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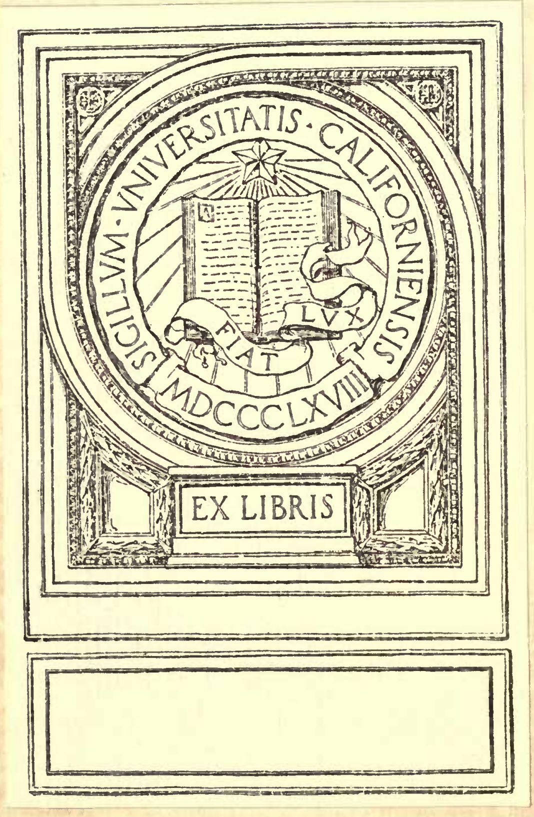
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# CHEMISTRY FROM THE INDUSTRIAL STANDPOINT

BY

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> “The farther researches we make into this admirable scene of things, the more beauty and harmony we see in them.”
>
> Stephen Hales, 1726

# PREFACE

Many people have a habit of exclaiming, when a fact bearing on chemistry is mentioned to them, "Oh! that's *Chemistry*," in much the same tone of voice that they would use to declare it was Sanskrit. During the war a rumour has spread that chemistry and chemists have something to do with explosives (particularly high ones), poison gases, and dyes; but the connection is not at all clear to the man in the street. He has an hereditary horror of "chemicals," and to him a chemist is another name for a druggist.

This book endeavours to explain to the inquiring mind that all things are chemicals, and that the chemist does not work miracles, but merely takes advantage of the behaviour of substances. It is not a catalogue of useful chemicals, but, using the methods of making some important substances as the basis, shows the fundamental lines on which chemical processes operate.

The use of formulæ, etc., has been introduced, not to appal the reader, but to give him an accurate means of noting the chemical reactions described. Any subject of study develops technical terms and methods, and it is not advisable to evade them or the subject has to be re-learnt later on.

The fact that large-scale operations have been described has necessitated pictures of the plant used. These have been simplified so far as possible, and in most cases show the structures in section. I have to thank my wife for preparing the drawings.

The reader must not expect to be able either to start a chemical works or pass an examination after reading this book. If he achieves some appreciation of the methods of chemistry and the way substances behave, its object will have been achieved.

For those who wish to know more than is here presented, lists of books are included at the end of some of the sections and at the end of the book. Similarly, some few chapters have summaries at the end; the reader is invited to summarise the others as a means of consolidating what he has learnt.

I have to thank many friends who have helped me to write the following pages, some personally, others in their books.

**P. C. L. THORNE.**

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# INTRODUCTION

### By H. V. A. Briscoe, D.Sc. (Lond.), A.R.C.S., D.I.C.

The war has brought home to us all that the position of this country in many industries is thoroughly unsatisfactory, more especially in those most largely dependent upon the application of scientific knowledge. The real trouble is that, broadly speaking, there exists no common ground of understanding upon which the scientist and business man can meet.

One can, of course, point to special industries in which our position is sound, but usually such cases are due to the fact that a business man of unusual determination and ability has turned himself into a scientific worker as well, or *vice versâ*. They are clearly exceptional, and their history generally discloses at some period a heavy battle between the scientist and the business community, and indicates that the success of the industry has been attained in spite of and not because of the attitude of the latter.

It is, perhaps, necessary to emphasise the point that this weakness in our industrial situation is not due to any lack of initiative, enterprise or energy. Our system of education and the natural tendency of the race does produce a good proportion of men who, lacking nothing of these qualities, are fitted to lead or direct ventures of all kinds—so long as these are of a pioneering character. When, however, as must happen sooner or later, the venture meets with competition, and the necessity arises for conducting it upon a closely reasoned basis, our men fail—because they lack the education which would fit them to comprehend the industry they operate.

I am continually astonished to find the real control of large industries in the hands of men who have not the haziest idea as to the basic principles upon which their industry depends.

All this, of course, is not the fault but the misfortune of the business man, who is practically always in the position of having to learn in the hard school of experience, at an undue cost, many things essential to success which should have been inculcated in his youth. In other words, the radical defect is in our system of education—and despite the efforts of the last few decades, the present system of education is still defective in the same general manner, if not quite to the same extent, as that which produced this deplorable result.

The fault lies partly at the door of the teacher himself; he has too often taught his subject on the basis that it is of interest for its own sake. This may do well for the hundredth pupil, who has a natural or acquired liking for that particular subject, but it leaves the ninety-nine stone cold. Their interest can only be awakened when they are brought to realise that the subject has an intimate relation to their daily life and that its study will help them to *live* in one or other sense of the word.

A praiseworthy prejudice against purely utilitarian education causes many teachers to handle their subjects in an atmosphere of entire detachment from their practical applications. Chemistry in particular has suffered in this way, and the book Mr. Thorne has now written is the first of its kind. It is a departure from standard practice which is, I believe, of the first importance.

Mr. Thorne's book appeals to me, and will, I believe, appeal to many, as a most interesting attempt to correlate the teaching of elementary chemistry with the ordinary events of daily life. The book is small, but much failure in the past teaching of chemistry has arisen because the teacher has not realised that his subject is very strong meat for the lay mind and can only be properly assimilated if given in small doses.

The study of chemistry, unless conducted on a basis of experiment, presents extraordinary difficulty. For obvious reasons, very few who have left school, and but a small proportion of those now at school, can have the advantage of much experimental study. The only real means, therefore, of bringing home to the majority of people the concepts of chemistry, is to illustrate them by phenomena with which all are familiar or can be made familiar by suitable textual description. This Mr. Thorne has attempted to do—and with a measure of success which should make his book of the greatest utility. Whilst he has thus made the book "popular," he has preserved a logical order which renders it entirely suitable as a text-book for elementary students.

For reasons which are, though very imperfectly, set forth above, I regard the publication of this book as an event of importance; and I very heartily commend it both to those who, having learned little of chemistry, now wish for any reason of utility or interest to become acquainted with its general principles, and to those who are responsible for the elementary teaching of chemistry or general science in our schools.

H. VINCENT A. BRISCOE.

*September*, 1919.

# SECTION A

## SOLIDS, LIQUIDS, AND GASES

## CHAPTER I

### SOLIDS AND LIQUIDS.

CHEMISTRY is a branch of science which attempts to classify the stuff of which the world is made, and to study the effects of reaction of one kind of stuff on another. As in all sciences dealing with tangible things, the method of study is to observe a number of effects, then classify them, and, by using the imagination, attempt to see what common principle underlies the observed effects. This conjecture is then tested by seeing if it fits in with further observations.

It is important to simplify the study so far as possible. For that reason methods of separating various substances from the mixture in which they are commonly found are important. In chemical industry, which aims at making useful substances from those which are found in Nature, the separation of mixtures is equally necessary. In this section of the book, therefore, we shall deal with such methods as are generally used, particularly those applied on the large scale in manufacturing practice.

Let us think for a moment of some of the things in the world—the ground we stand on, the paper on which this is printed, an iron poker, the glass in the windows: all these we can classify as *solids*.

But consider water; we cannot stand on it or grasp it; when put into a bottle it at once goes to the bottom and becomes the same shape as the inside of the bottle, whereas if we put small stones into a bottle they will not fill up the corners. Things which behave like water, such as paraffin oil, methylated spirit, and quicksilver, we can classify as *liquids*.

There is yet another class of things which is not quite so obvious to the senses as the other two. We are suddenly aware of a substance around us when the wind blows; if we turn on a gas-tap without lighting the gas, there comes from the pipe something which is like air in some ways (you cannot see it, for instance); there is also steam above the water inside the glass used to show the level of the water in a boiler, although the steam cannot be seen by the eye—turn the top tap and steam rushes out. Substances like air, coal-gas, and steam are called *gases*. They are not all invisible—for instance, chlorine, used as a "poison gas" in the late war, is green; and the vapour from iodine is violet.

Gases, unlike solids and liquids, when put into a vessel fill the whole of it, however big it is. For instance, the air pumped into an empty cycle tyre or football bladder does not sink to the bottom as water would, but fills the whole evenly. Of course, all ordinary vessels we call "empty" are really full of air, so that before we can fill them with any other gas we must first pump the air out.

Also, gases are easily compressed, whereas solids and liquids resist compression. Thus if we try to force a well-fitting cork into a bottle quite full of water, the bottle will break; but if the end of a cycle pump be covered with the thumb, the piston can be forced in part of the way, compressing the air, although no air escapes.

We see then that the stuff or matter which is around us can be classed as *solids*, *liquids*, and *gases*. It is obvious that this classification only applies at the ordinary temperature; for liquid water cooled becomes solid ice, and when heated becomes gaseous steam; lead melts when heated in a pot over the fire;

petrol becomes a gas in the carburettor. On allowing the temperature of the substance to come back to the ordinary temperature, the substance changes back to its ordinary state. We shall now consider the conditions under which these changes of the same substance from solid to liquid and gas on being heated take place; and, first, the change from solid to liquid known as *melting*, and from liquid to solid known as *freezing*.

The temperature at which water freezes or turns to ice is 32° F. or 0° C. Each solid has its own peculiar temperature at which it changes to a liquid, that temperature being called its *melting-point* (or freezing-point).

Water does not go suddenly to ice even at the freezing-point—a thin sheet is formed first which gradually thickens if it keeps cold. This is because heat has to be taken from it to make it freeze, even when it is at the freezing temperature; similarly, if a lump of ice is put into a saucepan and then heated, it takes a long time to melt, and the mixture of ice and water, if stirred, does not rise in temperature above the freezing-point until all the ice has melted. Actually, the heat required to melt a pound of ice is four-fifths of that needed to raise the water formed from the freezing-point to boiling.

Another important thing to note is that ice floats on water. This, naturally, is because it is lighter than the water. So that the pound of ice takes up more room than the pound of water it becomes on melting. This accounts for the bursting of water-pipes during a severe frost; the water on changing to ice requires more room and can only get it by splitting the pipe; of course, this is not noticed until the thaw, as the ice does not run out.

Water, however, is almost solitary in expanding when it becomes solid; most liquids contract, and the solid is heavier than the liquid, and thus sinks in it. Type metal behaves like water when cast, and expands to give a sharp edge to the letters in the type; castings from most metals have to be made somewhat larger than required and machined when cold if a clean surface is required.

### SUMMARY.

Matter exists in three forms: solid, liquid, and gaseous.

Solids become liquids on heating (unless they decompose, *e.g.* wood) when a certain temperature is attained.

Heat is absorbed by a solid in melting (and given up by the liquid in solidifying).

Most liquids contract on freezing, but water expands.

# CHAPTER II

## EXTRACTION OF SULPHUR. SOLUTION

THE well-known substance sulphur or brimstone is obtained from the earth by a process which consists of melting it in the ground and forcing up the liquid formed.

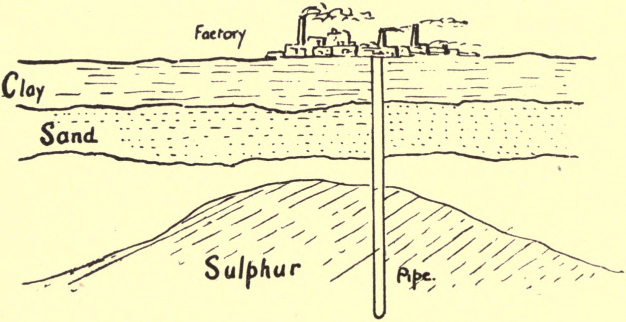

FIG. 1.—General view of sulphur mine, Louisiana.

The sulphur is found in Louisiana, U.S.A., under a layer of sand and clay nearly 500 ft. thick (see Fig. 1). A pipe of wrought iron 13 in. in diameter is sunk through the sand bed, and inside this another pipe (8 in.

diameter) is forced right into the sulphur bed. Within this tube are three others, 6 in., 3 in., and 1 in. respectively, which at the lower end are joined up as shown in Fig. 2. Water, superheated[1] under pressure to 170° C., is forced down the two outer pipes and escapes through the end of the 8 in. pipe and a series of holes in the 6 in. one into the sulphur bed. Now sulphur melts at 115° C.; hence a pool

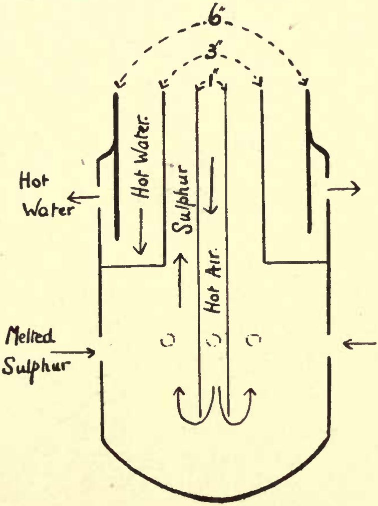

Fig. 2.—End of sulphur-extraction pipe.
(Note: 13 in. and 8 in. pipes are not shown.)

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[1] Water heated in an open vessel boils at 100° C., but when heated in a closed vessel boiling is prevented for some time and the water is said to be "superheated." See Chap. V.

of molten sulphur forms round the end of the pipe system. The liquid flows into the rounded end through another series of holes, and is carried up to the surface by a stream of hot compressed air passing down the 1 in. pipe—the froth of air and molten sulphur passing up between this pipe and the 3 in. one. On reaching the top end of the pipe, it is run into large wooden tanks, where it becomes solid. The sulphur so mined is very pure (99·9 per cent.), and about 250,000 tons is produced each year by this method. It is obviously a more simple and economical method than that of sinking a wide shaft and excavating the sulphur by hand or machinery.

§ *Sulphur* is a pale yellow crystalline solid which melts at 115° C. It boils at 445° C., and can be purified by distilling it. It is not soluble in water, but dissolves in carbon disulphide.

It is *used* as one of the ingredients of ordinary gunpowder ; to dust vines and other plants to prevent mildew, and for vulcanising rubber. It burns in the air with a blue flame, to produce a gas—sulphur dioxide—with a pungent, suffocating smell.

*Solution.* It is well known that when some solid substances are placed in a liquid (say, sugar or salt in water) they disappear and pass into the liquid, although it is far too cold for them to melt in the strict sense of the word.

The solid is then said to *dissolve* in the liquid; the resulting liquid consists of water *and* salt; whereas, in melting, the liquid formed contains nothing but the substance from which it was made.

Now suppose we continue to add salt to cold water, stirring to mix up the whole. It will continue to dissolve for some time, but in the end some salt will be left in the solid state. The water is then said to be *saturated* with salt.

If, however, the saturated water with a little solid salt in it is heated, more salt will dissolve; so that we can only say that the water is saturated at the temperature at which we are using it; the same water when heated will take up more salt.

Suppose we add salt to hot water until it will take up no more, forming a hot saturated solution—the water with the salt in it is called a *solution* of salt. We then pour the solution from the solid salt and allow it to cool. As it cools it is unable to dissolve as much salt as it did when hot, and consequently the solid salt reappears, frequently at the surface, as the solution there cools most quickly. The white shining particles are called *crystals* of salt; and it is as crystals that solids mostly reappear from a solution. With a magnifying-glass they can be seen to be tiny cubes. All crystals have a definite shape, the shape varying with the substance. We shall learn more about them later.

If now, instead of cooling the hot saturated solution, we boil away the water, the salt will soon begin to appear in the solid form, as there is no longer enough water to dissolve it. Of course, if we boil away all the water, we can get back all the solid salt.

Another way of getting rid of the water from a solution is to freeze it. So in North Russia sea-water is allowed to freeze, the ice (almost pure) taken out, and the solution, now nearer being saturated, frozen again. The liquid remaining after the second freezing is boiled to produce the solid salt. This is necessary, obviously, since when, by removing the ice, the solution becomes saturated at the freezing-point, salt will appear with the ice.

Salt is sometimes sprinkled on to ice in winter; the ice then melts as the salt dissolves. Thus the freezing-point of the water is lowered, and this happens whenever a solid is dissolved in a liquid.

Again, if a thermometer is placed in some water, salt added, and the mixture stirred, the temperature will be seen to fall. In fact, in some cases the cooling is great enough to be easily felt if the vessel containing the water is held in the hand, *e.g.* in dissolving ammonium chloride (sal ammoniac) to make a solution for an electric bell battery.

The importance of solutions in daily life is obvious. All our food must become soluble to be of any use to us after we have eaten it; the solution of foodstuff passes into the blood. Plants, also, must take up some of their food from the soil, and only dissolved substances can enter the roots and be taken up the stem to the other parts of the plant. We make a solution of gum every time we stick a stamp on a letter; soda is dissolved by the housewife to cleanse dirty dishes. Solutions in other liquids are also frequently used: bruises and sprains are painted with a solution of iodine in alcohol; a solution of rubber in an inflammable liquid is used to mend cycle tubes.

### Summary.

When a solid dissolves in a liquid, heat is absorbed; the liquid freezes at a lower temperature; only a limited quantity is dissolved at any particular temperature; more can be dissolved if the solution is warmed, but the excess reappears on cooling.

A saturated solution (at a particular temperature) is one which will dissolve no more of the solid.

# CHAPTER III

## THE EXTRACTION OF SALT

SALT is found (as *rock salt*) in layers in the earth, sometimes very thick and extensive, beneath other beds of clay. It is often stained brown by the presence of iron oxide, and the solid rock salt is only suitable for giving to cattle.

It is obtained for our use in one of two ways: either a shaft is sunk and the salt is mined by blasting, etc., in much the same way as coal is mined, or water is sent down the shaft, and when it is saturated with salt the brine is pumped up and the salt obtained from it.

The mining method is practised in Galicia at Wielicza, where the same mines have been worked for six hundred years.

In England (at Nantwich, Northwich, Middlewich, and Droitwich) it is more usual to adopt the brine pumping method.

At Nantwich the salt bed lies some 140 ft. below the surface, and is 75 ft. thick; below this is a sheet of marl 30 ft. thick, then the second salt bed over 100 ft. thick.

In order to obtain the salt a shaft about 10 ft. in diameter, lined with cast-iron cylinders, is sunk down to the layer of marl covering the salt. A hole is then forced through the marl, when the brine which lies above the bed of salt rushes partly up the shaft. This saturated solution of salt is then pumped up into reservoirs, usually of brick lined with clay. As fresh water flows into the salt bed the pumping can be continued until the whole bed is dissolved up, which at the present rate of working will be a very long time. Naturally, as there is nothing to replace the salt so removed, the land sinks in, often as rapidly as 1 ft. per year.

The salt is obtained from the brine by evaporating the water. In countries where fuel is scarce the brine is pumped to the top of a stack of brushwood and allowed to trickle down, so that some of the water is evaporated by mere exposure to the air; but much salt is lost by the brine being blown away as spray.

In any case, the final evaporation has to be done by heating the brine. In England large shallow pans are used (25 ft. by 20 ft. by 1 ft. 6 in. deep and upwards), made from a number of iron plates riveted together. The pan *A*, shown in section in Fig. 3, is heated by flues *B* underneath leading from a fire at one end, the walls of the flues serving to support the pan. As the water evaporates the salt crystallises out and is taken from the pan by a workman using a shovel with small holes in it, called a " skimmer." The salt is flung on to the " hurdles " or sloping shelves *C* at the sides of the pan, where it drains, the brine running into the gutter *D* at the edge, which leads back into the pan.

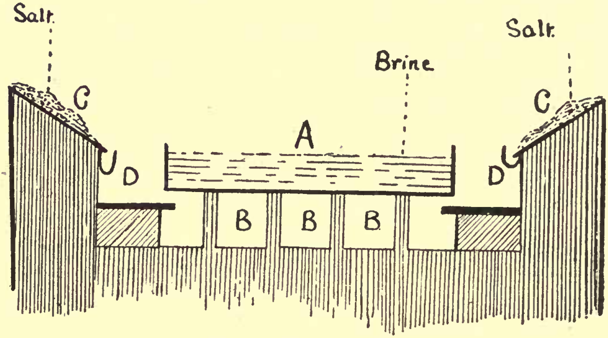

Fig. 3.—Pan for evaporating brine.

The kind of salt produced depends mostly on the temperature at which the evaporation is carried on, and on the frequency with which the salt is taken out of the pan.

For example, fine-grained table salt is obtained by actually boiling off the water in smaller pans than those described above, the salt being raked out continuously. The wet salt is put into wooden boxes, and on cooling more crystallises out from the liquid still remaining in the mass, forming a solid lump such as is ordinarily sold for cooking purposes.

For salting fish larger crystals are required. Evaporation is carried on at 40°–60° C., and the salt removed only once a week or once a fortnight.

Bay salt is coarser still. The temperature here is below 50°, and the crystals are taken out about once a month.

The liquor finally left contains impurities and is run to waste.

§ *Salt* (known in chemistry as sodium chloride) is a white solid crystallising in cubes. It is soluble in water, but the weight dissolved by 100 grams of boiling water is only 39 grams salt; whereas at the ordinary temperature 35 grams are dissolved. Thus it is not much more soluble in hot water than it is in cold water. It is a necessary addition to human food, and a useful preservative for meat and fish; enormous quantities are used to make soda in the alkali industry.

*Solution as a Means of Separating Solids.*—It is obvious that a great many substances do not dissolve in water, although, as a matter of fact, it can dissolve a greater variety of substances than any other liquid. So that, if we have a mixture of a soluble with an insoluble substance, on stirring up in water the soluble substance will dissolve, leaving the insoluble one as a deposit on the bottom of the vessel. The insoluble material can be completely separated by one of the methods of filtering discussed in Chapter IV. Thus, when common soda is made by one process the crude product is mixed with calcium sulphide and other materials not soluble in water. On treatment with hot water the soda dissolves, leaving the other materials. Such an operation is called *lixiviation.* Again, mercury is used to dissolve gold from the crushed quartz which contains it ; an amalgam, or solution of gold in mercury, is formed. Alcohol or methylated spirit is very useful as a solvent for many substances not soluble in water, particularly in extracting medicinal substances from the roots or herbs in which they occur. Usually hot alcohol is used in a closed plant to prevent losses, and by adapting the method of distillation described later, a comparatively small quantity of alcohol can be used over and over again. This method of removing soluble substances is known as *extraction* ; or, if performed with cold solvent, as is sometimes necessary to prevent decomposition of the drug, *percolation.*

The making of tea is an everyday example of extraction with hot water ; lemonade (made from real lemons) is another case in point; whilst an over-salted piece of bacon is rendered eatable by steeping for a short time in cold water to dissolve out some of the salt.

*Crystallisation as a Means of Purifying Substances.*—Let us consider the liquid from which a quantity of salt has been removed, as described earlier in the chapter—it is called the *mother liquor*. Clearly, it will be a saturated solution of salt at the temperature at which we are working; but the salt in the beds contains other substances besides pure sodium chloride, for instance, some magnesium chloride, in some cases as much as 1 per cent. Now when we dissolve the salt in water to a saturated brine, it will not be a saturated solution of magnesium chloride; for in the 35 grams of crude salt dissolved in 100 grams of water only 0·3 gram will be magnesium chloride, which, incidentally, is much more soluble in water than salt itself (100 grams of water at 15° C. dissolve 55 grams of magnesium chloride). So if the solution is partly evaporated the magnesium chloride will remain in the mother liquor, the crystals being purer salt.

However thoroughly the crystals drain, a little mother liquor will still cling to them, thus adulterating them with magnesium chloride. To remove this we must *wash* them, say, with water. This will dissolve some salt, but will remove practically all the magnesium chloride.

Again, if we wish to obtain as much of the salt as possible in a pure state, we can continue to evaporate the solution. But a time will come when the magnesium chloride accumulates to such an extent in the mother liquors that it crystallises out with the salt, thus defeating our object. This is only one example of the endless opposition between obtaining the greatest quantity of the product and maintaining the quality or purity.

This method of separating substances which are both soluble, by crystallising one of them from a solution of both, is very generally used as a means of purifying solids. It is known as re-crystallisation. We shall come across many examples of it later on.

The *solubility* of a substance is expressed accurately by the greatest weight dissolved by 100 grams of the liquid at the temperature named; thus the solubility of magnesium chloride is: At 0° C., 53 grams; at 50° C., 60 grams; at 100° C., 73 grams. Or, put another way, a saturated solution of magnesium chloride at 0° C. is made by dissolving 53 grams in 100 grams of water.

### SUMMARY.

Salt is obtained by dissolving the rock salt underground, pumping up the brine, and evaporating till it crystallises.

Small crystals are obtained by rapid evaporation and frequent removal of crystals; large crystals by slow evaporation, the crystals being removed less often.

Solution is used to separate mixtures—

(1). Of soluble and insoluble substances. The soluble substance dissolves, leaving the insoluble ones.

(2). Of various soluble substances. The more soluble is left in the mother liquor on crystallising.

# CHAPTER IV

## THE SEPARATION OF SOLIDS FROM LIQUIDS

It very frequently happens, as, for instance, in crystallising salt, that a mixture of a solid and a liquid is required to be separated as completely as possible into its two constituents.

The simplest way of doing this is to allow the mixture to stand. For instance, muddy water left undisturbed becomes clear by the heavier mud sinking to the bottom of the vessel, leaving the clear water above, which can then be tapped off.

The rate at which the solid settles depends largely on (1) the size of the solid particles, and (2) how much heavier they are than water. Thus in the muddy water the coarse gravel settles first, then the finer sand, and finally the very finest mud.

The fact that heavier substances settle more quickly is used to separate valuable minerals from the rock which is always mixed with them as they come from the mine or quarry.

Thus tinstone, which is nearly seven times as heavy as water (or, to put it accurately, has a specific gravity of 6·8), is easily separated from the earthy material mixed with it, which usually has a specific gravity between 2 and 3. Obviously, to get rid of the effect of the mere size of the lumps, it is necessary to grind the material to, roughly, the same size. Gold, similarly, is separated by this method of *elutriation*, the small nuggets remaining behind when the quartz, etc., is washed away.

Very fine pieces of solid, however heavy, settle slowly, and, when they are so small as to be invisible with a microscope, do not settle at all. Such a suspension is called a *colloidal solution*. These mixtures can be separated only by adding a substance which causes the fine particles to cohere and form larger ones.

The method of separating solids from a liquid by allowing them to settle is very slow, and even in the end the layer of solid on the bottom is very wet. It is usually necessary to get the solid more quickly and with less liquid clinging to it. This is done by *filtering* the mixture.

The simplest way of filtering a small quantity of, say, a mixture of sand and water is to pour the mixture into a funnel lined with a paper cone. (The cone can be easily made by folding a circular piece of filter paper—an unglazed and porous paper—as shown and then opening out one of the larger quarters.) The water flows through the pores of the paper, leaving the sand behind (see Fig. 4).

This method also is slow, and again the solid does not get very dry; so frequently the water is sucked through. Fig. 5 shows how this can be done in a *vacuum filter*. The plate *A* is perforated with holes, and is fixed across the large vessel *B*, and covered with a piece of filter cloth which fits well, *C*. The mixture of solid and liquid is poured or pumped into the top part of *B*, and the air is sucked

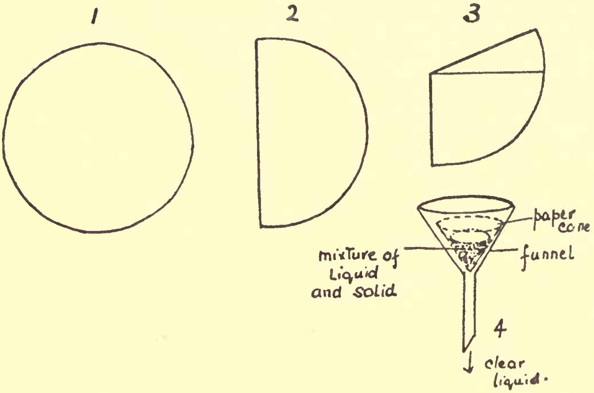

FIG. 4.—Folding a filter paper and filtration through it.

out of the lower part by connecting the outlet *D* to a vacuum pump. The liquid then runs through the cloth much more rapidly than it would do if just left to itself. When the lower part of *B* gets nearly full of the liquid, it can be tapped off from the pipe *E*.

This way of filtering has many disadvantages; for instance, the liquid evaporates more easily in the vacuum than in air, so that more is wasted if it is required to be kept. The solid cake in the upper part, also, has to be dug out when dry: it often develops cracks before all the liquid is removed, and these have to be filled up by scraping the surface solid into them; and also, if the solid is at all fine, the cake becomes hard and dry just above the

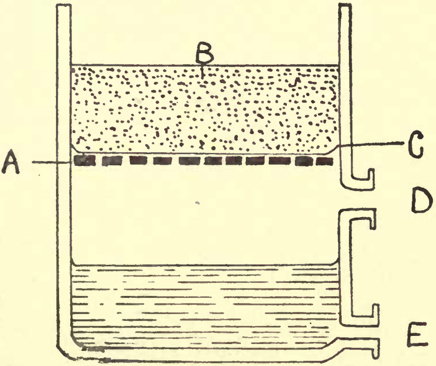

Fig. 5.—Vacuum filter.

surface of the cloth, and does not permit the rest of the liquid to go through.

It is useful, however, when only comparatively small quantities of material have to be dealt with; and the one filter can be used for many different products.

Another form of vacuum filter which is much more useful is the *rotary filter* (Fig. 6). This consists of a wheel *A* with a wide rim which is composed of a series of boxes from which pipes, as additional spokes, lead to the axle *B*, which is also hollow. The outside of the rim is perforated and covered with filter cloth *C*, held on by wire *D* which goes round and round the circumference of the wheel.

The lower half of the wheel is submerged in a tank *E* in which the mixture of solid and liquid is kept stirred by paddles or compressed air. The suction through pipe *F* on the immersed sectors causes a layer of solid to stick to the surface of the cloth, while some of the liquid is sucked through *F*. As the wheel rotates the sector comes out of the tank, and the adhering water is sucked from the layer of sludge. If necessary, the solid cake is washed by a jet of water spraying on to it, *J*. By the time the sector we are following has arrived at the top of the tank on the other side the cake is dry and has been loosened by a puff of compressed air delivered to the chamber by a separate pipe, *H.* It is then scraped off by an inclined plate *K*, and falls down either on to a travelling belt which conveys it to a truck, or direct into a heap below the scraper.

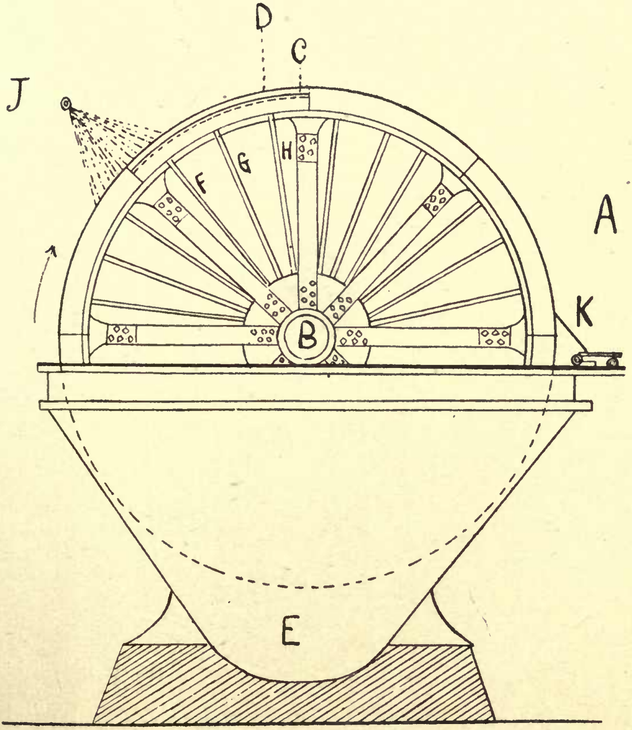

Fig. 6.—Rotary vacuum Filter. F, vacuum pipe for mother liquor; G, vacuum pipe for wash water; H, compressed air pipe.

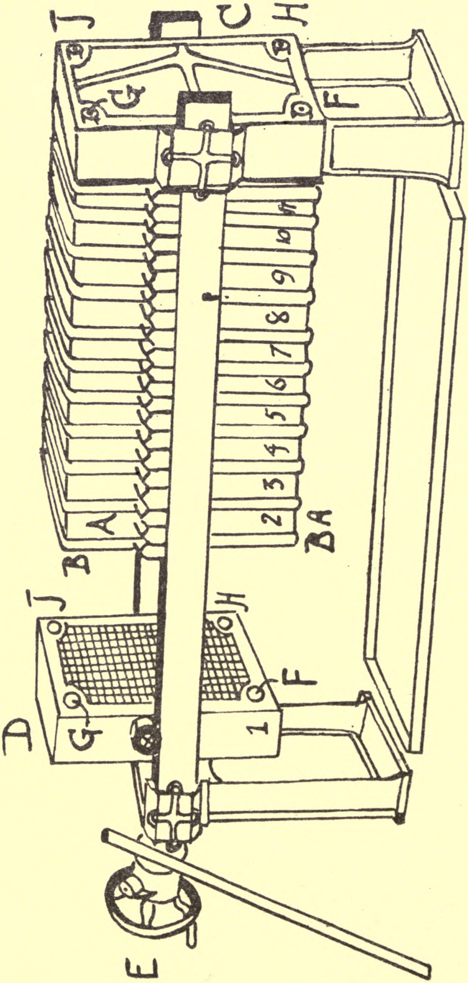

FIG. 7.—Filter Press.

The immense advantage of this type of filter is that it is continuous in action and requires little attention. It is most useful for fine crystals or sandy solids which require to be "de-watered."

Of more general utility is the *filter-press*, one type of which is seen in Fig. 7.

A strong iron frame supports the plates *A* and the frames *B*, which alternate with them. Two strong castings *C* and *D* form the two ends of the series, C being fixed to the iron framework, while *D* can move along the bars supporting the plates and frames. A screw *E*, the head of which can be turned by a lever inserted in slots in it, serves to move *D* and the plates and frames, so that when in use the whole is tightly pressed up against *C*. Filter cloths are arranged to cover both sides of the frames, so that a box is formed, the two sides of filter cloth, the edges by the frame. The mixture of solid and liquid is forced by a pump or compressed air or steam into the pipe *J*, which, formed by holes in plates and frames, runs the whole length of the press. Slots in the frames (see Fig. 8*a*) admit the mixture to the chambers formed by the filter cloths, and the liquid passes through the filter cloths, the solid remaining in the chambers. The liquid escapes along the corrugated surface of the solid plates and out by a pipe *F* at the bottom of each plate, when it can be collected if required. Eventually the chambers become full of solid (as shown by a rise in pressure at the pump). The press, when drained at *F*, is then unscrewed and the frames lifted out, the cloth stripped off, and the cake of solid material knocked out into a truck or other receptacle.

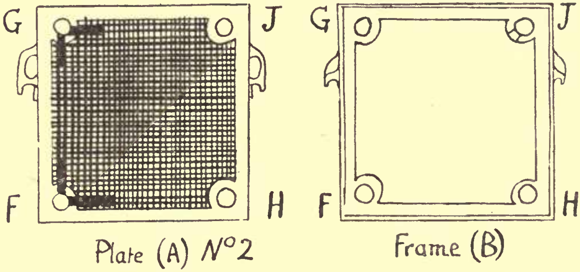

FIG. 8*a*.—Surface view of plate and frame. (Plates 1, 3, 5 . . . differ in having channels at H instead of G.)

If it is required to wash the solid free from a mother liquor, the plates and frames are further perforated with two other series of holes forming two pipes *G*, *H*, leading from cocks in the stationary headpiece. Water is pumped in at the lower of these, *H*, and admitted by slots to plates 1, 3, 5, etc. It percolates the solid cakes in the intervening frames and escapes by slots in plates 2, 4, 6, etc., into the upper main *G*.

The filter press is very generally used for separating such substances as can be pumped through pipe systems, from fine crystals to the slimes in crude oil. A great variety of forms are in use, each suited to deal with a particular mixture of solid and liquid. Its disadvantages include the waste of time in opening and removing cakes, and

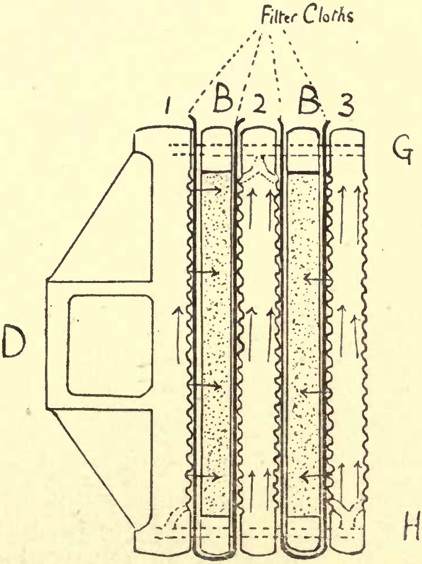

FIG. 8*b*.—Section through a few plates and frames in place. Arrows show direction of wash water.

the manual labour required for that operation.

Particularly with oil-bearing seeds, it is useful sometimes to extract the liquid by sheer pressure. The material is put into bags which are piled up on the base of the press, an iron plate between each bag. A plunger is then forced down on the pile, either by a screw or, more often, by hydraulic pressure. The oil or other liquid flows out of the bags into a gutter round the base of the press and thence to tanks for storage.

The centrifuge or hydro-extractor (Fig. 9) is a suitable means of thoroughly draining crystals or other solids not slimy in consistency. The mixture of crystals and mother liquor is placed in the basket *A*, which is made of perforated copper strengthened by steel bands on the outside and capable of being rotated at high speed (usually about 1,000 revolutions per minute). The solid is thus thrown up against the vertical wall of the basket, and the liquid streams out through the holes into the strong casing *B* to the gutter *C*. If washing is required, water is directed on to the solid in a fine spray. It is obviously necessary that the whole machine should be strongly built, as a break whilst going at full speed might easily cause loss of life. Centrifuges are largely used to dry sugar and starch, wood pulp, and many other substances. Laundries have found them useful for removing the bulk of the water from linen; similarly, they find application in

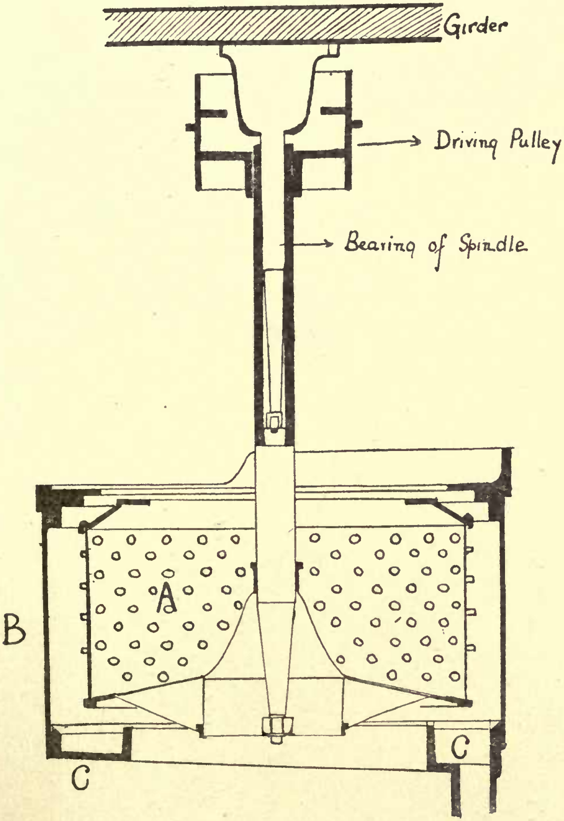

Fig. 9.—Hydro-extractor.

drying yarn and dyed goods in the textile manufactures.

The variety of apparatus used in the separation of solids from liquids is some indication of the great importance of this operation in chemical manufactures and, indeed, in manufactures generally.

# CHAPTER V

## THE CHANGE—LIQUIDS TO GASES

WE have seen in the first chapter how solids melt to liquids; we will now study the way liquids become gases.

The first obvious difference is that liquids can become gases to some extent at any temperature. A puddle of water will dry up without being heated; the petrol in the carburettor of a motor-car engine becomes vapour at the ordinary temperature.

Now a puddle of water, or linen on a clothes line, does not always dry at the same rate; on a dry (and, by preference, windy) day the water evaporates much more quickly than on a still, damp day. This is because the air round about the water which is evaporating can receive only a certain quantity of water, and the warmer it is the more it can take up. Wind assists evaporation by supplying fresh portions of air to be saturated with the water vapour.

For suppose we leave a corked bottle half full of water, the space above the water will in the course of time take up as much water vapour as it can. The air is then said to be *saturated,* in the same way that water becomes saturated with salt; and, like the salt solution, more is soluble at a higher temperature.

A difference is noticed, however, if the water is placed in a vacuum where there is no air; it vaporises to just the same extent as when exposed in air; so that it is not really a solution of water in air, as it occurs equally well without the solvent. The quantity of water which will vaporise at a given temperature in a vacuum is limited. Suppose, for instance, we admit a little water to the space above the mercury in a barometer, which space is ordinarily a vacuum. The water evaporates and, owing to the *pressure* exerted by the vapour, the mercury falls. If water is continuously admitted, little by little, the mercury eventually ceases to fall, and a layer of liquid water is left on the surface of the mercury. At 15° C., for instance, this occurs when the mercury has fallen 12·7 mm. Thus the *pressure of water vapour* at 15° C. is 12·7 mm. of mercury.

The pressure increases as the temperature is raised; at 100° C. it is 760 mm. of mercury —the normal pressure of the atmosphere. So that, if we continued the barometer experiment to this temperature, the mercury would fall the whole height of the original column. (See Fig. 10.)

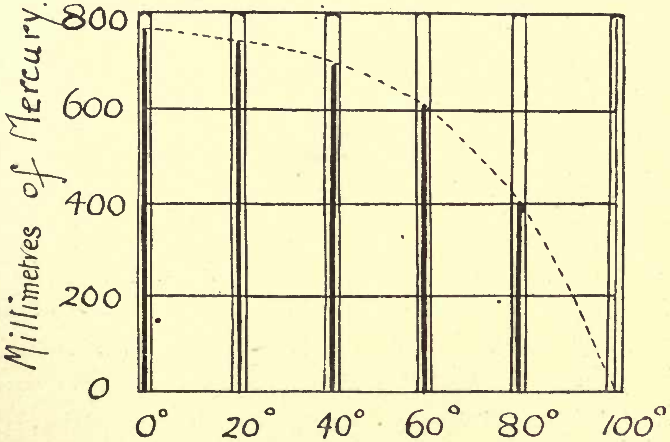

Fig. 10.—Series of barometers showing vapour pressure of water at different temperatures.

In ordinary language, water boils at 100° C., for liquids are said to boil when the vapour pressure becomes equal to the atmospheric pressure. At this temperature evaporation occurs, not only from the surface of the liquid as at lower temperatures, but also from the body of the liquid, which is converted into vapour as rapidly as the necessary heat is supplied to it.

For, just as a quantity of heat is necessary to convert ice into water without raising the temperature, so is it necessary to supply heat to convert water into steam. Actually, to change a gram of water (at 100°) to a gram of steam (also at 100°) 536 calories[1] are required.

A similar quantity of heat (somewhat greater as the temperature is lower) is always required to evaporate a liquid; and, unless supplied intentionally from outside, it is taken from the liquid itself or from objects in contact with it. The fact that one catches cold on remaining for some time in rain-soaked clothes, and the cooling of a bottle of wine by standing it in a draught with a damp cloth wrapped round it, are two everyday examples of this absorption of heat.

Thus when water is heated in a saucepan, say, starting from the ordinary room temperature of 15°, at first the heat is used up (1) in raising the temperature of the water, and (2) in vaporising that quantity which evaporates from the surface. At 100° the whole of the

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[1] Two units of heat quantity are in use: (1) the small calorie (cal.) is the heat required to raise the temperature of 1 gram of *water* from 0° to 1°. (2) The large Calorie (Cal.) is the heat required to raise the temperature of *1000* grams of *water* from 0° to 1°.

heat is used up in operation (2); evaporation proceeds from the body of the liquid, as can be seen by bubbles of vapour arising from all parts of it, and the temperature does not rise any higher.

When the steam or water vapour condenses again, the heat which it took up on conversion into vapour is liberated once more; this source of heat is often convenient to heat up a quantity of cold water in a vat or other vessel to which heat from a fire cannot readily be applied. It is used either as "live steam," in which case the steam is blown direct into the water, or by passing the steam through a coil or series of pipes immersed in the liquid. A scald caused by steam is much more serious than one produced by hot water, owing to the additional heat suddenly given out.

The condensation of the vapour of a liquid is a useful method for obtaining the pure liquid from a solution; for solids in solution do not contaminate the vapour, but remain behind in the liquid. This process is conducted by boiling the liquid in a still (*A*, Fig. 11), the vapour being led from the still head *B* to the condenser *C*. The latter consists essentially of a pipe or system of pipes kept cool, usually by being surrounded by flowing cold water. The vapour in the condenser, being cooled below the boiling-point, becomes liquid and can be run off continuously from the lower end of the condenser.

We must now return to the consideration of the influence of pressure on the change from liquids to gases. We have noticed that liquids boil when the pressure of the vapour becomes equal to that of the atmosphere—that is, in the space above the surface of the liquid. If, now, a liquid is heated in a closed vessel, which must of necessity be strongly

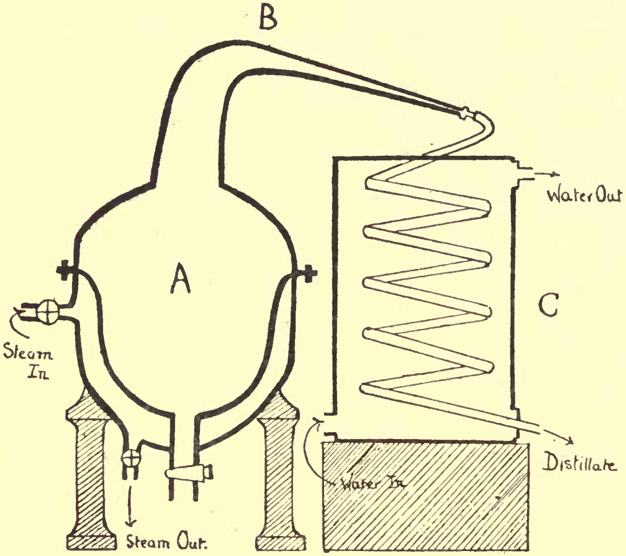


FIG. 11.—Steam-heated still and condenser.

made, the vapour will accumulate above the liquid, thus increasing the pressure, and the temperature of the boiling liquid will be found to rise. Thus water boils at 144° when the pressure is four times the ordinary atmospheric pressure. This important property is utilised, for instance, to extract gelatines from waste bones, etc.; or, again, tea-dust is extracted with benzene under pressure, as the caffeine is much more soluble at the higher temperature. Further, a number of chemical processes are much more rapid at the high temperature which can be attained by heating solutions in an *autoclave*, as such a closed vessel is called.

On the other hand, if the air (and vapour) is pumped out of the vessel containing the liquid, it boils at a lower temperature. Thus, if the pressure in the containing vessel is reduced to 17·4 mm. of mercury, water will boil at 20°. This pressure is the vapour pressure of water at that temperature; and, generally, when the pressure in a vessel containing a liquid is reduced to the value of the vapour pressure at that temperature, the liquid boils.

We shall consider technical applications of this important property in Chapter VI.

The question now arises as to whether the substances which are ordinarily gases can be reduced to the liquid state. Let us take the case of carbon dioxide—a gas formed when carbon (*e.g.* coke, charcoal, etc.) is burnt, and when limestone is heated (see Chapter VIII). This gas can be made liquid by compressing it at the ordinary temperature (50 atmospheres is required at 20°). This operation really amounts to raising the boiling-point (normally − 78°) by increasing the pressure. There is, however, a temperature above which no mere increase of pressure will cause liquefaction of the particular gas in question. This temperature is called the *Critical temperature* of the gas. For carbon dioxide it is 31°.

The existence of this maximum temperature when mere compression becomes effective, means that with gases of low boiling-point it is necessary to cool as well as to compress. For instance, oxygen (the active fifth part of the atmosphere) boils at −182°, and its critical temperature is − 118°. So thus it is necessary to cool to − 118° before compressing. In recent methods this cooling is brought about by allowing the compressed gas (at about 200 atmospheres pressure) to escape through a small hole, the sudden release cooling it considerably; the colder gas is led away over tubes conducting the compressed gas to the pin-hole. The oncoming gas is thus cooled before expansion cools it yet more. Eventually it becomes so cold that expansion cools it below the boiling point and it becomes liquid.

The liquefied gases, at still lower temperatures, freeze to solids; the cooling in this case is brought about by allowing a quantity of the liquid to evaporate rapidly when the heat absorbed in evaporation is sufficient to cool the remaining liquid to the freezing-point.

# CHAPTER VI

## DISTILLATION

The separation of two liquids which do not mix, like oil and water, can easily be done after the fashion of the first method of separating solids from liquids—that is, by allowing the heavier liquid to settle to the bottom of a tank and tapping it off first.

A difficulty arises, however, if the quantity of one of the liquids is small compared with that of the other; for example, the water from the exhaust of a steam-engine is contaminated with a small proportion of oil, which forms an *emulsion*. Such a mixture has many of the properties of a suspension of fine particles of solid matter—a colloidal solution—which we have already noticed in Chapter I. It is then necessary to filter the emulsion through a filter which will retain the oil drops, *e.g.*, if it is desired to use the water again in the steam boiler.

Liquids dissolve in other liquids in a somewhat similar way to solids; but generally the range of solubility is greater, and the property is often described as *miscibility*. Thus water and alcohol, water and glycerin, dissolve mutually in any proportions in which we may choose to mix them, and are therefore said to be completely miscible. If, on the other hand, ether and water are shaken together in equal proportions, two layers soon separate—the upper, a solution of water in ether; the lower, a solution of ether in water. These two liquids are therefore only partially miscible; and we can speak of the solubility of ether in water, and of water in ether, in just the same terms as we did of salt in water in Chapter II. The separation of the two substances is much the same problem whether they are completely or only partially miscible.

Consider, for instance, a mixture of alcohol and water. Pure alcohol boils at 78°, water at 100°. It appears at first sight simple enough to separate a mixture of the two liquids by pouring into a still of the type shown in Fig. 11, and heating the liquid to 78°, when we might expect the alcohol to distil over, leaving the water behind. But we must remember that at 78° water has a considerable vapour pressure, and consequently a good deal will evaporate with the alcohol.

We can, of course, get a liquid stronger in alcohol by re-distilling the liquid condensed. In practice this operation is performed in a simple way by fixing a " head " to the top of the still, the condenser being attached to the upper end of the head. Fig. 12 shows a still with such a head. The head, or *fractionating column A* for use with alcohol, is made of copper and covered with wood (to prevent too rapid cooling). It will be noticed that the vapour rising up the head can enter each chamber only by the valves *V*, whilst the descending liquid must lie on the floor of each chamber as it can escape only by the tubes *d*. Now just as the alcohol is the first to vaporise, so the water is the first to condense. The layer on the floor of a given chamber is heated by the oncoming vapour, which really re-distils it, so that the rising vapour is stronger in alcohol. This process is repeated in each chamber. In the figure shown two columns are arranged side by side known as the analyser *A* and the rectifier *B*, the vapour from the first being led to the bottom of the second. The rectifier is cooled by a series of pipes *C*, through which the liquid from which the alcohol is being distilled (the wash) is pumped ; this liquid is thereby heated and actually admitted to the top of the analyser, so that a good deal of its alcohol is removed before it reaches the still *S*, which is heated by live steam. The

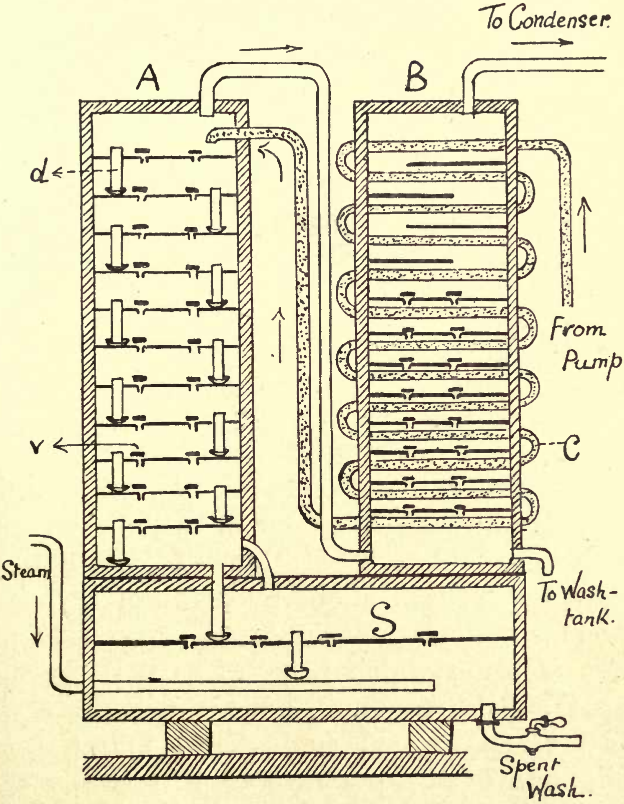


FIG. 12.—Still for rectifying alcohol.

spent wash is removed from the bottom of the still from time to time; and the pipe from the top of the rectifier leads to a worm condenser, where the alcohol, almost free from water, is condensed. The distillation can be controlled by taking the density of the liquid condensed, from which the proportions of alcohol can be found by consulting tables.

The alcohol thus obtained is further purified by a second fractional distillation, the still in this case being heated by external steam; the first fractions are collected separately, as they contain more volatile impurities; also the last portions, which contain fusel oil, a mixture of other alcohols of higher boiling-point. Even then the alcohol is not quite dry (*i.e.*, free from water), and it is necessary to add quicklime to take up the traces of water, and after filtration to re-distil the alcohol.

This is an example of one of the many cases where a *complete* separation of two liquids cannot be brought about by distillation owing to the formation of a "*constant boiling mixture*," *i.e.*, a solution which behaves as if it were a simple substance and distils unchanged. It is necessary to add some third material to retain one of the partners in this temporary combination, such as the quicklime used in this case. Another important instance of this behaviour is met in the case of nitric acid, where the mixture contains 68 per cent. acid;

the water can be removed by distilling with sulphuric acid, which retains it.

In the previous chapter we noted that whilst an increase of pressure in the containing vessel raises the boiling-point, so a decrease of pressure causes the liquid to boil at a lower temperature. This latter property is very useful when, for instance, a liquid decomposes at, or even below, the boiling-point. By distilling *in vacuo*, as the process is not very accurately called, many liquids can be purified which would otherwise have to be treated in some less satisfactory way. Thus hydrogen peroxide decomposes rapidly into water and oxygen when even a weak solution is boiled. But if distilled in a closed system in which the pressure is reduced by a pump to 15 mm. of mercury, the hydrogen peroxide can be distilled unchanged at 70–80°.

The method is also important in the case of liquids with a high boiling-point. Thus aniline boils at 184°, and to reduce the wear of plant and permit the use of steam instead of direct fire as a heating agent, it is frequently distilled *in vacuo*. The exhaust pump to produce the partial vacuum is connected to the receiver, which for such distillations must be connected airtight to the end of the condenser—a precaution not necessary when distilling under ordinary pressure. Fig. 13 shows the connections to the receivers, which are in duplicate, so that one can be emptied, while the other is filling, without admitting air to the plant. Thus when receiver I is full, taps *B* and *C* are closed and *A* is opened, admitting air, when the aniline can be run out from the bottom tap. Meanwhile tap *A* on receiver II is closed, and first *C*, then *B*, is opened. The gauge glasses show when the receivers are full.

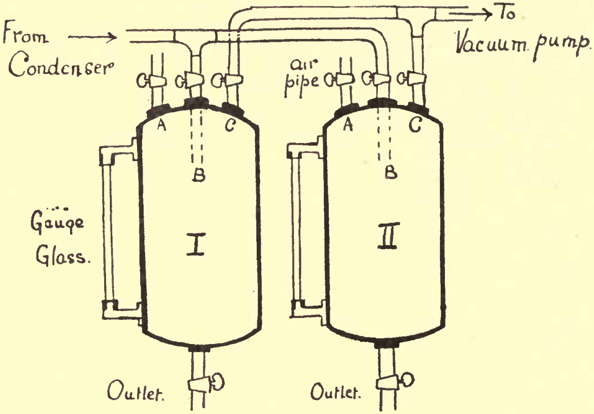


Fig. 13.—Receivers for distillation in vacuo.

The rest of the plant is not shown, as it is similar to an ordinary still and condenser, except that it is strongly made to resist pressure from the outside, and that the condenser must be more efficient than is necessary in plain distillation. A vacuum gauge on the still shows the pressure of working, whilst a plain tube some 15 ft. high serves as a still head.

What is practically a special form of vacuum still is used for removing small quantities of liquid from solids by evaporation. The *vacuum drier* consists of a strong cast-iron chamber fitted with hollow shelves, on which the solid is spread and which can be heated by steam. One side of the chamber is a heavy door, which can be closed airtight once the drier is filled. A pipe leads from the drier through a condenser to the vacuum pump. The liquid is rapidly evaporated, leaving the dry solid, and the temperature is easily controlled, so that the plant is most useful where a substance has to be dried rapidly at a low temperature.

The principle of vacuum distillation is also applied to great advantage in evaporating solutions for crystallisation. The old method described for the evaporation of brine in Chapter III is obviously wasteful of heat, space, and time. In fact, such a crude process has been to a considerable extent supplanted by the use of *evaporators*, as these vacuum evaporation plants are commonly called.

Fig. 14 shows (much simplified) a type of evaporator. Steam is admitted to the wide outer tube *A* through *B*, condensed water being let out through *C*. The interior of *A* is fitted with a large number of tubes *D*, up which the solution to be evaporated (for instance, sugar juice) is pumped, entering by pipe *E*.

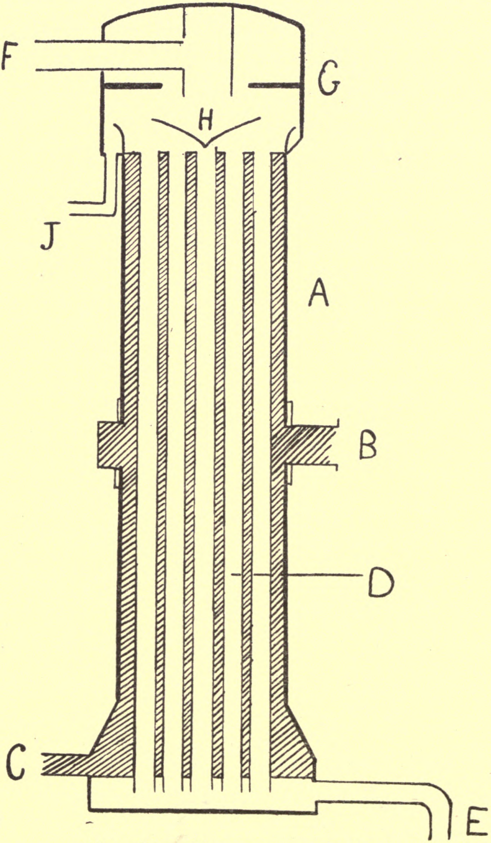


FIG. 14.—Vacuum evaporator.

An exhaust pump, connected through a condenser with the outlet pipe *F*, maintains a vacuum in the pipe system *D* and the head of the evaporator *G*. The solution entering the pipes therefore boils vigorously, the steam bubbles propelling it at great velocity up the pipes. The mixture of vapour and concentrated solution, on reaching the top of the tubes, is forced into a spiral motion by the baffles *H*, which effectually separate the liquid, which flows down to the bottom of *G* and out by pipe *J*, from the steam which escapes by *F* to the condenser.

An obvious economy is to use the steam from the first evaporator, as it issues at *F*, to heat a second one instead of using steam from the boiler as in *A*. To accomplish this, *F* is joined to the inlet corresponding with *B* in a second system. In practice this "double effect," as also "triple" and "quadruple" effects, is commonly used.

The quantity of water evaporated from a given solution depends clearly on the rate at which the liquid is pumped in at *E*. This is so arranged that the concentrated solution issuing at *J* crystallises on cooling.

# CHAPTER VII

## VARIOUS SEPARATIONS

THERE are a number of miscellaneous, but important, points in connection with the separation of the various possible mixtures of solids, liquids, and gases which we will now consider.

The *drying of solids* has been touched on only with reference to the vacuum drier, which obviously has but a limited application owing to its expense and small capacity. Generally, materials are dried by a current of hot, and by preference, dry air. Furnace gases can be used if they do not harm the substance being dried, *e.g.*, for ores. In other cases the air must be heated in other ways so that it remains clean, such as by waste steam in pipes or by hot gases in flues. Dryness of the air used to remove moisture is obviously desirable, though it is not so often insisted on as it should be, owing to the fact that removal of water vapour from air on a large scale is not a very simple operation. One method is to send the air through a moving belt of flannel as it enters the drying chamber, the flannel in another part of its course passing over a steam-heated drum to remove the absorbed moisture. The most effective way of drying the air is to cool it, when the bulk of the moisture is deposited as dew or hoar-frost; but here again the dry air must be re-heated before entering the chambers containing the solid, if the maximum water is to be taken up there.

The solid should be kept in motion during drying. This is often accomplished by rotating a cylinder in which the solid is placed and through which air is blown. The cylinder is heated, and if arranged to slope, the drying is continuous, dry solid issuing from the lower end of the revolving tube. With lumpy solids the ends of the cylinder are closed and heavy balls placed inside, thus crushing the material as it dries. Such a ball mill drier can also be adapted to use under vacuum.

The *removal of* solid *dust* from gases is an important problem in metallurgical industries. This is partly achieved by passing the gas through zigzag pipes or flues, when the solid is deposited. Filters of cloth can be used for cold gases, and fine sprays of water are also effective. The most important method, however, as it can be used for either hot or cold gases, is the Cottrell method of electrical precipitation. In copper smelting, for instance, the fumes contain much sulphur dioxide, a poisonous gas, together with a considerable quantity of the ore in the form of dust. The sulphur dioxide can be dispersed by leading it up a high shaft, but the valuable ore is then lost; if the ore is separated by filters the gases must be cooled, and will then rise very little, and, settling down after coming out of the shaft, blast the surrounding vegetation. It is found that if conductors carrying a high-voltage current are inserted in the hot gases the dust is deposited on the conductors, the gases passing on free of dust.

The electrical method of precipitation can also be applied to *mists*—that is, suspensions of liquid particles in gases. Usually the older methods are still used as in removing tar particles from coal gas. The gas, for example, is passed into a cylinder with many small holes punched in the side. This is surrounded by another cylinder furnished with slots, which do not come opposite the holes in the inner cylinder. The gas is thus forced into a devious route and the tar deposited on the cylinders.

The *separation of* various *gases in a mixture* composed merely of gases can scarcely be generalised. We have already mentioned the method of removing water vapour from air by freezing, and this indicates a general method of separation, viz., cool the mixture down until the desired component liquefies. The air can be separated into its two main parts by liquefying the whole and allowing the nitrogen to distil off. Clearly this can be used as a method of separation only when nothing simpler is possible.

Frequently one of the gases in the mixture is soluble in water or in some other solvent. Thus in crude coal gas there is present a good deal of ammonia, which has to be removed, as it is a valuable product, and if left in would merely reduce the heating power of the gas. In contact with water it dissolves easily, so that to remove it it is only necessary to scrub with water. In order to expose a large surface of the water to the action of the gas it is best to allow the water to flow down over bricks or coke packed loosely in a tower up which the gas passes; or to project sprays of water into the gas. A series of towers is so arranged that the water nearly saturated with the gas to be absorbed encounters the fresh mixture containing much of the soluble gas, whilst fresh water in a further tower removes the last traces from the mixture; or, put generally, the water moves in the opposite direction to the gas.

*Solids which pass direct into gases* and back again to solids without going through the liquid stage are fairly common. All solids give off vapour to a certain extent, noticeably the solids which have a smell, *e.g.*, camphor. Thus at a particular temperature a solid, like a liquid, has a definite vapour pressure. Now in some cases the vapour pressure becomes equal to the pressure of the atmosphere at a temperature below the melting-point of the solid, so that the solid is completely transformed into vapour without melting. On cooling it goes back again to the solid form without passing through a liquid stage. In cases where this occurs it forms a very convenient method of purifying the solid from other matter which does not *sublime*, as this effect is named. Thus iodine, camphor, and sal ammoniac are all purified in this way, the simplest apparatus being a pot of suitable material in which the substance is heated. The vapour condenses as solid on the lid, which can with advantage be made hollow and a stream of cold water passed through it. The impurities remain behind in the bottom of the pot.

We have dealt in a brief manner in this section with some of the important properties of solids, liquids, and gases in general, and with the methods used in handling them and in effecting their separation one from another. Further details than it is possible to give here can be found in the books listed at the end of the section, as well as in volumes dealing with engineering only.

## LITERATURE.

Besides the information in special books, some mentioned below, a great deal can be learned from the catalogues of the various firms dealing in engineering appliances for the chemical industries, and from their advertisements in technical journals, such as (in English) the *Journal of the Society of Chemical Industry, the Chemical Trade Journal, the Chemical Age, Metallurgical and Chemical Engineering*, the *Journal of Industrial and Engineering Chemistry*, etc., as also from the papers in the body of these journals.

### *Books.*

Elements of Chemical Engineering: Grossman.
The Mechanical Appliances of The Chemical and Metallurgical Industries: O. Nagel.
The Function and Scope of the Chemist in a Pharmaceutical Works: C. A. Hill (Institute of Chemistry, 1913).

(*See also list of general literature at end of book.*)

# SECTION B

## CHEMICAL CHANGES

# CHAPTER VIII

## COMBINATION AND DECOMPOSITION

OUR first section has dealt only with the changes which are called physical—that is, those in which the *substance* is not changed, although it may be melted, vaporised, or dissolved; when recovered it is the same substance. We have now to consider the more fundamental changes in which two (or more) substances undergo changes which form *new substances*.

The operation of slaking quicklime is familiar to anyone who has watched building operations. When water is poured on to a lump of lime it crumbles up to a loose white powder and gets very hot. It actually *combines* with about one-third its weight of water.

Frequently, more water than this is used, and the slaked lime allowed to drain, as in this way soluble impurities are washed out, which, if left in the lime, produce a less perfect mortar.

If a portion of such slaked lime is dried in an oven heated to a temperature just above that at which water boils (say, 110° C.), the uncombined water evaporates, leaving the actual compound of quicklime with water.

Working accurately, it is found that 28 parts by weight of lime take up 9 parts by weight of water; this is always the same, however much water is used to slake it, provided, of course, that the excess is driven off. If less than this weight is used and the lime is left in damp air, it will absorb water up to its proper quantity.

These facts indicate a difference between this absorption of water and, say, solution of a substance in water; for in the latter case various solutions of different composition—in fact, of continuously varying composition—can be obtained, saturation itself being dependent on temperature. In the slaked lime the quantity of water retained is quite fixed.

The ammonia obtained in the distillation of coal for the production of coal gas is usually converted into ammonium sulphate for use as a manure. We have already seen that, in the first instance, the ammonia is dissolved by water (Chapter VII). The solution is then boiled, usually with milk of lime, when the ammonia is expelled (with the steam) as a gas. The mixture of steam and ammonia passes up a fractionating column to keep back most of the steam, whilst the ammonia is led by pipes into sulphuric acid, with which it combines, forming ammonium sulphate.

Thus the ammonia, a colourless gas of pungent odour, combining with the acid, a heavy corrosive liquid, forms ammonium sulphate, a white crystalline substance without smell or harmful action.

In weight, 17 parts of ammonia combine with 49 parts of sulphuric acid to give 61 parts of ammonium sulphate.

So much heat is evolved in the combination that there is no need to evaporate the liquid in which the ammonia is absorbed, to cause crystallisation of the sulphate—the evaporation proceeds concurrently with the absorption, and the crystals can be taken out continuously.

Other common examples of this act of combination of substances are found when things burn in the air. The products, of course, may be solids, liquids, or gases. With metals a solid is usually formed. Thus magnesium as used in flashlight powders in photography produces a white powder, which, if carefully collected, weighs 66 per cent. more than the magnesium used, as it has combined with two-thirds its weight of the oxygen in the air.

Zinc, again, is burned in a furnace on a manufacturing scale to produce its oxide (or compound with oxygen), known to the painter as zinc white. The powder volatilises owing to the heat of the furnace, and is condensed in a series of chambers, the coarser material being found nearer the furnace, while the finer and more valuable part of the product is carried to the more distant chambers. Here the increase in weight of oxide over zinc is about 25 per cent. (accurately, 65 parts of zinc give 81 parts of oxide), again due to the oxygen with which it has combined.

When many other substances burn the products are gases. Thus coke, consisting mainly of carbon, gives rise to the invisible gas, carbon dioxide, when completely burnt. Other fuels, which contain varying proportions of carbon and hydrogen, burn to form carbon dioxide and hydrogen oxide, which is water. For every 12 lb. of carbon burnt 44 lb. of carbon dioxide are formed; whilst each pound of hydrogen in a fuel forms 9 lb. of water.

The case of fuels shows very clearly an attendant factor which is present whenever substances combine together—the production of heat and sometimes of light, more generally the liberation of energy. The combination of the definite weights of two substances produces a fixed quantity of heat or other energy. With a fuel this is known as its calorific value, when determined for a kilogram (or pound) by burning in compressed oxygen in a steel bomb immersed in water, to which the heat is transmitted and there measured. For 1 gram of average coal 7500–8000 calories are developed on burning; pure carbon (*e.g.*, diamond) gives 8080 calories, petroleum 12,000, and so on.

More generally we speak of the heat of formation of the final substance, or the heat of combination of the original substances. These terms will be defined accurately at a later stage.

We see thus that when substances combine chemically: (1) they do so in definite weight proportions; (2) the product is utterly different in properties from the original substances; and (3) energy (usually heat) is given out.

We will now proceed to a few typical cases where the opposite occurs—a complex form of matter breaks up to form simpler substances.

The lime we have already mentioned is made by "burning"—that is, strongly heating—chalk, limestone, or marble, all of which are naturally occurring forms of what is known to chemistry as calcium carbonate.

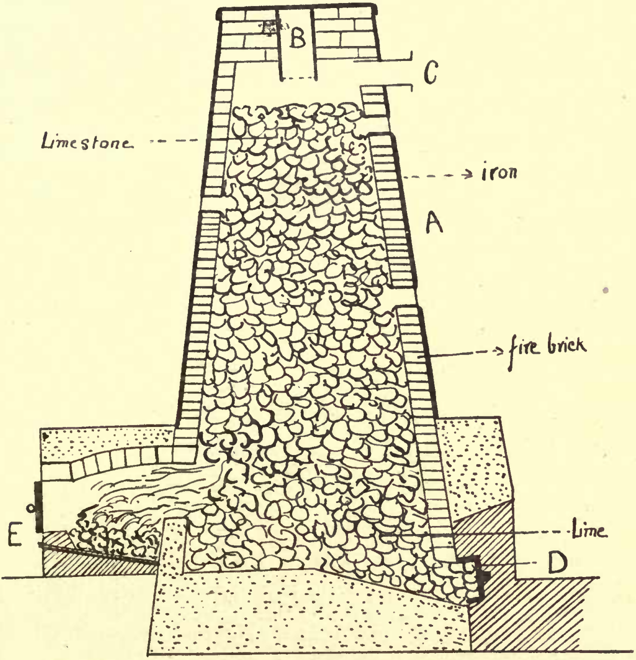


FIG. 15.—Lime kiln.

When heated at about 1000° C., these substances break up into carbon dioxide, a gas, and lime. Industrially, the decomposition is conducted in tall furnaces with arrangements for leading away the carbon dioxide, and continuously adding fresh limestone and removing the lime.

Types of furnace vary with the method of firing, the fuel being either mixed with the limestone or separately burnt. Fig. 15 shows a typical kiln fired by separate fuel.

The kiln *A* is of iron lined with firebrick, a few " windows " being left in order that the progress of the burning may be observed. The limestone is fed in through the top *B*, which is closed after each addition to prevent loss of carbon dioxide, which normally escapes through the tubes *C*. The finished lime is raked out from the bottom of the tower *D*. The mass in the tower is heated by coal burned in hearths shown at *E*, the temperature being regulated by the fire-dampers. Three hearths are placed round the kiln and alternate with three openings for discharging the lime.

Coke can be used for firing when the fuel is mixed with the limestone, but obviously the lime will be contaminated with the ash of the coke; on the other hand, the carbon dioxide produced is of a higher degree of purity.

Allowing for slight impurities in the limestone (mostly silica, alumina, and iron oxide), which are almost unaltered in the heating, 100 parts by weight of limestone yield 56 parts of lime and 44 of carbon dioxide; and to bring about the decomposition of 1 kilo. of calcium carbonate, 425 Calories are required.

We have in this case, therefore, the breaking up of a compound into two simpler substances; definite weights of each are produced from a given weight of the limestone, and energy must be supplied in definite quantity to effect the rupture of the original substance.

We will now consider two cases in which the energy required to split up a compound is supplied in the form of an electric current.

Aluminium, a metal important, owing to its lightness, in the construction of aeroplanes and airships, is now made entirely by decomposing aluminium oxide into aluminium and oxygen by means of the electric current.

The apparatus used is shown in Fig. 16. An iron box *A* is packed with carbon blocks *B*, and is connected to the negative pole of the source of current. The hearth in the centre is filled with sodium aluminium fluoride (in the form of the mineral cryolite), and about 20 per cent. of pure aluminium oxide is added. A bundle of carbon rods *C* dips into the mixture, and is joined to the positive terminal of the dynamo. On passing the current the cryolite fuses, and the temperature is maintained at 900°–1000° by the mere heating effect of the current. The aluminium oxide is decomposed, the molten aluminium sinking to the bottom of the hearth at *D*, whence it is tapped off periodically at *E*. The oxygen passes off at the positive pole, where it causes the carbon rods to burn.

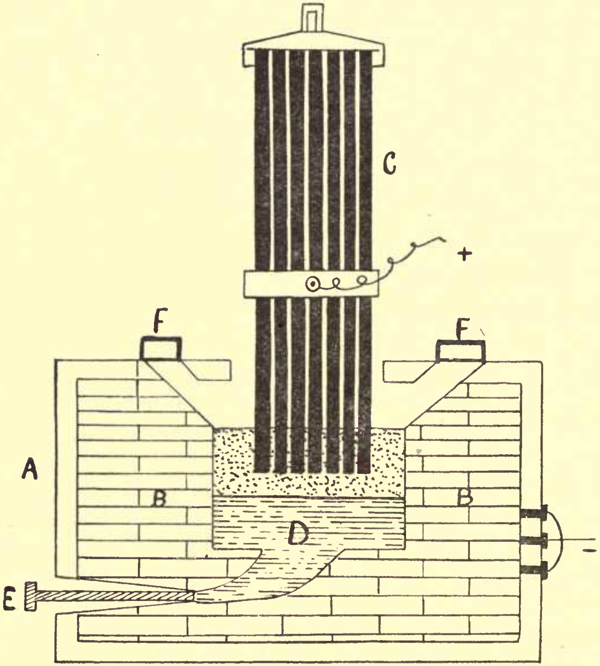


FIG. 16.—Furnace for producing aluminium from its oxide.

Fresh alumina is added as required by the holes *F*. The cryolite is unchanged during the process, and is added merely to lower the melting-point of the alumina.

We have thus an instance where a substance, alumina, which is a white powder, is decomposed into two other materials—the well-known metal aluminium and the gas oxygen—of which it is made up. It is found that 17 parts of alumina yield 9 parts of aluminium and 8 parts of oxygen. Similarly, when aluminium is burnt in the air (*i.e.* re-combines with the oxygen) 9 parts of the metal give 17 parts of alumina.

A somewhat similar case is the decomposition of common salt (sodium chloride) into its two components, sodium and chlorine. Here again the reaction occurs at a high temperature, as it is necessary to fuse the salt.

The apparatus is shown in Fig. 17, and consists of a U-tube in which one limb *A* is made of fireclay, the other, *B*, of iron, being joined to the negative pole of the current source. The junction of the two limbs is made by a ring of solidified salt caused by water circulating through an annular tube *T*. The positive pole consists of a stout carbon rod *C* in the fireclay limb. Fresh salt is fed in through the basket *D*. On passing the current sodium is set free in the iron limb, where it eventually overflows by a side pipe; the chlorine, which appears at the carbon pole, rises through the molten salt *S* and escapes by the pipe *E*.

Here again definite quantities are produced by the decomposition, 58·5 parts of salt giving 23 parts of sodium and 35·5 parts (by weight) of chlorine.

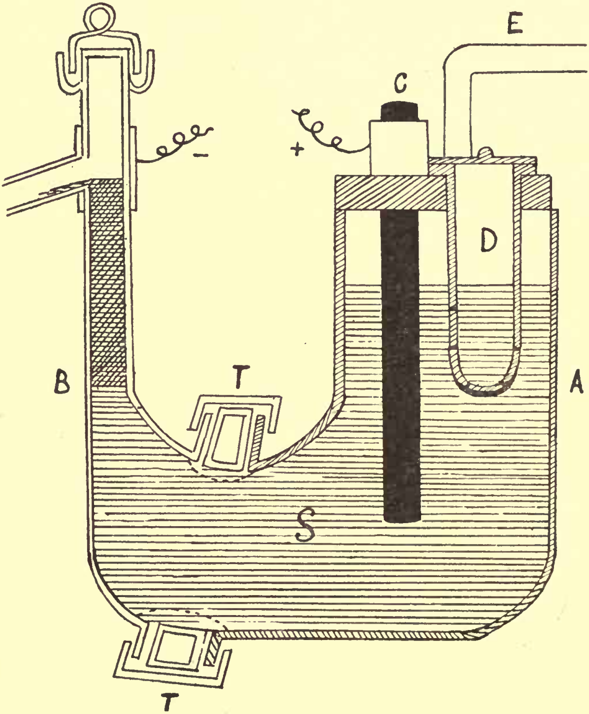


FIG. 17.—Decomposition of molten salt into sodium and chlorine.

In the last two decompositions studied the products, aluminium and oxygen, and sodium and chlorine, cannot be further broken up by any known process. Such ultimate substances are called *elements*. With chalk, on the other hand, the substances formed by roasting are known to be made up of two elements in each case—lime, of calcium and oxygen; carbon dioxide, of carbon and oxygen. These more complex bodies containing more than one element are called *compounds*.

From a qualitative point of view the most astonishing thing about the combination of substances is the great difference in almost all properties between the compound formed and the substances from which it is made. The salt of every day is formed from the soft metal sodium and the choking green gas chlorine. Alumina, which forms a large part of clay, bricks, and pottery, is formed from the white metal aluminium and the gas oxygen. These facts are not explained by calling salt sodium chloride or by the use of symbols, although these scientific terms are useful in describing and comparing the compounds; such astounding results of chemical reaction must at present be accepted as some of the wonders of the world, now many more than seven.

# CHAPTER IX

## ELEMENTS AND COMPOUNDS

We saw in the previous chapter that substances can unite together to make more complex bodies, and, in the reverse way, some substances can be split up by suitable means into two or more different and simpler kinds of matter.

In the end we come to certain sorts of stuff which cannot be decomposed any further. Zinc is one of these, and so far it has not been broken down into two different substances. Similarly with aluminium and with sodium. All new substances made from these contain, say, zinc *plus* something else. These fundamental substances, of which the universe is made, are called *elements*.

The two tests which an element must satisfy are, therefore: (1) it cannot be decomposed into other substances; (2) it cannot be made by the combination of other substances.

Take, for instance, water, which was

considered to be an element for a very long time. It is not easy to decompose it if quite pure, but it can be easily made by the combination of hydrogen and oxygen. Thus it is not an element.

Lime, similarly, can be made by burning calcium in oxygen; in fact, it is calcium oxide—a *compound* of these two elements.

Alumina is broken up by the electric current into the two elements from which it is made—aluminium and oxygen.

A complete list of the elements at present recognised is given at the end of the book.

We have, therefore, a new way of classifying matter (as compared with that used in Chapter I—solids, liquids, and gases), that is, elements, and compounds—new substances made by combination of two or more elements.

For instance, suppose we mix the two elements aluminium and sulphur, both finely powdered. We can easily make various *mixtures* by using more or less of one of the two elements.

If we heat such a mixture, the two elements unite with great vigour, giving out heat and forming a grey powder quite different from either sulphur or aluminium in its properties. It is called aluminium sulphide, and when wetted with water emits an evil-smelling gas.

Again, unless the correct mixture is made before combination occurs we shall have either some aluminium or sulphur left over unchanged. But, using, say, 9 grams of aluminium and 16 grams of sulphur, the whole of both elements is used up in making the compound.

Thus compounds (1) have a fixed composition; (2) are formed with evolution (or absorption) of heat; and (3) have different properties from the mixture of the elements composing them.

As a further example we can note the formation of zinc oxide from zinc, described in Chapter VIII. This compound is a white powder quite different from the metal (and element) zinc which it contains. Also 65 grams of zinc yield 81 grams of zinc oxide, the difference (16 grams) being oxygen, which has come from the air.

If, on the other hand, zinc is heated with sulphur, we find that 65 grams of zinc form 97 grams of zinc sulphide by uniting with 32 grams of sulphur. Also, when sulphur burns, 32 grams unite with 32 (*i.e.* 2 × 16) grams of oxygen to form 64 grams of sulphur dioxide.

Cases like this can be quoted without end, in which, say, multiples of 16 parts by weight of oxygen unite with a fixed number of parts by weight of other elements.

It is therefore supposed that the union occurs between very small particles of oxygen of weight corresponding with the number 16 and of zinc of weight corresponding with the number 65. These very small pieces of the element are called *atoms*, and these numbers the *atomic weights*.

It is found that hydrogen has the smallest atomic weight of all, so in order to avoid fractions this is called 1, and the others are calculated from it. A complete list is given at the end of the book. Thus the atomic weight of oxygen is 16, of zinc 65, of sulphur 32, and so on.

As a kind of shorthand the initial letter of the name of the element is generally used to indicate an atom; where several begin with the same letter a small letter is added to distinguish them (thus Aluminium, Al; Arsenic, As). When dealing with more than one atom the number is shown by adding a small figure to the bottom right hand of the *symbol*, as these letters are called (*e.g.* $O_2$ means "two atoms of oxygen"; $Al_3$, "three atoms of aluminium," and so forth).

When two or more different atoms combine to form a compound, this is shown by writing the symbols side by side, thus: $ZnO$ is zinc oxide; $Al_2S_3$ is aluminium sulphide, made by two atoms of aluminium uniting with three of sulphur. It will be seen how clearly this method of writing shows what the compound is made of, though naturally the facts have to be found out before the symbols can be written. The collection of symbols representing a compound is called a *formula.*

We can now write a complete summary of what happens when zinc burns in air to form zinc white, as follows:

$$Zn + O \longrightarrow ZnO,$$

or, one atom of zinc combines with one atom of oxygen to form zinc oxide. This method of showing a chemical reaction is called the *equation* of the reaction, as the total weights on the two sides of the arrow are the same.

The small particle of the compound zinc oxide produced from one atom of each of its components is called a *molecule* of zinc oxide. Its weight is the sum of the weights of the atoms which compose it (in the case of zinc oxide $65 + 16 = 81$) and is called its *molecular weight.*

We have thus two different kinds of small particles: *atoms,* the small portions of an *element* that take part in chemical processes;

and *molecules*, the smallest portions which exist separately, whether of an element or of a compound. Thus in the case of oxygen the atom O (weight 16) is joined in pairs in the gas, forming molecules $O_2$ (molecular weight, 32). Salt, of formula NaCl, has a molecule made up of one atom of sodium (Na) and one of chlorine (Cl).

We cannot study here the methods by which atomic and molecular weights are fixed. The latter can be found easily in the case of *gases* by determining the density, *i.e.* how many times heavier than hydrogen the other gas is. For instance, the density of oxygen is 16, and, as in all cases, by doubling this figure the molecular weight is obtained (in this case 32). Little is known as to the molecular weights of liquids, and less still with regard to solids. In these latter cases it is the practice to use the simplest formula, *e.g.* in the case of common salt NaCl, and in that of aluminium oxide $Al_2O_3$.

In the case of atomic weights it is easy to find by careful experiment the weights of two elements which combine to form a compound, *e.g.* 8 grams of oxygen unite with 1 gram of hydrogen to form 9 grams of water. Now the molecular weight of water (in the form of steam) is found to be 18. Thus a molecule will be made of 2 parts by weight of hydrogen and

16 of oxygen. The atomic weight of hydrogen being 1, the formula of water must contain $H_2$. The 16 parts of oxygen may represent one atom or several. But as it is found, in a large number of compounds, that no less quantity than 16 of oxygen occurs *in one molecule*, the atomic weight is taken as 16.

We will now see in one or two cases the great use of equations, etc.

Suppose, for instance, we wish to know how much zinc white we can possibly get from one ton of pure zinc. To be quite accurate we must double our previous equation (for the oxygen atoms, as mentioned above, are joined in pairs in the gas, thus making its formula $O_2$):

$$\begin{array}{ccc} 2Zn + O_2 & \rightarrow & 2ZnO \\ (2 \times 65) + (2 \times 16) & \rightarrow & 2 \times (65 + 16). \end{array}$$

and we can insert the weights beneath the formula after looking them up in the table of atomic weights.

Thus

$(2 \times 65)$ parts of zinc yield
$2 \times (65 + 16)$ parts of zinc white.

$\therefore$ 130 parts of zinc give 162 parts of zinc oxide.

So 1 ton of zinc gives $\frac{162}{130} = 1{\cdot}246$ tons of zinc white.

Or, if lime is being made from limestone (calcium carbonate), we can again calculate the requisite quantities. The equation in this instance being

$$\begin{array}{ccccc} CaCO_3 & \longrightarrow & CaO & + & CO_2 \\ (40+12+48) & & (40+16) & & (12+32) \end{array}$$

$$\textit{i.e.}\quad \left.\begin{array}{c}100\\\text{parts of}\\\text{calcium}\\\text{carbonate}\end{array}\right\}\text{give}\left\{\begin{array}{c}56\\\text{parts of}\\\text{lime}\end{array}\right\}\text{and}\left\{\begin{array}{c}44\\\text{parts of}\\\text{carbon}\\\text{dioxide}\end{array}\right\}$$

In slaking the lime, also,

$$\begin{array}{ccccc} CaO & + & H_2O & \longrightarrow & CaO.H_2O \\ 56 & & 18 & & 74 \end{array}$$

We shall come across many more cases of the uses of symbols, formulæ, and equations. It is important to beware of writing equations on the evidence of the imagination alone; they should in all cases represent the result of someone's accurate weighing of the substances concerned.

We have already mentioned the heat of formation of compounds. This quantity of energy is accurately defined as the heat evolved when the molecular weights (in grams) of the two combining substances react. Thus carbon burning to carbon dioxide evolves 97,000 calories per gram-molecule.

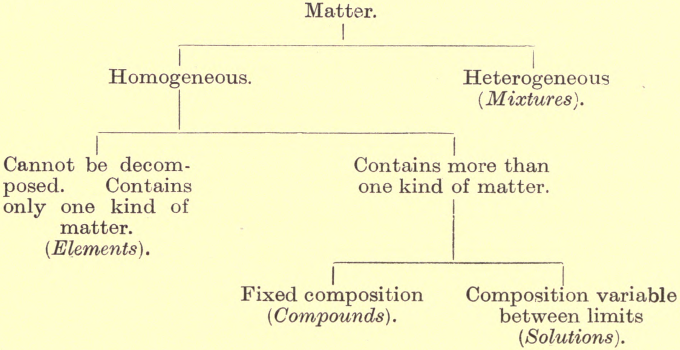
$$C + O_2 \longrightarrow CO_2 + 97{,}000 \text{ cals.}$$

Compounds, like carbon dioxide, formed with evolution of heat are classed as *exothermic* compounds; a few, like carbon disulphide, are formed with absorption of heat:

$$C + S_2 \longrightarrow CS_2 - 28{,}700 \text{ cals.}$$

and are called *endothermic* compounds.

The following scheme is an outline of the classification of matter we have dealt with so far:



# CHAPTER X

## SIMPLE CHEMICAL CHANGES (1)

We will now consider a number of simple but important chemical changes in the light of the atomic and molecular theories.

A common type is that in which one element, which we will call $A$, takes the place of another element, $B$, in a compound, say $BX$. Thus, starting with $BX$ and $A$, we produce $AX$ and $B$. This kind of reaction is most important as applied in winning metals from their ores, in which the metals are combined with such elements as oxygen, sulphur, or oxygen and carbon together. A cheaper element, usually carbon, is used to take the place of the metal in the compound, thus setting the metal free.

As a concrete example we will take the replacement of iron in iron oxide by aluminium. Naturally, this is not a commercial process on a large scale, for aluminium is much more expensive than iron; but it is extremely useful where a small quantity of molten iron is required at a particular spot, *e.g.* to weld two tram-lines together, or to mend a crack in a large casting. The aluminium powder is well mixed with iron oxide in the form of hammer scale, and the mixture (known as thermit) is placed in a clay mould round the place where the molten iron is wanted. The action is started by a small piece of magnesium ribbon stuck into a small heap of a mixture of aluminium and barium peroxide—the burning of this mixture gives a sufficient temperature at that point to set the main reaction going. The products are aluminium oxide and iron, the heat developed being great enough to melt both. The heavier iron sinks to the bottom and is covered by the slag of aluminium oxide.

Expressed in the atomic notation,

$$\underset{\text{Iron oxide}}{3Fe_3O_4} + \underset{\text{Aluminium}}{8Al} \rightarrow \underset{\text{Aluminium oxide}}{4Al_2O_3} + \underset{\text{Iron}}{9Fe}$$

from which we can see that the aluminium has taken the place of the iron which was originally combined with the oxygen.

This method of smelting is used in commerce only when it is desired to produce a metal more expensive than aluminium itself—for instance, tungsten, manganese, or chromium.

For instance, tungsten is frequently made by using up to ten tons of the mixture of tungstic oxide and aluminium in a large mould of sand.

The metal produced is mostly used in making alloys. Tungsten steels have the property of retaining their hardness at high temperatures, and are thus used for high-speed tools. Here the reaction is

$$\underset{\text{Tungstic oxide.}}{WO_3} + 2Al \rightarrow Al_2O_3 + W$$

More generally, *carbon* is used to replace the metal required free, as in smelting most of the common metals. In the case of iron, for instance, the ore, after a preliminary roasting to remove water, carbon dioxide, and some other impurities, is mixed with a flux which will form a slag with the earthy impurities in the ore—in England limestone is used. It is further mixed with coke, and finally fed into the top of a blast furnace. This form of furnace is cylindrical and some 80 ft. high and 20 ft. in diameter at the widest part, lined with firebrick and cased in riveted iron plates. It narrows towards the top to a cup and cone feeder, below which a side tube carries off the furnace gases. At the bottom the sides again slope inwards to the hearth of diameter 8 ft., where the molten iron, and above it the slag, collect. Openings are provided for tapping off both these products, and also for the tuyères—water-cooled nozzles through which a blast of hot and preferably dry air is blown into the furnace. The reactions which occur in the various parts of the furnace are complex, but in general (1) the carbon replaces the iron in the ore,

$$Fe_2O_3 + 3C \longrightarrow 3CO + 2Fe,$$

thus setting free iron which dissolves some carbon and flows down to the bottom of the furnace. (2) The limestone decomposes as in an ordinary kiln, the lime forming a slag with silica, alumina, etc. With silica the reaction

$$SiO_2 + CaO \longrightarrow \underset{\text{Calcium silicate.}}{CaSiO_3}$$

occurs, the molten silicate flowing down and settling above the iron. (3) The gases evolved at the top of the furnace contain about 25 per cent. of carbon monoxide (CO) mixed with carbon dioxide ($CO_2$) and nitrogen. The monoxide is combustible and is burnt,

$$2CO + O_2 \longrightarrow 2CO_2,$$

to heat the air for the tuyères.

Similarly, tinstone (tin oxide) is smelted with coal, after a preliminary roast to remove sulphur, the carbon taking the place of the tin in its combination with oxygen.

$$SnO_2 + 2C \longrightarrow 2CO + Sn.$$

This reaction occurs at a much lower temperature than the corresponding reduction of iron ores.

Lead and bismuth are sometimes obtained

from their sulphide ores by using iron to replace the more valuable metal. Thus with galena (lead sulphide),

$$PbS + Fe \longrightarrow Pb + FeS,$$

and in the case of bismuth glance,

$$Bi_2S_3 + 3Fe \longrightarrow 2Bi + 3FeS.$$

Copper is smelted by a more complex method, but it is often useful to precipitate copper from waste liquors by means of metallic iron. Thus burnt pyrites containing as little as 1 per cent. of copper is exposed to the air and then treated with sulphuric acid, forming copper sulphate. When scrap iron is put into the solution, ferrous sulphate and metallic copper are produced, the latter being collected and refined.

$$CuSO_4 + Fe \longrightarrow Cu + FeSO_4.$$

This simple replacement of one metal in a salt in solution by the addition of a second metal can easily be observed by placing a knife-blade in a solution of copper sulphate. Zinc also sets free copper from solution of its sulphate; copper will become covered with gold if put into a solution of gold chloride. In fact, a list of the metals can be made in which a particular metal will displace metal following it in the list, and be displaced by those which precede it. The order for the common metals is: Mg, Al, Zn, Fe, Ni, Sn, Pb, Sb, Bi, As, Cu, Hg, Ag, Pt, Au. Further, if plates of two different metals are immersed in dilute acid and joined by a wire, an electric current flows from the metal later in the list to the one earlier. Other conditions being the same, the farther apart the two metals are in the list the stronger the current, *i.e.* the greater the voltage produced. This is the fundamental fact on which the ordinary electric cell is based; a further discussion is deferred to Section E. Chemically, it is expressed by saying that the elements first in the list are more *electro-positive* than those that come later. Hydrogen, which in this connection behaves like a metal, occupies a place between lead and antimony; metals before it in the list replace it in acids, and often in water. Thus zinc liberates hydrogen from acids and from steam; whereas copper, a post-hydrogen element, sets free no hydrogen from acids, and hydrogen itself takes the place of copper in copper oxide when that substance is heated and hydrogen passed over it:

$$H_2 + CuO \longrightarrow Cu + H_2O.$$

We have thus a number of examples of the type of chemical reaction in which one element replaces another in a compound. We shall discuss some more cases in the next chapter.

# CHAPTER XI

## SIMPLE CHEMICAL CHANGES (2)

ELEMENTS other than metals can replace one another in much the same way as metals, and this method is used to obtain some of them in the free state from compounds which occur in Nature. Thus in the Stassfurt salt deposits there is about 1 per cent. of magnesium bromide in the bulk of crude potassium chloride, and after the potassium chloride has been crystallised the mother liquor becomes rich in magnesium bromide, the more soluble substance.

The bromine is obtained from this mother liquor by treating it with chlorine gas, which takes the place of the bromine, thus :

$$MgBr_2 + Cl_2 \longrightarrow Br_2 + MgCl_2.$$

The reaction is allowed to take place in towers made of sandstone, with partitions similar to those in an ordinary fractionating column. The mother liquor is heated and admitted to the top of the column, when it meets the upward stream of chlorine sent in at the bottom. The liberated bromine is swept upwards and passes out of the tower by a side pipe near the top, to an earthenware coil immersed in water, in which it condenses and so is collected.

It is important to prevent the escape of bromine vapours into the air; so the receiver at the end of the coil only opens to the air through a tube containing damp iron filings, which combine with the bromine,

$$2Fe + 3Br_2 \longrightarrow 2FeBr_3,$$

forming iron bromide.

Chlorine itself can be set free from its compound with hydrogen (hydrogen chloride) by the use of oxygen under conditions which we discuss in a later chapter. The other product is the compound of hydrogen with oxygen—water:

$$4HCl + O_2 \longrightarrow 2H_2O + 2Cl_2$$

In other circumstances the reverse action occurs—for example, when a solution of chlorine in water is left in sunlight:

$$2Cl_2 + 2H_2O \longrightarrow 4HCl + O_2.$$

The replacement of the hydrogen of steam by carbon, with liberation of the hydrogen, is an important method of producing a gaseous fuel suitable for heating retorts, ovens, etc., in an equable manner. Coke is burnt in a draught until a temperature of over 1000° is produced in the mass. Then steam is blown through it, and the following reaction occurs:

$$\mathrm{C + H_2O \longrightarrow H_2 + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO}}$$

The mixture of hydrogen and carbon monoxide is led away by pipes and burnt where required. The reaction, however, absorbs heat (about 2900 calories for each 12 grams of carbon gasified), so that the mass of coke must be re-heated after about four minutes, with an ordinary plant. The heating is accomplished by blowing air through for about ten minutes, the two operations alternating in this fashion. The gas produced is known as *water-gas*, and when properly made consists of a mixture of equal volumes of hydrogen and carbon monoxide, though about 7 per cent. of non-burning gas is often present. Frequently the steam and air are blown in together to avoid the discontinuity of the above procedure, but the gas thus produced contains 50 per cent. of incombustible nitrogen. Such a gas is called *producer-gas*, as also one made without the use of steam at all, such as the gas which burns with a blue flame on the surface of a clear coal fire.

We can indicate only briefly the advantages of the use of water- or producer-gas over the direct combustion of the solid fuel where heat is needed. The cleanliness of the gas, the ease with which it is controlled, and the fact that it burns without smoke and requires very little air above that needed for complete burning are all points in its favour. The energy of combustion of the gas can also be converted direct into mechanical power by its use in gas-engines.

The replacement of one element by another is important in the more complex compounds of carbon. Thus the hydrogen in benzene ($C_6H_6$) is capable of being replaced wholly or in part by various elements (*e.g.* Cl, Br, I), as also by various combinations of elements, such as OH, $NH_2$, $NO_2$, $SO_3H$, etc. A typical instance is the replacement of one of the six atoms of hydrogen by chlorine to form monochlorbenzene. The benzene, which boils at 80°, is heated in a still surmounted by a fractionating column, leading in the usual way to a condenser. The benzene which distils over runs into a vessel containing masses of iron and iron chloride, which serve to hasten the reaction. Chlorine from a cylinder of liquefied gas is bubbled in and reacts with the benzene. The hydrogen which is replaced does not appear as the free element, but combines with the chlorine thus:

$$\underset{\text{Benzene.}}{C_6H_6} + Cl_2 \longrightarrow \underset{\substack{\text{Monochlor-}\\\text{benzene.}}}{C_6H_5Cl} + \underset{\substack{\text{Hydrogen}\\\text{chloride.}}}{HCl}.$$

The chlorinated liquid flows back into the original still, where the substitution product, which boils at 132°, accumulates. The plant is arranged in this way so that there is always an excess of benzene in the chlorinating vessel, otherwise compounds with more than one atom of hydrogen replaced are formed. Finally, any excess benzene is removed by distillation, the monochlorbenzene being also purified by this means.

# CHAPTER XII

## DOUBLE DECOMPOSITIONS—MANUFACTURE OF POTASSIUM NITRATE AND OF NITRIC ACID

We have so far considered (besides simple combination and decomposition as met with in Chapter VIII) only reactions in which a free element takes part. Much more frequent are the cases in which a number of compounds undergo change resulting in a number of new compounds, none of the elements being free. Such reactions are called " double decompositions," and taking the simplest instance of two compounds, which we will call *AX* and *BY*, we find at the end of the reaction *AY* and *BX*, two new arrangements of atoms, produced.

Such reactions are commonly carried out in solution. Thus, in preparing crystalline aluminium chloride a solution of aluminium sulphate is made, and to this is added a solution of barium chloride, when the following reaction occurs :

$$\underset{\text{Aluminium sulphate.}}{\mathrm{Al_2(SO_4)_3}} \underset{+}{+} \underset{\text{Barium chloride.}}{3\mathrm{BaCl_2}} \underset{\text{give}}{\longrightarrow} \underset{\text{Aluminium chloride.}}{2\mathrm{AlCl_3}} \underset{+}{+} \underset{\text{Barium sulphate.}}{3\mathrm{BaSO_4}}$$

Now as barium sulphate is almost insoluble in water, it settles out as a fine white powder; the barium chloride is added until a small portion of the mixture, filtered, gives no further barium sulphate with a drop of barium chloride, when the whole is filtered or allowed to settle clear. The liquid freed from barium sulphate is evaporated to obtain the aluminium chloride as crystals, which contain water combined with the chloride and have for formula $AlCl_3.6H_2O$.

The above simple example indicates some of the many problems to which such reactions give rise. The raw materials (on the left hand of the equation) must be mixed or otherwise brought into such contact that the reaction occurs; equally important is the separation of the products (right hand of equation). Where one is not soluble, as barium sulphate, the separation is not difficult; in other cases the varied means of separating solids, liquids, and gases from mixtures as set forth in Section A must be applied, if we require to obtain the products each in a pure state.

In many cases both the products, as well as the raw materials, are soluble in water (or in the other solvent which may be used). Chile saltpetre, for instance, is mainly sodium nitrate and cannot be used direct for making gunpowder, as it absorbs moisture from the air.

It is therefore converted into potassium nitrate, which remains dry, this transformation being usually accomplished by adding potassium chloride to the sodium nitrate in solution in water thus :

$$\underset{\substack{\text{Sodium}\\\text{nitrate.}}}{NaNO_3} + \underset{\substack{\text{Potass.}\\\text{chloride.}}}{KCl} \longrightarrow \underset{\substack{\text{Sodium}\\\text{chloride.}}}{NaCl} + \underset{\substack{\text{Potass.}\\\text{nitrate.}}}{KNO_3}$$

Now both the products—sodium chloride and potassium nitrate—are soluble in water ; hence, if solutions of the raw materials are merely mixed, nothing appears to have happened. In order to separate pure potassium nitrate advantage is taken of differences in solubility, which we shall now discuss.

Fig. 18 shows diagrammatically the solubility of sodium chloride and of potassium nitrate at various temperatures. The curves have been obtained by determining the solubility of the salts at various temperatures, plotting the results on graph paper graduated in grams on the vertical scale, and in degrees Centigrade on the horizontal one. It is thus possible to read off from either curve the quantity of substance which can be dissolved in 100 grams of water at any particular temperature, and also to get a picture of the relative solubilities of the two substances at various temperatures. Thus it will be noticed that, at

20°, 32 grams of $KNO_3$ are dissolved and 36 grams of NaCl; whereas, at 100°, 246 grams

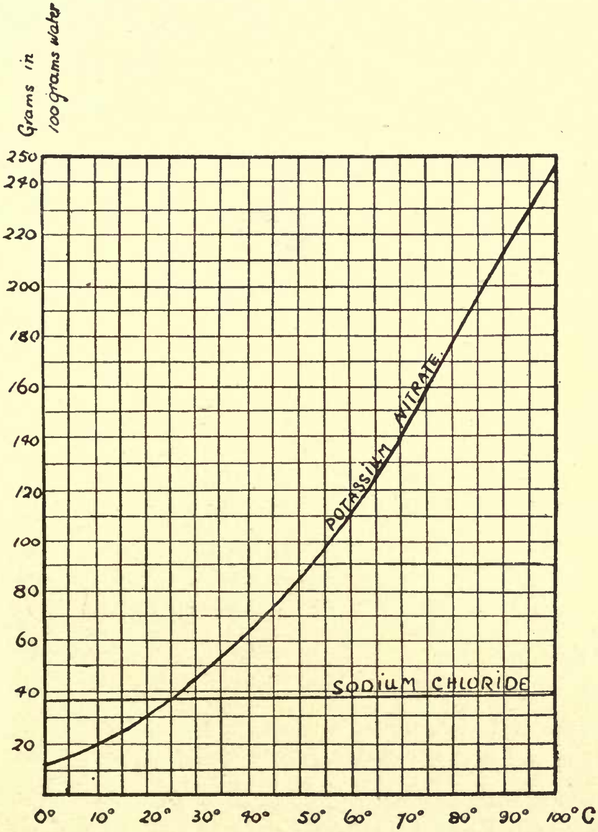


FIG. 18.—Solubility curves of potassium nitrate and sodium chloride.

of $KNO_3$ and 39·6 grams of NaCl are the respective solubilities. So that, generally speaking, salt (sodium chloride) is somewhat more soluble in cold water than nitre, whereas in boiling water nitre is very much more soluble than salt. In practice the mixture of sodium nitrate and potassium chloride, as calculated from the equation above, is put into an iron pan with rather less than half its weight of water—enough to dissolve all the potassium nitrate formed, but not all the salt. The pan is heated by external steam, and the solution of nitre filtered from the salt while still hot. The liquid deposits crystals of crude nitre containing a few per cent. of salt; whilst the salt retains a little nitrate solution. The salt, after a wash with a little water, is pure enough to sell for curing meat. The nitre is dissolved once again and allowed to crystallise, when, on filtering the crystals in a centrifugal machine and washing with cold water in small quantity, nitre containing less than 0·1 per cent. of salt is obtained.

Where one of the products of the reaction is a liquid, the others being solid, it is comparatively simple to distil off the liquid. Thus nitric acid is made from Chile saltpetre by adding sulphuric acid and distilling off the nitric acid set free thus:

$$NaNO_3 + H_2SO_4 \longrightarrow \underset{\text{Sodium bisulphate.}}{NaHSO_4} + HNO_3$$

The sodium nitrate and sulphuric acid are put in that order into a cylindrical cast-iron still fixed in brickwork with the axis of the cylinder horizontal, about equal weights being used—5 tons in all. The still is heated directly by a fire, and the nitric acid vapour is condensed in a series of earthenware receivers joined by inverted U-shaped pipes of earthenware (see Fig. 20), the last traces of the acid being absorbed in towers down which water trickles over earthenware balls.

The whole process is now sometimes conducted *in vacuo* with considerable economies in fuel and improvement in the quality of the acid, which is always slightly decomposed under ordinary conditions of working.

It is possible to use only half the quantity of sulphuric acid shown in the equation above, producing sodium sulphate in place of bisulphate, viz. :

$$2NaNO_3 + H_2SO_4 \longrightarrow \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + 2HNO_3$$

A temperature much above the 150° of the ordinary process is, however, required to carry out this reaction; more nitric acid is thus decomposed, and the sodium sulphate is difficult to remove from the still, whilst the bisulphate (" nitre cake ") can be run out at the bottom of the still in a molten condition.

# CHAPTER XIII

## THE LEBLANC SODA PROCESS

MANY of the chemical manufactures carried on on a large scale are merely a chain of double decompositions. We shall now deal with two of these—both processes for manufacturing soda (sodium carbonate).

The Leblanc process is the oldest method, and is only slowly being ousted by more modern processes. The first reaction in it is the treatment of salt with sulphuric acid. About half a ton of broken rock-salt or salt coarsely crystallised is shot into a shallow iron pan *A* (Fig. 19), heated from below by furnace gases, and an equal weight of sulphuric acid run in from a storage tank. The following reaction occurs :

$$2NaCl + H_2SO_4 \longrightarrow HCl + NaHSO_4 + NaCl.$$

The hydrochloric acid, which is formed together with sodium bisulphate from half the salt used, escapes as a gas up a flue *B* in the dome-shaped roof of the chamber in which the pan is built.

The reaction proceeds at a low temperature, and when it is largely completed the semi-liquid mass is raked out of the pan through a door *C* into a firebrick chamber *D*, also heated by the flues *F* that heat the pan, but nearer the furnace *E*. At the higher temperature thus obtained the second half of the salt is attacked, thus:

$$\mathrm{NaCl} + \mathrm{NaHSO_4} \longrightarrow \mathrm{Na_2SO_4} + \mathrm{HCl},$$

with evolution of more hydrochloric acid and the formation of sodium sulphate.

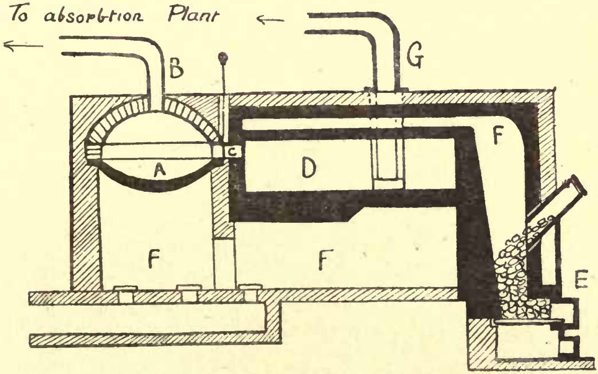


FIG. 19.—Salt cake furnace.

The hot sodium sulphate is raked out of the chamber into trucks provided with lids, and run away to be ground up for the next stage. It is known in the industry as *salt cake*.

The hydrochloric acid passes up a pipe *G* from the chamber, which, with the pipe from the roof of the pan chamber, leads to the absorption plant (Fig. 20). The gas is absorbed by water which passes in an opposite direction through fifty or sixty earthenware jars *A*, joined by small pipes *B* half way up the side for the water circulation, and by large and tall inverted U-tubes *C* luted on at the top for the transference of the gas (Fig. 20). A tower, as usual, ends the absorption system. Though really a by-product, and originally allowed to escape into the air with disastrous results to the surrounding countryside, the hydrochloric acid is now an essential part of the economy of the Leblanc process.

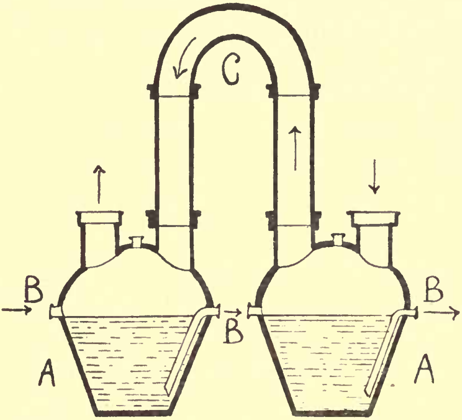


FIG. 20.—Absorption vessels for hydrochloric acid.

In the second stage the sodium sulphate

from the original treatment is mixed with coal slack and limestone and roasted, frequently in a revolving furnace (Fig. 21), to avoid the hand-stirring which is otherwise essential. The charge of 2 tons of salt cake, 2 tons of limestone, and 1 ton of coal, all having been crushed, is put into the revolving cylindrical furnace *A* through a manhole at the top. The furnace is heated by flames from a fire *C* which pass through it in the direction of its axis, which is horizontal and about which it revolves, thus turning the charge over and exposing it to the heat of the flames. The end of the reaction can be detected by experienced workmen; the rotation is then stopped with the manhole in the cylinder at the bottom of its course, and the charge run out into trucks.

The reactions which take place in the furnace are somewhat complex, but in the main the changes proceed as follows:

(1) The coal reacts with the salt cake, forming sodium sulphide:

$$Na_2SO_4 + 2C \longrightarrow \underset{\text{Sodium sulphide.}}{Na_2S} + 2CO_2$$

(2) The sodium sulphide then reacts with the limestone, forming sodium carbonate and calcium sulphide:

$$Na_2S + CaCO_3 \longrightarrow Na_2CO_3 + Cas.$$

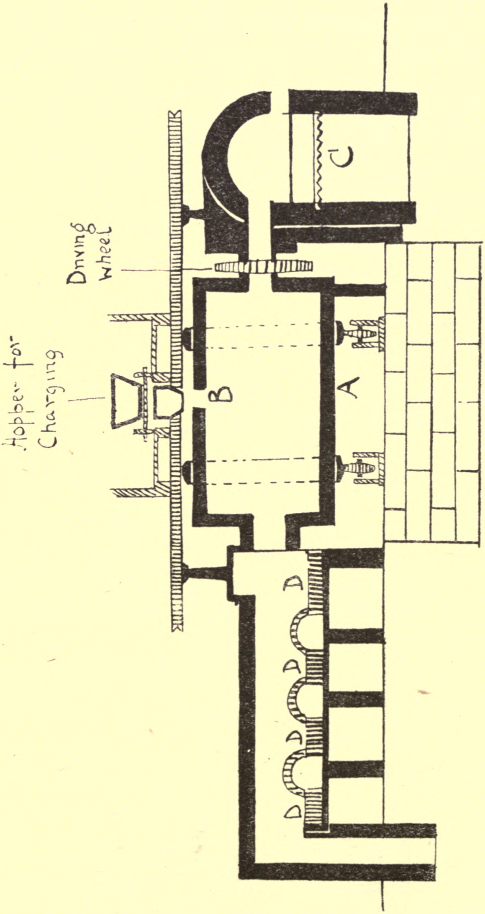


FIG. 21.—Revolving black-ash furnace.

Other reactions occur which are important in the next stage of the process; thus, as an excess of coal and limestone is used, these react as in the limekiln:

$$CaCO_3 \longrightarrow CaO + CO_2$$
$$CO_2 + C \longrightarrow 2CO$$

The material from the furnace known as "*black ash*" has roughly the following composition:

| | Per cent. |
|---|---|
| $Na_2CO_3$ | 45 |
| CaS | 30 |
| CaO | 10 |
| Coal | 5 |
| Other substances | 10 |

and the next procedure is to lixiviate the black ash with hot water to extract the soluble portion. The black ash is placed on the perforated false bottom of an iron tank into which water is run and heated to 50° by live steam. An overflow pipe reaching to the bottom of the tank causes the heavier solution at the bottom to flow over into another tank, the system of tanks being so arranged that the more concentrated solution in the last tank is in contact with fresh black ash, whilst the nearly exhausted ash is treated with fresh water. The solution of soda thus obtained is allowed to settle and treated in two different ways, according to the final product desired.

To make sodium carbonate from the liquid it is necessary to blow carbon dioxide through the solution to convert the caustic soda present into sodium carbonate, thus :

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O.$$

The caustic soda is found during lixiviation by the action of the lime on the sodium carbonate :

$$Ca(OH)_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaOH.$$

The soda solution is then filtered by a filter-press and evaporated, usually by the waste heat in the gases from the furnaces in the earlier operations, the pans *D* being set on flues as salt pans are (see Fig. 21). The soda crystallises out and tends to cake on to the bottom of the pan ; so the pans are often made hemispherical in cross-section (see Fig. 22), and rotating scrapers *S* remove the soda from the bottom as fast as it is formed. An evaporating pan of this type is known as a Thelen pan. The crystals formed are dropped over the side of the pan as the stirrer revolves and, after draining, are further heated to remove water. The product—a white powder—contains 98–99 per cent. of sodium carbonate and is sold as "soda ash."

Owing to the fact that the ammonia–soda process described in the next chapter can make purer soda ash at a lower cost, the liquid from the lixiviation tanks is now often worked up direct for caustic soda (NaOH). The reaction is brought about by treating the solution with

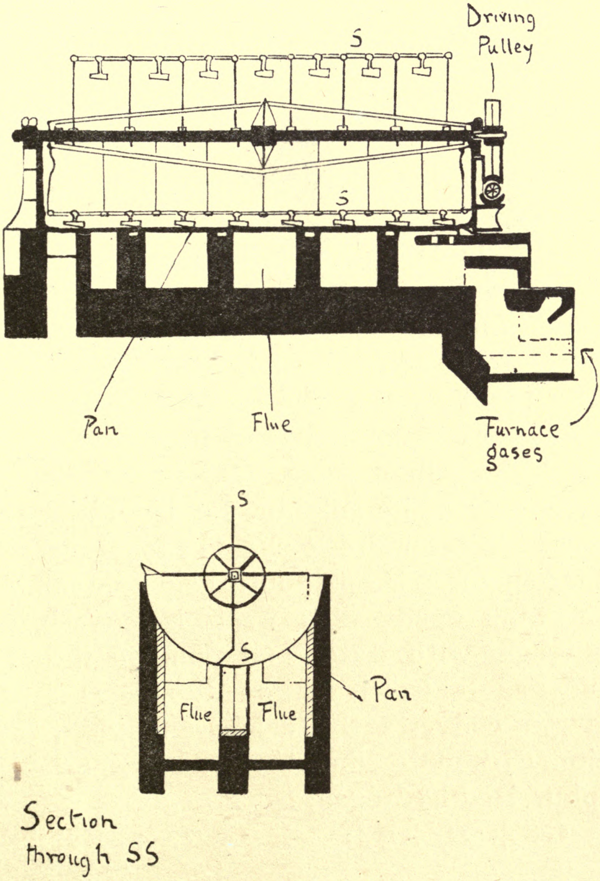


FIG. 22.—Thelen pan.

lime in pans stirred both mechanically and by a stream of air.

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow 2NaOH + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3}.$$

The calcium carbonate produced is insoluble and settles out. The solution is then run off and concentrated in vacuum evaporators, and finally in large cast-iron pans over a fire, where the caustic soda fuses after all the water has been driven off. It is then poured into drums for sale.

The insoluble matter left in the lixiviation tanks from the black ash stage, consisting of calcium sulphide, calcium carbonate, and unchanged coal, was originally a great nuisance to the alkali works and anyone near them. For this *tank waste*, if left in the air and rain, emits foul-smelling gases. It is now used for the recovery of its sulphur, for it will be seen in following through the chain of reactions that all the sulphur in the sulphuric acid used remains in the tank waste. The waste is made into a thin cream with water and pumped into tall cylinders into which carbon dioxide is blown. This gas converts the calcium sulphide into calcium carbonate, liberating hydrogen sulphide (sulphuretted hydrogen):

$$CaS + CO_2 + H_2O \longrightarrow CaCO_3 + \underset{\substack{\text{Hydrogen}\\\text{sulphide.}}}{H_2S}$$

This gas is collected in gas-holders and, after mixing it with the requisite quantity of air, is passed into a Claus furnace, which contains iron oxide spread on shelves. Here the hydrogen sulphide partially burns, forming water and sulphur by the oxygen replacing the sulphur in it:

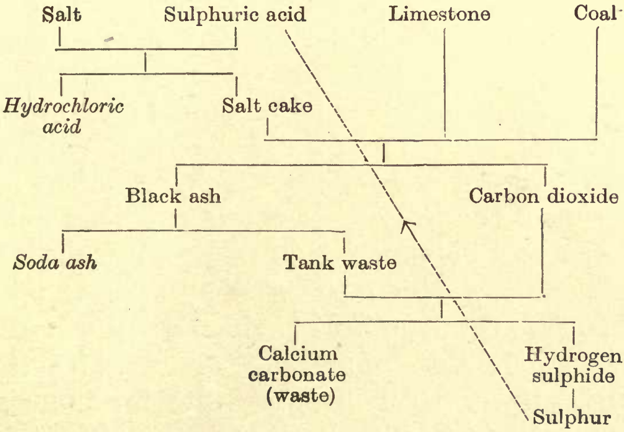
$$2H_2S + O_2 \longrightarrow 2H_2O + 2S.$$

The sulphur is collected in the solid state and can be sold as such or burnt in a good stream of air to form sulphur dioxide,

$$S + O_2 \longrightarrow SO_2,$$

which is used for the production of sulphuric acid. (See Section D.)

General Scheme—Leblanc Process.



# CHAPTER XIV

## THE AMMONIA–SODA PROCESS

THE ammonia–soda process for making sodium carbonate depends on one fundamental reaction. When brine is treated with ammonia and carbon dioxide, sodium bicarbonate appears as a solid, leaving ammonium chloride in solution. Thus

$$NaCl + CO_2 + NH_3 + H_2O \longrightarrow \underset{\text{Sodium bicarbonate.}}{NaHCO_3} + \underset{\text{Ammonium chloride.}}{NH_4Cl}.$$

We will now consider the various necessary stages in detail.

First, the brine, which should be saturated with salt, is made to dissolve ammonia by passing down towers up which ammonia gas is passed, the interior of the iron towers being obstructed in much the same way as is a fractionating column. These " absorbers " must be cooled, as much heat is given out during the absorption. Coils of iron pipe are often inserted in the tower with arrangements for allowing cold water to flow through the coils. The temperature is thus kept below 60°. The ammonia gas used to saturate the brine contains some carbon dioxide, which causes most of the calcium and magnesium impurities to be precipitated as insoluble carbonates. To remove these, the liquid is led into large tanks in which the carbonates settle as a mud and the clear purified brine overflows at the top.

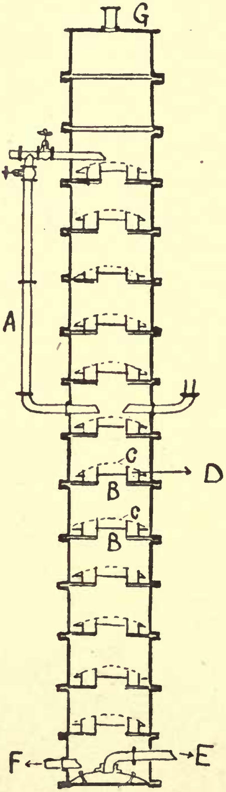


FIG. 23.—Solvay carbonating tower.

The ammoniacal brine is next treated with carbon dioxide in towers, of which one is shown in Fig. 23. After being cooled down to 30° by passing through the tubes of an "evaporator," through the outside of which cold water circulates (see Fig. 3), the brine is delivered by a pipe *A* about half-way up the tower. The latter consists of a number of cast-iron drums, 3 ft. high by 5 ft. in diameter, fixed above one another to form a tower 70–90 ft. high. Each drum is open at the top and has a hole *B*, 15 in. in diameter, in its base. Above the hole is a mushroom of iron perforated with fine holes, *C*, and supported by vertical stays *D*. The carbon dioxide, delivered in by pipe *E*, at $1\frac{1}{2}$–$2\frac{1}{2}$ atmospheres pressure, streams up through the holes in the plates *C* in a series of fine bubbles through the ammoniacal brine, in which it dissolves, giving out heat in so doing. It is essential, however, to keep the liquid at about 30°, for at a higher temperature the bicarbonate is formed in lumps, and more is left in solution, while excessive cooling causes the formation of a cream difficult to filter. Coils through which cold water circulates are therefore placed in some of the drums (they are not shown in the diagram). The sludge of fine bicarbonate crystals is run out at *F*, whilst the excess of carbon dioxide (5–10 per cent.) escapes by the top pipe *G*. As this gas contains a little ammonia, it is bubbled through an absorber against a stream of fresh brine. After about a fortnight's working the perforations in the iron plates *C* become stopped up by crystals of bicarbonate, and it is necessary to wash out the tower with hot water, in which this substance is much more soluble than in cold water. Otherwise the towers work continuously, fresh brine being fed in as the finished mixture of bicarbonate crystals and mother liquor is run out at *F*.

This sludge is filtered by a rotary vacuum filter (see Fig. 6) and washed by a small quantity of cold water. The mother liquor contains a little free ammonia with the ammonium chloride, and is used as described later to regenerate the ammonia.

The bicarbonate must be heated to convert it into soda ash, thus:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2.$$

This decomposition is effected in furnaces, or more usually, in a long pan of semicircular cross-section provided with mechanical scrapers like the ordinary Thelen pan of the Leblanc process. As in this case the pan must be closed so that the carbon dioxide may be recovered, the scrapers merely move backwards and forwards over the circular bottom instead of executing a complete rotation as when previously mentioned. The bicarbonate is fed in at one end by a gastight screw conveyer, and the finished carbonate removed similarly at the other end, the scrapers being arranged to give the material a slow drift along the pan.

The mother liquors from the filtration of the bicarbonate are pumped direct into stills, and the requisite quantity of slaked lime added to set free the ammonia, thus:

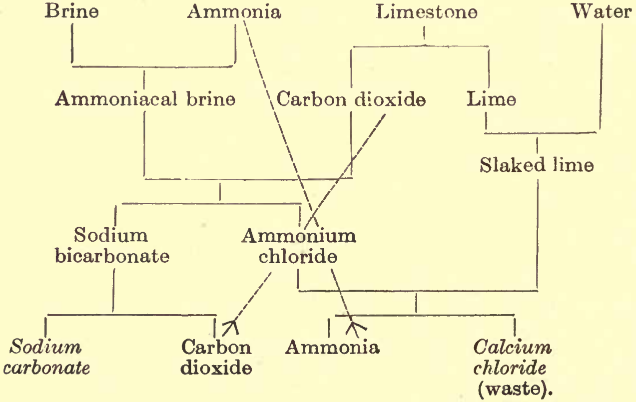
$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Slaked lime.}}{Ca(OH)_2} \longrightarrow 2NH_3 + 2H_2O + \underset{\text{Calcium chloride.}}{CaCl_2}$$

The mixture is boiled and the ammonia goes off as a gas and is led away to saturate more brine.

The slaked lime is produced by roasting limestone in kilns (which also provides the necessary carbon dioxide). The hot lime is slaked with the minimum quantity of hot water and run to storage tanks ready for the stills in which the ammonia is recovered.

The calcium chloride from these stills is a waste product, and is usually run away when all the ammonia has come off. As will be seen clearly from the following synopsis of the process, this substance, and also the soda ash, are the two final products of the series of reactions we have considered, the ammonia and carbon dioxide being returned as shown by the dotted lines to be used again in the earlier stages.

General Scheme—Ammonia-Soda Process.



# SECTION C

## ELEMENTS AND COMPOUNDS

# CHAPTER XV

## THE ELEMENTS—(1) NON-METALS

In the previous section we have considered the general nature of elements and compounds, with some simple types of the reactions which occur between them. We will now proceed to a very general survey of the whole of the elements and of some outstanding types of compounds which they form. It is obviously not possible or desirable within the limits of this book to give details as to the properties and behaviour of all these bodies; these must be sought for in formal text-books or dictionaries.

Of the eighty or so recognised elements, the bulk are solids and metals. Two only are liquids—mercury and bromine; ten exist as gases, and none of these are metals. Naturally, these descriptions apply only to the ordinary temperature, as the transformations from solid to liquid and gas apply equally to elements as to compounds when the temperature is changed.

The division of the elements into metals and non-metals is more fundamental than it would be if based on the properties of the element alone—the distinction persists in the compounds they form and in the properties of these compounds. There are naturally some elements capable of behaving in their compounds both after the manner of metals and of non-metals.

Of the gaseous non-metals *oxygen* is of outstanding importance. It forms as the free element one-fifth part by volume of the air, and is essential for breathing to both plants and animals. In pure oxygen living beings are much more vigorous than in air, but life is short as well as gay. Similarly, processes of burning consist essentially in the combination of the fuel with oxygen, and they are likewise more fierce in pure oxygen. Naturally, therefore, oxygen is found in many compounds. It forms about one-half of the earth's crust so far as that is explored—that is, the top half-mile. Water, also, contains nearly 89 per cent. of oxygen combined with hydrogen. Oxygen made on the large scale by liquefying air and is allowing the nitrogen to boil off.

*Hydrogen*, on the other hand, does not occur in the free state in Nature, but it forms 11 per cent. of water, and is found in all animals and vegetables in the combined state. As it is fourteen times lighter than air, it is used to fill balloons and airships, although, as it burns easily in the air (combining with the oxygen to form water), it is dangerous when used for this purpose in warfare. When a jet of the proper mixture of oxygen and hydrogen (*i.e.* two volumes of hydrogen and one of oxygen, for the equation is $2H_2 + O_2 \rightarrow 2H_2O$) is lit, an intensely hot flame is produced which is used for cutting steel, melting platinum and other metals of high melting-point, and also for heating a block of lime for the limelight. It also serves for heating and lighting in coal gas, in which it is present up to 50 per cent. It is made by displacing the hydrogen of acids, alkalis, or water, by means of metals, or by decomposing water by an electric current.

*Nitrogen*, the remaining four-fifths of the air (in which it serves to dilute the oxygen), is less active than oxygen or hydrogen under ordinary conditions; but when electric sparks are passed through a mixture of it with these two elements severally, oxides of nitrogen and ammonia are formed respectively. As nitrates, such as Chile saltpetre, it is found in dry regions. In this form, or as salts of ammonia, it is essential to plant life, and so, to eke out the natural supplies, such compounds are now being made by the electric process indicated above. A further important method of "fixing" atmospheric nitrogen is to cause it to combine with a carbide (usually calcium carbide),

$$CaC_2 + N_2 \longrightarrow CaCN_2,$$

the compound formed being calcium cyanamide, which can be used direct as a manure.

*The Five Inert Gases.*—Oxygen and nitrogen together form roughly 99 per cent. of the atmosphere when water vapour and carbon dioxide have been removed. The remaining 1 per cent. comprises five gases—argon, helium, neon, krypton, and xenon—which have been separated by liquefying the mixture and distilling off the more volatile ones first. They are also found in some springs and minerals, whence, for instance, helium has been collected in quantity in America as a substitute for hydrogen in dirigible airships, the advantage being that it is incombustible. Argon forms the bulk of the 1 per cent. residue in the air. None of these gases have so far been found to form any compounds, nor, apart from helium, have they been put to any use.

*The halogens* are an interesting series of non-metal elements—*fluorine*, *chlorine*, *bromine*, and *iodine*—showing a gradation of properties in the order given above. The first two are gases; bromine is a liquid and iodine a solid, but the two latter gasify easily, iodine without melting. The vapours show a colour gradation —yellow, green, red-brown, violet. Unlike the gases we have just mentioned, the halogens are notably vigorous in reacting with other elements. With hydrogen, fluorine unites explosively even in the dark; but chlorine unites with hydrogen in sunlight only, and but slowly in diffused light; whilst bromine and iodine have to be heated with the hydrogen before they combine, and even then only a certain proportion of the mixture forms the compounds HBr and HI. All these hydrogen compounds are gases, very soluble in water, giving strongly acid solutions—hydrofluoric, hydrochloric, hydrobromic, and hydriodic acids respectively. These elements can all be obtained by decomposing solutions of fluorides, chlorides, etc., by the electric current, although, as fluorine decomposes water, it is necessary to use a solution in liquefied hydrofluoric acid. Industrially, chlorine is most used, either liquefied or as bleaching powder (a compound of it with slaked lime) as a bleaching and disinfectant agent. Iodine and some compounds (*e.g.* iodoform) are of great use in medicine and surgery, while bromine is similarly used in its compounds, many of which induce sleep. Fluorine is at present mostly a curiosity, but its hydrogen compound is useful in etching glass.

Of the solid non-metals, *sulphur* we have already met with in Chapter II., as found free in Nature, where it also occurs combined with metals as sulphides, and with metals and oxygen as sulphates.

*Carbon*, in its various forms as diamond and graphite, and with various impurities, as lamp-black, charcoal, coke, and coal, is too well known to merit physical description. That these varied products are all carbon can be shown by burning them, when the product is the same in quantity and kind—carbon dioxide. Carbon cannot be fused, but in the electric arc it volatilises. As graphite it is used in pencils, blacklead, and for making crucibles.

*Silicon*, an element similar in many respects to carbon, is either a dark brown powder or grey crystals (corresponding roughly with lamp-black and graphite respectively). It is not found free in Nature, but occurs in great quantities in the earth's crust in the form of its oxide (silica) as sand, sandstone, and quartz, and as compounds of silica with other oxides, forming silicates. The bulk of rocks not composed of carbonates are silicates. Thus orthoclase is a potassium aluminium silicate; serpentine, a magnesium silicate; and emerald, a beryllium aluminium silicate. From sand the element can be obtained by strongly heating with magnesium powder:

$$SiO_2 + 2Mg \longrightarrow Si + 2MgO,$$

and when silicon is heated it burns to form silica again.

*Boron*, the element of borax and boric acid, resembles silicon and carbon in being an inert brownish powder or a crystalline body. It can be made as they are by heating its oxide ($B_2O_3$) with sodium or magnesium. Its compounds only are made use of—boric acid ($HBO_3$) for preserving (*e.g.*, cream), and borax (sodium borate, $Na_2B_4O_7.10H_2O$) as a flux in brazing and as a glaze for earthenware.

*Phosphorus* is an element somewhat similar in chemical behaviour to nitrogen. It is essential to animal and plant life; for instance, the skeleton of bone is largely made up of calcium phosphate ($Ca_3PO_4$). The element is made from this compound by heating with carbon (or carbon and sand) to a high temperature (see Section E). The element—which can be obtained either as a yellow waxy solid or as a red-brown powder—is largely used in the manufacture of matches.

Three elements allied to phosphorus—arsenic, antimony, and bismuth—graduate in that order into the metallic character.

*Arsenic*, unlike phosphorus, is found free in the earth in small quantities, but more frequently as its compounds with sulphur (realgar, $As_2S_2$, and orpiment, $As_2S_3$) and as arsenical pyrites, FeAsS.

The element can be prepared from the latter by heating with carbon ; but it is more usual to use its oxide ($As_2O_3$), " white arsenic," the form in which it is usually met with in commerce. It can be obtained in various conditions—*cf.* carbon—and is used now only to harden lead shot.

# CHAPTER XVI

## THE ELEMENTS—(2) THE METALS

In ordinary life we know metals as bodies which have a characteristically bright lustre when polished, and a capacity for conveying heat and electricity. We can hammer most metals into thin sheets or draw them into fine wires. Chemically, these well-known properties are associated with others no less important. If an electric current is passed through a solution of a compound of a metal with a non-metal—for example, copper and chlorine (copper chloride, $CuCl_2$)—the metal is set free at the negative pole, and the non-metal at the positive pole: that is, metals are electro-positive, non-metals electro-negative (see Section E). Further, when burnt in air to form oxides, and the product is dissolved in water, the non-metals give rise to acids, whilst the metals give alkalis or bases—substances which we shall consider in detail later. So that, although it is difficult to define a metal in few words, the general distinction from non-metals is well known.

*Sodium* and *potassium*, the two important alkali metals, contained in soda and potash respectively, are soft white metals melting at 96° and 63°. They tarnish very rapidly in the air and decompose cold water, thus:

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2,$$

forming caustic soda and hydrogen. It is therefore necessary to keep both these metals under petroleum or some similar liquid which does not contain oxygen. On the large scale, after being wetted with oil, they are packed in airtight soldered tins.

They can be manufactured by heating sodium or potassium carbonates to a high temperature with carbon; but this method has now been replaced completely by electrical methods of preparation from the fused chloride (Chapter VIII) or the fused hydroxide. Metallic potassium is little used, but sodium, which is cheaper and serves the same purposes, is important for preparing some of the less common metals, as well as some complex carbon compounds, whilst much is burnt direct to form sodium peroxide, $Na_2O_2$.

Both these metals are widely distributed in Nature as compounds. They are found in the bodies of plants and animals, and it is often necessary to add potassium compounds to the soil as manures.

*Magnesium*, *calcium*, *strontium*, and *barium*, form a second group of metals less alkaline in character than sodium and potassium. They are known collectively as the metals of the alkaline earths. With the exception of strontium, all are found freely in Nature in combination with other elements, *e.g.*, calcium as chalk, limestone, calcspar ($CaCO_3$), gypsum, alabaster ($CaSO_4$), and in most egg- and sea-shells; barium as heavy spar ($BaSO_4$) and witherite ($BaCO_3$); magnesium as magnesite ($MgCO_3$) and dolomite [$MgCa(CO_3)_2$]. The metals are all prepared by the use of an electric current as fused compounds, but magnesium is the only one used to any extent, *e.g.*, for flashlights in photography, in fireworks, etc. It is less easily converted into oxide in the air than are the others, which resemble sodium in this respect. But magnesium ribbon or filings are always coated with a thin layer of oxide. The solutions of the oxides in water are in all these cases strongly alkaline.

*Aluminium* resembles magnesium in many ways, and is also widely distributed in compounds, *e.g.*, clays, etc. Its preparation has already been described in Chapter VIII. Owing to its lightness (specific gravity 2·7), it is widely used in the construction of aircraft, and its general cleanliness and convenience are increasing its application to domestic and industrial vessels of all kinds. It is normally coated with a thin layer of oxide, which prevents further action of the air. Alkalis, *e.g.*, washing soda, attack it rapidly, thus limiting its usefulness. A method of soldering it has only recently been elaborated, and it is soft enough to clog a file if such a tool is used on it. Its alloys with other metals are exceedingly useful, *e.g.*, aluminium bronze (copper + 3 per cent. aluminium), magnalium (aluminium +1–2 per cent. magnesium), which latter lacks many of the disadvantages of pure aluminium. The use of aluminium for producing other metals by the thermit process we have already described (Chapter X).

The "metalloids" *antimony* and *bismuth* lie on the border-line between metals and non-metals. Antimony (Lat. *Stibium*, hence Sb) is mined as the sulphide, antimonite ($Sb_2S_3$), bismuth as bismuthine, $Bi_2S_3$, and both are often smelted by the use of iron as a replacing agent; otherwise the ore must be roasted to burn away sulphur, leaving the oxide of the metal, which is then heated with carbon. Both these metals are more brittle than the general run of metals; they do not tarnish in the air, but burn to oxides if heated. Antimony is largely used as a constituent of alloys, *e.g.*, type metal (antimony—tin—lead), anti-friction metal (antimony—zinc—copper) used for bearings, Britannia metal, etc. Bismuth enters into the composition of a number of easily fusible alloys, used as fuse wires, fusible plugs in boilers, etc.; using various proportions of bismuth, lead, and zinc, almost any desired melting-point from 60° to 268°—the melting-point of pure bismuth—can be obtained.

*Tin* and *lead* are extremely useful metals which have been long known to man. The chief ores are cassiterite or tinstone ($SnO_2$) and galena (PbS). Tinstone is smelted with coal in the usual way, and owing to the fact that the silver-white metal thus produced is unaltered in the air or by water, it is used to coat less resistant metals. For making "tins" thin sheets of mild steel, after pickling in acid, are dipped into molten tin. Copper vessels are likewise often tinned inside. Common alloys containing tin are solder (tin—lead) and bronze (tin—copper), whilst tin foil alloyed with some lead is used to wrap up substances like chocolate and tobacco, which deteriorate if freely exposed to air. Lead is not quite so simple to prepare from galena. In some places the ore is roasted in air, thus converting part of it into lead oxide and lead sulphate :

$$4PbS + 7O_2 \longrightarrow \underset{\substack{\text{Lead}\\\text{oxide.}}}{2PbO} + \underset{\substack{\text{Lead}\\\text{sulphate.}}}{2PbSO_4} + 2SO_2$$

On further heating, these two compounds react with the unaltered ore, giving molten lead, thus :

$$2PbO + PbS \longrightarrow 3Pb + SO_2.$$
$$PbSO_4 + PbS \longrightarrow 2Pb + 2SO_2.$$

If the ore is not so pure, it is usual to roast till all becomes lead oxide, and then to reduce with coal.

Owing to the fact that it is but slowly altered in the air, lead is used for roofing, where durability rather than cheapness is an object. It is of great use in chemical industry for tanks, as it resists sulphuric and other acids ; but it is important to prevent any compound of lead entering articles for human consumption (*e.g.*, drugs), as they act as slow poisons. Its use for pipes is based on the ease with which it bends when required to adapt itself to awkward junctions, or slow strains under the ground. Its use in alloys has already been mentioned.

*Zinc* is found as calamine ($ZnCO_3$) and blende ($ZnS$), and obtained therefrom by roasting. The roasting removes carbon dioxide and sulphur respectively, and finally the remaining oxide is reduced with carbon. As the metal melts at 418° and boils at 730°, the smelting is carried on in retorts of fireclay, and the zinc distilled off and led into chambers to condense.

Zinc, like aluminium, becomes coated with a layer of oxide in the air, thus preventing further action. It is therefore used to coat iron as wire for telegraphs, sheets for roofs, and many kinds of vessels. The iron is simply dipped into molten zinc, the process being called "galvanising"—a rather misleading term. As a constituent of alloys it enters into brass (copper—zinc) and German silver (copper—zinc—nickel). In galvanising also it alloys with the surface of the iron.

*Mercury* has the distinction of being the only liquid metal. It is found almost exclusively as its sulphide, HgS, known as cinnabar, from which it is obtained by roasting in a current of air. The sulphur burns away, and mercury distils with the sulphur dioxide formed:

$$HgS + O_2 \longrightarrow Hg + SO_2.$$

The ore is fed into a heated kiln traversed by baffles shaped like an inverted V, so that it is finely broken up and exposed to the action of the heat, the mercury vapour being led away and condensed in inverted, water-cooled, earthenware U-tubes. The whole plant is put under a slight vacuum to avoid casual escapes of vapour, as the fumes are exceedingly poisonous. The mercury is purified by squeezing through cloths, and finally by distillation, preferably *in vacuo.*

As a liquid, mercury dissolves many metals, the solutions being called *amalgams.* It is therefore largely used for extracting gold and silver from the earthy matter in which these elements are found free. A tin amalgam is used to coat mirrors. Mercury itself is used in thermometers, as it expands regularly on heating and does not boil till a temperature of 357° is attained; and in barometers, for it is 13·5 times as heavy as water, so that a column only 30 in. high serves to balance the pressure of the atmosphere. Generally it is of immense service in scientific experiments as a heavy, dry liquid which does not vaporise much at ordinary temperatures.

# CHAPTER XVII

## THE ELEMENTS—(2) THE METALS (*continued*)

*Copper* is notable for its beautiful red colour and its high capacity for conducting electricity. It can also be drawn into wires, and beaten into plates or foil very easily. The chief ore is chalcopyrite (CuS.FeS), a double sulphide of copper and iron, from which the copper is obtained by a process of double smelting somewhat similar to that already described for lead. Details can be found in books on metallurgy. It is finally refined electrically, as described in Section E.

In the air copper is little altered if kept dry, but in moist air a coating of verdigris (a copper carbonate) is developed, as, for example, on outdoor bronze statuary. It easily forms a black oxide when heated in the air. Owing to its high conductivity of electricity, it is almost always used for wiring and in the construction of electrical apparatus. Its alloys are also very important; brass, bronze, and German silver we have already mentioned. Bell metal is a tin alloy with about 75 per cent. of copper, whereas brass contains zinc (25 per cent.) with the copper. Small quantities of phosphorus in bronze increase its tensile strength, while manganese makes it very hard. *Silver* and *gold* are like copper in some ways, particularly in chemical behaviour. All three are found free in Nature. Silver is a regular constituent of lead ores to the extent of about 1 per cent. It is separated by burning the lead to the molten oxide, beneath which the silver collects. Various other methods are used for other ores. The metal does not oxidise even on heating in the air, and hence is classed as one of the "noble metals"; although it is easily dissolved by nitric, and to some extent by sulphuric, acid. These acids are used to "part" silver and gold, the latter metal being unattacked. British silver coinage contains about 7·5 per cent. of copper to 92·5 per cent. of silver, this being the standard for "sterling silver," of which silver-plate is made. The pure metal is too soft for use as coinage. Much silver is used for plating, usually on articles of the alloy German silver (see Section E). Gold is found mostly in the free state, but in minute quantities, in many rocks. It is extracted by various methods of solution after the gold-bearing rock has been "concentrated" by running water—the gold is left behind, when the rock is largely washed away. The residue is finely crushed and run over copper plates coated with mercury, in which most of the gold dissolves; the amalgam is scraped off at intervals, and the mercury distilled off, leaving gold. The undissolved gold is recovered by solution in potassium cyanide, which in presence of air converts gold into a soluble complex cyanide:

$$4Au + \underset{\text{Potassium cyanide.}}{8KCN} + 2H_2O + O_2 \longrightarrow 4KOH + \underset{\text{Potassium gold cyanide.}}{2KCN.AuCN}$$

The metallic gold is obtained from the solution by scrap zinc, which replaces it, or by an electric current, as in plating. Gold coinage is 22-carat, *i.e.*, $\frac{22}{24}$ gold and $\frac{2}{24}$ copper. The use of the metal in the arts needs no reference here. It can be beaten out into very thin sheets (gold leaf), which are used for gilding; gold amalgam is also used for this purpose, but generally a method of electro-plating is now used, as for silver.

*Platinum* is another noble metal and, like gold, is soluble only in a mixture of hydrochloric and nitric acids (known as aqua regia), other acids having very slight action on it. It is found free in sand, mostly in the Ural Mountains. It melts at 1760° and is usually fused by the use of the oxyhydrogen blowpipe. It is largely used in scientific apparatus, in spite of its price, because of its high melting-point and resistance to attack by other substances. In fact, many operations in the laboratory can scarcely be performed without it.

*Iron* is the most commonly met with of all the metals. The usual method of smelting has already been dealt with in Chapter X. The pure metal is rarely used, but small quantities of carbon and other metals modify its properties immensely, as also does the method of working; so that every variety from brittle cast iron to the most flexible steel can be produced. We shall discuss some of these alloys in the general section on such materials, but details must be looked for elsewhere. The many uses of iron also are left to the reader to tabulate from his own experience. Iron ores are very abundant, *e.g.*, magnetite, $Fe_3O_4$; hæmatite, $Fe_2O_3$; spathic iron ore, $FeCO_3$; and iron pyrites, $FeS_2$. The last is always roasted to utilise the sulphur dioxide formed for the manufacture of sulphuric acid (Section D).

*Nickel,* mined mostly as a silicate, is smelted by the aid of limestone and coke. To obtain pure nickel from the crude product the process of Ludwig Mond is largely used. The 80 per cent. regulus is heated to 300° in a tower, and water gas passed over it to reduce any oxide; it is then put into a "volatiliser," in which a current of carbon monoxide (CO) is passed over it at a temperature of 100°. The nickel forms a volatile compound with the carbon monoxide, $Ni(CO)_4$, which distils into a tower heated to 180°. It is here decomposed into nickel, which is deposited, and carbon monoxide which is used to treat more crude material. The white metal obtained in this way finds its main applications in nickel plating (for it does not tarnish in the air), and the manufacture of alloys, such as German silver, and nickel coins, which contain 75 per cent. copper and 25 per cent. nickel. *Cobalt* is a somewhat similar metal, but much less used, and its ores are mainly worked to obtain compounds, many of which are useful as pigments.

The remaining metals, other than rare ones, are mostly of importance in their compounds, under which heading we shall mention tantalum (used as metal for filaments in electric lamps), chromium, manganese, zirconium, thorium, and radium.

*Further Classification of the Elements.*—Besides the main groups, metals and non-metals, we have seen that a number of elements can be roughly grouped together as having similar properties, thus: fluorine, chlorine, bromine, iodine; calcium, strontium, barium; sodium, potassium; and so on. It was noticed first by Newlands that, if the elements are arranged in order of their atomic weight, those with similar properties recur at fixed intervals in the list—usually every eighth element is similar. This method of classification has been elaborated by Lothar Meyer and Mendeléeff into the Periodic Classification of the elements, details of which will be found in ordinary text-books of chemistry.

*Alloys.*—Originally used as a term to denote the debasing of noble metals by the introduction of inferior ones, alloy is now a general name for a metal containing more than one metallic element.

Metals combine with one another to form definite compounds with the characteristic evolution of heat. Thus copper and tin unite when melted together to form a compound represented by the formula $Cu_3Sn$. Such compounds form one class of alloys.

Again, molten metals dissolve one another in a manner similar to other liquids. Thus lead and tin are miscible in all proportions, giving a continuous series of alloys, of which pewter (Pb,4; Sn,1) and the various solders are examples. In other cases the solubility is limited; thus zinc and lead are soluble only to a slight extent in one another, and on cooling two layers are formed in just the same way as with ether and water. The solutions may remain as such in the solid metal when it cools, but in some cases the two components separate out in fine, but separate, crystals.

The compounds of the metals with one another, as also with non-metals, often dissolve in other metals. Thus iron carbide, $Fe_3C$, is soluble in iron, forming steel, while cast iron contains much of its carbon deposited in separate graphite crystals. Iron phosphide is also soluble, having a bad effect on the properties of the steel.

Frequently minute traces of other metals produce changes in a main compound out of all proportion to their quantity. A mere trace of tin or arsenic in copper greatly reduces its power of conducting electricity. In these cases some fundamental alteration in the metal seems to have been brought about comparable with that from yellow to red phosphorus.

Alloys can be made in many cases by melting the constituents together. If one metal is volatile, such as zinc, it is usual to melt the other metal first and add the volatile one to the molten mass. An alternative method is to smelt the ores mixed together—this is seldom adopted except where the mixture is already there.

The structure of an alloy is often investigated by polishing a flat surface of the metal and etching it with acids. An examination under the microscope then reveals the nature of the particles which make up the mass. Compounds and solutions which remain as such show a mass of similar crystals. Any components separated out appear as crystals distinct from other portions of the metal. The microscopic examination is correlated with the mechanical properties of the alloy, and in this way many new and useful alloys have been brought into commerce.

# CHAPTER XVIII

## COMPOUNDS OF NON-METALS WITH OXYGEN: ACIDS

We have already come across many cases in which elements burn in the air, or otherwise combine with oxygen. Many of these compounds are very important and useful, as also are the further compounds produced when these oxides, as they are called, combine with water.

In the case of non-metals the oxides vary greatly in physical character. Some are solids, many are gases. On combining with water, acids are formed—that is, substances with a sour taste, which cause many blue colouring matters such as litmus or the juice of the pickle cabbage, to turn red. Most acids poured on to common soda or chalk cause an effervescence due to the escape of carbon dioxide. Vinegar is the most familiar acid, and from its Latin name (*acetum*) the term itself is derived.

Sulphur, for instance, burns easily in the air, forming a gaseous oxide, sulphur dioxide, $SO_2$, easily soluble in water. The acid thus formed is sulphurous acid, $H_2SO_3$, but the combination is not strong, for on heating the acid the gas $SO_2$ is expelled. The gas itself is easily reduced to the liquid state (it boils at $-10°$ at atmospheric pressure). It is mostly used as a bleaching agent for straw, sponges, and other materials which cannot be bleached satisfactorily with chlorine.

In the presence of certain substances (see Section D) sulphur dioxide combines with more oxygen to form a trioxide, $SO_3$. This appears as a fog and condenses to silky, crystalline masses which dissolve in water with a hissing noise. Sulphuric acid is formed:

$$H_2O + SO_3 \longrightarrow H_2SO_4,$$

which, when freed from water by distilling off the latter, is a clear, heavy, oily liquid. It has a great affinity for water, so much so, indeed, that it abstracts water from wood, paper, etc., producing a charred effect. It is most useful in expelling other acids from their metallic compounds (salts), as we have seen above in the case of nitric acid (from sodium nitrate) and hydrochloric acid (from salt).

Sulphuric acid is the most widely used of any of the acids. Enormous quantities take part in the preparation of superphosphate of lime for manure. Soap manufacture, tinning and galvanising, dyeing, the manufacture of nitroglycerine, trinitrotoluene, and other explosives, and of dyes all consume quantities of sulphuric acid. Petroleum is purified by its means. In fact, it is scarcely possible to mention a manufactured article which has not come into contact with sulphuric acid at some stage of its preparation.

Sulphur trioxide dissolves in sulphuric acid itself to produce *oleum*. If an extra molecule is added, pyrosulphuric acid is formed:

$$H_2SO_4 + SO_3 \longrightarrow H_2S_2O_7.$$

It is used for purposes similar to those in which sulphuric acid is applied, for some of which it is a more effective reagent.

Nitrogen combines with oxygen only under special conditions, but many oxides are known, prepared in various other ways. Nitrous oxide, $N_2O$, is made by heating ammonium nitrate cautiously:

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O,$$

and is mostly used as an anæsthetic (the "gas" of dentists). It has a sweet taste and is moderately soluble in water; the solution, however, is not acid. Oxides which give acids on combination with water are called the *anhydrides* of those acids; the other non-metal oxides, like $N_2O$, are called neutral oxides. Nitric oxide, NO, is formed when nitrogen does combine with oxygen. It is a colourless gas, but in contact with more oxygen is at once converted into nitrogen peroxide, a red-brown gas:

$$2NO + O_2 \longrightarrow 2NO_2.$$

It is scarcely soluble in water and is a neutral oxide. The peroxide dissolves easily in water, giving a mixture of nitric and nitrous acids:

$$2NO_2 + H_2O \longrightarrow \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{HNO_2} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{HNO_3}$$

Nitrous acid is very unstable, and when required for use, *e.g.*, in making dyes, it is prepared as needed from sodium nitrite.

Nitric acid is a colourless liquid which fumes strongly in the air. It dissolves almost all metals except gold and platinum, forming nitrates. With organic substances such as sawdust its action is very violent, sometimes causing fire. This is owing to the ease with which it gives up oxygen:

$$2HNO_3 \longrightarrow H_2O + 2NO + 3O.$$

It is essential to the manufacture of modern explosives (most of which contain the group of atoms $NO_2$), *e.g.*, picric acid, trinitrotoluene, guncotton, and nitroglycerine. These are only special examples of its action on complex compounds of carbon (organic substances). Others are intermediate stages in the production of most dyes and drugs made artificially. The anhydride of nitric acid is nitrogen pentoxide, $N_2O_5$. It can be obtained by removing water from nitric acid itself by the use of phosphorus pentoxide.

The element phosphorus forms two oxides when burnt. In a deficient air supply the trioxide is formed:

$$4P + 3O_2 \longrightarrow 2P_2O_3.$$

This oxide forms phosphorous acid, $HPO_3$, with water. The more important pentoxide is formed when more air is available during the burning of the phosphorus:

$$4P + 5O_2 \longrightarrow 2P_2O_5.$$

This oxide, a soft white powder, has a greater avidity for water than almost any known substance. It is therefore used in scientific work for abstracting traces of water from gases. It is the anhydride of phosphoric acid which is formed on its energetic combination with water:

$$P_2O_5 + 3H_2O \longrightarrow 2H_3PO_4.$$

This acid is sold as crystals, melting at 38°, or in the form of a thick syrup. It is used in making phosphates, and also in the manufacture of hydrogen peroxide.

Arsenic forms two similar oxides, $As_2O_3$ (white arsenic) and $As_2O_5$, which give arsenious acid, $H_3AsO_3$, and arsenic acid, $H_3AsO_4$.

The oxide of silicon, silica, is very common as sand, sandstone, and quartz. A great deal is used in the manufacture of glass, pottery, etc. Silica fuses at a high temperature, and vessels made of it can be plunged white-hot into cold water without cracking, owing to the fact that the material expands little on heating. It is therefore extremely useful for apparatus and plant, especially as it also resists almost all acids.

This oxide, $SiO_2$, is scarcely soluble in water in its natural state. If fused with alkalis such as soda, silicates are formed, and on treatment with hydrochloric acid a white jelly is formed, commonly called silicic acid. It has not a definite composition, the quantity of water depending on the temperature at which it is dried. On strongly heating the jelly, pure silica is left as a white powder.

Carbon forms two important oxides, the dioxide, $CO_2$, and the monoxide, $CO$. The former is readily soluble and easily made liquid. In water it forms the unstable carbonic acid, $H_2CO_3$. Such a solution is sold as "soda water," and the gas is dissolved in most alcoholic beverages, in which it is produced during the fermentations in manufacture. Carbon dioxide is formed when carbon in any form is burnt completely, by the breathing of animals and plants. Quantities are also formed in burning limestone to make lime, and in most fermentation processes. We have already described its use in the ammonia–soda process; sugar refineries use it to remove lime from the juice. The gas is sold liquefied in strong steel cylinders.

Carbon monoxide is also a colourless gas, but is difficult to liquefy and is but little soluble in water. It is the main product when carbon is burnt at a high temperature, under which condition it is more stable than the dioxide. The monoxide is poisonous and forms a considerable part of water-gas and producer-gas, which, as we have already seen, are used for heating and power. Carbon monoxide burns in the air with a blue flame, forming the dioxide:

$$2CO + O_2 \longrightarrow 2CO_2.$$

Although really a neutral oxide, it is obtainable from formic acid, $H_2CO_2$, by the use of water-removing agents like sulphuric acid; so that it may be regarded as the anhydride of this acid. Formic acid is one of an enormous number of the complex acids of carbon: acetic acid in vinegar, citric acid in lemon-juice, malic acid in apples, and tartaric acid in wine-lees are a few of the commoner examples. We shall not deal with them in detail here, as the study of complex carbon compounds is a science in itself.

The oxide of boron, $B_2O_3$, is a white powder which fuses to a glassy mass, but does not volatilise below white heat. It slowly absorbs water even from the air, forming boric acid, $H_3BO_3$. This substance, also called boracic acid, is found in jets of steam issuing from the ground in Tuscany. It is also prepared by treating calcium diborate (the mineral borocalcite) with nitre cake.

$$CaB_4O_7 + 2NaHSO_4 + 5H_2O \longrightarrow CaSO_4 + Na_2SO_4 + 4H_3BO_3.$$

The product is filtered in a filter press to remove the calcium sulphate and the boric acid crystallised from the liquid.

The oxides of hydrogen are neutral. Water, $H_2O$, is too well known to merit physical description. It can be purified from non-volatile substances by distillation, for ordinary tap water contains various salts and gases in solution which it has abstracted from the air and soil in its passage through them. To prepare it for drinking purposes it is necessary to remove bacteria by exposure to the air, filtration, or the addition of bleaching powder or free chlorine; frequently also it must be softened by the addition of lime. In the case of sea-water distillation is necessary to remove the salt in solution. The importance of water, not only in industry but in every-day life, is so great that no attempt will be made to summarise its uses. This can be done with advantage by the reader for himself.

The other oxide of hydrogen, $H_2O_2$, is called its peroxide, and is the parent substance of the metallic peroxides, from which it is obtained by the action of dilute acids. Thus if barium peroxide is sifted into dilute sulphuric acid, barium sulphate (insoluble) is formed, and hydrogen peroxide remains in solution :

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2.$$

The solution must be concentrated by distillation *in vacuo*, as when heated to the ordinary boiling-point it decomposes into water and oxygen:

$$2H_2O_2 \longrightarrow 2H_2O + O_2.$$

It is thus a convenient source of oxygen and, like many bodies that give up oxygen easily, is a bleaching agent (used for fine fabrics, feathers, ivory, etc.). It is also a safe though effective disinfectant.

# CHAPTER XIX

## ACID HYDRIDES. GENERAL NOTES ON ACIDS

Besides those acids formed from the oxides of non-metals, some of their compounds with hydrogen behave as acids in solution in water.

Thus chlorine combines readily with hydrogen to form gaseous hydrogen chloride, HCl, which when dry has no acid reaction. It is very soluble in water, and the solution is a very useful acid—hydrochloric acid. On the large scale it is made by the action of sulphuric acid on salt, as in the Leblanc process. Hydrochloric acid as sold is a liquid which fumes in the air, and contains 43 per cent. of HCl. On heating, the gas is partly given off, until at 110° a liquid containing 20 per cent. HCl distils over. This is a constant boiling mixture, as referred to in Chapter VI, and the gas cannot be further removed from the water by distillation. The ordinary acid dissolves many metals, and when mixed with nitric acid ($3HCl,1HNO_3$) dissolves even gold and platinum. The bulk of the acid produced is made into chlorine by the use of compounds which easily part with their oxygen (*e.g.*, manganese dioxide), this element replacing chlorine in the acid thus :

$$2HCl + O \longrightarrow H_2O + Cl_2.$$

It is also used in a large number of miscellaneous manufactures, *e.g.*, dyes, pigments, glue, etc., as well as for making various chlorides.

The hydrides of bromine and iodine, HBr and HI, are somewhat similar substances to hydrogen chloride. They cannot, however, be made by the reaction of sulphuric acid with bromides and iodides, as the acid is partly decomposed, thus :

$$2HBr + H_2SO_4 \longrightarrow Br_2 + 2H_2O + SO_2.$$

They are therefore prepared by the action of water on the bromine and iodine compounds of phosphorus :

$$PI_3 + 3H_2O \longrightarrow 3HI + H_3PO_3.$$

These acids are not much used outside laboratories.

Hydrofluoric acid, on the other hand, is very useful, and can be made by a method similar to that employed for hydrochloric acid. The native calcium fluoride, fluorspar, $CaF_2$, is heated with sulphuric acid :

$$CaF_2 + H_2SO_4 \longrightarrow 2HF + CaSO_4.$$

As the acid rapidly attacks glass, earthenware, and most metals, the preparation is carried out in leaden vessels, and the solution of hydrogen fluoride in water must be kept in lead bottles or in glass vessels coated inside with paraffin-wax. It is poisonous and produces slow-healing sores if spilt on the hands. Its disinfecting action is used in washing out beer-vats, in which undesirable organisms are killed. In contact with glass, hydrofluoric acid attacks the silica, forming a gas—silicon fluoride :

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O.$$

It is therefore used for etching glass ; the glass is coated with wax and the parts to be etched are bared by removing the wax ; the glass is then exposed to the fumes of the acid, and the part uncovered is partly removed by the action of the acid. Similarly, hydrofluoric acid is used to dissolve silica from crude graphite.

Hydrogen sulphide (also called sulphuretted hydrogen and hydrosulphuric acid) is formed in the putrefaction of organic matter containing sulphur. Thus its smell is usually likened to rotten eggs. It is a gas boiling at – 74° and is moderately soluble in water. It burns in air with a blue flame, giving water and sulphur dioxide :

$$2H_2S + 3O_2 \longrightarrow 2H_2O + 2SO_2.$$

With insufficient air, only the hydrogen burns, and the sulphur is deposited as such, as we have already seen in the method of recovering sulphur in the Leblanc process. The solution deposits sulphur when exposed to air by the same oxidation of the hydrogen. It is only a feeble acid in solution, but is the parent acid of the important class of substances known as sulphides. It is therefore made by acting on sulphides (usually iron sulphide) with hydrochloric acid. It is very useful in the laboratory for making insoluble sulphides, and is used on the large scale for removing undesirable substances, such as arsenic, in a similar way.

*General Notes on Acids.*—We have now considered a number of the more important acids, and it will be useful to summarise at this stage some of their more general properties :

(1). The sour taste and action on vegetable colouring matters are common to all the acids.

(2). It will be noticed that all the acids mentioned contain hydrogen. Many also contain oxygen, although, as witness the acid character of the hydrides discussed in this chapter, this element is not essential.

(3). Many acids dissolve metals, frequently evolving their hydrogen in so doing. Thus with dilute sulphuric acid and zinc :

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2.$$

In all cases it will be noticed that the metal takes the place of the hydrogen in the molecule. Even with nitric acid, which gives rise to nitrogen oxides when copper acts on it, copper nitrate, $Cu(NO_3)_2$, is formed, in which the copper is in the place lately occupied by the hydrogen. Compounds thus produced by the replacement of the hydrogen in an acid by a metal are called *salts*. It will have been noticed that there is a simple connection between the name of the acid and the salt derived from it. Thus nitr*ic* acid gives nitr*ates* ; nitr*ous* acid gives nitr*ites* ; hydrochloric acid gives chlor*ides*, *-ide* being the usual termination to indicate a compound containing only two elements. The metal which forms the salt need not be presented to the acid as free metal ; its oxide, hydroxide, or salt of some other acid can also be used, as we shall see later.

(4). Hydrochloric acid (HCl) has only one atom of hydrogen per molecule ; sulphuric acid ($H_2SO_4$) has two ; phosphoric acid ($H_3PO_4$) has three. This composition is indicated by saying that the acids are mono-, di-, or tribasic. In acids other than monobasic the hydrogen may be replaced by metal in stages ; thus we have already met with sodium *bi*sulphate, $NaHSO_4$. Substances are thus obtained which are part acid, part salt, and are called *acid salts*.

(5). Several cases have been mentioned in which an acid is prepared by the action of another acid on its salt, *e.g.*, hydrochloric, nitric, and hydrosulphuric acids. This action is very common, and one gets a general impression of stronger acids displacing weaker ones from salts of the latter. This sulphuric acid, under ordinary conditions, displaces almost any other acid; but this is often due to the fact that the other acid is more volatile and is removed from the scene of the struggle for the metallic part of the salt.

(6). Solutions of acids in water conduct electricity easily, and hence can be considered in the light of a theory which has been worked out as to the state of substances in solution. Salt, for example, behaves in many ways in solution as if it were split up into sodium and chlorine particles electrically charged. That is to say, a molecule of salt ($NaCl$) dissolved in water masquerades as an atom of sodium *plus* electric charge, and an atom of chlorine also *plus* electric charge. In very concentrated solutions these tactics cease and the molecules appear as such; but the more water is added to a solution the more molecules split up into these *ions*, as the atom *plus* electric charge is called. Not all ions are atoms, however; sulphuric acid becomes $2H^{\cdot}$ and $SO_4''$, the dot ($^{\cdot}$) showing one positive charge, the dash ($'$) a negative one. Now all acids ionise in solution like sulphuric acid to produce hydrogen ions, thus :

$$\begin{aligned} HNO_3 &\longrightarrow H^{\cdot} + NO_3{}' ; \\ HCl &\longrightarrow H^{\cdot} + Cl' ; \\ H_2S &\longrightarrow 2H^{\cdot} + S'' ; \end{aligned}$$

and so forth.

So general is this behaviour that we can say not merely that all acids contain hydrogen, but also that they all give hydrogen ions in solution.

### SUMMARY OF METHODS OF PREPARING ACIDS

(1). Combination of hydrogen and non-metal, *e.g.*, HCl.

(2). Combination of oxide of non-metal and water, *e.g.*, $H_2SO_4$.

(3). Displacement from a salt by another acid, *e.g.*, $HNO_3$.

A solitary example has been given in each case. The reader will be able to add others from the information in the last few chapters.

# CHAPTER XX

## COMPOUNDS OF METALS WITH OXYGEN

THE oxides of the metals, as has already been indicated, are opposite in their chemical nature to those of the non-metals. They often combine in a similar way with water, giving hydroxides, which, when soluble in water, have a burning taste and turn red litmus blue.

The monoxides of sodium and potassium are unimportant ($Na_2O$, $K_2O$), but their compounds with water, sodium hydroxide (caustic soda), NaOH, and potassium hydroxide, KOH, are among the most useful of manufactured substances. They can be made as described under the Leblanc process by boiling a solution of the carbonate with slaked lime :

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH.$$

Caustic soda is marketed as a white solid which in the air rapidly absorbs moisture (and carbon dioxide). It is extremely soluble in water, and the water in its molecule is so finely combined that it is not converted into the oxide when heated, like almost all other hydroxides. The most important use of caustic soda is in the manufacture of soap. It is likewise essential to the manufacture of most dyes and organic chemicals, and is often used for mercersing cotton. Potassium hydroxide is less used, being more expensive, but its properties are much the same.

Caustic soda reacts with acids, and if solutions of this alkali and, say, hydrochloric acid are mixed until, when tested with litmus papers, no colour change is seen either to red or blue, the acid is said to be neutralised, and on evaporating the solution a salt (in this case common salt) is found. We can see from the equation

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

that the hydrogen of the acid has been replaced by the metal presented to it as a hydroxide. The hydrogen of the acid has hereby combined with the hydroxyl (OH) of the alkali to form water.

A solution of ammonia ($NH_3$) in water behaves in many respects like a solution of the hydroxides of sodium and potassium, and it is commonly supposed to form ammonium hydroxide:

$$NH_3 + H_2O \longrightarrow (NH_4)OH.$$

The group of atoms ($NH_4$) is known as "ammonium" and behaves in many respects like a metal. Solutions of ammonia neutralised with acids give ammonium salts, *e.g.*, chloride, $(NH_4)Cl$, sulphate, $(NH_4)_2SO_4$, etc., with formulæ similar to the salts of the alkali metals.

Phosphorus hydride forms similar salts less stable than the ammonium salts, *e.g.*, phosphonium iodide, $(PH_4)I$; but the hydroxide is unknown, and the hydride has no alkaline properties like ammonia.

Calcium and barium oxides are usually made by roasting the carbonates, as already described in the preparation of lime ($CaO$). Like many metallic oxides, they are very refractory—that is, difficult to melt. Lime, for example, melts at about 1900°, and volatilises at a slightly higher temperature. As it emits a white light when hot it is used in the limelight, in which a stick of lime is heated in an oxy-hydrogen or oxy-gas flame. These oxides form hydroxides on slaking with water, much heat being given out. These hydroxides [$Ca(OH)_2$, $Ba(OH)_2$] are not very soluble in water, slaked lime less so than baryta. The chief use of lime is in building, where, mixed with sand, it is used to make joints in brickwork. The lime combines with the carbon dioxide in the air, forming calcium carbonate, which firmly binds the mass:

$$CaO + CO_2 \longrightarrow CaCO_3.$$

(Incidentally, this is an instance of a salt formed by the union of a basic with an acidic oxide.) It is also used in the manufacture of caustic soda; to liberate ammonia from its compounds (see ammonia–soda process); to absorb chlorine, forming bleaching powder ($CaOCl_2$), whereby the chlorine is made portable and easily available. In general, it is used whenever a cheap, strong alkali is required.

Magnesium oxide, $MgO$, is used as a furnace lining. It is scarcely soluble in water, and a hydroxide can be prepared by adding sodium hydroxide to a solution of magnesium salt. The barely soluble $Mg(OH)_2$ has a faint alkaline reaction.

The hydroxides of practically all the other metals are jelly-like substances scarcely soluble in water. They are prepared generally by adding a solution of caustic soda or ammonia to a solution of a salt of the metal. Thus ferric chloride gives red-brown ferric hydroxide on addition of ammonia:

$$FeCl_3 + 3NH_4.OH \longrightarrow Fe(OH)_3 + 3NH_4Cl.$$

Copper sulphate with caustic soda gives pale blue copper hydroxide:

$$CuSO_4 + 2NaOH \longrightarrow Cu(OH)_2 + Na_2SO_4.$$

If the solutions are mixed hot in this case, the hydroxide loses water and the black copper oxide is formed :

$$Cu(OH)_2 \longrightarrow CuO + H_2O.$$

With other hydroxides it is necessary to heat more strongly to remove the water, and in many instances it has been shown that the water content depends merely on the temperature of drying, so that formulæ for hydroxides must be viewed with suspicion. The reverse process—formation of hydroxide by the addition of water to the oxide—does not occur with oxides other than those of Na, K, Ca, Ba, Sr, Mg. In some cases the hydroxide is soluble in excess of the alkalis used to precipitate it ; thus if ammonia is used to form copper hydroxide, we get first a blue precipitate of the hydroxide, but on adding more ammonia it dissolves to form an intensely blue liquid, which has the astonishing property of dissolving cellulose (*e.g.*, paper).

The hydroxides of aluminium and zinc are soluble in excess of caustic soda, but not in ammonia. In this case the effect is due to the hydroxide behaving as an acid and forming a salt (sodium aluminate). Thus

$$Al(OH)_3 + NaOH \longrightarrow \underset{\text{Sodium aluminate.}}{NaAlO_2} + 2H_2O$$

This reaction is used to free alumina from iron, as the hydroxide of iron is not soluble and settles out from the solution. The salt is very unstable—even carbonic acid evicts the aluminium hydroxide from the aluminate.

The hydroxides generally are soluble in dilute acids, forming salts; thus the greenish chromium hydroxide, $Cr(OH)_3$, gives chromium sulphate when dissolved in sulphuric acid:

$$2Cr(OH)_3 + 3H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 6H_2O.$$

The ease of solution is reduced if the hydroxide has been allowed to stand or is partially dried.

The main use of hydroxides in industry is based on their property of taking up dyes from solution and forming coloured solid compounds called *lakes*. In ordinary dyeing it is frequently necessary to treat the fabric with a *mordant* before placing it in the dye-bath. Such mordants are the acetates and nitrates of aluminium, iron, etc., which easily decompose, leaving a layer of hydroxide in and on the fibres of the cloth. When placed in the dye-bath a lake is formed on the fabric.

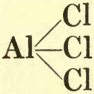
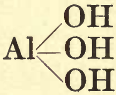
The oxides of metals other than the alkali and alkaline earth metals are mostly powders of high melting-point. Many are soluble in acids, but become less so when strongly heated.

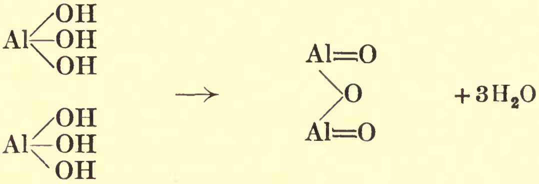
They give salts and water in so dissolving, thus:

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O.$$

The oxides of aluminium ($Al_2O_3$), zinc ($ZnO$), tin ($SnO$ and $SnO_2$), antimony ($Sb_2O_3$ and $Sb_2O_5$), and bismuth ($Bi_2O_3$) are white or yellowish. Manganese dioxide ($MnO_2$), cupric oxide ($CuO$), silver oxide ($Ag_2O$), and magnetic iron oxide ($Fe_3O_4$) are black. Others have various colours and are useful as pigments. Thus woodwork is often treated with a paint containing a good deal of red lead ($Pb_3O_4$) before its final colour is put on; such a paint is also useful in making screw joints in pipe systems. Cuprous oxide ($Cu_2O$) is a dull red-coloured powder used in anti-corrosion paint for the hulls of ships. Ferric oxide ($Fe_2O_3$) forms a rough brown-red paint for iron constructions, and appears also as rouge. The white oxides, particularly zinc oxide (zinc white, Chinese white), are also used in paints.

The reader may have been astonished at the very varied formulæ given to the oxides both of metals and of non-metals; and also at the fact that many elements form two or more oxides. As explained in Chapter IX, these formulæ are based on the results of analyses. We will now consider a simple theory which correlates these miscellaneous formulæ.

The simplest way of viewing the union of hydrogen and chlorine to form hydrogen chloride is to consider that an atom of each of these elements is possessed of one means of attaching itself to the other. This linking power is usually indicated by attaching a small line to the symbol of the element, thus: H—, and Cl—. The union is indicated by joining the two lines thus: H—Cl. The formula of water, again, is $H_2O$. Here one atom of oxygen is joined to two of hydrogen. The atom of oxygen must therefore be possessed of two bonds, as they are often called. We can thus write the formula H—O—H. Potassium and sodium form oxides similar in formula to water: K—O—K, Na—O—Na. The hydroxide is, similarly, Na—O—H. Calcium has two bonds per atom, like oxygen, so that its oxide is Ca=O, its chloride Cl—Ca—Cl. Elements having one bond per atom are termed "monovalent"; with two, "divalent"; and so on. Aluminium is trivalent, its chloride being  $\mathrm{Al}{<}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\\ \mathrm{Cl}\end{matrix}$ and its oxide O=Al—O—Al=O, derived from its hydroxide,  $\mathrm{Al}{<}\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{matrix}$ by the loss of water from two molecules, thus:



Some elements behave as monovalent in one set of compounds, and as divalent in another. Thus copper is divalent in copper sulphate, $CuSO_4$, in cupric chloride, $Cu{<}^{Cl}_{Cl}$, and in cupric oxide (black), $Cu{=}O$. In the cupr*ous* compounds (thus called to distinguish them) it is monovalent, thus: cuprous chloride, $Cu{-}Cl$; cuprous oxide, $Cu{-}O{-}Cu$. Obviously, with elements that are more than monovalent, further compounds are possible owing to the varied arrangement of the bonds. The whole of the theory of organic chemistry is based on tetravalent carbon and the permutations of its four bonds.

In salts, etc., which are soluble in water, monovalent atoms or groups give ions with one electric charge on each; divalent atoms or groups have two charges, and so on. Thus sulphuric acid ionises into two monovalent hydrogen ions with one charge each, and a divalent complex ion $(SO_4)$ with two charges:

$$H_2SO_4 \longrightarrow H^{\cdot} + H^{\cdot} + (SO_4)''.$$

This indicates an electric view of the phenomenon of chemical combinations.

*Peroxides.*—Many higher oxides of metals give hydrogen peroxide on treatment with acids and are then known as peroxides. Thus sodium peroxide, $Na_2O_2$, produced by burning sodium, gives $H_2O_2$ with acids:

$$Na—O—O—Na + 2HCl \longrightarrow H—O—O—H + 2NaCl.$$

Barium peroxide has already been quoted in this connection.

### SUMMARY OF METHODS OF MAKING OXIDES

(1). Burning the element (or otherwise causing it to combine with oxygen), *e.g.*, also most metallic oxides: $SO_2$, $P_2O_5$, NO, $CO_2$.

(2). Removing water from the hydroxide, *e.g.*, all metal oxides except Na, K; $SiO_2$, $SO_2$, $B_2O_3$.

(3). From another oxide containing more or less oxygen, *e.g.*, $CO_2$ from CO; $SO_3$ from $SO_2$; PbO from $PbO_2$.

(4). Heating a salt, *e.g.*, CaO from $CaCO_3$. Many oxides from nitrates of metals; $N_2O$ from $NH_4.NO_2$.

Other examples can be supplied by the reader.

# CHAPTER XXI

## SALTS

WE have already considered salts as the products of the replacement of the hydrogen in acids by metals ; we have further seen that the metal is often presented in the form of its oxide or hydroxide, the acid and alkali losing their distinctive properties and forming a salt. Oxides and hydroxides which are capable of neutralising an acid in this way are called *bases* ; so the alkalis are merely soluble bases.

Salts can be viewed from two other points of view. Suppose we have solutions of caustic soda and nitric acid in separate vessels. The substances will be ionised in solution, giving

$$\begin{aligned} NaOH &\longrightarrow Na^{\cdot} + OH' ; \\ HNO_3 &\longrightarrow H^{\cdot} + NO_3'. \end{aligned}$$

On mixing the solutions in quantities which produce neutrality in the mixture, sodium nitrate and water are produced. Written in ions, the reaction is

$$Na^{\cdot} + OH' + H^{\cdot} + NO_3' \longrightarrow Na^{\cdot} + NO_3' + H_2O ;$$

and it will be seen that all that has really happened is that the $OH'$ ions of the base have combined with the $H^{\cdot}$ ions of the acid to form water, which is scarcely ionised. That this is so is further indicated by the fact that the heat evolved during the reaction, using a gram-molecule of each substance, is 13,700 calories, *whatever acid and base are used*, provided other complications do not arise. It will be seen further that, whilst the characteristic acid properties can be attributed to the $H^{\cdot}$ ion, and the general properties of bases to the $OH'$ ion, the properties of salts in solution will depend on both the ions present. Thus cupric salts are blue in solution, due to the cupric ion $Cu^{\cdot\cdot}$; in other cases the anion is coloured, as in chromates; the $CrO_4''$ ion is yellow.

Salts can often be made by the direct combination of the basic oxide with the anhydride of the acid; we have already instanced the formation of chalk from quicklime and carbon dioxide. We can show this view of the composition of calcium carbonate by writing its formula $CaO.CO_2$. In a similar way, if silica is fused with caustic soda, sodium silicate, $Na_2SiO_3$, is formed; we can write the formula to show that it is formed by the union of sodium monoxide with silicon dioxide, thus: $Na_2O.SiO_2$. This method of showing the composition of salts is freely used for minerals; thus orthoclase, $K_2O.Al_2O_3.6SiO_2$; serpentine, $3MgO.2SiO_2$, etc.

Salts are typically soluble in water. Of the insoluble ones barium sulphate, $BaSO_4$ (mined as heavy spar), is used as the basis of paint pigments, as it is a heavy white powder (*blanc fixé*); the chlorides, bromides, and iodides of silver are used on photographic films, as they blacken when exposed to light. All carbonates, silicates, and chromates are insoluble, except those of Na, K, $NH_4$. Nitrates are soluble without exception.

When crystallised from water some salts reappear with no water in their composition, *e.g.*, sodium chloride, NaCl, potassium nitrate, $KNO_3$. In many cases, however, the crystals contain water combined in definite proportions with the salt itself. Thus washing soda crystallises from cold solutions in clear crystals having the composition $Na_2CO_3.10H_2O$; when heated the water is driven off and the *anhydrous* white salt, $Na_2CO_3$, left behind. Similarly, copper sulphate crystallises in fine blue masses, known as blue vitriol, of composition $CuSO_4.5H_2O$. On heating, the water is lost and a white powder, $CuSO_4$, is left behind. Often the water is lost in stages; thus sodium sulphate can be obtained as $Na_2SO_4.10H_2O$, $Na_2SO_4.7H_2O$, and the anhydrous salt cake, $Na_2SO_4$. It is comparatively easy, moreover, to remove four of the five molecules of water from copper sulphate, $CuSO_4.5H_2O$, by heating to 100°; the compound, $CuSO_4.H_2O$, must be heated to 250° before it loses the last molecule of water of crystallisation.

The tendency of hydrated salts to lose water is represented by a definite vapour pressure. Thus with $Na_2SO_4.10H_2O$ this pressure is 28 mm. of mercury. Now the ordinary vapour pressure of the water in the air is only 8 mm. of mercury; hence we should expect the crystals of sodium sulphate to give off water in the air; and when sodium sulphate crystals are left in the air they gradually give up moisture and crumble to a white powder, anhydrous $Na_2SO_4$. This phenomenon is known as *efflorescence*, and can be readily noticed in crystals of washing soda. If, however, water-free calcium chloride, $CaCl_2$, and ferric chloride, $FeCl_3$, are exposed to the air, they absorb moisture, forming $CaCl_2.6H_2O$ and $FeCl_3.6H_2O$. This *deliquescence*, as it is called, is accounted for by the fact that the vapour pressures of the hydrated salts are 3 mm. and 6 mm. of mercury respectively.

Salts not only combine with water when they crystallise from solution; they often combine with one another, if several are present. Thus if a solution containing potassium sulphate,

$K_2SO_4$, and aluminium sulphate, $Al_2(SO_4)_3$, is crystallised, the two salts do not appear as separate crystals, but as crystals of a *double salt*, alum. The composition of the alum crystals is quite definite, viz.:

$$K_2SO_4.Al_2(SO_4)_3.24H_2O.$$

The crystals are different in shape from those of the component salts; and the fact that the two components are always present in the proportion of their molecular weights shows that they can be no mere mixtures. Ordinary alum of the above formula is merely one example of the series of alums, for similar double salts can be made by the use of other mixtures of sulphates. Thus chrome alum is obtained from potassium and chromium sulphates and has for formula $K_2SO_4.Cr_2(SO_4)_3.24H_2O$. Iron in the ferric (trivalent) state can also take the place of aluminium in the typical alum formula, while potassium may be replaced by sodium, ammonium, or silver. It is interesting to note that, whatever metals are in the two positions in the alum formula, the shape of the crystals is the same. This is quite a general rule with crystals—similar formula, similar crystal shape. Common alum and chrome alum are used in tanning and as mordants in dyeing.

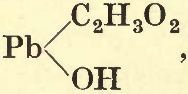
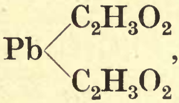
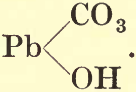
Many other salts form double compounds.

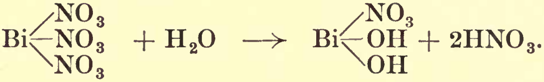
They are very common in Nature; for instance, at Stassfurt an important source of potassium salts, carnallite, $KCl.MgCl_2.6H_2O$, and kainite, $K_2SO_4.MgSO_4.MgCl_2.6H_2O$, occur in large quantities. Dolomite is a double carbonate of calcium and magnesium, $CaCO_3.MgCO_3$.

In solution, double salts behave as mixtures of their components—that is, the ions are those of the separate salts.

We have already noted that acid salts can be produced by replacing only part of the hydrogen in a di- or tri-basic acid. Similarly, compounds known as basic salts can be prepared in many cases from metallic hydroxides containing more than one $-OH$ group in the molecule. Thus if copper hydroxide is heated with only half the theoretical quantity of sulphuric acid, a compound of copper oxide and copper sulphate is formed:

$$2Cu(OH)_2 + H_2SO_4 \longrightarrow \underset{\text{Basic copper sulphate.}}{CuO{\cdot}CuSO_4} + 2H_2O.$$

Many basic salts are important in commerce; thus basic lead acetates, such as  $Pb\begin{matrix}C_2H_3O_2\\OH\end{matrix}$, are formed by heating litharge (PbO) with ordinary lead acetate,  $Pb\begin{matrix}C_2H_3O_2\\C_2H_3O_2\end{matrix}$, in one process for making white lead. This pigment itself is a basic carbonate,  $Pb\begin{cases} CO_3 \\ OH \end{cases}$. Bismuth subnitrate, an insoluble white powder, used in medicine, is formed from bismuth nitrate, $Bi(NO_3)_3$, by adding a concentrated solution of the nitrate to a large bulk of water :



$$Bi\begin{cases} NO_3 \\ NO_3 \\ NO_3 \end{cases} + H_2O \longrightarrow Bi\begin{cases} NO_3 \\ OH \\ OH \end{cases} + 2HNO_3.$$

Thus basic salts are formed by replacement of part of the hydroxyl of a base by acid radicles.

The general method of making salts can be written

$$\text{Acid} + \text{base} \longrightarrow \text{salt} + \text{water}.$$

In many cases the reverse action occurs—water acts on a salt to form free base and acid again. The formation of bismuth subnitrate is one example of this, in which the salt is partly converted into hydroxide. If the subnitrate is washed repeatedly with water it is eventually converted into hydroxide, $Bi(OH)_3$. This reverse action, known as *hydrolysis*, occurs when most salts are dissolved in water, but the effects are most noticeable when a weak acid has neutralised a strong base, or a weak base [*e.g.*, $Bi(OH)_3$] is combined with a strong acid (*e.g.*, $HNO_3$).

When sodium carbonate (washing soda) is dissolved in water the solution shows all the alkaline reactions, although this body is a salt. This effect is due to hydrolysis:

$$Na_2CO_3 + 2H_2O \longrightarrow 2NaOH + H_2CO_3,$$

though naturally only a small proportion of the soda is changed in this way. In this case the base is strong and the acid weak, "strong" meaning largely converted into ions in water, and "weak" meaning scarcely ionised. Thus, written in ions, the equation becomes

$$2Na^{\cdot} + CO_3'' + 2H_2O \longrightarrow 2Na^{\cdot} + 2OH' + \underset{\text{(Un-ionised.)}}{H_2CO_3}$$

so that the reaction of the products on the right-hand side will be that of the OH′ ions—that is, alkaline.

Similarly, ferric chloride and aluminium sulphate give acid solutions in water; thus

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{Un-ionised}}{Fe(OH)_3} + 3HCl.$$

In this case, if the solution is put into a bag of parchment paper suspended in water, the acid goes through the paper, whereas the ferric hydroxide is unable to diffuse. If the water is frequently changed, practically all the acid can be removed in this way.

This fact is used in dyeing, where salts, such as the acetates of aluminium and iron, tin, chloride, etc., are used as mordants. The fabric is treated with a solution of these salts, and on steaming or drying the goods hydrolysis occurs and the volatile acids go off, leaving the hydroxide. On immersing the material in the dye-bath, the dye attaches itself to the hydroxide.

The application of hydrolysis of salts in industry is limited, but the phenomenon is so general that it must be guarded against or controlled in many cases.

# SECTION D

## The Rate of Chemical Change

# CHAPTER XXII

## THE PROGRESS OF CHEMICAL CHANGES

We have so far taken a wide view of chemical change as a phenomenon which occurs when certain substances are brought together and treated in a definite way. The products of a number of reactions have been studied, together with the means used to carry out the reactions. We will now consider certain factors which affect the course of reactions in general.

There is undoubtedly some force which causes substances to combine together, and in many cases the more opposite the characters of the substances the more eagerly they appear to react. This force does not operate until the substances are in actual contact, so that it is quite different either from the force of gravitation, which causes bodies to move towards the centre of the earth, or from the attracting force of a magnet. The avidity of the one substance for the other—for instance, of lime for carbon dioxide—is completely satisfied with a certain weight of the second substance, as we have seen in Chapter IX, and this weight is always the same.

Substances which do not react are said to have no affinity for one another, *e.g.*, caustic soda and oxygen. It was at one time thought possible to measure the affinity of a pair of substances for one another by the heat evolved when they combined. But this suggestion cannot include cases where heat is not given out, but absorbed—endothermic reactions. Moreover, in many cases reactions can proceed in either direction, as we shall see later. If we consider a case of simple replacement which behaves in this way—the action of steam on iron :

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2$$

—we find not only that iron will decompose steam, forming iron oxide and hydrogen, but that hydrogen decomposes iron oxide, leaving iron and forming steam. So that in one case the affinity of the iron for oxygen is greater than that of hydrogen, while in the reverse reaction it is less.

It is therefore clear that the chemical affinity of substances depends on conditions to a great extent, and consequently only a general idea can be formed of the relative affinities of reacting substances. The actual combining force is probably electrical.

We shall confine ourselves to a consideration of the practical factors which affect chemical change.

All reactions take a definite time to complete their course. If a mixture of oxygen and hydrogen in a tube is fired by a spark, the flame travels at a measurable rate along the tube; similarly, ionised substances in solution react as a rule very rapidly, but not instantaneously.

Let us consider the simple case of the action of a metal on an acid (*e.g.*, the " killing " of hydrochloric acid by zinc, as carried out to make a cleaning liquid for soldering). The reaction starts off briskly, and hydrogen is given off rapidly; but gradually, as the acid gets used up, it slows down, and finally ceases completely when all the acid or all the zinc is consumed. Accurately expressed, the rate depends on the number of gram-molecules of acid per litre of the liquid (*i.e.*, the molecular concentration). As this quantity is gradually reduced the rate of reaction—that is, the gram-molecules of zinc dissolved per second—becomes also less and less.

Practically the rapid removal of the products of the reaction is as important as the supply of raw material if the reaction is to proceed rapidly. Thus, if we attempt to make carbon dioxide by the use of dilute sulphuric acid and chalk :

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O,$$

the reaction does not proceed to completion, as the particles of chalk become coated with a layer of the not very soluble calcium sulphate. It is only possible to obtain a good yield if the carbonate is powdered. If, on the other hand, hydrochloric acid is used, the calcium chloride produced as a by-product is soluble in the water present and the reaction proceeds unimpeded ; in fact, too rapidly for many purposes, unless the carbonate is in the form of chips of marble.

The thorough mixing of the reacting substances is also indicated as an advantage, so that the concentrations may not become low in places. The regular use of mechanical stirrers on the large scale for reactions in solution, and of rotating furnaces in the Leblanc process and in making cement, are examples of the application of this principle to liquids and fused masses. Where gas is to react with a liquid, the gas is usually sent up a tower down which the liquid trickles, as in the ammonia–soda process. This arrangement has also the advantage of causing a high concentration of the gas at the base of the tower, where the brine concentration is low, so as to urge the completion of the reaction. Similarly, at the top of the tower the high brine concentration is able to react with the low carbon dioxide content of the liquid.

We mentioned above the case of the action of steam on iron—a reaction used practically for the preparation of hydrogen for military purposes. The reaction proceeds in the direction

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2,$$

when steam is blown over heated iron. The hydrogen is removed from the sphere of action as rapidly as it is formed, so that its concentration is maintained very low; but as an excess of steam is used its concentration is kept high.

If, on the other hand, hydrogen is driven through a heated tube containing magnetic iron oxide, steam is formed and the oxide reduced to the metal, thus:

$$Fe_3O_4 + 4H_2 \longrightarrow 4H_2O + 3Fe.$$

Here the reverse conditions obtain. The steam is swept away by the stream of hydrogen, of which the concentration is obviously high. In actual practice the iron is liberated from the oxide by the use of producer-gas :

$$Fe_3O_4 + 4CO \longrightarrow 4CO_2 + 3Fe,$$

after which the metallic mass can be used again for the production of hydrogen.

Let us consider the hypothetical case of a quantity of iron heated with steam in a closed tube in quantities demanded by the first equation above. Here the hydrogen will accumulate, and its concentration thus increase, with a tendency to cause the reaction to go backward. Eventually the tendency is so great that the forward reaction stops (or, to speak more accurately, both proceed at the same rate). The system is then said to be in *equilibrium*, and a reaction like this one, which can go in either direction, is called *reversible*, the equation being written with double arrows :

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + 4H_2.$$

Many authorities regard all reactions as being theoretically reversible ; those we consider complete having the equilibrium position very close to the complete end.

We have already seen that the general reaction

$$\text{Acid} + \text{Base} \underset{\text{Hydrolysis}}{\overset{\text{Neutralisation}}{\rightleftarrows}} \text{Salt} + \text{Water}$$

is reversible to a greater or less extent, the forward reaction being called neutralisation, and the reverse hydrolysis. Here, again, the influence of concentration is seen. In the case of bismuth subnitrate, for example, the hydrolysis is favoured by the presence of much water, and by the fact that one of the products is removed from the scene of the reaction (solution in the water) by being precipitated as a basic salt. Hydrolysis, again, is prevented by the presence of excess of free acid.

Generally speaking, a rise in temperature accelerates chemical changes. In fact, many changes we have dealt with proceed so slowly as to be unnoticed at the ordinary temperature. Often, when the reaction proceeds with liberation of heat, it is only necessary to heat the substances to a minimum temperature and the change will go on of itself, becoming faster and faster unless the heat produced escapes. The burning of coal is an instance of this. It oxidises slowly at the ordinary temperature; when heated, with a sufficient supply of air to burn it and remove the products of combustion, the temperature rises until the mass is radiating or otherwise losing heat as fast as it produces it.

In the case of reversible reactions the speed of both the forward and backward reactions may be increased. As they are not always increased in the same ratio, it is clear that the equilibrium stage will not only be reached more quickly, but, when it is arrived at, may consist of different quantities of the compounds concerned.

The extended use of heat in bringing about chemical reactions has therefore two objects in view: (1) to supply energy required to bring about a reaction which absorbs it (*e.g.*, formation of lime and carbon dioxide from chalk); and (2) so to increase the rate of reaction that the end desired is arrived at in a reasonable time.

A very striking instance of the effect of temperature on the rate of chemical change is the fact that many reactions which proceed rapidly at the ordinary temperature cease almost completely if the reacting substances are cooled in liquid air.

Increase of pressure brings about a similar hastening to increase in temperature, but is seldom used.

We shall discuss in the next few chapters the important use of some chemical substances, called *catalysts*, which have a profound influence on the rate at which other substances react.

## SUMMARY

The rate of a chemical change is increased by—
(1). Increased concentration of the reacting substances.
(2). Decreased concentration of the substances produced.
(3). Rise of temperature or pressure.
(4). The pressure of catalysts.

# CHAPTER XXIII

## CATALYSTS: THE CONTACT PROCESS FOR SULPHURIC ACID

SOME chemical changes proceed only very slowly, even when conditions favour them in many respects. Even in the case of gases, where the mixture of the changing substances is complete, the action may proceed only slowly or not at all. For instance, hydrogen and oxygen mixed in the proportion required to form water, as summarised:

$$2H_2 + O_2 \longrightarrow 2H_2O,$$

may be left at the ordinary temperature for years without any appreciable union taking place. If, however, a small piece of spongy platinum is brought into contact with the mixture, the reaction takes place almost instantaneously.

The platinum is itself unchanged, so far as we know. At any rate, it is there just the same when the reaction has finished. Also a very small quantity only is necessary to cause the union of a great quantity of the two gases.

A substance which stimulates a sluggish chemical action in this way is called a *catalyst*, and its action is described as *catalytic*. In some cases it forms temporary compounds with the other substances involved; but in a truly catalytic action it is found to be unchanged in weight and kind after it has done its work. All kinds of substances can be used as catalysts, but often they must be in a finely divided state, which leads us to suspect that their surface is where the action occurs. Thus fine nickel powder is used to add hydrogen to certain oils; and sulphur is useful in hastening the action of chlorine on acetic acid; a small quantity of manganese dioxide quickens the rate at which oxygen is evolved from potassium chlorate.

We shall now study in detail a few cases in which these accelerators are used in commercial manufacture.

As was mentioned in Chapter II, sulphur burns in air, producing sulphur dioxide ($SO_2$). This gas can be made to unite with more oxygen to give another oxide, thus:

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

—sulphur trioxide. When this oxide—a solid crystalline substance—dissolves in water, the very important compound sulphuric acid is produced :

$$SO_3 + H_2O \longrightarrow H_2SO_4.$$

There are two main methods in use for producing sulphuric acid—the contact process and the older chamber process. Together they make some seven to eight million tons of acid annually.

We shall first study the contact process, which is a simple example of catalysis.

We must first consider the general factors governing the combination of sulphur dioxide and oxygen. At 400° C. union occurs very slowly ; the mixture, passed through a tube heated to 600°, gives a product containing about 30 per cent. trioxide ; a higher temperature gives less, for the reaction is reversible, thus :

$$2SO_2 + O_2 \xrightleftharpoons[\text{above } 600^\circ]{400^\circ\text{—}600^\circ} SO_3.$$

Now many of the catalysts that might be used (quartz, brick, ferric oxide, etc.) increase the rate of reaction only at 600° or over ; thus, owing to the back action, they can never convert *all* the mixed gases to sulphur trioxide. On the industrial scale it is essential to do so, as it is not simple to separate the remaining dioxide.

Further, the action proceeds, when it does begin, with evolution of heat, the energy equation being

$$SO_2 + O_2 \longrightarrow 2SO_3 + 45{\cdot}2 \text{ cals.}$$

On the large scale, therefore, care has to be taken to cool the apparatus once the action has started, otherwise again the yield will be reduced.

In the process patented by the Badische Anilin- u. Soda-Fabrik, asbestos coated with platinum is used as the catalyst. This is made by soaking the asbestos in a solution of platinum chloride, drying, and heating to redness, when the salt is decomposed and platinum metal in a fine condition remains attached to the asbestos. This is then placed on the perforated shelves which occur up the whole length of the tubes *A*, shown in Fig. 24. To begin with, the whole chamber is heated to about 400° by means of the gas-ring *G* at the bottom. The mixture of sulphur dioxide and air, with rather more air than is theoretically necessary, is admitted by the tube $v_1$, and enters the main chamber through holes in its wall. The gases flow round the outside of the tubes *A*, so that on arriving at the top they, too, are heated to the necessary temperature. They proceed downwards past the baffles *B*, and stream down through the platinum layers in *A*.

By the time the bottom is reached from 96–98 per cent. of the sulphur dioxide is converted, and the remaining gases, in which the trioxide

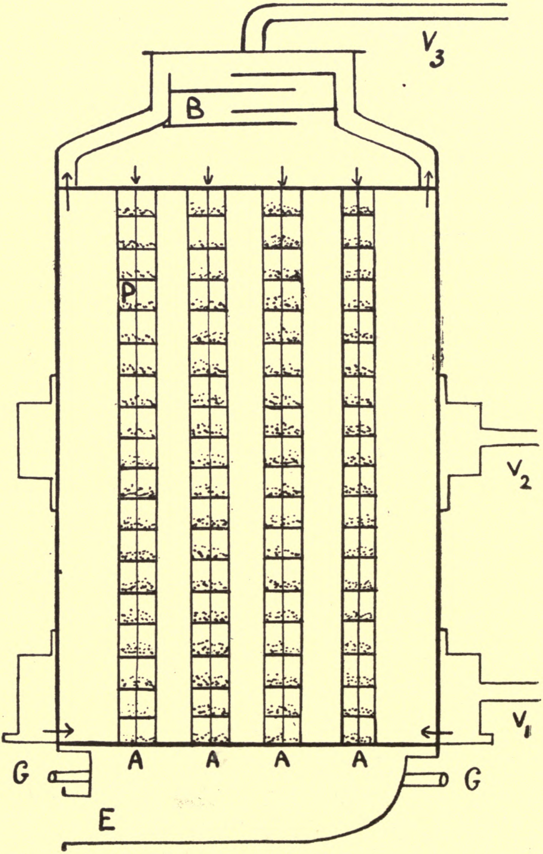


Fig. 24.—Platinum contact apparatus for sulphur trioxide.

forms a white fog, go out through the common main *E*. The temperature must be carefully watched, and should it rise too much the tubes are cooled by allowing some of the mixture to enter from pipes $v_2$ or $v_3$, in which case the gases will obviously get less heated before coming to the platinum.

To make sulphuric acid from the trioxide thus formed is not so simple as would appear. When obtained in solid crystals it can be dissolved easily in water; but the mist coming from the outlet *E* is quite difficult to clear with water only. It is found best to absorb it in water which has already taken up a good deal of trioxide—that is, in sulphuric acid itself. So *E* is connected to a series of towers of earthenware packed with balls of the same material, over which the acid trickles. This obviously produces a solution containing more sulphur trioxide than sulphuric acid. Such an acid, which is useful and even essential in many chemical processes, is called technically "oleum." To make ordinary sulphuric acid from this it is necessary to add water in the proper proportion, or a weaker acid.

The sulphur dioxide required for this process is usually made by burning iron pyrites—an iron ore of composition represented by the formula $FeS_2$. When heated in a stream of air the sulphur and iron both burn, giving their respective oxides, $SO_2$, and ferric oxide, $Fe_2O_3$.

The pyrites, however, is not pure. In particular it contains some arsenic. Now arsenic, and some other substances, have a bad effect on the platinum catalyst. A very little arsenic will soon prevent its acting as a catalyst at all —it is said to be " poisoned." So it is necessary before allowing the gases to enter the reaction chamber, to purify them. This is done by scrubbing them in towers with (1) jets of steam, (2) jets of cold water, and, finally, (3) a stream of sulphuric acid, which dries them.

This clearly is a troublesome business, and in the Mannheim plant it is largely avoided. In this the air is dried before going to the pyrites ; and the whole plant being kept closed, it remains dry.

We noticed earlier in this chapter that ferric oxide was a catalyst for the reaction, although not suitable to give a complete result. It is, however, much less sensitive than platinum to the dust and arsenic in the gases from the pyrites burners ; moreover, being infinitely cheaper, it can be renewed (from the *burnt* pyrites) when it gets sluggish.

The gases from the burners *B*, which are fed with dry air through the pipes *A*, are therefore led direct up a tower containing

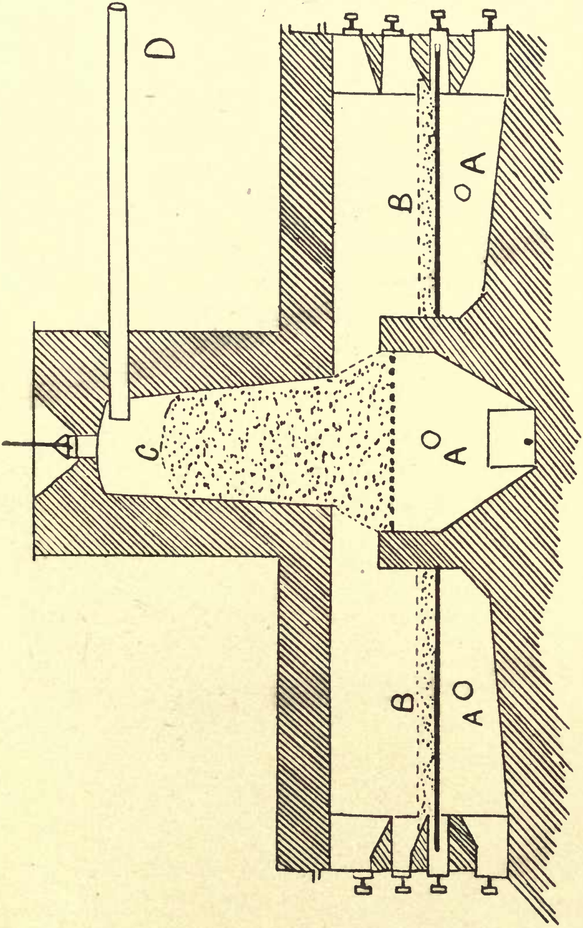


FIG. 25.—Mannheim plant for sulphur trioxide.

burnt pyrites *C* in lumps. The dust is caught here, and some 60 per cent. of the sulphur dioxide is converted to trioxide. The gases, now cleaned, pass on by pipe *D* to a platinum apparatus to finish the reaction (Fig. 25).

The contact process generally is simpler than the chamber process, which we shall deal with in the next chapter; the high cost of platinum makes it expensive to set up, and with recent improvements the chamber process competes very favourably with it as a method of making sulphuric acid.

# CHAPTER XXIV

## THE CHAMBER PROCESS FOR SULPHURIC ACID

THE main reaction in the chamber process is the same as that in the contact process, viz.

$$2SO_2 + O_2 \longrightarrow 2SO_3,$$

and in this case also the reaction is brought about by the use of a catalyst. We have already mentioned that nitric oxide (NO) combines with oxygen spontaneously to form nitrogen peroxide ($NO_2$). This gas gives up its oxygen under certain conditions, leaving nitric oxide once more. It is this reaction which is used to add oxygen to the sulphur dioxide. The nitric oxide left, in contact with more air, is once more converted into nitrogen peroxide, and the process is repeated. The nitric oxide therefore acts as a " carrier " of the oxygen of the air.

Fig. 26 gives a simplified view of the plant used, and reference will be made to it in describing the stages of the process.

The sulphur dioxide is ordinarily produced by burning iron pyrites, $FeS_2$, of which that commonly used contains an average of 45 per cent. of sulphur. Other sulphides, such as

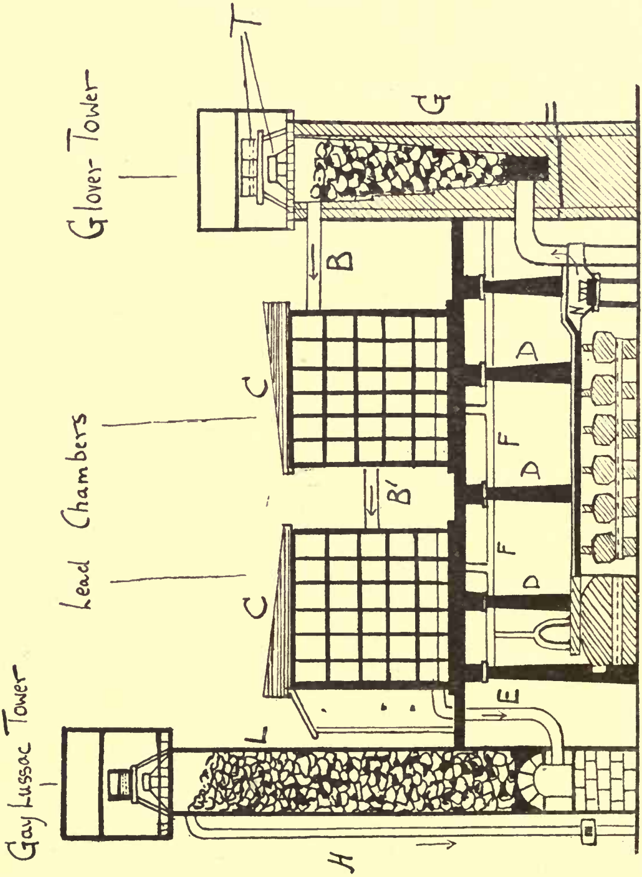


Fig. 26.—Chamber plant for sulphuric acid.

zinc blende ($ZnS$) and galena ($PbS$), are used in works which also smelt these metals, but are not so convenient, as they contain less sulphur and the oxides are more volatile than the oxide of iron. The iron hydroxide which has been used in gasworks to abstract sulphur from coal gas is also sometimes used, while to obtain a pure sulphuric acid free from arsenic sulphur itself is burnt in special kilns.

The iron pyrites is converted into ferric oxide,

$$4FeS_2 + 11O_2 \longrightarrow 8SO_2 + 2Fe_2O_3,$$

and, once started, burns by itself like a fuel. It is important to regulate the supply of air to the pyrites burners, as with insufficient air sulphur will be left unburnt, while excess cools the furnace and dilutes the sulphur dioxide. The pyrites burners are ordinarily made like a common furnace with grate, etc., but only coarse lumps can be burnt thus. A row of burners is shown at *A* in Fig. 26. Finer material is burnt in mechanical roasters, in which it is continually raked by the water-cooled arms of a central rotating spindle.

It is important to remove dust from the gases produced. They are either led into long flues or given a spiral motion to separate dust. The Cottrell method of electric precipitation of dusts is also applied.

The burner gases contain 7 per cent. of $SO_2$ and a little $SO_3$, and are led from the dust catcher (not shown in Fig. 26) over the nitre pots *N* to the Glover tower *G*. The nitre pots contain Chile saltpetre and sulphuric acid to provide the oxides of nitrogen for the oxidation of the sulphur dioxide. The nitric acid evolved from the pots is decomposed by the hot gases :

$$2HNO_3 \longrightarrow H_2O + NO + NO_2 + O_2,$$

and the products swept on up the Glover tower.

This tower is constructed of acid-proof earthenware bricks or of a compact lava at the base, and is packed with flints or with hollow cylinders of earthenware. The packing is designed to allow free passage of the gases upward whilst distributing evenly the acids which pour down the tower from tanks *T* at the top of it.

The gases, in passing up the tower, take up more nitrous fumes from the descending acids, and pass by a wide lead tube *B* to the lead chambers.

The lead chambers are made of pure soft lead about 0·1 in. thick, the joints being welded by the oxyhydrogen flame. The chambers are supported by a framework of wood, to which they are attached by lead straps welded on to the chambers, and the whole is raised on pillars *D* clear of the ground. The chambers *C*, of which two only are shown in the figure, though more are often used, are connected by pipes *B′*, and a further lead pipe *E* connects the last in the series to the Gay Lussac tower *L*. These pipes are furnished with glass windows, through which the colour of the passing gases can be observed.

The main reaction, which occurs partly in the Glover tower, completes itself in the lead chambers. Water is supplied by numerous fine jets producing sprays in the chambers, and the reaction which takes place can be represented simply by the equation

$$NO_2 + SO_2 + H_2O \longrightarrow H_2SO_4 + NO.$$

Almost certainly it is not so simple as here represented; but to give the various speculations would merely confuse the reader.

The sulphuric acid formed flows down the walls of the chambers to the base, in which the edge is turned up to make a shallow tank, from which the acid is periodically run off to reservoirs by pipes *F*. It is essential to mix the gases in the chambers thoroughly. This is accomplished by fans, or, in some types of chamber, by admitting the gases tangentially into a round chamber.

The residual gases contain much nitric oxide, which must be recovered. They are led by *E* to the bottom of the Gay Lussac tower, down which a stream of concentrated sulphuric acid trickles over coke or more systematic packing. The nitrogen peroxide combines with the sulphuric acid to form nitrosyl-sulphuric-acid, thus :

$$2NO + O + 2H_2SO_4 \longrightarrow \underset{\text{Nitrosyl-sulphuric acid.}}{2NOHSO_4} + H_2O.$$

The remaining gases escape by pipe *H* to the main shaft. The nitrosyl-sulphuric acid is pumped to a tank at the top of the Glover tower, where it trickles down and the hot furnace gases decompose it :

$$2NOHSO_4 + SO_2 + 2H_2O \longrightarrow 3H_2SO_4 + 2NO.$$

The nitric oxide is swept on into the chambers and serves to convert more sulphur dioxide into acid. Frequently two Gay Lussac towers are used, so that the nitrous fumes are more completely recovered. The reaction between sulphur dioxide and oxygen, even when catalysed by nitric oxide, takes some time to complete ; hence several chambers are necessary. The reaction occurs more rapidly if more nitrous fumes are used, but this not only greatly increases the expense of production, but also causes the chambers to corrode more rapidly. With a more rapid action fewer chambers are necessary, but, in any case, repairs are a heavy item. It is now the custom, however, to work the chambers "intensively," and as much as 10 kg. of chamber acid per cubic metre of chamber can be obtained, although formerly half this rate of production per twenty-four hours was considered good. The shapes and sizes of modern chambers are designed to increase this factor, to diminish or facilitate repairs, and to increase the rate of cooling of the chambers; for, as we saw in the contact process, the formation of sulphur trioxide is accompanied by evolution of heat, and obviously the heat produced in a given time increases with intensity of working. The temperature of the chambers should not rise above 90°, and that of the last in a series is often as low as 40°.

The yield of acid, calculated as 100 per cent. $H_2SO_4$, is about 290 per cent. of the sulphur burned in the pyrites—about 94 per cent. of the quantity theoretically obtainable. To obtain 100 kilos. of acid, 0·5–1·0 kilo. of sodium nitrate must be used to make up for unavoidable losses of nitrous fumes; otherwise the nitric oxide is a true catalyst—unchanged when its work is completed, able in small quantity to convert a large bulk of sulphur dioxide to the trioxide. The sulphuric acid produced is of various concentrations, depending on the point at which it is removed from the plant. Thus the acid condensing in the chambers—chamber acid—contains 60–70 per cent. $H_2SO_4$. This is suitable for many industrial purposes, particularly for making superphosphate of lime.

A quantity of the chamber acid is concentrated by allowing it to stream down the Glover tower with the nitrosyl-sulphuric acid. The acid which runs off at the bottom of the tower contains 78 per cent. $H_2SO_4$ and is sold as Glover acid. It frequently acquires impurities in this stage, as the tower packing is seldom completely acid-proof.

The chamber acid is concentrated by heating in lead pans if a purer quality is required. It can be concentrated in this way only up to the strength of Glover acid, as, if heated longer, the lead pans are attacked. It is therefore necessary to heat in vessels other than lead in order to achieve a higher concentration. Basins are constructed of fused silica, fused alumina, alloys of iron and silicon (such as "ironac," "tantiron," "duriron," etc.), and other acid-resisting materials. Each basin is provided with a long lip, and they are set on a kind of staircase above flues. The bottom of the staircase is hottest, and the acid flows from one pan to the next down the " cascade " until on reaching the bottom the acid is sufficiently concentrated. Alternatively the acid is caused to stream down towers (Galliard towers), up which hot gases from a " producer " are passing. The towers are unpacked, but the chamber acid is sprayed in evenly at the top of the tower.

A small proportion of the sulphuric acid produced is still concentrated up to 94–96 per cent. of acid by evaporation in glass or platinum —iridium pans.

The whole question of the concentration of sulphuric acid has been revolutionised by the development of the contact process. We saw in the last chapter how that process normally produces only fuming sulphuric acid (oleum). It is therefore always possible to make a concentrated acid from chamber acid by adding to it the requisite quantity of oleum. In fact, many chamber plants now have a contact plant working side by side with them to produce oleum for concentrating the normal product of the first process in this simple and economical way.

A comparison of the economic efficiency of the two systems is not easy to make at present. Generally, for producing 97 per cent. acid the costs for the contact process are somewhat less than for an old-fashioned chamber plant, but rather more than for a chamber system comprising the latest improvements. The contact process is also being improved, with a consequent cheapening of its product. At the moment, as we have seen, they may be treated as two separate manufactures—the one producing oleum, the other sulphuric acid of various concentrations.

# CHAPTER XXV

## THE DEACON CHLORINE PROCESS

We have already mentioned that oxygen is capable of replacing the chlorine in hydrochloric acid to produce free chlorine and water in the forward sense :

$$4HCl + O_2 \rightleftarrows 2Cl_2 + 2H_2O.$$

At low temperatures this reaction proceeds almost completely from left to right, whereas at higher temperatures the reverse reaction proceeds more quickly.

Both these reactions, however, go far too slowly for practical use, unless a catalyst is present. The usual catalyst employed is cupric chloride, $CuCl_2$, although many other substances, notably the chlorides of nickel and manganese, and even pumice-stone, function in the same manner.

The best temperature for working is about 450° C.; below this temperature equilibrium is attained slowly, while at a higher temperature the copper chloride volatilises appreciably, and the reverse reactions set in with greater speed. In no case is the reaction complete in the forward direction, so that the chlorine is contaminated with hydrochloric acid.

The plant used on a large scale is indicated diagrammatically in Fig. 27. The hydrochloric acid fumes from the salt-cake pans and roasters of the Leblanc process enter by the pipe *A*. A mixture of 5–20 per cent. of HCl with air is found to be best, for it will be seen from the equation that excess oxygen increases the rate of the forward reaction. The mixture passes up the condenser *B* to remove dust, drops of sulphuric acid, etc. Frequently a stream of sulphuric acid trickling over coke in *B* serves to dry the gas, which then passes to the heater *C*. The heating is effected by passing the gas through twenty-four inverted U-tubes arranged in a firebrick chamber heated by the gases from a small furnace *D*. The temperature is here raised to 470°, and the gases pass on to the reaction chamber *E*. This firebrick room is heated to 450° by gases from the furnace *D*, and contains six compartments filled with lumps of clay which have been soaked in copper chloride solution and baked. The gases are sent from above downwards in the first chamber, then up through the second, and so on alternately through the series. About

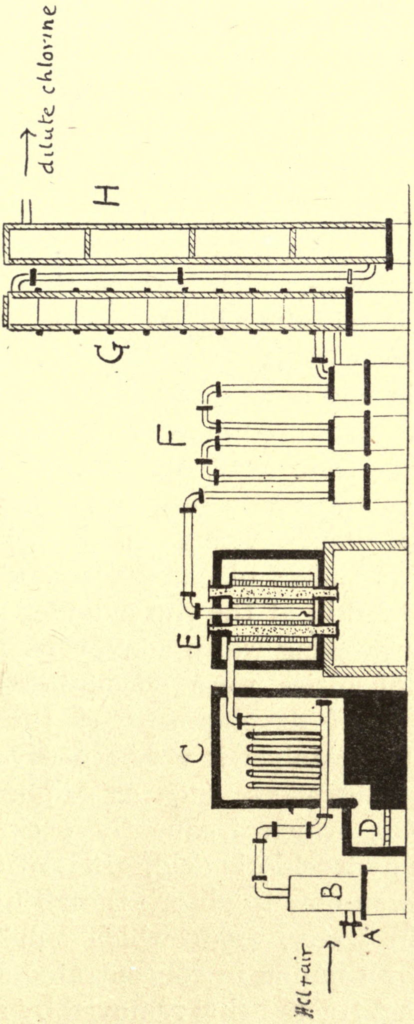


Fig. 27.—Deacon plant for chlorine.

65 per cent. of the HCl is converted into chlorine, and the mixture is cooled in a series of cooling tubes *F*, where most of the steam and hydrochloric acid is condensed. It is essential, if the chlorine is to be converted into bleaching powder, to remove all hydrochloric acid from the issuing gases. They are therefore passed up the tower *G*, down which a spray of water is pumped over coke, which dissolves the remaining hydrochloric acid and a little chlorine. A second tower *H* serves to dry the gas. In it a stream of sulphuric acid flows down also over coke.

The final gases are not very rich in chlorine; they contain from 5–12 per cent. of this gas, which is usually made into bleaching powder by a special plant. The gas is passed through a series of cylinders placed horizontally, along which lime fed in at the top cylinder is caused to drift by rotating worm conveyers.

Many difficulties were encountered in the early stages of development of the Deacon process. The catalyst is very sensitive to dust and other substances, such as sulphuric acid, arsenic, etc., which frequently occur in the unpurified hydrochloric acid. It is often found desirable even now to absorb the HCl from the furnaces in water, from which solution it is liberated by running in concentrated sulphuric acid, the last traces being removed by a current of air. The water from tower *K* can obviously be used with advantage at this stage.

The loss of copper chloride is considerable—about 50 per cent. in ten days, unless the gases are sent through the mass in the manner described above. Recently the double chloride of copper and sodium, $CuCl_2.NaCl$, has been used with success, as it is not appreciably volatile even at 550°.

The Deacon process is so far the most effective means of preparing chlorine from hydrochloric acid. The great advantage is that the oxygen used is derived from the air and so costs nothing.

In the alternative process, devised by Weldon, manganese dioxide is used as the source of oxygen, thus :

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O.$$

It will be noticed that only one-half of the chlorine in the hydrochloric acid is set free—in practice about one-third ; and although the manganese can be recovered and used again to treat more acid, the chlorine in the manganese chloride is run to waste as calcium chloride in the recovery process.

It will be noted that this method is not catalytic, as the manganese dioxide takes a definite part in the chemical reaction.

# CHAPTER XXVI

## THE HYDROGENATION OF OILS

A LARGE number of oils and their acids, which are liquid at the ordinary temperature, are converted into solid fats on combination with hydrogen. Thus oleic acid (m.pt. 14°) is converted into stearic acid (m.pt. 69°):

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + H_2 \longrightarrow \underset{\text{Stearic acid.}}{C_{18}H_{36}O_2}.$$

Similarly, cotton-seed oil is changed into a fat of the consistency of lard and can then be used in the manufacture of margarine. Fish oils lose most of their powerful odour and can be used in soap-making.

These fats do not combine with hydrogen in the ordinary way. A certain proportion can be changed by passing hydrogen through the hot oil, which is simultaneously subjected to a silent electric discharge; but the accumulation of the hydrogenated oil reduces the speed of reaction, so that the conversion comes to a standstill with only about 20 per cent. yield.

Very much better results have been obtained by the use of various catalysts, particularly nickel.

We will now describe generally the method of carrying out the transformation.

The oil is mixed in a tank with the requisite quantity of catalyst and pumped into the reaction vessel shown in Fig. 28, which it enters at *A*. It is there heated to 175–190° by means of coil *B*, which is supplied with superheated steam or hot oil. The temperature is recorded by an electric thermometer (not shown). Hydrogen is admitted through *C*, the air having been swept out of the vessel, before filling with oil, by a stream of hydrogen. *D* is a safety device to prevent a possible explosion passing further along the tube; it is usually a wider tube plugged loosely with steel wool. The pressure of hydrogen maintained in the hydrogenator is indicated by the gauge *E*, and varies from ordinary atmospheric pressure to 25 lb. per square inch.

It is essential to mix the oil and the hydrogen thoroughly. The most obvious way to achieve this effect is to pump the hydrogen in at the bottom of the vessel and thus maintain a circulation. There are great difficulties in pumping hot hydrogen, and much of the gas is liable to be lost. The oil is therefore continuously pumped out of the vessel by the pump *F* and delivered by the tube *G* at the nozzle *H*. The stream of oil passing from *H*

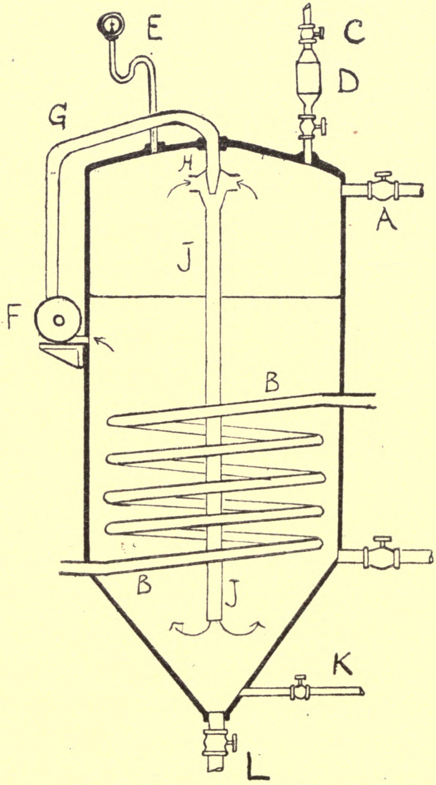


FIG. 28.—Vessel for hydrogenating oils

into the wider tube *J* drags hydrogen with it to the bottom of *J*, whence the hydrogen bubbles up through the liquid. Continuous circulation and mixing are thus maintained. When a sample of oil, which can be taken at pipe *K*, shows the required hardness, the contents of the hydrogenator are run out through *L* to a tank heated by steam coils.

The oil from these tanks is pumped through a steam-heated filter press to remove the catalyst, and the clear oil run into tanks, where it solidifies and can be used for making margarine, soap, etc.

The catalyst for this process must be carefully prepared. Nickel, when used, must be in the form of a fine powder, such as is produced from the oxide by the action of hydrogen. It is also usual to deposit the nickel on some form of support, such as pumice, kieselguhr, or crushed glass. To make the catalyst, therefore, a solution of a nickel salt (*e.g.*, the sulphate) is precipitated by an alkali with the "carrier" present in the vat, the whole being thoroughly mixed. The nickel hydroxide thus formed is filtered in a press and thoroughly washed free of salts. The filter cakes are then dried and ground. The reduction of the nickel oxide thus formed is carried out in a rotating iron drum, through which a brisk current of hydrogen is passed. The drum is heated to about 360°—the lower the temperature of reduction the more active the catalyst. The finished product is dropped from the drum direct into oil through a hopper filled with hydrogen; for it frequently fires if brought into contact with air, and, in any case, rapidly deteriorates; presumably owing to a slow oxidation.

Many other substances have been proposed, and some used, as catalysts of the hydrogenating reaction. Nickel oxide and palladium (a rare metal like platinum) are the most important. Nickel carbonyl is a useful source of metallic nickel for catalytic purposes. The carbonyl dissolves in oil, and when heated to 180°, as in the Mond process, the free nickel is distributed in extremely fine particles through the mass.

Little is known as to the way in which the catalyst brings about the reaction. Nickel and palladium both take up considerable quantities of hydrogen to form either a compound or a kind of solution, and undoubtedly this effect is important in the action.

The hydrogen required for the hydrogenation process must of necessity be free from substances which poison the catalyst or react with the oil itself. In the case of oils to be made into edible fats special care is necessary. The liquefaction of the carbon monoxide in water-gas; the decomposition of compounds of carbon and hydrogen by heat; the action of steam on iron, as quoted earlier in this section; and the electrolysis of water containing some caustic soda, are among the more promising methods at present in use.

The above account of the conversion of oils into solid fats by the use of hydrogen is necessarily general, for the whole method has developed only in the present century. Undoubtedly it is an industry which will assume far greater importance than it does even at present; for the increased development of margarine manufacture has so raised the price of solid fats that soapmakers are ready to buy the cheaper fats produced by this process. It is, indeed, a notable instance of rapid development in chemistry, for only in 1897 a great authority on oils and fats confessed his inability to bring about a reaction now conducted on an enormous scale by the use of catalysts.

# SECTION E

## USE OF ELECTRICITY IN CHEMICAL CHANGE

# CHAPTER XXVII

## THE ELECTRIC FURNACE

THE relations between electricity and chemistry are manifested in two converse ways: (1) by the use of chemical reactions to produce an electric current, and (2) by the use of the electric current to bring about chemical reactions. The energy which we have seen is liberated in the formation of compounds can often be obtained in the form of electrical energy in place of the otherwise universal production of heat; and, similarly, the energy required to break up a compound into its simpler constituents can, and often must, be supplied in the electrical form for a particular decomposition to take place.

The details of the means used to harness chemical energy to the production of an electric current can here be dealt with only in a general way; the various forms of cell will be found described in books on electricity. Mostly, when a metal is placed in a solution of its sulphate, it becomes electrically charged with respect to the solution, *i.e.*, a difference of potential exists between it and the solution. For instance, zinc becomes negatively charged in contact with zinc sulphate, the difference of potential being about 0·5 volt; copper, on the other hand, becomes positively charged when placed in a solution of its sulphate, the potential difference being 0·6 volt; so that, if we have zinc and copper sulphates in solution in two compartments of a vessel separated by a porous partition, and place plates of the metals in their respective sulphates, the total potential difference will be 1·1 volts. This arrangement is in effect a Daniell cell, a form largely used in telegraphic work. When the two plates are joined outside the solution by a wire, a current passes from the copper (+ ve) to the zinc (− ve), the energy being derived from the solution of the zinc in the zinc sulphate.

Other cells in common use merely have different metals in different solutions producing various potential differences. Such cells are used only in chemical work for producing current for small-scale experiments. For manufacturing purposes the electric current is produced by dynamos.

One of the simplest cases in which the electric current is applied to a chemical operation is that in which it is desired to apply heat at a particular point, usually inside a furnace. The fact that an electric current develops heat in a conductor is manifest in electric lamps and heaters. The heat developed varies with the square of the current used, and directly with the resistance of the part of the circuit under consideration. Thus to obtain a heating effect at a given part it is necessary to arrange a high resistance at that point. We will now proceed to consider a case where electric heating has supplanted direct firing—the manufacture of carbon disulphide.

This compound is made by passing the vapour of sulphur over hot carbon. It is one of the few compounds which are formed with absorption of heat (endothermic), thus:

$$C + S_2 \rightarrow CS_2 \quad - 28{,}700 \text{ cals.}$$

It was manufactured originally by heating charcoal in retorts and allowing molten sulphur to run down into them. More recently it is made by use of the plant shown in Fig. 29. The cylindrical furnace *A* is packed with coke, which can be fed in at the top. The wider base of the furnace *B* is furnished with four electrodes placed crosswise, of which two (*E*, *E*) are shown. Sulphur, fed in through the hand holes *S*, *S*, is melted by the heat of the furnace and runs down to the base of the furnace. The

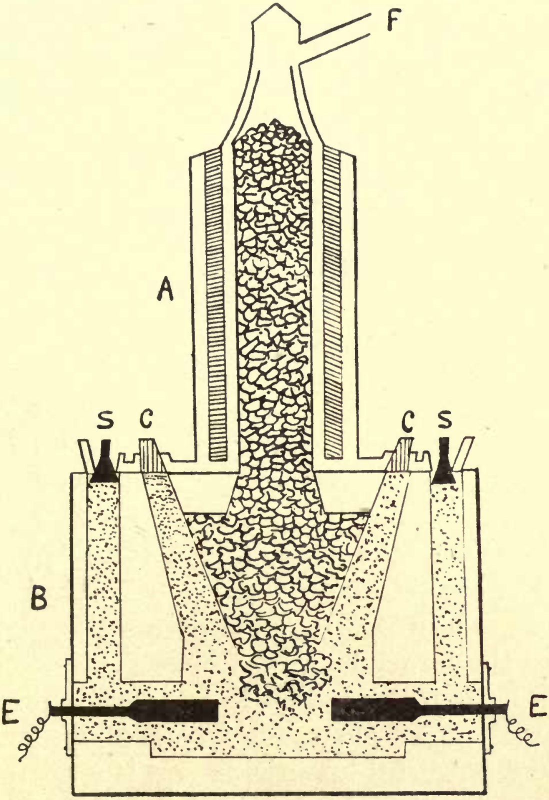


Fig. 29.—Electric furnace method of making carbon disulphide.

current (of voltage as low as 50, but high amperage) passes from the two electrodes to those directly opposite, and as the intervening space conducts badly, great heat is developed in the centre of the cross. The carbon disulphide formed passes with sulphur vapour up the furnace and out by the pipe *F*, whence it is led to very long worm condensers. The tower of coke, acting as a fractionating column, serves to retain most of the sulphur vapour. Fresh carbon in the form of fragments of gas carbon is added as required through *C*, *C*. A furnace of the type shown (40 ft. high by 16 ft. in diameter) will run continuously for a year, without renewals of electrodes or clearing out, with a daily output of seven to ten tons of carbon disulphide. The electrical process has the advantages of being continuous and much less liable to leaks both of heat and of product than the old retort process. The sulphur itself in the modern process acts as a very efficient lag for the larger base portion.

The carbon disulphide thus made is purified and used as a solvent for fats and rubber; it is also a powerful insecticide and is used to kill wireworms, etc., in the soil and weevils in grain, the grain being unharmed by it. Owing, however, to its great volatility—it boils at 46·5°—and the fact that it catches fire easily, it is often replaced for these purposes by less wasteful or less dangerous solvents. A further important use is the manufacture from it of carbon tetrachloride ($CCl_4$) by the direct action of chlorine, with a trace of iodine as catalyst, or by the use of sulphur chloride :

$$CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S.$$

The preparation of phosphorus, again, was originally carried out by heating calcium metaphosphate (made from bone ash by treatment with sulphuric acid) with carbon in fireclay retorts in a furnace :

$$3Ca(PO_3)_2 + 10C \longrightarrow 10CO + Ca_3(PO_4)_2 + 4P.$$

It is now made (at Niagara) by electrically heating a mixture of ordinary calcium phosphate, sand, and carbon in a furnace somewhat similar to the one used for carbon disulphide, when the following reaction occurs :

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 \longrightarrow 5CO + \underset{\text{Calcium silicate.}}{3CaSiO_3} + 2P.$$

The phosphorus distils off in either case, and by passing the expelled gases into water the phosphorus condenses and the carbon monoxide passes away.

It will be noticed in the electrical method that sand is used, forming a molten slag with the calcium present, which can be tapped off periodically; the mixture to be heated is continuously fed into the furnace by a gastight screw conveyer. The same economies due to internal heating and continuous working are obtained as in the previous manufacture described; moreover, it will be noticed from the equations of the reactions that by using sand the whole of the phosphorus is set free, whereas in the old method two-thirds only is liberated, and in practice less than a half of the phosphorus present is reduced.

Some products can be made on a large scale only by the use of an *electric furnace*, as the method of heating we have described is often called. Such is calcium carbide, which has risen to such importance in this century—as a source of acetylene for lighting and the oxyacetylene blowpipe, as a reducing agent for obtaining metals, and for the preparation of calcium cyanamide. In this instance the base of the furnace, which also forms one of the electric poles, often consists of a truck covered with a layer of compact coke; the other electrode, also of carbon, is lowered from the top of the furnace on to a thin layer of the mixture of 56 parts of quicklime and 36 of coke, and when this is fused more is added through a hopper. The reaction

$$CaO + 3C \longrightarrow CaC_2 + CO$$

occurs at about 3000°, and when a sufficient quantity is formed on the base of the furnace the whole is allowed to cool, and the truck is then run out and the product broken up. A current of 2000 amperes at 60–100 volts is necessary, and the carbon monoxide formed must be allowed to escape freely, otherwise the reverse reaction sets in.

When nitrogen is blown into the calcium carbide in the furnace, calcium cyanamide is formed :

$$\mathrm{CaC_2 + N_2} \longrightarrow \underset{\substack{\text{Calcium}\\ \text{cyanamide}}}{\mathrm{CaCN_2}} + \mathrm{C}.$$

This substance contains commercially 12–20 per cent. of nitrogen, and is thus a valuable manure, for in the soil it is decomposed into compounds of ammonia by the action of bacteria. The nitrogen required for its production is obtained by liquefying air, when the nitrogen distils off first.

This process is thus one of the important methods of " fixing " (*i.e.*, bringing to the solid form) the nitrogen of the air. Plants are unable to use free nitrogen, and for use as manure it must be converted into ammonium salts or nitrates, or substances which will form such compounds in the soil. Practically all the methods in use and suggested for the fixation of atmospheric nitrogen involve the use of electricity as in the cyanamide process.

Nitrogen and oxygen combine to form nitric oxide when blown through an electric arc. In practice the arc is spread into a disc of flame by the use of electromagnets outside the furnace, and air blown through the disc; on emerging from the arc the gases contain 1–1·5 per cent. of nitric oxide, and are further mixed with air, forming nitrogen peroxide ($NO_2$), which, absorbed by lime, forms calcium nitrate. An excess of lime is used to give a basic nitrate, which keeps dry and can be easily used as a manure. This "Norwegian saltpetre" contains about 13 per cent. of nitrogen and combines the merits of a nitrogenous manure with those of the addition of lime to the soil.

The above are a few typical examples of the use of an electric current in chemical reactions where a high local temperature is required. For this purpose it is immaterial whether the current is direct or alternating; in the operations discussed in the next chapter, where the current is used to effect decompositions which can be done only by its means, it is essential that a direct current should be used.

# CHAPTER XXVIII

## ELECTROLYSIS

In the previous chapter we have considered only those cases in which an electric current is used as a convenient internal heating agency. We must now consider certain uses of this important form of energy in which reactions peculiar to it are carried out, particularly in decomposing dissolved substances.

We have already seen that in aqueous solution many substances, particularly acids, salts and bases, split up into ions consisting of atoms or groups of atoms electrically charged. Thus copper sulphate ionises in $Cu^{\cdot\cdot}$ and $SO_4''$—that is, copper ions, each carrying two positive charges, and the compound sulphate ions, each carrying two negative charges.

The electric current may be passed through the solution by placing in it, out of contact with each other or other conductors, two plates joined by wires to the source of the electric current. These plates are known as poles or electrodes, the one connected to the negative pole of the current source being called the *cathode*, the other, joined to the positive pole, the *anode*. The current thus passes into the solution at the anode and leaves it by the cathode (Fig. 30).

The ions in the solution, which when subjected to this process of *electrolysis* is termed generally the *electrolyte*, begin to move as soon as the current begins to pass through the solution. The copper ions, for example, move towards the cathode, as they are charged with electricity of the opposite sign; similarly, the $SO_4''$ ions travel in the direction of the anode. On reaching the cathode each copper ion gives up its charge and is deposited on the cathode,

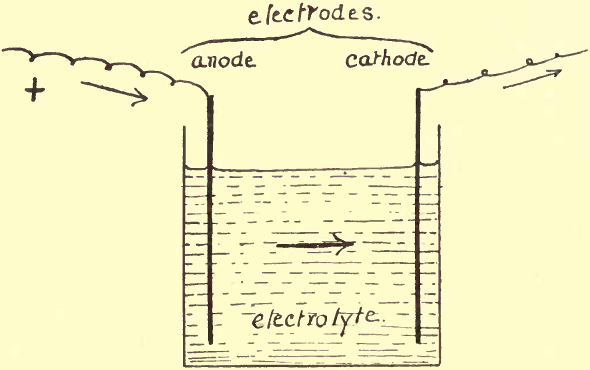


Fig. 30.—Diagram of electrolysis.

thus forming a layer of copper on that conductor. This is the simplest effect of electrolysis—the deposition of the material of the ions on the surface of the electrode of the opposite charge.

In many cases, however, other reactions occur when the ion reaches the electrode. For example, in this case of copper sulphate the $SO_4''$ ions, on arriving at the anode, give up their charge, and when thus liberated react either with the material of the anode or with the water in which the salt is dissolved. A copper anode is itself attacked, forming fresh copper sulphate, which dissolves in the water. This effect has an important application in preparing pure copper from the crude product of smelting, the latter, cast into blocks, being used as the anodes in an acid solution of copper sulphate; the cathodes—sheets of pure copper $\frac{1}{20}$ in. thick—are gradually coated with pure copper when a current is passed, the metal being in effect transferred to them *via* the solution from the anodes, producing 99·9 per cent. copper from the 97–98 per cent. copper of the cathodes.

This method also has an important application in electroplating and electrotyping. For the former the object to be plated is made the cathode, and a sheet of the pure metal with which it is to be coated (*e.g.*, silver) is used as the anode. It is found that more complex salts than, say, silver nitrate are best for producing a firm adhering deposit. Double cyanides of silver and potassium are most often used—for example, KCN.AgCN, made by dissolving silver cyanide in potassium cyanide solution.

Electrotyping is the act of producing a facsimile of an object, such as a coin, in metal. An impression of the surface to be copied is taken in wax or plaster and the surface of the cast painted over with fine graphite to act as a conductor. The graphite is then made the cathode in a suitable bath, as for electroplating, and a layer of metal deposited on it; when thick enough the form thus copied is filled in with fusible metal.

Frequently the solvent is attacked by the ions instead of the anode; thus if the anode in the copper sulphate solution is made of platinum it remains unattacked, and the $SO_4''$ ions, on release, decompose the water at the anode, liberating oxygen, thus:

$$2SO_4 + 2H_2O \longrightarrow 2H_2SO_4 + O_2.$$

As another example we may take the electrolysis of common salt solution, which is ionised into $Na^{\cdot}$ and $Cl'$. The $Na^{\cdot}$ ions, arrived at the cathode, which may be made of iron, decompose the water present, forming caustic soda and liberating hydrogen :

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2.$$

The chlorine at the anode (usually of carbon) merely forms the molecule of chlorine and appears free as such. Now all these three substances are of value, and if the chlorine and caustic soda are to be isolated from the solution they must be prevented from mixing, for the chlorine dissolves in the water and reacts with caustic soda. The mixing is usually prevented by interposing partitions of porous material between the anode and the cathode which prevent the motion of liquid, although as the electrolyte soaks the diaphragms the current can still pass.

In some cases, in place of a solution of the salt, it is possible to use the salt in a fused state, thus obviating the action of the water on the liberated substances. The effects under these conditions are otherwise much the same as when a solution is used.

We can thus summarise the qualitative results of electrolysis as the liberation of the ions at the electrodes, with the consequent production of substances which are either the material of the ions themselves or the products of the action of the liberated ions on the electrodes or on the solvent.

The quantitative aspect of these reactions was worked out in the main by Michael Faraday early in the nineteenth century. The first important fact is that the quantity of substance decomposed is accurately proportional to the quantity of electricity passed through the solution. The unit quantity of electricity (1 coulomb) deposits 0·00118 gram of silver from a solution of silver nitrate, 1 coulomb passing per second being the well-known unit of current—an ampere—which is defined in this way.

In the second place, the quantities of various elements liberated by the same current, as, for instance, when various solutions are electrolysed in the same circuit, are proportional to the chemical equivalents of the elements. The equivalent of silver (108 grams) is set free by 96,540 coulombs, as can be seen by calculation from the above definition of a coulomb. Similarly, this quantity of electricity (96,540 coulombs) will liberate the equivalent of copper (31·8 grams) from copper sulphate; 1 gram of hydrogen from an acid; 8 grams of oxygen in cases where it is set free; 35·5 grams of chlorine from salt, and so on. It is therefore possible to calculate what amperage is required to produce a given quantity of any product in a given time.

The electromotive force (E.M.F.) or voltage of the current is also an important factor. Every compound has a definite decomposition voltage, and this difference of potential must be maintained between the electrodes or the action will cease. Thus for dilute acids and alkalis a minimum of 1·7 volts is required, so that one dry cell is insufficient to electrolyse dilute sulphuric acid, as the maximum voltage of the cell is never more than 1·5 volts. Silver nitrate requires 0·7 volt, sodium chloride 4 volts. The theoretical minimum decomposition voltage (always exceeded in practice) can be calculated from the heat of formation of the compound, for electrolysis is merely a convenient way of supplying the energy required for decomposition. Practically, the decomposition voltage is the expression of a tendency for the electrodes to become coated with the products of electrolysis (*e.g.*, a layer of hydrogen and oxygen respectively when dilute acids are electrolysed) when these layers produce a "back E.M.F." tending to produce a current in the opposite direction.

Apart from these effects, the electrolyte behaves as an ordinary conductor of electricity, and the general laws of the electric current are applicable.

Having now dealt with the elementary facts of electrolysis, we shall proceed in the next chapter to describe in detail the methods used in producing important substances by this means.

## NOTE.

### CALCULATION OF DECOMPOSITION VOLTAGE FROM HEAT OF FORMATION.

Take the case of water; the heat of formation of water at 0°, starting from 2 grams of hydrogen and 16 grams of oxygen, is 68,000 calories. Thus to produce one equivalent of each from water (1 gram of H and 8 grams of O from 9 grams of $H_2O$) 34,000 calories must be supplied.

Now 1 calorie = 4·19 volt-coulombs.

So that the energy required = 34,000 × 4·19 volt-coulombs.

One equivalent of any element is set free by 96,540 coulombs, and thus the requisite voltage is

$$\frac{34{,}000 \times 4{\cdot}19}{96{,}540} = 1{\cdot}47 \text{ volts.}$$

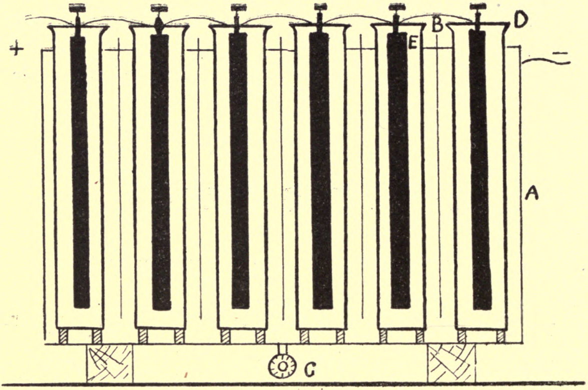
We have already noted that in practice 1·7 volts is the minimum.

# CHAPTER XXIX

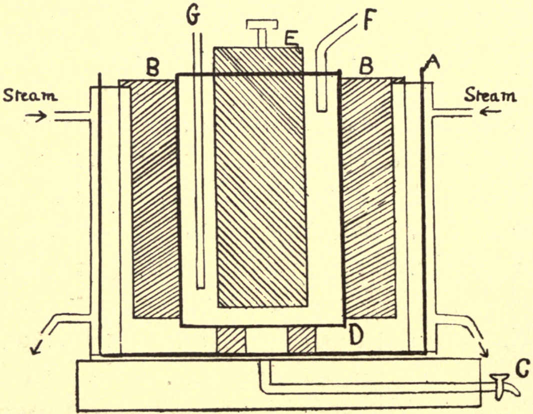
## ELECTROLYSIS IN INDUSTRY

THE manufacture of caustic soda, sodium carbonate, and chlorine from salt is one of the most important industries in which electrolysis has been successfully employed.

We have seen already that the ordinary result of the electrolysis of brine is the production of chlorine at the anode, and caustic soda, by reaction of the sodium with water, at the cathode. An apparatus much used on the Continent for isolating these two products is shown in Fig. 31. An iron tank *A* is supported on wooden blocks and traversed by sheets of iron *B*, which extend almost to the bottom and from side to side of the tank. The outside of the tank is steam-jacketed, and lagged to prevent loss of heat. The tank itself, with the iron sheets, forms the cathode, and the caustic soda solution produced in it is run off by a pipe in the bottom, *C*. Between the plates are placed



Elevation



Section

Fig. 31.—Electrolytic cell for preparation of caustic soda and chlorine from salt.

closed boxes *D* made of cement mixed with salt and hydrochloric acid in making them, and thus on soaking in water the salt is removed, leaving a porous skeleton. Each box contains an anode *E* made of fused magnetite ($Fe_3O_4$), which is used in preference to carbon to avoid contaminating the chlorine with carbon dioxide. The pipe *F* serves to carry away the chlorine, and fresh brine is added through *G*.

The brine is saturated and kept at 80–90°, as at this temperature the decomposition voltage is lower than when it is cold. It is run in at such a rate that about one-third of the salt is converted into caustic. If the electrolysis continues above this concentration, oxygen is produced with the chlorine at the anode. Each cell as described is kept at 4 volts difference of potential, and a current of 10–20 amperes per square foot is used.

The caustic soda is obtained by evaporation, when the salt present crystallises out and is removed. The chlorine is either liquefied or, after dilution with air, led over lime to produce bleaching powder.

A somewhat different arrangement is used by an alkali works at Middlewich, in which sodium carbonate (a product much more largely consumed than caustic soda) is formed.

The tank, shown in section in Fig. 32, is

10 ft. by 2 ft by 5 ft. deep, and is built up of slabs of sandstone clamped together. Two asbestos diaphragms about $\frac{1}{8}$ in. thick *A*, *A*, divide it lengthwise into three compartments and are supported on the outside by sheets of copper gauze of the same size *C*, *C*, which form the cathodes. Pipes *S*, *S* convey steam and carbon dioxide into the empty outside compart-

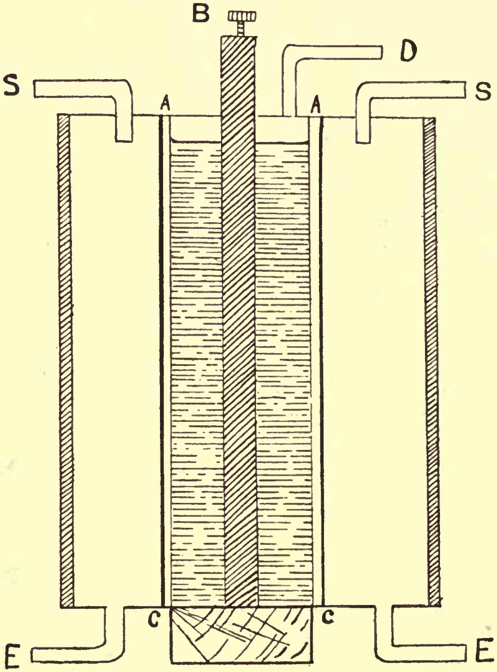


FIG. 32.—Electrolytic cell for direct preparation of sodium carbonate.

ments. The anodes are carbon rods *B*, placed in the central chamber, which is filled with saturated brine, circulation being arranged so that the brine is removed when about 66 per cent. is converted into soda. On passing the current, chlorine is set free in the central chambers and escapes by pipes *D*. The caustic soda is formed at the cathodes in the empty outer chambers and at once converted into sodium carbonate by the carbon dioxide admitted through *S* with the steam, the concentrated solution running away by pipes *E* to crystallising pans.

Usually twelve cells are run in series, using 2000 amperes (*i.e.* a current density of 20 amps. per square foot), the pressure being 4–4·5 volts for each cell. In twenty-four hours about 240 tons of salt is converted into sodium carbonate, giving some 220 lb. of $Na_2CO_3$; also 360 lb. of bleaching powder is made from the chlorine, of which it contains 37 per cent.

It will be noticed at once how much more simple and direct is this method of producing soda from salt than the older Leblanc and ammonia–soda processes.

By the use of modified apparatus many other useful products can be obtained by the electrolysis of salt. Thus if a diaphragm is not used the chlorine mixing with the caustic soda forms in the cold sodium hypochlorite:

$$2NaOH + Cl_2 \longrightarrow \underset{\text{Sodium hypochlorite.}}{NaClO} + NaCl + H_2O.$$

This substance, which is stable only in weak solutions, is a useful bleaching agent, and small plants are used to produce sufficient for the needs of individual bleaching works.

Sodium chlorate ($NaClO_3$) is produced when the temperature of the bath is about 45–50°, and by electrolysing the chlorate in solution perchlorate ($NaClO_4$) is produced, of which the potassium and ammonium salts, made therefrom, are used in explosives.

We have already become acquainted with two instances of the electrolysis of fused substances in Chapter VIII—the smelting of alumina dissolved in cryolite to form aluminium, and the decomposition of fused salt into sodium and chlorine collected as such. In the first case only the alumina is decomposed, as the necessary voltage in this case is only 2·8 volts, whereas for sodium fluoride and aluminium fluoride (the components of cryolite) it is 4·7 volts and 4 volts respectively. Many attempts have been made to apply the electric current to the direct winning of metals from their ores, but only in a few cases, of which the above are two, with any success.

Much more promising has been the use of electrolysis in producing the complex compounds of carbon known as organic substances, particularly in Germany. Thus iodoform, vanillin, saccharin, and a large number of dyes are formed in commercial quantities by electrolytic methods.

Generally speaking, the application of the electric current to chemical operations is at present in its infancy. With cheap power there seems no reason why enormous developments in this line should not occur in the near future.

### LITERATURE.

Applications of Electrolysis in Chemical Industry : A. J. Hale.
Electrochemistry of Organic Compounds : Löb & Lorenz.
Practical Electrochemistry : B. Blount.

# APPENDIX.

## LITERATURE.

### *General and Popular in Style.*

Everyman's Chemistry: Hendrick.
Modern Chemistry (2 vols.): Sir William Ramsay.
Chemistry of Common Life: Johnstone & Church.
Chemistry in the Service of Man: Findlay.
Achievements of Chemical Science: Philip.
Some Chemical Problems of To-day: Duncan.
The Chemistry of Commerce: Duncan.
Chemistry of Familiar Things: Sadtler.

### *Books on Chemistry as Such.*

Of the innumerable text-books on pure chemistry published the following are selected:

Modern Inorganic Chemistry: Mellor.
Inorganic Chemistry: A. Smith.
Treatise on Chemistry, vols. I. and II.: Roscoe & Schorlemmer.
Modern Inorganic Chemistry (several volumes): edited by J. N. Friend.
Elements of Chemistry: Bassett.

### *Books on Industrial Chemistry and its Branches.*

Dictionary of Applied Chemistry: Thorpe.
Industrial and Manufacturing Chemistry (3 vols.; also published in smaller sections): G. Martin.
Sulphuric Acid and Alkali: Lunge.
Coal-Tar and Ammonia: Lunge.

And many other volumes on special branches (*e.g.*, "Monographs of Chemical Technology," now being published). Also many books in German, of which Ullmann's "Enzyklopädie der technischen Chemie" may be mentioned.

## *International Atomic Weights.*

| | Symbol. | Atomic weight. |
|---|---|---|
| Aluminium | Al | 27·1 |
| Antimony | Sb | 120·2 |
| Argon | A | 39·9 |
| Arsenic | As | 74·96 |
| Barium | Ba | 137·37 |
| Bismuth | Bi | 208·0 |
| Boron | B | 10·9 |
| Bromine | Br | 79·92 |
| Cadmium | Cd | 112·40 |
| Cæsium | Cs | 132·81 |
| Calcium | Ca | 40·07 |
| Carbon | C | 12·00 |
| Cerium | Ce | 140·25 |
| Chlorine | Cl | 35·46 |
| Chromium | Cr | 52·0 |
| Cobalt | Co | 58·97 |
| Columbium | Cb | 93·1 |
| Copper | Cu | 63·57 |
| Dysprosium | Dy | 162·5 |
| Erbium | Er | 167·7 |
| Europium | Eu | 152·0 |
| Fluorine | F | 19·0 |
| Gadolinium | Gd | 157·3 |
| Gallium | Ga | 70·1 |
| Germanium | Ge | 72·5 |
| Glucinum | Gl | 9·1 |
| Gold | Au | 197·2 |
| Helium | He | 4·00 |
| Holmium | Ho | 163·5 |
| Hydrogen | H | 1·008 |
| Indium | In | 114·8 |
| Iodine | I | 126·92 |
| Iridium | Ir | 193·1 |
| Iron | Fe | 55·84 |
| Krypton | Kr | 82·92 |
| Lanthanum | La | 139·0 |
| Lead | Pb | 207·20 |
| Lithium | Li | 6·94 |
| Lutecium | Lu | 175·0 |
| Magnesium | Mg | 24·32 |
| Manganese | Mn | 54·93 |
| Mercury | Hg | 200·6 |
| Molybdenum | Mo | 96·0 |
| Neodymium | Nd | 144·3 |
| Neon | Ne | 20·2 |
| Nickel | Ni | 58·68 |
| Niton (radium emanation) | Nt | 222·4 |
| Nitrogen | N | 14·00 |
| Osmium | Os | 190·9 |
| Oxygen | O | 16·00 |
| Palladium | Pd | 106·7 |
| Phosphorus | P | 31·04 |
| Platinum | Pt | 195·2 |
| Potassium | K | 39·10 |
| Praseodymium | Pr | 140·9 |
| Radium | Ra | 226·0 |
| Rhodium | Rh | 102·9 |
| Rubidium | Rb | 85·45 |
| Ruthenium | Ru | 101·7 |
| Samarium | Sa | 150·4 |
| Scandium | Sc | 44·1 |
| Selenium | Se | 79·2 |
| Silicon | Si | 28·3 |
| Silver | Ag | 107·88 |
| Sodium | Na | 23·00 |
| Strontium | Sr | 87·63 |
| Sulphur | S | 32·06 |
| Tantalum | Ta | 181·5 |
| Tellurium | Te | 127·5 |
| Terbium | Tb | 159·2 |
| Thallium | Tl | 204·0 |
| Thorium | Th | 232·15 |
| Thulium | Tm | 168·5 |
| Tin | Sn | 118·7 |
| Titanium | Ti | 48·1 |
| Tungsten | W | 184·0 |
| Uranium | U | 238·2 |
| Vanadium | V | 51·0 |
| Xenon | Xe | 130·2 |
| Ytterbium (Neoytterbium) | Yb | 173·5 |
| Yttrium | Yt | 89·33 |
| Zinc | Zn | 65·37 |
| Zirconium | Zr | 90·6 |

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