 4% of tin and 1% of zinc.

Copper is easily distinguished from other metals by its warm red colour. It is not attacked at the ordinary temperature by oxygen which is free from carbon dioxide, nor is it attacked at any temperature by water; but when exposed for a long time to air, it becomes covered with a green incrustation of basic copper carbonate by the joint action of the oxygen, moisture and carbon dioxide in the air. Although still a comparatively soft metal, copper is considerably harder than silver.

It will not dissolve in dilute sulphuric acid, but when heated with concentrated sulphuric acid it produces copper sulphate and sulphur dioxide according to the equation—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$

At the same time some of the sulphuric acid is reduced still further, so that the mixture rapidly becomes black from formation of copper sulphide. Copper is readily attacked by nitric acid, the copper being converted into copper nitrate, and the nitric acid reduced for the most part to nitric oxide, the equation being—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Copper forms two sets of salts, the *cupric salts* with the

radical $Cu^{\cdot\cdot}$, which are the ordinary salts of copper, and the *cuprous salts*, with the radical $Cu^{\cdot}$, which are comparatively rarely met with.

The most common copper salt is bluestone or **blue vitriol**, $CuSO_4,5H_2O$. This substance can be made by dissolving copper in oil of vitriol, and crystallising the copper sulphate thus produced from water; or it can also be made, as has already been indicated above, by the action of atmospheric oxygen on the natural sulphide. It crystallises in large blue crystals, and is moderately soluble in water. When heated to 100°, it loses four-fifths of its water of crystallisation, but only parts with the remaining fifth when the temperature rises to about 200°.

The **nitrate** can be prepared by dissolving copper in nitric acid. The solution thus obtained deposits blue crystals with the formula $Cu(NO_3)_2,3H_2O$. These crystals are deliquescent, and when heated leave a black residue of cupric oxide CuO.

Cupric chloride is easily prepared by heating cupric oxide with hydrochloric acid, and allowing the solution to crystallise. The chloride separates in the form of green crystals, having the formula $CuCl_2,2H_2O$.

A concentrated solution of cupric chloride is green, but when diluted with water it becomes blue like the other soluble cupric salts.

Cuprous chloride, CuCl, can be readily procured by boiling cupric chloride and concentrated hydrochloric acid with metallic copper, the reaction which takes place being represented by the equation—

$$CuCl_2 + Cu = 2CuCl$$

The solution obtained in this way is brown in colour, but when poured into a large quantity of water it deposits a white precipitate. This white precipitate consists of cuprous chloride, which is insoluble in water, though soluble in concentrated hydrochloric acid. A solution of cuprous chloride in hydrochloric acid is frequently employed in gas analysis for absorbing carbon monoxide, which it readily dissolves.

Corresponding to the two sets of copper salts we have two oxides of copper, **cupric oxide**, CuO, and **cuprous oxide**, Cu_2O. We have already seen that cupric oxide can be made by heating copper nitrate. Cuprous oxide is easily produced as a bright

red precipitate when a solution of copper sulphate is boiled with glucose and excess of caustic alkali. The glucose serves to reduce the copper from the cupric to the cuprous state. When copper is heated in the air both of these oxides are formed. The ordinary copper scale produced on copper in this way is cupric oxide on the outside and cuprous oxide in the interior.

When sodium hydroxide is added to a soluble cupric salt, a blue precipitate of **cupric hydroxide** is obtained according to the equation—

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4$$

When the liquid containing this precipitate is heated to the boiling point, the cupric hydroxide loses water, and becomes black from formation of cupric oxide—

$$Cu(OH)_2 = CuO + H_2O$$

Soluble copper salts give deep blue solutions when ammonia is added to them in excess, the production of which is one of the most characteristic tests for copper compounds.

Basic carbonates of copper are found as minerals in nature. They have either a blue or green colour, the most valuable varieties being known as *malachite* and *azurite*. The blue precipitate obtained by adding sodium carbonate to copper sulphate solution is also a basic carbonate.

Cuprous sulphide, Cu_2S, occurs in large quantity in nature, and is one of the chief ores of copper. **Cupric sulphide,** CuS, which also occurs in nature, but in much smaller quantity, can be easily prepared in the laboratory as a black precipitate by passing sulphuretted hydrogen through a solution of a cupric salt—

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

MERCURY

Mercury or quicksilver, which presents absolutely no physical resemblance to metallic copper and belongs to a different natural family, is yet very similar to copper in many of its chemical actions. Metallic copper is a red, moderately hard metal of high melting point; mercury is a pure white metal, which is liquid even at the ordinary temperature. Mercury, like copper, occurs in small quantity in the metallic state, but it is chiefly found in the form of mercuric sulphide, HgS, which is commonly known as *cinnabar*. The

extraction of metallic mercury from cinnabar is a very simple affair. The mercuric sulphide is roasted in kilns in an adequate supply of air. The sulphur is converted into gaseous sulphur dioxide, and the metallic mercury comes off as vapour at the high temperature generated by the combustion. The mercury vapour is cooled and condensed in large chambers or in aludels (fig. 42) to liquid mercury, which may then be purified, first by squeezing through wash leather, and, finally, by distillation.

Fig. 44.—Aludels for Condensing Mercury.

These aludels are earthenware vessels, which are used in long series, the stem of each fitting into the neck of its successor.

Mercury, which, when sufficiently cooled, is a hard crystalline metal, melts at $-39°$, and boils at 360°, the molecular formula of the vapour being Hg. It is used, on account of its being liquid through so great a range of temperature, for filling thermometers, and also in the construction of barometers and many other scientific instruments. Its chief practical use, however, is in the extraction of silver and gold by amalgamation processes. The "silver" on the back of mirrors is sometimes an alloy of tin and mercury, or tin amalgam, the alloys of mercury being always called *amalgams*.

Mercury is not attacked by air at the ordinary temperature, and retains its bright surface permanently. It has already been stated that when heated in air for a long time at its boiling point it gradually combines with oxygen to produce mercuric oxide, HgO, which, however, easily splits up again into its elements on further heating. Mercury does not decompose water at any temperature. It does not dissolve in hydrochloric acid, or in dilute sulphuric acid. Like copper, it forms two sets of salts, *mercurous* salts, with the radical Hg', and *mercuric* salts, with the radical Hg''.

When heated with concentrated sulphuric acid, it behaves like copper, forming **mercuric sulphate** and sulphur dioxide, according to the equation—

$$Hg + 2H_2SO_4 = HgSO_4 + 2H_2O + SO_2$$

It also dissolves readily in nitric acid. When the nitric

acid is warm and dilute, **mercurous nitrate** is produced in accordance with the equation—

$$3Hg + 4HNO_3 = 3HgNO_3 + NO + 2H_2O$$

When the nitric acid is more concentrated, **mercuric nitrate** is produced according to the equation—

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 2NO + 4H_2O$$

The dilute nitric acid thus oxidises the metallic mercury to the mercurous state of oxidation, whilst the hot concentrated nitric acid oxidises it further to the mercuric stage.

Both the nitrates of mercury are easily soluble in water containing a little nitric acid, but when they are treated with pure water, they decompose with formation of a quantity of insoluble basic nitrates and liberation of nitric acid. The solutions of mercuric or mercurous nitrate, therefore, which are used in the laboratory always contain a considerable quantity of free nitric acid.

The two chlorides of mercury are the commonest mercury compounds. **Mercuric chloride**, $HgCl_2$, is prepared by dissolving metallic mercury in concentrated sulphuric acid, evaporating the mercuric sulphate thus obtained to dryness, and then distilling it with common salt. Double decomposition takes place according to the equation—

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

and the mercuric chloride, being the most volatile of the substances concerned in this reaction, distils off, leaving a residue of sodium sulphate. The mercuric chloride vapour condenses to a crystalline mass which can readily be purified further by sublimation. On account of the ease with which mercuric chloride can be sublimed it is frequently known by the name of *corrosive sublimate*.

Mercuric chloride is easily soluble in boiling water, but not very soluble in cold water. It is a very poisonous substance, and can only be administered as a drug in small doses.

Mercurous chloride, HgCl (or, as it is sometimes written, Hg_2Cl_2), is prepared by adding metallic mercury to the

mixture of common salt and mercuric sulphate before subliming.

$$HgSO_4 + 2NaCl + Hg = 2HgCl + Na_2SO_4$$

When mercuric chloride and mercury are vaporised together, the vapours on cooling combine to produce mercurous chloride, which again is largely dissociated into mercuric chloride and mercury on resublimation.

$$HgCl_2 + Hg \rightleftarrows 2HgCl$$

Mercurous chloride or *calomel* produced in this way is usually in the form of an amorphous powder which is practically insoluble in water and in dilute acids. Like mercuric chloride, calomel is also used in medicine, but on account of its not being nearly so soluble it may be administered in much larger doses.

When sodium hydroxide is added to a soluble mercuric salt, a yellowish precipitate of **mercuric hydroxide** is obtained, which on drying leaves a red residue of **mercuric oxide**, HgO. This oxide, when heated, decomposes, as we have already seen, into metallic mercury and oxygen. When sodium hydroxide is added to a solution of a mercurous salt, a black precipitate is obtained which is supposed to consist of **mercurous oxide**, Hg_2O. This substance, however, if it exists, is very readily decomposed into mercuric oxide and mercury.

$$Hg_2O = HgO + Hg$$

Mercury sulphide, HgS, is not only found in nature as the red mineral *cinnabar*, but is manufactured on a large scale and used as a red pigment under the name of *vermilion*. When precipitated from a solution of a mercuric salt it is black.

Mercury salts behave in a peculiar way when treated with a solution of ammonium hydroxide. In general, if a hydroxide is precipitated from a solution of a metallic salt by sodium hydroxide, the same precipitate is obtained when ammonium hydroxide is used as precipitant. In the case of mercury, however, it is quite different. If a solution of ammonia is added to a mercuric salt, a white precipitate is produced, instead of the reddish yellow precipitate which is obtained with sodium hydroxide. This **white precipitate** contains mercury,

but no longer as the positive radical. The mercuric mercury has replaced some of the hydrogen in the ammonium radical, so that the white precipitate contains a complex positive radical into which mercury, nitrogen, and hydrogen enter. The formula of the chloride is usually represented as $(NH_2Hg)\cdot Cl'$. When ammonia solution is added to a mercurous salt, a black precipitate is formed. This precipitate is not mercurous oxide or hydroxide, but again contains a complex ammoniacal positive radical.

The oxidation of a mercurous to a mercuric salt can easily be effected by strong nitric acid, and a mercuric salt can be easily reduced to a mercurous salt by means of stannous chloride.

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$$

This reaction is made use of in testing for mercury. When stannous chloride is added to the solution of the mercuric salt, a white precipitate of mercurous chloride is immediately obtained, which may afterwards become grey by further reduction to minute globules of metallic mercury.

It will be seen from what has preceded, that there is considerable resemblance between silver, copper, and mercury in their chemical properties. The metals themselves have no action on water at any temperature, and are not attacked by hydrochloric or dilute sulphuric acid. They all dissolve, however, in concentrated sulphuric acid and in nitric acid. Silver forms only one set of salts, copper and mercury each forms two sets; and the similarity that there is between silver compounds on the one hand, and copper or mercury compounds on the other, exists between the silver salts and the less oxidised salts of the copper or mercury. Thus, while cupric chloride and mercuric chloride are soluble in water, cuprous chloride and mercurous chloride are, like silver chloride, quite insoluble in water. The same holds good for many other mercurous and cuprous compounds.

CHAPTER XXXVIII

GOLD AND PLATINUM

GOLD

GOLD is found almost entirely in the metallic state in nature, although a compound with tellurium is worked as a gold ore in Western Australia. The principal supplies of gold come from South Africa, Western North America and Australia. In gold mining larger particles of gold are separated from the quartz and other rocks with which they may be associated, by taking advantage of their high specific gravity, in virtue of which it is possible to wash away the specifically lighter rock particles from the crushed ore without carrying off the particles of gold which are about eight times denser. Gold may also be extracted by dissolving it in mercury, or by acting upon it chemically, and converting it into a soluble gold compound. The reagents employed for the last-named process are either chlorine in aqueous solution, which extracts it as chlorauric acid $HAuCl_4$, or else potassium cyanide in presence of the oxygen of the air, which reacts as follows :—

$$4Au + 8NaCN + O_2 + 2H_2O = 4NaAu(CN)_2 + 4NaOH$$

Chlorauric acid and sodium gold cyanide are easily soluble in water, and from the solutions so obtained gold may readily be precipitated by the action of a reducing agent or of a metal, usually zinc.

Gold is a yellow metal of specific gravity nearly 20. It is exceedingly malleable and ductile, so that it can be readily beaten into gold leaf which is so thin as to transmit a light of greenish or bluish colour when held between the eye and the source of light. It is so soft that for use it is generally alloyed with silver or copper in order to harden it. Gold resists the action of ordinary acids, but dissolves readily in a mixture of nitric and hydrochloric acids, the so-called *aqua regia*. The nitric acid of this mixture oxidises hydrochloric acid with production of chlorine, which together with the remaining

hydrochloric acid attacks gold according to the following equation:—

$$2Au + 3Cl_2 + 2HCl = 2HAuCl_4$$

The **chlorauric acid** thus produced has definite salts, of which the sodium salt $NaAuCl_4$ is largely used in photography for gold toning. Both the acid and the salts are sold under the name of *gold chloride*.

Colloidal solutions of gold may be readily prepared by reducing dilute solutions of gold chloride by means of almost any neutral or faintly alkaline reducing agent. The pale yellow solution of the chloride under such circumstances assumes a ruby-red, purple or blue colour, the particular colour obtained depending on the conditions of the reduction. Many of these colloidal solutions of gold are very stable, whilst others gradually become turbid, and deposit minute particles of gold.

PLATINUM

Platinum, like gold, occurs almost entirely in the metallic state in nature, chiefly in the Ural Mountains. It resembles gold in many of its properties. Thus it has a very high specific gravity, its density being greater even than that of gold—namely, 21.5. It is not oxidised by heating in air at any temperature. It resists the action of all acids with the exception of aqua regia, and it forms compounds, the chemical properties of which are closely analogous to those of the corresponding compounds of gold. It differs from gold in one important particular—namely, that its melting point lies at 1755° instead of being 1063°, as is the case with gold. This property enables it to withstand the temperature of all coal-gas and air flames without fusion, and thus renders it very useful for many physical and chemical purposes.

When dissolved in aqua regia it is converted into **chloroplatinic acid**, H_2PtCl_6, which is commonly called *platinum chloride*. This acid has definite salts corresponding to it, and of these the potassium salt K_2PtCl_6 may be noted as being one of the few very sparingly soluble of salts of potassium. Platinum compounds, like gold compounds, are all easily decomposed by heat, with production of the metal.

Platinum is remarkably efficacious in promoting the catalysis of many reactions between gases. This action is most strongly evident when the platinum is finely divided, so as to expose a great surface to the gas to which it is exposed. An example of this catalytic action has already been noted in the commercial oxidation of sulphur dioxide to sulphur trioxide by means of air (p. 211).

Platinum, like gold, can be obtained in colloidal solution; most readily by passing electrical sparks between two platinum wires held close together in pure water. The colloidal solution is brown, and exhibits the catalytic activity of the metal itself.

CHAPTER XXXIX

TIN—LEAD

TIN

METALLIC tin is scarcely ever met with in the free state in nature. It almost invariably occurs oxidised in the form of *tin-stone*, which is more or less pure tin dioxide, SnO_2.

After a mechanical treatment and a preliminary roasting in air to get rid of impurities, the tin-stone is heated in a reverberatory furnace (compare fig. 45) along with powdered coal, which takes the oxygen of the tin dioxide and liberates metallic tin, the equations for the action being—

$$SnO_2 + 2C = Sn + 2CO$$
$$SnO_2 + C = Sn + CO_2$$

Tin is a pure white metal which generally has a marked crystalline structure. At the ordinary temperature it is very malleable, and can easily be rolled into the thin sheet known as *tin-foil*. Its melting point is only a little above 200°. Metallic tin resists the action of air at the ordinary temperature, but it can scarcely be used in the pure state for the manufacture of utensils or boxes on account of its comparatively high cost. When a perfectly clean plate of iron, however, is dipped into molten tin, the tin will adhere to it, and cover it with a uniform coating, which protects it from the action of the air which otherwise would rust the iron. This iron, with a covering of tin, is what we know as *tin-plate*, and is the material of which "tin" cans, etc., are made.

Tin is a constituent of many alloys—such as *solder* and *pewter*, which are alloys of tin and lead—and *gun metal* and *bronze*, which are alloys of tin and copper.

Tin, although not acted upon by air at the ordinary temperature, combines readily enough with oxygen when heated. Thus, if a piece of tin-foil is held in a bunsen flame it will melt, and at the same time oxidise with pro-

duction of copious white fumes of tin dioxide, the equation for the combustion of tin being—

$$Sn + O_2 = SnO_2$$

Tin does not decompose water at a boiling heat, but if steam is passed over red-hot metallic tin, hydrogen is produced according to the equation—

$$Sn + 2H_2O = SnO_2 + 2H_2$$

In accordance with this power to decompose water, metallic tin decomposes hydrochloric and sulphuric acids at the ordinary temperature with production of hydrogen—

$$Sn + 2HCl = SnCl_2 + H_2$$

Tin is not dissolved by nitric acid, but is oxidised to an insoluble white powder called **metastannic acid**, the equation for the formation of which is—

$$3Sn + 4HNO_3 + H_2O = 3H_2SnO_3 + 4NO$$

The chief soluble compounds of tin are stannous chloride $SnCl_2$, and stannic chloride $SnCl_4$.

Stannous chloride, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid, the chloride crystallising out as $SnCl_2,2H_2O$, when the concentrated solution is cooled. Stannous chloride is a reducing agent, and a solution of it on exposure to the air absorbs oxygen. This oxidation may be prevented by adding some hydrochloric acid to the solution and keeping it in contact with metallic tin.

Examples of the reducing action of stannous chloride have already been given (p. 173), the reduction of mercuric chloride to mercurous chloride (p. 282) being the most characteristic, and one frequently used as a test for tin in the form of stannous salt.

Pure **stannic chloride**, $SnCl_4$, may be obtained by heating metallic tin in a current of dry chlorine, the formation taking place according to the equation—

$$Sn + 2Cl_2 = SnCl_4$$

A solution of stannic chloride is prepared by heating metallic tin with a mixture of hydrochloric and nitric acids, the nitric

acid serving to oxidise the tin from the stannous to the stannic stage of oxidation.

Stannic chloride has none of the characteristics of a salt. It is a liquid boiling at a temperature not much above that of the boiling point of water, and is easily decomposed by alkalies and even water, with formation of the corresponding hydroxide—

$$SnCl_4 + 4H_2O = Sn(OH)_4 + 4HCl$$

This hydroxide is scarcely a base but rather a very feeble acid, being generally known as **stannic acid.**

Stannous sulphide, SnS, and **stannic sulphide,** SnS_2, may be formed by the action of sulphuretted hydrogen on the corresponding chlorides, thus—

$$SnCl_2 + H_2S = SnS + 2HCl$$
$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

The former is a brown and the latter a yellow precipitate. Stannic sulphide prepared in the dry way in the form of golden-yellow scales is called "mosaic gold."

LEAD

Metallic lead occurs in excessively small quantities in nature. It is chiefly met with when in the form of sulphide, and occasionally in the form of carbonate or sulphate.

The mineral *galena* or lead sulphide, PbS, is by far the most important ore of lead, and nearly all commercial lead is prepared from it. The preparation of metallic lead from lead sulphide consists first in the partial oxidation in a reverberatory furnace of the lead sulphide to lead oxide and lead sulphate. These compounds are then reduced by fusing them with the unoxidised lead sulphide, which contains the reducing element sulphur. The equations for the actions are as follows. First there are the two equations of oxidation—

$$PbS + 2O_2 = PbSO_4$$
$$2PbS + 3O_2 = 2PbO + 2SO_2$$

Then there are the two equations of reduction—

$$PbSO_4 + PbS = 2Pb + 2SO_2$$
$$2PbO + PbS = 3Pb + SO_2$$

Sulphur dioxide is the only other product besides metallic lead.

It was stated under the heading of silver that most lead ores contain a small quantity of silver ores, and that the silver ultimately finds its way into the metallic lead. It is profitable in many cases to extract the silver from lead, and various processes have been devised for this extraction.

One of the simplest of these is *Pattinson's process*, which takes advantage of the fact that the first solid which separates

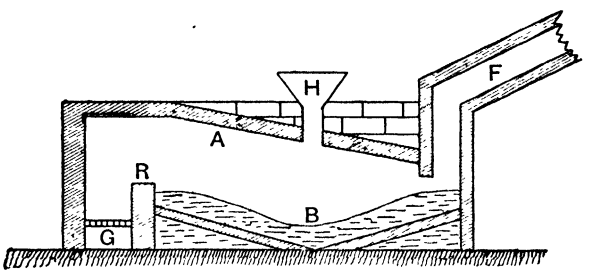


Fig. 45—Reverberatory Furnace for Leading-smelting.

In a reverberatory furnace the fuel is burned on a grate *G*, and is separated from the bed of the furnace *B*, on which the chemical process takes place, by a bridge *R*. The flames and hot gases from the fire strike the roof *A* and are reflected or "reverberated" back on the bed of the furnace, which in this case is hollowed out to collect the molten lead. The gases pass off by the flue *F*. *H* is a hopper to introduce the ore, here lead sulphide.

out from a molten mixture of lead and silver is pure lead. If, therefore, a considerable proportion of the molten argentiferous lead is allowed to solidify, and is then removed, nearly all the silver remains in the liquid residue. By systematically carrying out this separation the silver may be concentrated in a comparatively small quantity of lead. This rich lead is then subjected to a process called **cupellation**. Cupellation consists in the oxidation of metallic lead to lead oxide by heating the molten lead to bright redness in air. The skin of oxide which forms on the surface of the molten metal is soaked up by a porous bone-ash hearth or *cupel*, in which the molten lead is contained. A fresh surface of lead is thus exposed, and this in turn becomes oxidised. The oxide is again absorbed: and so the process goes on until all the lead has been removed, and the metal which remains is pure silver.

Metallic lead is chiefly useful on account of its softness and easy fusibility. It can be readily formed into wire or pipe by squirting the soft metal through a steel die, and can also be rolled into sheet lead, which may be beaten into the shape of any object which it may be desirable to line or cover with it. Metallic lead does not decompose water alone, although it does so in presence of oxygen; and is not attacked by hydrochloric acid or dilute sulphuric acid. Even concentrated sulphuric acid attacks metallic lead only slowly, so that lead vessels are very often employed on the large scale in operations where sulphuric acid is used. Nitric acid dissolves lead with production of lead nitrate.

Lead nitrate, $Pb(NO_3)_2$, and **lead acetate**, $Pb(C_2H_3O_2)_2$, are the commonest soluble salts of lead. The former may be made by dissolving metallic lead in nitric acid, and the latter is made by dissolving lead monoxide in acetic acid.

When sodium hydroxide is added to a soluble lead salt a white precipitate of **lead hydroxide** is produced.

$$Pb(NO_3)_2 + 2NaOH = Pb(OH)_2 + 2NaNO_3$$

This precipitate when heated loses water, and a residue of lead monoxide or **litharge**, PbO, remains. This oxide can be produced directly by heating lead in air—*e.g.* during cupellation. It has no tendency to give up oxygen on further heating, but rather absorbs oxygen from the air and is converted into the oxide Pb_3O_4—

$$6PbO + O_2 = 2Pb_3O_4$$

This oxide is an important one, for when properly prepared it forms the pigment known as *red lead.*

Red lead, Pb_3O_4, is not a basic oxide, and no series of salts corresponds to it. When it is treated with nitric acid it behaves as if it were a mixture of lead monoxide, PbO, and lead dioxide, PbO_2. The lead monoxide dissolves in the nitric acid with production of lead nitrate—

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$$

and the lead dioxide, or lead peroxide as it is usually called, remains as a black residue.

Lead dioxide, PbO_2, has very feebly basic properties. Owing to its reluctance to act as a basic oxide, lead dioxide

does not dissolve readily in acids, and in particular is quite insoluble in nitric acid. When warmed with hydrochloric acid it acts like manganese dioxide (p. 184), yielding lead chloride and chlorine.

When hydrochloric acid or a soluble chloride is added to a soluble salt of lead, a white precipitate of **lead chloride**, $PbCl_2$, is immediately formed. This chloride is very sparingly soluble in cold water, but dissolves readily in boiling water, from which it is re-precipitated in crystalline scales on cooling.

When a soluble sulphate is added to a lead salt, a white precipitate of **lead sulphate**, $PbSO_4$, is obtained. It is almost insoluble in water, but dissolves in concentrated sulphuric acid.

Normal **lead carbonate**, $PbCO_3$, occurs in nature as the mineral *cerussite*, and can also be prepared by precipitating a solution of lead acetate with ammonium carbonate. If sodium carbonate is used to precipitate a solution of a lead salt, a basic carbonate is produced, the composition of which varies. A basic carbonate of lead having the composition $2PbCO_3$, $Pb(OH)_2$, is very extensively used as a pigment, and is known as **white lead**.

Lead sulphide, PbS, not only occurs as galena, but can easily be formed by precipitating any soluble lead salt with sulphuretted hydrogen. Both the natural and precipitated varieties are black.

Tin and lead belong to the same natural family and are the chief metallic representatives of the tetrad group of which the important non-metallic elements are carbon and silicon.

CHAPTER XL

ZINC—ALUMINIUM

ZINC

ZINC does not occur in nature in the metallic state, but occurs chiefly as *zinc blende*, which is the sulphide ZnS, or as *calamine*, which is the carbonate $ZnCO_3$. The production of metallic zinc from these ores is very simple. The sulphide and carbonate are first heated strongly in the air, and converted into zinc oxide, the equations for the roasting being—

$$2ZnS + 3O_2 = 2ZnO + 2SO_2$$
$$ZnCO_3 = ZnO + CO_2$$

The zinc oxide obtained in this way is then heated in long fireclay retorts, together with carbon in the form of coal (fig. 46). The carbon reduces the zinc oxide to metallic zinc—

$$ZnO + C = Zn + CO$$

which, at the temperature of the reaction, is above its boiling point. The zinc, therefore, comes off as vapour, and is condensed in iron tubes attached to the open end of the long fireclay retorts.

Zinc is a metal which in many ways resembles tin. It can be distinguished from tin, however, by its bluish colour. It melts below a red heat, and at the ordinary temperature is not attacked by air or by water. When heated in air it burns with production of zinc oxide ZnO. This may be seen by holding a strip of zinc foil in the bunsen flame, the zinc oxide which is produced appearing as copious white fumes.

When water in the form of steam is passed over heated zinc, it is decomposed with evolution of hydrogen.

$$Zn + H_2O = ZnO + H_2$$

Zinc, like tin, is often used to form a protective coating for iron. The iron to be protected is carefully cleaned and then

dipped into a bath of molten zinc. The zinc adheres to the clean iron surface and protects it from the action of the air. Iron which has been treated in this way is called *galvanised iron*, although no galvanic action is used in its production.

Zinc dissolves readily in all acids, hydrogen being evolved with hydrochloric acid or dilute sulphuric acid. The soluble salts of zinc can thus be easily made by dissolving the metal in the appropriate acid. The most common of soluble zinc salts is **zinc sulphate** or zinc vitriol, $ZnSO_4,7H_2O$. This substance may be made on the large scale by roasting zinc sulphide at a carefully regulated temperature. The sulphide combines with oxygen, according to the equation—

$$ZnS + 2O_2 = ZnSO_4$$

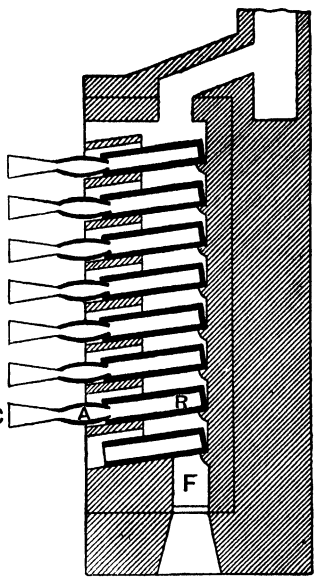


Fig. 46.—Retort for Reduction of Zinc Oxide.

The oxide and carbon are heated together in the fireclay retorts *R*, which are attached by means of the adapters *A* to the iron condensers *C*, which project beyond the furnace used for heating the retorts. The fuel is burnt on the grid F.

and the zinc sulphate thus produced may be dissolved in water and purified by recrystallisation.

When sodium hydroxide is added to a solution of zinc sulphate, a white precipitate of **zinc hydroxide** is produced—

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

This hydroxide readily dissolves in excess of sodium hydroxide to form sodium zincate Na_2ZnO_2—

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

Zinc oxide produced by heating the hydroxide, or by burning zinc in air, which is the method adopted for its commercial production, is a pure white substance which has the characteristic property of becoming bright yellow on heating. On

being cooled it regains its pure white colour. It is employed as a pigment under the name of *zinc white.*

When a solution of sodium carbonate is added to a soluble zinc salt, a white precipitate of **basic zinc carbonate** is produced.

Although the zinc blende which occurs in nature is almost invariably coloured black by admixture with ferrous sulphide, pure **zinc sulphide** is colourless. It may be produced as a white precipitate by adding a solution of an alkaline sulphide to a soluble zinc salt—

$$ZnSO_4 + Na_2S = ZnS + Na_2SO_4$$

Zinc chloride, $ZnCl_2$, is prepared by dissolving zinc oxide or metallic zinc in hydrochloric acid. Its concentrated solution has a very caustic action, and will dissolve paper or cotton. It is usually cast in the form of sticks, which have a remarkable attraction for water, and are frequently used for removing traces of water in certain chemical actions.

ALUMINIUM

Aluminium is a metal which never occurs in the free state in nature. It is always found in the oxidised condition, chiefly in the form of silicate. *China clay* or kaolin is a very nearly pure hydrogen aluminium silicate. Ordinary *clay* consists chiefly of hydrous aluminium silicate, but contains silicates of iron and other metals which give it its colour. Clays which contain much iron have a red colour; china clay is colourless; while pipeclay contains very little iron and is almost without colour. *Fireclay* consists of ordinary clay incorporated with silica.

Aluminium oxide or **alumina**, Al_2O_3, is a very hard substance, the pure mineral being termed *corundum.* An impure variety of corundum is largely used on account of its hardness as a polishing powder under the name of *emery.* Some precious stones, such as *sapphire* and *ruby*, consists of nearly pure alumina. A mineral known as *bauxite*, which contains about two-thirds of its weight of alumina, has recently attained importance as a source of the metal aluminium.

In order to prepare **metallic aluminium** from bauxite, the

mineral is first fused with sodium carbonate, when sodium aluminate is formed, according to the equation—

$$3Na_2CO_3 + Al_2O_3 = \underset{\text{Sodium aluminate}}{2Na_3AlO_3} + 3CO_2$$

This being a sodium salt is soluble in water, and the aluminium may thus be removed from iron and other impurities which remain behind in the form of insoluble oxides. By passing carbon dioxide into the solution of sodium aluminate, the aluminium may be precipitated as aluminium hydroxide, decomposition occurring according to the equation—

$$2Na_3AlO_3 + 3CO_2 + 3H_2O = 2Al(OH)_3 + 3Na_2CO_3$$

This aluminium hydroxide is then heated to convert it into oxide—

$$2Al(OH)_3 = Al_2O_3 + 3H_2O$$

When the aluminium oxide thus obtained is dissolved in fused cryolite, Na_3AlF_6, and a current of electricity is passed through the fused material, electrolysis takes place, metallic aluminium being liberated at the cathode, and oxygen being discharged at the anode. At the high temperature of the electric furnace the metallic aluminium is liquid and can be drawn off as requisite. The oxygen attacks the carbon anode to form carbon dioxide. One type of electric furnace is shown in fig. 47.

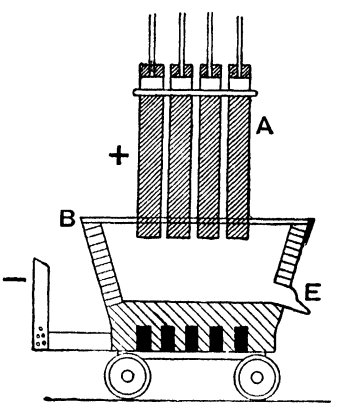


Fig. 47.—Electric Furnace for the Production of Aluminium.

The body of the furnace *B* is kept negatively charged by means of metallic and carbon conductors. The carbon anodes *A* dip under the surface of the electrolyte, which is kept in a state of fusion by the heavy current passing through it. The molten aluminium is withdrawn at the tap-hole *E*.

Aluminium is a pure white metal which resists the action of air and water at the ordinary temperature. This property, along with its strength and low specific gravity (which is only about one-third of that of iron), renders it very useful, and it is now being used for the manufacture of many metallic articles in which lightness combined with strength is desired.

Although it does not decompose water at the ordinary temperature, except when amalgamated with mercury, it decomposes steam when highly heated. It is scarcely attacked by nitric acid, and is not easily attacked by dilute sulphuric acid, but it dissolves readily in hydrochloric acid, according to the equation—

$$2Al + 6HCl = 2AlCl_3 + 3H_2$$

When aluminium is heated to a high temperature in the air it burns, and is converted into aluminium oxide Al_2O_3.

The commonest compound of aluminium is **alum**, which is a double sulphate of aluminium and potassium or ammonium, the formulæ of the compounds being respectively—

$K_2SO_4,Al_2(SO_4)_3,24H_2O$ — Potassium alum

$(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$ — Ammonium alum

Ordinary alum may be either of these compounds or a mixture of both.

Alum may be prepared from a silicate of aluminium, say pipeclay, in the following manner:—The clay is ground to a fine powder and heated with concentrated sulphuric acid until it forms a paste, which is then exposed to the air for some weeks. The sulphuric acid attacks the aluminium silicate, with formation of silicic acid H_2SiO_3, and aluminium sulphate $Al_2(SO_4)_3$. This aluminium sulphate is soluble, and may be separated from the other materials, which are insoluble, by treating the mass with water. When the solution is evaporated, aluminium sulphate crystallises out, but is not easy to purify by crystallisation. It is, therefore, mostly dissolved up again, and to the solution is added either potassium or ammonium sulphate, when the sparingly soluble alums separate out and can readily be purified by recrystallisation. Both alum and aluminium sulphate are extensively used in dyeing and paper-making.

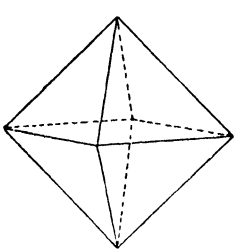


Fig. 48.—Crystal of Alum.

The alums crystallise in the form of a *regular octahedron*, an eight-sided solid, with all the faces equilateral triangles.

When a soluble hydroxide is added to a solution of an

aluminium salt, **aluminium hydroxide** is precipitated, the equation being—

$$Al_2(SO_4)_3 + 6NaOH = 3Na_2SO_4 + 2Al(OH)_3$$

This aluminium hydroxide, like the corresponding hydroxide of zinc is amphoteric (p. 237). With strong acids it behaves as a base. Thus, it will dissolve in hydrochloric acid with formation of aluminium chloride, as follows:—

$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$$

But with strong bases it can also behave as an acid. Thus, if excess of caustic soda is used in precipitating the solution of an aluminium salt, the aluminium hydroxide first formed dissolves up in the excess of sodium hydroxide, with production of the soluble sodium aluminate, the equation for this action being—

$$Al(OH)_3 + 3NaOH = Na_3AlO_3 + 3H_2O$$

Here the aluminium hydroxide acts as an acid with respect to the sodium hydroxide. It is only with regard to strong bases, however, that the aluminium will act in this way. If, for example, we take ammonia instead of caustic soda, we find that the precipitated aluminium hydroxide is much less easily dissolved up again. That is on account of ammonium hydroxide being so much weaker a base than sodium hydroxide, that it is unable to remain permanently combined with the very feeble acid aluminium hydroxide, unless it is present in a very large excess so as to make up by its quantity for its lack of strength.

Aluminium hydroxide is not only very feeble as an acid, it is also very feeble as a base. Although its salts with strong acids are stable enough, being only slightly hydrolysed in solution (p. 152), aluminium acetate when boiled with water is decomposed, the whole of the aluminium being precipitated as a basic acetate and the weak acetic acid being liberated. With an acid so weak as carbonic acid, aluminium hydroxide can form no salt at all. Thus, when sodium carbonate is added to a solution of aluminium sulphate, although a white precipitate is produced, this precipitate is not aluminium carbonate, as we might expect: it is aluminium hydroxide. We may, if we choose, imagine that aluminium

carbonate is first produced from the aluminium sulphate and sodium carbonate, according to the equation—

$$Al_2(SO_4)_3 + 3Na_2CO_3 = 3Na_2SO_4 + Al_2(CO_3)_3$$

but that this aluminium carbonate, being a compound of a very weak base with a very weak acid, is at once decomposed by water with formation of aluminium hydroxide and carbonic acid—

$$Al_2(CO_3)_3 + 6H_2O = 2Al(OH)_3 + 3H_2CO_3$$

Sulphuretted hydrogen like carbonic acid is a very weak acid. Although it is possible to prepare aluminium sulphide in the dry way, the product is decomposed by water with formation of aluminium hydroxide and liberation of hydrogen sulphide—

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S$$

The precipitate which separates when sodium or ammonium sulphide is added to a soluble aluminium salt is thus not aluminium sulphide, but aluminium hydroxide.

Although zinc and aluminium belong to different periodic groups, there is a considerable resemblance between them, as a comparison of their corresponding compounds will show.

CHAPTER XLI.

IRON

IRON occurs in the metallic state only in very small quantity, chiefly in meteorites, which are not of terrestrial origin at all. It is found combined very abundantly with oxygen and with sulphur. The commonest compound with sulphur is iron pyrites FeS_2, which, although a convenient source of sulphur, is not to be classed amongst *iron ores*—*i.e.* minerals from which metallic iron can be profitably extracted. The chief ores of iron are oxides and the carbonate, which occur in a more or less pure condition, their composition being indicated in the following table :—

Ferrous carbonate (spathic iron ore) . . .	$FeCO_3$
Ferric oxide (red hæmatite)	Fe_2O_3
Ferric hydroxide (in brown hæmatite) . .	$Fe(OH)_3$
Ferroso-ferric oxide (magnetic iron ore, lode-stone)	Fe_3O_4

Metallic iron can be obtained from these ores by first of all roasting them to get rid of carbon dioxide and certain impurities, and then reducing them in a blast furnace by means of carbon in the form of coke, or of charcoal, if a very pure iron is desired. The actions which go on in a blast furnace are very complicated, but it would appear that the carbon dioxide which is produced by the union of the oxygen of the hot air blast which is blown in at the bottom of the furnace with the carbon of the fuel, is reduced, in the higher portions of the furnace, to carbon monoxide, which in its turn reduces the ferric oxide to metallic iron. This reduction occurs in a comparatively cold part of the furnace, the temperature being insufficient to melt the pure metallic iron, which is one of the least fusible of metals. The metallic iron, however, is capable of taking up carbon, partly to form a carbide of iron, and the resulting product, known as *cast iron*, is easily fusible and sinks

to the bottom of the furnace, from which it can be withdrawn as required. At the same time the silica and lime found associated with the iron compounds in the ores, or specially added along with them, unite together to form a fusible slag, containing chiefly calcium silicate, which lies as a layer on the surface of the fused cast iron and protects it from oxidation by the blast.

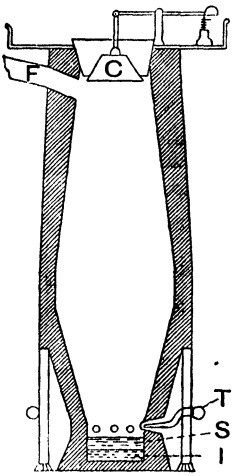


Fig. 49.—Blast Furnace.

In a blast furnace the fuel and ore are mixed together in the body of the furnace, and not separated as in a reverberatory furnace (fig. 45). A blast of hot air is blown in through a series of tubes *T* at the bottom of the furnace to supply the oxygen necessary for the combustion. The top of the furnace is closed by the cone *C*, which is lowered when a fresh charge has to be introduced. The furnace gases escape by the flue *F*. The molten cast-iron *I* collects on the hearth of the furnace, and is covered by a layer of fused slag *S*, formed from impurities in the ore, which protects it from oxidation by the air-blast.

Cast iron as it leaves the furnace is made to run into moulds and is there allowed to solidify in the form of bars. It consists of iron with from 2 to 5 per cent. of carbon, partly as carbide, and partly crystallised throughout the bar in the form of graphite. When cast iron is treated with acid, the iron dissolves and hydrogen is given off. This hydrogen, however, is by no means pure, as it contains quantities of hydrocarbons derived from the iron carbide, just as the hydrocarbon acetylene is derived from calcium carbide. There remains also a black residue which does not dissolve in acids, and consists chiefly of carbon in the form of graphite. Cast iron, as its name implies, can be cast in a mould to any desired form. This is on account of the comparatively low temperature at which it fuses, and also on account of its expanding slightly on solidification, so that it enters the smallest crevices of the mould and reproduces the details exactly.

Wrought iron or malleable iron may be produced from cast iron by removing its carbon. This may be effected in various ways, but in principle they are all the same. If the cast iron is melted and exposed to air, the oxygen of the air combines with the carbon in preference to the iron, so that at a high temperature the whole or nearly the whole of the carbon may be removed in the form of gaseous

oxides of carbon, a pasty mass of wrought iron remaining behind. Wrought iron is much less easily fused than cast iron and cannot be used for making casts. It is worked into shape by being rolled or hammered to the desired form when hot. It is not brittle like cast iron, but tough and fibrous.

Steel is intermediate in composition between cast iron and wrought iron. It contains about $\frac{1}{2}$ per cent. of carbon, but the quantity may vary according to the quality of steel which is desired. *Mild steel* contains a comparatively small quantity of carbon, and approximates in character to wrought iron. *Tool steel* contains a larger proportion of carbon, and is more like cast iron in its properties. The most valuable property of this variety of steel is its capability of being *tempered*. If a piece of steel is heated to redness and is then suddenly chilled in water or oil, it becomes extremely hard, but is at the same time very brittle. The hardness and brittleness may be removed to any required degree by heating the steel to moderate temperatures and allowing it to cool. If the steel is heated only slightly it loses very little of its hardness and brittleness. If it is heated to a higher temperature it becomes tough and elastic, and at intermediate temperatures it may be made to assume intermediate properties. The hardest steel easily scratches glass and is excessively brittle, but the same steel may be tempered down until it acquires the elasticity and toughness of a watch spring. The temper of a knife-blade is intermediate between these two extremes.

Steels which are desired to possess special mechanical properties frequently contain, besides iron and a small proportion of carbon, considerable quantities of other metals. Thus there are nickel steels which are used for the manufacture of armour plates owing to their toughness and power of resisting shock, chromium steels, manganese steels, and the like. Steels containing vanadium are also largely employed; and tungsten steels, used as rapid tool steels, are not only very hard, but maintain their hardness up to a high temperature. The so-called "stainless" steel for table cutlery contains both chromium and tungsten.

Pure iron may be most easily prepared by electrolysis, or by reducing an oxide of iron by means of aluminium (see p. 168), the equation in the latter case being—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe$$

Pure iron has a very high melting point, the temperature being estimated at about 1500°.

Iron is not attacked by oxygen or air which is free from moisture or carbon dioxide. In ordinary air, however, which contains both of these substances, iron is slowly attacked at the atmospheric temperature with formation of rust, which is chiefly ferric hydroxide $Fe(OH)_3$. The action of rusting seems to consist in water and carbon dioxide jointly attacking the iron, with production of ferrous carbonate $FeCO_3$, which is afterwards oxidised to ferric hydroxide $Fe(OH)_3$ with liberation of carbon dioxide. Iron does not attack water at the ordinary temperature, but if steam is passed over red-hot iron, the iron is oxidised, and hydrogen is set free. The equation usually given for this reaction is—

$$3Fe + 4H_2O = \underset{\text{Ferroso-ferric oxide}}{Fe_3O_4} + 4H_2$$

but it is doubtful if the oxide actually formed has the exact composition here represented.

Iron is readily attacked by dilute sulphuric, hydrochloric, and nitric acids, but it presents a peculiarity in resisting the action of concentrated sulphuric and concentrated nitric acid. No entirely satisfactory explanation of this behaviour has yet been arrived at.

Iron forms two sets of salts, the *ferrous* salts containing the radical $Fe^{\cdot\cdot}$, and the *ferric* salts containing the radical $Fe^{\cdot\cdot\cdot}$. The commonest soluble ferrous salt is **ferrous sulphate** in the form of *green vitriol* or *copperas* $FeSO_4,7H_2O$. This is usually manufactured on the large scale by the slow atmospheric oxidation of moist iron pyrites FeS_2. The soluble ferrous sulphate is extracted by water and recrystallised. It can also be readily obtained by dissolving iron in diluted sulphuric acid, and crystallising the solution. Ferrous sulphate, like all other soluble ferrous salts, tends to take up oxygen from the air, especially when in solution, and become oxidised to a ferric salt. A solution of ferrous sulphate, therefore, always contains some ferric sulphate, unless when freshly prepared. Ferrous sulphate, on account of the ease with which it oxidises to a ferric salt, is often used as a reducing agent. It is also extensively used in the manufacture of black dyes, and of ink.

The commonest ferric salt is **ferric chloride**, $FeCl_3$, which

can be prepared in the anhydrous state by passing chlorine over heated metallic iron. At a high temperature it sublimes in the form of black scales. A solution of ferric chloride from which the hydrate $FeCl_3,6H_2O$ may be obtained by evaporation is usually prepared by dissolving iron in hydrochloric acid, and then oxidising the ferrous chloride thus formed by boiling with a little nitric acid. The equation for this action is—

$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + NO + 2H_2O$$

Ferrous salts are almost invariably oxidised to ferric salts in this way by means of nitric acid. **Iron alum** $K_2SO_4, Fe_2(SO_4)_3, 24H_2O$ which crystallises in the same form as ordinary alum (p. 296) is another common ferric salt.

When sodium hydroxide is added to a solution of ferrous sulphate quite free from ferric salt, a white precipitate of **ferrous hydroxide**, $Fe(OH)_2$, is produced—

$$FeSO_4 + 2NaOH = Fe(OH)_2 + Na_2SO_4$$

The precipitate obtained from an ordinary ferrous solution is always dark green in colour, owing to the presence of a little ferric salt in the ferrous solution.

Sodium hydroxide, when added to a solution of a ferric salt, gives a reddish brown precipitate of **ferric hydroxide**—

$$FeCl_3 + 3NaOH = Fe(OH)_3 + 3NaCl$$

This hydroxide is the base corresponding to the ferric salts, and when heated yields the basic oxide Fe_2O_3.

Between ferrous oxide, FeO, and ferric oxide, Fe_2O_3, there exists a **ferroso-ferric** oxide, Fe_3O_4, which is distinguished by being magnetic like metallic iron. It occurs in nature, and on account of its magnetic properties is sometimes known as *lodestone*. It is not a basic oxide in the sense of having a definite set of salts corresponding to it. When dissolved in acids it yields a mixture of ferrous and ferric salts—

$$Fe_3O_4 + 4H_2SO_4 = \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Ferric sulphate}}{Fe_2(SO_4)_3} + 4H_2O$$

Ferric hydroxide is by no means a strong base, and solutions of its salts are always acid on account of partial hydrolysis. Like aluminium, it can neither form a carbonate nor a sul-

phide in aqueous solution. Thus when a solution of sodium carbonate is added to a solution of ferric sulphate, ferric hydroxide is precipitated, and carbon dioxide is evolved.

$$Fe_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 3Na_2SO_4 + 3CO_2$$

Ferrous hydroxide is a considerably stronger base than ferric hydroxide, and is capable of forming a carbonate. Thus, when sodium carbonate is added to a pure solution of ferrous sulphate **ferrous carbonate** is precipitated.

$$FeSO_4 + Na_2CO_3 = \underline{FeCO_3} + Na_2SO_4$$

This carbonate occurs in nature as *spathic iron.*

CHAPTER XLII

NICKEL—COBALT

NICKEL

THE metal nickel closely resembles iron in the properties of its principal compounds. It is found in nature as sulphide, as arsenide and as silicate, the chief ore being a silicate of nickel and magnesium found in New Caledonia and a magnetic iron pyrites in Canada, which contains up to 8 per cent. of nickel. The method of extraction varies according to the nature of the ore, but, generally speaking, the ore is converted into oxide of nickel, which is reduced by means of carbon. Mond's process for the separation of nickel from other metals depends upon the formation of a volatile compound, **nickel carbonyl**, formed by the union of metallic nickel with carbon monoxide—

$$Ni + 4CO \rightleftarrows Ni(CO)_4.$$

The oxide of the crude metal is reduced in a tower by means of water-gas at a comparatively low temperature. The metal afterwards meets with a gas rich in carbon monoxide, which attacks the finely divided nickel at a temperature below 100°, and leaves the other metals unaffected. At this temperature nickel carbonyl, which is liquid at the ordinary temperature, is above its boiling-point, and passes on as gas to a chamber heated to about 200° in which small balls of nickel are kept in a state of constant agitation. The nickel carbonyl decomposes, and the metal is deposited on the balls of nickel present in the chamber, while the carbon monoxide passes back to the bottom of the tower in which the nickel carbonyl is produced. Metallic nickel formed in this way is practically free from other metals.

Nickel is a nearly white metal which tarnishes only slowly in the air and does not rust like iron, on which account it is often used to electro-plate iron or steel objects. It is slightly

heavier than iron and is magnetic at the ordinary temperature, although it loses its magnetism on heating. It is used to alloy with iron in the production of the hard nickel steel employed in the manufacture of armour plates, etc. It is alloyed with copper and with copper and zinc for the production of hard white alloys like German silver.

There is only one salt-forming oxide of nickel—namely, the basic oxide NiO. The common salt of nickel is **nickel sulphate** $NiSO_4,7H_2O$, which may be formed either by dissolving this oxide or the metal itself in dilute sulphuric acid. The sulphate corresponds exactly to ferrous sulphate $FeSO_4,7H_2O$, but differs from it in showing no tendency to oxidise. The double nickel ammonium sulphate $NiSO_4,(NH)_2SO_4,6H_2O$ is used in nickel plating—*i.e.* the deposition of a coating of nickel by electrolysis. These salts, like the other common compounds of nickel, are green in colour.

The oxide Ni_2O_3 corresponds to ferric oxide. It is produced as a black precipitate by oxidising a nickel salt with alkaline hypochlorite. It is not, however, a basic oxide like ferric oxide, but behaves in general as a peroxide, liberating chlorine when boiled with hydrochloric acid.

$$Ni_2O_3 + 6HCl = 2NiCl_2 + Cl_2 + 3H_2O.$$

COBALT

Cobalt is found in nature combined with sulphur and with arsenic and may be obtained in the metallic form by reducing any of its oxides with carbon. The metal itself resembles nickel in its appearance but has a reddish tinge which is absent from nickel. It is not used as metal to any great extent, but some of its compounds are important.

It resembles iron and differs from nickel in having two basic oxides, CoO and Co_2O_3, to which the cobaltous and cobaltic salts respectively correspond. The **cobaltous salts** are generally of a red or pink colour in solution. Cobaltous chloride $CoCl_2,6H_2O$ forms red crystals which, when heated, lose water and become dark blue. Advantage is taken of this change in colour in the use of a dilute solution of cobaltous chloride as a sympathetic ink. The dilute solution leaves practically no trace on paper, but when the paper is warmed the hexahydrate is decomposed and the blue tetrahydrate

or the blue anhydrous salt is produced, and the writing becomes visible. When a cobalt salt or oxide is fused with potassium carbonate and silica, a deep blue glass is obtained, the commercial preparation being known as smalt and used as a pigment. The cobaltous salts do not oxidise spontaneously, but **cobaltic salts** may, however, be produced under special conditions. They are not, as a rule, stable, one of the most stable being the alum $K_2SO_4,Co_2(SO_4)_3,24H_2O$, which has a deep blue colour. Cobaltic oxide Co_2O_3 is readily formed, like the corresponding nickel compound, by oxidation of a cobaltous salt with alkaline hypochlorite.

CHAPTER XLIII.

CHROMIUM—MANGANESE

CHROMIUM

THE chief compound of chromium occurring in nature is a double oxide of iron and chromium of the formula $FeCr_2O_4$, which is known as *chrome iron ore* or *chromite*. It is difficult to attack by ordinary chemical reagents and is generally converted into soluble chromium compounds by simultaneous oxidation and fusion with alkali.

There are two principal oxides of chromium—namely, chromic oxide Cr_2O_3 and chromic anhydride CrO_3. The former is a basic oxide; the latter is a purely acidic oxide, being the anhydride of chromic acid, to which the salts known as chromates and bichromates correspond. In chrome iron ore, which may be written FeO,Cr_2O_3, the chromium is in the lower stage of oxidation. When oxidised it passes into chromic anhydride, which, on account of its acidic nature, readily combines with alkalies to form soluble salts. The iron, on the other hand, when simultaneously subjected to oxidation, forms no acidic oxide capable of combining with alkalies, and so the separation of the two metals can be easily effected. In practice the chrome iron ore is mixed with an alkaline carbonate and calcium carbonate, the object of the latter being to prevent complete fusion. The mixture is heated to redness in a reverberatory furnace, to which air has free access, the charge being continually stirred in order to expose a fresh surface for oxidation. During the process sodium chromate Na_2CrO_4, calcium chromate $CaCrO_4$ and ferric oxide Fe_2O_3 are produced. The cooled mass is broken up and boiled with a solution of sodium carbonate, which reacts with calcium chromate as follows:—

$$CaCrO_4 + Na_2CO_3 = CaCO_3 + Na_2CrO_4.$$

All the chromium then passes into solution as sodium chromate,

and may be filtered off from the insoluble calcium carbonate and ferric oxide. From this salt the other chromium compounds are prepared.

Chromic anhydride CrO_3 may be produced from a solution of a soluble chromate by addition of concentrated sulphuric acid. It separates from solution in crimson needle-shaped crystals, which are filtered off through glass wool or asbestos, since the solution attacks filter paper. They are purified by washing with concentrated nitric acid to remove sulphuric acid and sulphates with which they may still be mixed. On subsequent exposure to a current of warm, dry air, the nitric acid evaporates and they are obtained practically pure. Chromic anhydride dissolves in water to form an orange-red solution which contains chromic acid H_2CrO_4, and bichromic acid $H_2Cr_2O_7$. On evaporation of the solution, however, only crystals of the anhydride are obtained. When chromic anhydride is heated to a temperature of about 250° it decomposes, losing oxygen and being converted into chromic oxide—

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

Chromic anhydride is capable of combining with bases in different proportions, in this respect behaving similarly to sulphuric anhydride SO_3, and phosphoric anhydride P_2O_5. The two chief sets of salts are the **chromates** and **bichromates**, which will be seen to correspond to the sulphates and pyrosulphates respectively—

SO_3	Sulphate Na_2SO_4	Pyrosulphate $Na_2S_2O_7$
CrO_3	Chromate Na_2CrO_4	Bichromate $Na_2Cr_2O_7$.

For a given amount of base the proportion of acidic anhydride in the bichromate is twice as great as in the chromates. The soluble chromates have a pure yellow colour; the soluble bichromates, on the other hand, have a deep reddish-orange colour. The bichromates may be prepared from the chromates by the addition of acid. For example, the crude sodium chromate prepared from chrome iron ore is generally converted into sodium bichromate, because the latter salt may be more easily purified by crystallisation. The conversion is effected by adding the requisite quantity of sulphuric acid to a solution of chromate, the equation representing the reaction being as follows:—

$$2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O.$$

On concentrating the liquor the sodium sulphate crystallises out first and is removed; on further evaporation sodium bichromate separates. If potassium carbonate is used in the treatment of chrome iron ore instead of sodium carbonate, the corresponding potassium compounds are obtained, and may be more readily purified on account of their smaller solubility in water. *Lead chromate* $PbCrO_4$, and *barium chromate* $BaCrO_4$, which may be prepared by precipitation, are yellow insoluble compounds, and are frequently used as pigments.

Chromic anhydride, and chromates or bichromates in conjunction with acid, are frequently used as oxidising agents, the chromium during the reaction being reduced from the stage of CrO_3 to that of Cr_2O_3.

Chromic oxide Cr_2O_3 is prepared on a large scale by heating a bichromate with starch. The starch acts as reducing agent and converts the chromate into a mixture of chromic oxide Cr_2O_3 and alkaline carbonate, the necessary carbon coming from the starch. It is a dark green powder and is sometimes used as a colouring matter. If it has been prepared at a high temperature it dissoves in acids very slowly, but when prepared at a low temperature it dissolves to give the ordinary **chromic salts** of which the chloride $CrCl_3$ and the sulphate $Cr_2(SO_4)_3$ are the chief examples. These salts correspond in composition to the ferric salts. Chromic sulphate forms an alum like ferric sulphate or aluminium sulphate, the composition of the potash *chrome alum* being— $K_2SO_4,Cr_2(SO_4)_3,24H_2O$. These chromic salts may occur in either of two modifications, one variety yielding green solutions and the other purple solutions. Thus, a solution of chrome alum is generally purple, but the chromic salt produced by the reduction of a chromate or bichromate in acid solution is generally green. When a solution of the purple salt is boiled it usually passes into the green modification.

Metallic chromium may be prepared by reduction of the oxide by means of carbon at the high temperature of the electric furnace—

$$Cr_2O_3 + 3C = 2Cr + 3CO.$$

In the laboratory it is most conveniently obtained by igniting

a finely divided mixture of chromic oxide and aluminium (compare p. 301)—

$$Cr_2O_3 + 2Al = 2Cr + Al_2O_3.$$

Chromium is an extremely hard grey metal of very high melting-point. It is used in the preparation of chrome steels.

MANGANESE

Manganese occurs in nature either in the form of the sulphide MnS, *manganese blende*, or of various oxides, the chief of which is *pyrolusite* MnO_2. **Metallic manganese** can be prepared from the oxide either by reduction with carbon at a high temperature or else by reduction with aluminium, the methods being thus analogous to those adopted for the preparation of chromium. Like chromium, manganese is chiefly used to alloy with iron, in order to produce steels of definite properties.

Manganese forms numerous **oxides**, some of which are acidic and some basic. The formulæ of these oxides are given in the following table:—

Manganous oxide	MnO	Basic
Manganous-manganic oxide	Mn_3O_4	Basic
Manganic oxide	Mn_2O_3	Basic
Manganese dioxide	MnO_2	Amphoteric
Manganic anhydride	MnO_3	Acidic
Permanganic anhydride	Mn_2O_7	Acidic

The lower oxides are basic, and the higher oxides acidic, manganese dioxide possessing intermediate properties. The manganous salts correspond to manganous oxide, the formula of the sulphate being, for example, $MnSO_4$. The manganic salts correspond to the oxide Mn_2O_3, the sulphate having the formula $Mn_2(SO_4)_3$. The oxide Mn_3O_4 is intermediate between these two, and although it forms no set of salts itself, it has a basic character, giving rise with acids to mixtures of manganous and manganic salts. In this respect it resembles the corresponding ferroso-ferric oxide Fe_3O_4.

The **manganous salts** when precipitated with an alkaline hydroxide yield a nearly white precipitate of manganous hydroxide $Mn(OH)_2$, which rapidly darkens by oxidation, be-

coming converted into manganic hydroxide $Mn(OH)_3$. In this respect manganese resembles iron, but it should be noted that solutions of manganous salts show no tendency to oxidise to manganic salts in the air, and therefore differ in behaviour from the ferrous salts. The manganous compounds—*e.g.* the sulphate $MnSO_4,7H_2O$—have, in general, a pale pink or flesh colour, the dilute solutions being practically colourless.

Manganic salts are rarely met with, manganese alum being the common example of this type of compound. Its formula is analogous to that of the other alums, being $K_2SO_4,Mn_2(SO_4)_3,24H_2O$.

Manganese dioxide has both feebly acidic and feebly basic characters. When treated with concentrated hydrochloric acid in the cold, a dark brown solution is obtained, which, on heating, gives off chlorine and becomes practically colourless. The brown solution is that of a higher chloride of manganese which decomposes, yielding chlorine and manganous chloride. The reactions are probably expressed by means of the following equations :—

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O$$
$$MnCl_4 = MnCl_2 + Cl_2.$$

Manganese dioxide or the corresponding hydroxide also forms somewhat unstable compounds with bases, which are termed *manganites*. By oxidation of manganous compounds, or by reduction of manganates and permanganates in alkaline solution, a brown precipitate having the formula $MnO(OH)_2$ may be obtained. This is a hydrated form of manganese dioxide, into which it is converted by loss of water on heating—

$$MnO(OH)_2 = MnO_2 + H_2O$$

Manganates and Permanganates

When manganese dioxide is fused with potassium hydroxide or potassium carbonate, together with potassium chlorate as oxidising agent, the manganese is oxidised from the stage of MnO_2 to that of manganic anhydride MnO_3, which combines with the base to form **potassium manganate** K_2MnO_4. **If**

the fused mass is treated with water a deep green solution of the manganate is obtained. When a current of carbon dioxide is passed through the green solution after dilution, the colour changes to deep red, owing to the occurrence of the following reaction :—

$$3K_2MnO_4 + 2CO_2 + H_2O = 2KMnO_4 + MnO(OH)_2 + 2K_2CO_3.$$

The hydrated manganese dioxide appears as a brown precipitate which may be filtered off, the filtrate being then concentrated by evaporation. On cooling, the red solution deposits dark prismatic crystals of **potassium permanganate** $KMnO_4$. The manganate may also be electrolytically oxidised at the anode, the formation of hydrate peroxide being thus avoided. Potassium permanganate is extensively used as an oxidising agent, both in acid solution, when it is reduced to a manganous salt, and in neutral or alkaline solution, when it is reduced to hydrated manganese dioxide. Very mild reducing agents may reduce it in alkaline solution only to the stage of potassium manganate, which is easily recognised by its green colour. It should be noted that in the formation of potassium permanganate from potassium manganate by acid no oxidising agent is used, although part at least of the manganese is raised from the stage MnO_3 to the stage Mn_2O_7; at the same time, however, another part of the manganate is reduced from the stage MnO_3 to the stage MnO_2. There is thus a splitting up of the manganese in one stage of the oxidation into two others, one of which is at the higher and one at the lower stage of oxidation than the original compound. Both manganates and permanganates are used as disinfectants, red Condy's fluid containing chiefly calcium permanganate.

The elements nickel and cobalt belong to the same natural family as iron, the elements chromium and manganese to other families. Yet there is a considerable resemblance between the five elements in the lower oxides. Thus we have the dyad and triad series

FeO	CoO	NiO	CrO	MnO
Fe_2O_3	Co_2O_3	Ni_2O_3	Cr_2O_3	Mn_2O_3.

These are all basic oxides except Ni_2O_3, which behaves entirely as a peroxide, and has no salts corresponding to it.

CHAPTER XLIV.

TECHNOLOGICAL USES OF SOME RARER ELEMENTS

THE comparatively rare metals, titanium, cerium, thorium, vanadium and tungsten, and some of their compounds, have important industrial applications. Their characteristic oxides have the following formulæ :—

$$TiO_2, \quad CeO_2, \quad ThO_2; \quad V_2O_5; \quad WO_3.$$

The symbol W for tungsten is derived from wolframium, a former name given to that element. The general chemical nature of these elements may be ascertained by reference to the periodic table on p. 256. Titanium, cerium and thorium are members of a sub-group of tetrad elements different from that containing tin and lead. Vanadium does not belong to the arsenic series of pentads, but to another rarer sub-group. Tungsten is a member of the same natural family of hexads as chromium.

Titanium

The chief minerals containing titanium are *rutile* TiO_2, and *ilmenite* $FeTiO_3$. When powdered ilmenite, which is a fairly abundant mineral, is mixed with aluminium powder and ignited like a thermit mixture (p. 168), an alloy of iron and titanium or ferro-titanium is produced. Ferro-titanium is extensively used as an addition to steel in the fused state, the product being thereby improved in strength and durability. The titanium passes entirely into the oxidised slag, as the resulting steel is free from the element. It therefore apparently acts as a cleansing agent, removing gaseous elements from the steel, and rendering it more homogeneous and dense.

Titanium compounds are also used in the dyeing industry.

Cerium and Thorium

These elements occur together in the *monazite* deposits of

North Carolina, Brazil, etc. They are chiefly used in the form of their oxides for the production of **incandescent gas mantles.** The oxide of thorium ThO_2 when heated in a Bunsen flame emits a light, much brighter than that emitted by other white oxides—*e.g.* calcium oxide, under the same conditions. It was observed that when the thorium oxide contained 1 to 2 per cent. of cerium oxide CeO_2 as impurity, the brilliance of the light was greatly increased, but fell off again if more cerium oxide were added. When threads of cotton, ramie or artificial silk are impregnated with a concentrated solution of the nitrates of these metals, and are afterwards heated, they leave a coherent residue of the oxides, which emit the brilliant light of the incandescent gas mantle when placed in a non-luminous flame.

Metallic cerium is a component of the **pyrophoric alloys** used in gas-lighters or cigar-lighters. These are essentially alloys of cerium and iron, and may contain up to 30 per cent. of the former. When struck or scratched with hardened steel they throw off glowing sparks which can ignite coal gas or a combustible vapour such as that of methyl alcohol or petrol. The sparks are due to rapid oxidation of the metals in air.

Tungsten

The chief mineral containing tungsten is wolfram or **wolframite,** a tungstate of iron and manganese varying in composition between $FeWO_4$ and $MnWO_4$. It is found abundantly in the United States, and also in Cornwall, associated with tin-stone.

When wolfram is fused with sodium carbonate, sodium tungstate Na_2WO_4 is produced, and may be dissolved out by water. From this salt tungstic acid H_2WO_4 is precipitated by means of a strong acid. When heated the acid yields the anhydride WO_3, from which the metal is obtainable by reduction with aluminium,

$$WO_3 + 2Al = 2Al_2O_3 + W,$$

or with carbon in the electric furnace.

Metallic tungsten is remarkable for its high specific gravity, 19, approaching that of gold, 19.3, and platinum, 21.5; and also for its high melting-point 3000°, which exceeds that of any

other metal. It is largely employed for hardening steel (p. 301) and in making lamp filaments.

Incandescent Electric Lamps

The carbon filaments formerly employed in the bulbs for incandescent electric lighting have now been almost entirely superseded by metallic filaments. A high melting-point is an essential property of the metal if it is to be used as a filament, since the temperature required to give a light of the necessary brilliancy is high. The metals hitherto employed for the purpose are tantalum (melting-point 2300°), osmium (melting-point 2500°), and especially tungsten (melting-point 3000°). Difficulty was at first experienced in getting tungsten filaments of sufficient fineness and uniformity, but this is overcome by the employment of the colloidal metal, or by alloying with another metal which can afterwards be volatilised by heat.

CHAPTER XLV.

THE INERT GASES AND THE RADIO-ACTIVE ELEMENTS

The Inert Gases

In the chapter dealing with the atmosphere it was stated that an invariable constituent of atmospheric air is the inert elementary gas argon, an element which is entirely devoid of chemical properties. A thorough investigation of the atmospheric gases led to the discovery of other gases of the same character, although the proportions of them existing in the atmosphere were very minute. The complete series or natural family of inert gases, with their atomic weights, is given in the following table:—

Name . .	Helium	Neon	Argon	Krypton	Xenon	Niton
Symbol . .	He	Ne	Ar	Kr	Xe	Nt
Atomic weight	4	20	40	83	130	222.5

Neon, krypton and xenon have only been found in minute proportions in the atmosphere, and can be prepared from liquid air.

Helium is obtained in small quantities when minerals containing uranium and thorium are dissolved or heated. Before its preparation from these terrestrial sources it was known to exist in the sun, and in many stars, owing to a characteristic line in its spectrum. It is a product of the disintegration of certain radio-active elements, the properties of which are referred to below. It is the most difficult of all elements to liquefy, the boiling-point of liquid helium being -268.7—*i.e.* only 4.3° above the absolute zero.

The element niton, or radium emanation, is itself a radio-active substance, and is produced by the radio-active disintegration of the metallic element radium.

Radio-active Elements

Certain elements exist which undergo spontaneous transformations different in character from any chemical transforma-

tions that have hitherto been considered. These elements have received the name of radio-active elements because their transformations are associated with the production of radiations, the presence of which can readily be detected in a variety of ways. These radiations (1) act upon a photographic plate in the dark, (2) dissipate the charge of a charged electroscope, (3) excite fluorescence in certain substances, such as those used for X-ray screens.

The existence of the radiations was first of all detected photographically in the case of the metal uranium and its salts, all of which are feebly radio-active. The careful investigation of the uranium ores then led to the discovery of very highly radio-active substances—in particular, of the element radium, 1 part of which exists in about 10,000,000 parts of the ore.

Radium, from the ordinary point of view, is a metal of the alkaline earths, its compounds resembling closely those of barium in their properties. For example, radium sulphate $RaSO_4$ is still less soluble in water than barium sulphate. The chloride and bromide $RaCl_2,2H_2O$ and $RaBr_2,2H_2O$, on the other hand, are soluble, and of the same crystalline form as the corresponding compounds of barium, $BaCl_2,2H_2O$ and $BaBr_2,2H_2O$. These salts impart a characteristic coloration to the Bunsen flame, as do the other members of the alkaline earth group. The metal itself has been prepared and exhibits properties such as might be expected from a study of the other metals of the alkaline earths.

Notwithstanding this similarity in general chemical properties radium differs from the other members of the same family in possessing a highly developed radio-activity which is altogether absent from the rest. A quantity of radium bromide (which is the salt of radium most commonly employed) of weight less than a milligram, will rapidly discharge a charged electroscope, show visible fluorescence on a screen and affect a photographic plate enclosed in a black envelope. The radiations to which it gives rise are of three kinds: alpha (α) rays, which consist of positively charged material particles; beta (β) rays, which are streams of electrons, or particles of negative electricity; and gamma (γ) rays, which are not material at all and of the same general character as light, or, more specifically, as X rays.

The α rays consist of charged atoms of the element helium moving with extreme velocity. The charge which the helium atoms carry is always positive and constant in amount, the quantity of helium indicated by the formula He—*i.e.* 4 grams—being always associated with 2 faradays of positive electricity. It is owing to the high speed with which these particles move and not to their electrical charges that they possess the properties of α radiation. When they become slowed down by passing through a few centimetres of air, owing to their collisions with the gaseous molecules, they lose these characteristic properties entirely.

The radium which has in this way produced helium, is itself transformed into another new element called **radium emanation** or niton, which is gaseous at the ordinary temperature. We have here then a decomposition of the element into two new elements which may be represented by the equation—

$$\mathrm{Ra} = \mathrm{Nt} + \mathrm{He},$$

so that the element radium would, after all, appear to be in reality a compound. Such a compound, however, is of an entirely different character from those substances which are generally called by that name, and we still place radium in the list of the elements, despite the fact that it is subject to a process of spontaneous decomposition.

Niton, although one of the chemically inert gaseous elements, is even more radio-active than radium, and rapidly disintegrates to form other radio-active elements, the last product of the series of successive radio-active transformations being the non-radio-active element lead, which is stable and undergoes no further change.

Such phenomena are difficult to understand on older views as to the practically immutable nature of atoms, but the modern electrical theory of the structure of atoms (p. 79) succeeds in harmonising them with other well-ascertained facts in a satisfactory manner.

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Aluminium	Al	27.1	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	Ar	39.9	Neon	Ne	20.2
Arsenic	As	75.0	Nickel	Ni	58.7
Barium	Ba	137.4	Niton	Nt	222.5
Bismuth	Bi	208.0	Nitrogen	N	14.0
Boron	B	11.0	Osmium	Os	190.9
Bromine	Br	79.9	**Oxygen**	**O**	**16**
Cadmium	Cd	112.4	Palladium	Pd	106.7
Cæsium	Cs	132.8	Phosphorus	P	31.0
Calcium	Ca	40.1	Platinum	Pt	195.2
Carbon	C	12.0	Potassium	K	39.1
Cerium	Ce	140.2	Praseodymium	Pr	140.6
Chlorine	Cl	35.5	Radium	Ra	226.5
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	59.0	Rubidium	Rb	85.4
Columbium	Cb	93.5	Ruthenium	Ru	101.7
Copper	Cu	63.6	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorine	F	19.0	Silver	Ag	107.9
Gadolinium	Gd	157.3	Sodium	Na	23.0
Gallium	Ga	69.9	Strontium	Sr	87.6
Germanium	Ge	72.5	Sulphur	S	32.1
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.0	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.5
Indium	In	114.8	Thulium	Tm	168.5
Iodine	I	126.9	Tin	Sn	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.8	Tungsten	W	184.0
Krypton	Kr	82.9	Uranium	U	238.5
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.1	Xenon	Xe	130.2
Lithium	Li	6.9	Ytterbium	Yb	172.1
Lutecium	Lu	174.0	Yttrium	Yt	89.0
Magnesium	Mg	24.3	Zinc	Zn	65.4
Manganese	Mn	54.9	Zirconium	Zr	90 6
Mercury	Hg	200.6			