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CHEMISTRY FOR MATRICULATION

BY

G. H. BAILEY, D.Sc. Lond., Ph.D. Heidelberg

LATE LECTURER IN CHEMISTRY AT THE VICTORIA UNIVERSITY OF MANCHESTER

AND

H. W. BAUSOR, M.A., A.I.C.

LATE SCHOLAR OF CLARE COLLEGE, CAMBRIDGE

AUTHOR OF "CHEMICAL CALCULATIONS," "AN INTRODUCTORY COURSE OF CHEMISTRY," ETC.

Ninth Impression (*Second Edition*)



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PREFACE.

ACCORDING to modern standards a good secondary school education should include a general acquaintance with the elements of science, and also a fairly detailed study of at least one branch. Without this deeper knowledge of one branch the educational value of the science course is seriously diminished. It is the object of this book to provide such a course of more detailed study in chemistry.

It is now generally conceded that for work of this standard a judicious combination of the heuristic and didactic methods of teaching should be used. The elements of systematic chemistry are required, and if these are taught by the purely heuristic method, progress is needlessly slow, and the knowledge obtained is needlessly scrappy and incomplete. At the same time the treatment must still be experimental, for personal contact with the phenomena under discussion is still necessary if the student is to appreciate fully the points at issue. These are the main principles in accordance with which this volume has been prepared.

The book is divided into four Sections. *Section I.* is an Introductory Course of the approved type, based on a series of experiments by which the fundamental principles of the science are established in their proper sequence Special care has been devoted to the treatment of the Laws of Constant and Multiple Proportions, Avogadro's Hypothesis, and the meaning and use of Chemical Formulae and Equations.

Section II. consists of a systematic treatment of the non-metals illustrated by numerous experiments: the heuristic and didactic methods are both used, the choice depending on the nature of the subject-matter.

In *Section III.* some common metals and their compounds are treated on the lines of Section II., and a chapter on the Phenomena of Electrolysis is also included.

Section IV. consists of a chapter on Chemical Calculations, with full discussion of the principles and methods involved.

Since the time at the disposal of the student will not as a rule be sufficient to enable him to perform the whole of the experiments in the text, the more difficult have been starred (*e.g.* ***Exp. 45**) and should be omitted if time presses. A few experiments should not be attempted by the student in any case except under the immediate supervision of the teacher; these have been indicated by a dagger (*e.g.* †**Exp. 75**).

This book has been prepared by Mr. H. W. Bausor, M.A., but is based on the well-known work by Dr. G. H. Bailey previously published under the title of *The New Matriculation Chemistry*. The alterations have, however, been very extensive both as regards contents and methods of treatment. The new matter inserted—mainly experimental—has made the new book larger than the old, despite the fact that large portions of the old book have been omitted, including the whole section on the Chemistry of Daily Life.

NOTE TO THE SECOND EDITION.

THE Second Edition differs from the First Edition mainly in the inclusion of a more detailed account of catalytic action, pp. 223-4, in a reduction of the number of questions at the end of Chapter XIV., and in the revision of pp. 171, 303, 377.

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SECTION I.—INTRODUCTORY.

CHAPTER I.

PHYSICAL AND CHEMICAL CHANGES

1. The Method of Scientific Inquiry.—Let a person unacquainted with the aims and the conduct of scientific inquiry examine some material object, say a mineral, a piece of rock, or a pebble from the sea-shore, and let him then detail the points of interest which occur to him as the result of his examination. He may be struck by its form, its colour, its hardness, the nature of its surface, or he may be disposed to ask whence it came and how.

In what respects do his questionings differ from those of one trained in the methods of scientific investigation? In this, that the scientist is accustomed to grouping his observations, he is trained by experience to the recognition of likenesses and unlikenesses in such bodies so as to reject the trivial details, and hold firmly to the essential and characteristic ones.

Investigation by a process of comparison and classification, however, opens up such a wide field, that it becomes necessary to proceed step by step, and press the inquiry along well-defined lines, each with a distinct purpose.

The geologist, desirous of determining the history of the strata, will devote himself to the observation of existing strata, their essential and prevailing characters, their origin and mode of formation. The biologist, on the other hand, studies the structure of living organisms, classifying them according to their forms and functions, and tracing historically the occurrence and evolution of the different

types. The physicist interests himself with the phenomena associated with matter, whilst the chemist deals with matter itself and its identification.

Now to all these, such objects as we have mentioned in the opening paragraph will appeal in a variety of ways. A piece of chalk, limestone, or marble are very different objects to the geologist, but may be much the same thing to the chemist if he finds them to be composed of the same kind of matter. A piece of glass rubbed briskly with silk becomes capable of attracting small light bodies; this observation is of little direct importance to the chemist if he finds that the substance of the glass has not changed or its mass become greater, though to the physicist such an observation may be of great significance.

A piece of iron, so far as the chemist is concerned, retains its identity as iron whether it be in the form of a solid bar, the finest wire, or an impalpable powder; it may grow warmer and expand or by cooling contract; it may be endowed with the property of attracting other particles of iron or not, and yet its composition and mass may remain unchanged. So long as any modification of aspect or behaviour is such as experience has taught him belong to matter which he identifies as *iron*, he maintains that no alteration in substance has taken place.

To sum up, we may say that the method of scientific inquiry as applied to Chemistry consists in experiment, observation, and inference.

2. Transmutation of Metals.—The earlier chemists believed that they could change the baser metals into noble metals, quicksilver into gold or lead into silver, and most of their researches were pursued with this object in view. The more searching methods of inquiry adopted in later times have, however, shown that their conclusions were fallacious.

So also, even to the time of Lavoisier, towards the close of the eighteenth century, chemists failed to realise what takes place when iron rusts or metals burn, although an actual change of substance has taken place, and matter is indeed added to the metals during the process.

These misunderstandings arose from two main sources:

(1) Failure to appreciate the *essential and characteristic* properties of the substance under consideration.

(2) Failure to test whether any *apparent* alteration of substance had been accompanied by increment or loss of substance during the experiment.

At each step the balance must be called upon to say whether any increment or loss of substance has taken place, and if so the source of this change in mass must be traced.

All conclusions, and especially those which form the foundation of further investigation, require to be fully and critically examined in order to see that the deductions drawn are justified by the facts.

3. The Field of Inquiry for the Chemist.—The aim of the chemist is then to investigate matter with a view to recognising and classifying the *essential* characters of each kind of matter, and to follow the changes which ensue whenever those changes involve a redistribution of matter.[1]

Let us then follow the course of investigation by experiment, which will enable us to see how the information we require is to be obtained, and what deductions may be fairly made from the observations.

Exp. 1. *An apparent transmutation of iron into copper.* —Into a solution of copper sulphate ("blue vitriol") dip the bright blade of a penknife. After a short time remove the knife. Observe that the part of the blade which was immersed in the liquid has acquired the appearance of copper.

Apparently the iron of which the blade is composed has been changed into copper, and if you were to leave the investigation at this stage you might conclude that you had

[1] Whether in the operations which he performs matter may be created or destroyed must for the present remain untouched. An appeal to his later observations must decide this.

succeeded in bringing about a transmutation of iron into copper. Not until you have carried out an exhaustive inquiry, and performed a series of somewhat complex experiments will you be in a position to decide what is the nature of the change you have observed. And this you are not in a position to undertake at present.

4. The Art of Weighing.—Reference has already been made to the importance of the *balance* in Chemistry, and as it will be immediately brought into requisition a short account of the instrument and of the method of using it will now be given.

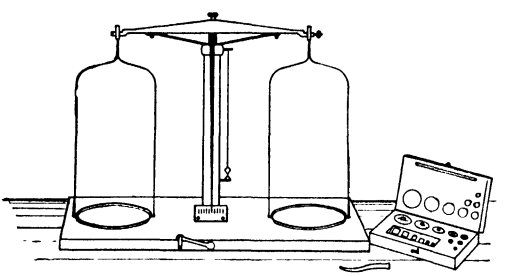


Fig. 1.

A suitable balance for a beginner is one which shows differences of weight of 1 cgm. between loads of 50 gm. in each pan.

Of course greater accuracy in weighing can be obtained, but the beginner's errors of experiment will generally prevent any increase in accuracy from being obtained through more accurate weighing. An accurate set of weights is, however, of importance, especially those which run from 10 gm. downwards.

The balance in general use has a brass beam and three agate or steel knife-edges, the two side edges being at equal distances from the centre one, and all three in a straight line. The beam rests on the middle knife-edge, which stands upon two plates of agate or steel, while the

scale pans are suspended from the end knife-edges by stirrups of the same materials. A long pointer with its end over a small ivory scale is fixed to the middle of the beam and a movable weight to one end (Fig. 1).

When the balance is not being used the beam and pans are supported on rests, but when we wish to weigh, we place the object to be weighed on one pan and the weights on the other, and by *gently* turning a metal axle cause the pointer to swing across the scale. If the needle swings to points at equal distances from the zero of the scale, the object and the weights are of equal mass, and the process of weighing has been accomplished.

In chemical work, weights of substances are nearly always determined by difference, so that the substances are not weighed upon the pans, but in or upon some vessel: for example, the weight of a quantity of liquid or solid is obtained by weighing the substance in some vessel (*e.g.* a beaker or crucible) and then subtracting the weight of the vessel.

The method of carrying out a weighing is illustrated in the following experiment.

Exp. 2. *To weigh some water in a beaker.*—Take a small beaker and place it upon the left-hand scale-pan; take the largest weight from the box, and place it on the right pan (using a pair of forceps). Next *slowly* turn the axle and allow the beam to swing. The needle probably moves at once to the left and shows no tendency to swing back; this indicates that the right pan is too heavy. Turn the axle back to its first position (*always* do this before adding or removing a weight) and try the next weight, replacing the first. At length you will find a weight which is too light, the one before it having been too heavy. Keep the light weight still on the pan and place beside it the next smaller one. If these are too heavy, remove the smaller one and try still smaller ones in succession. You will gradually work down from the grams to the decigrams, and finally to the centigrams.

As you get to the smaller weights, you must allow the needle to swing once or twice to each side before taking the readings. (If you read first, say, on the left, you must

take the *next* reading on the right.) At last you will find that a certain weight on the right pan is too large, whilst a centigram less makes it too small. The actual weight obviously lies between these, but it will be sufficient to take the weight which gives the nearest approach to equal swings on each side of the zero.

Now count up the gram weights on the pan, write the total down, then count up the decigrams, and then the centigrams, in order. Having written down the weight of the object, restore the weights to the box, checking them over to see if the total agrees with the weight you have noted down.[1]

Now pour a little water into the beaker and repeat the process of weighing. The difference between the two weighings gives the weight of the water.

Enter your results thus:—

Weight of beaker	=	10·24 grams (say)
„ „ beaker + water	=	17·91 „ („)
Weight of water	=	7·67 grams.

Articles with any liquid attached to them should never be placed on the pans; nor should any article be weighed when hot. It is advisable to have a small camel-hair brush for removing dust from the pans and weights. A pair of forceps is usually provided with each box of weights for lifting them from the box to the pan, etc.; weights should never be lifted with the fingers. As the student becomes more practised he will be able to save much time in weighing, by choosing a weight somewhere near that of the object instead of working down from the largest in the box.

5. The Nature of Physical and Chemical Change.—At the outset of any inquiry relating to the science of chemistry it is necessary to acquire clear ideas as to the nature of chemical change and the distinction between this

[1] This precaution is very necessary, especially to beginners—it prevents many erroneous weighings which would simply undo all the other work of the experiments.

and physical change, and we shall find that in such an inquiry the use of the balance is indispensable.

Exp. 3.—Take the following objects —

1. A small test-tube.
2. A porcelain crucible.
3. A few inches of platinum wire.

Weigh each of these carefully (seeing that they are quite dry and clean), and enter the weights in the column provided below, and also any notes descriptive of the objects. Now heat them for some minutes in the non-luminous flame of a Bunsen burner ; observe the alterations which ensue during the heating, *e.g.* change of colour, softening, and enter these observations also in the table. In heating a crucible it will be desirable to support it on a pipe-clay triangle as shown in Fig. 2.

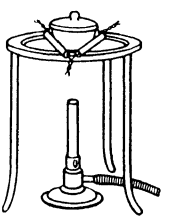


Fig. 2.

Allow the objects to cool, and see how far they resume their original character. Weigh them when quite cold, and enter these results alongside the others.

Weight		Description as to Colour, Texture, etc.		
Before Heating.	After Cooling	Before Heating.	During Heating.	After Cooling.

Now perform similar experiments with the following bodies, and make observations upon them in the same way, entering all your observations in tabular form :—

4. A small quantity of "flowers of sulphur" in a test-tube.[1]
5. A fragment of wax in a test-tube.
6. A few crystals of iodine in a test-tube.

Carefully observe and note down any changes during the application of the heat, and also what takes place during the period of cooling. A pocket lens will be of assistance to you in some of your observations.

Do not press the heating so strongly as to drive vapours out of the mouth of the tube. [Find out, however, in the last example how it would affect the records you have made if you do so drive off vapours.]

Exp. 4.—Heat for at least fifteen minutes in small porcelain crucibles, and record your observations in the same way :—

7. Some small pieces of magnesium ribbon (with crucible cover loosely on).
8. Some copper turnings (without cover).
9. Some small pieces of wood (without cover).

Having now before you the records of all your observations arranged in an orderly manner, you will notice that in the examples given you may collect them, *i.e.* generalise them, under the following heads :—

(*a*) Those cases (1-6) in which there is no substantial[2] alteration of weight, and in which, though whilst the heat was being applied changes of colour, etc., may have been evident, yet on cooling, the substance had, so far as we can judge, returned to its original form and character.

While hot the test-tube softened, became out of shape, and gradually acquired a red colour, the porcelain crucible became red-hot, and the platinum wire white-hot and softer so that it could be more easily drawn asunder; but all

[1] See Note at the end of this chapter on the "Use of a Spatula."

[2] It will be useful to consider how very small variations having no particular bearing on the inquiry may occur, and how precautions might be taken to eliminate them.

three objects regained their original appearance on cooling, though the test-tube remained out of shape.

Again the sulphur and wax melted on heating but solidified on cooling, and then exactly resembled other fragments of the original substances; the iodine volatilised without melting, forming violet vapours, but when the test-tube was allowed to cool these vapours condensed on the sides of the tube in the form of greyish-black crystals exactly like those originally taken.[1]

(*b*) Those cases (7-9) in which alteration of weight (gain or loss) has taken place, and in which it will be observed that a distinct change in character and properties has been brought about.

Thus the magnesium was converted into a very light fluffy white powder, whilst the copper became coated with a greyish-black brittle scale which tended to peel off, and[2] in both cases there was an increase in weight. The wood on the other gradually burned away with loss of weight, leaving a small amount of white ash.

We thus recognise a striking difference in behaviour under the action of heat. Later on we shall examine more closely into the remarkable fact that substances often gain in weight under the action of heat, for it was this which led the earlier inquirers to the conclusion that heat was a ponderable substance, and that the increase in weight was due to the addition of matter which they called "caloric" to the body which was exposed to it.

For the present, however, let us confine our attention to the cases under Exp. 3, in which no alteration of weight has been found to take place and no permanent alteration of properties.

Many familiar examples of this class of phenomena will readily occur to you. Water is well known by its appearance and character, and is presented to us commonly as rain, or collected in rivers and in the sea. In the depth of winter, however, we see it become transformed into solid

[1] This phenomenon (of volatilising without melting) exhibited by iodine on heating is called *sublimation*.

[2] Reserve these residues for a later experiment.

ice or snow, and later changing once more into water. The inhabitant of the Arctic regions is more familiar with it as ice, and the liquid water is to him a rarity. In tropical regions the reverse is the case, ice or snow being seldom seen. Yet we can readily satisfy ourselves, with the aid of the balance, that ice passes into water or water into ice without change in weight or substance; and, similarly, we may examine the relation between steam or water vapour and water itself.

In the solid form it is ice or snow, in the liquid form it is water, in the gaseous form it is steam or vapour. The matter is the same, the form of its occurrence is different That matter may exist in solid, liquid, or gaseous forms and yet be in substance the same is not the exception but the rule. The difference of character is a difference of *physical state.*

Whether the substance is present to us as ice, or water, or vapour, depends on the *physical conditions* which prevail, and we realise by ordinary experience that *temperature* is the controlling factor. Yet ice may be transformed into water by *pressure* alone, or by sprinkling it with common salt.

Exp. 5.—Make a mixture of three parts by weight of snow or crushed ice and one part by weight of common salt. Stir it well together until the ice or snow is nearly all melted. Now dip into the mixture the bulb of a thermometer, and note how the quicksilver shrinks (record the lowest reading of the thermometer).

Transfer the thermometer to hot water and see how the quicksilver increases in volume, occupying a greater space than it did before. Weigh the (dried) thermometer before and after one of these operations, and show that there is no change in the mass of the glass (which also contracts and expands) and quicksilver of which the thermometer is made.

Exp. 6.—Fit a small dry flask with a cork and glass tube[1] of the form shown in Fig. 3, and let it dip into a

[1] See Notes at the end of this chapter on cork-boring, glass bending, etc.

vessel containing liquid. Now place the flask in the mixture of ice and salt and afterwards in hot water, and note how the air in the flask contracts (sucking up some liquid into the tube) and subsequently expands (expelling this liquid and probably some air), just as the quicksilver did, but in greater degree.

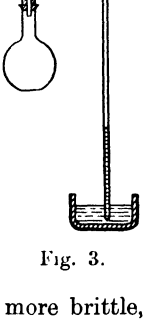


Fig. 3.

Summarising the results which these and similar observations bring home to us we find:—

(1) That matter may change in form (expand or contract), it may change in state (gaseous, liquid, solid), it may change in character (an impalpable powder, a crystalline solid), or it may become softer or more brittle, porous or more dense, without any alteration of mass or variation of substance.

Such temporary modifications of character are classed as *physical changes.*

(2) That matter may undergo modifications in the properties which it exhibits in response to the communication from without of heat, light, electricity, which are capable of being stored up by it, but which are imponderable, and therefore likewise bring about no alteration of mass.

Such properties are termed *physical properties.*

On the other hand the permanent modifications of character which matter undergoes when its mass is altered (as in Exp 4) are classed as *chemical changes,* and those properties of matter which it exhibits when it undergoes chemical change are termed *chemical properties.*

Notes on Cork-boring, Glass-bending, etc.

To bore a Cork.—The cork must first be softened by being rolled gently but firmly under the foot. It will shrink somewhat during this process, so that a cork somewhat wider than the hole into which it is to fit, *e.g.* the neck of a bottle, should be chosen. Take now a round file

and press the sharp end gently into the cork, turning it round all the time. The file will gradually penetrate to the far side, leaving a small hole, which can be enlarged by filing away different parts of the wall, until it is slightly less than the tube it has to contain.

More regular holes can be made by means of proper cork-borers, which are brass tubes of different sizes, with one end sharpened and the other perforated to admit a steel rod. The borer having been chosen of slightly less diameter than the tube for which the hole is intended, the sharp end is dipped in water, and the rod is inserted in the hole at the other end. The edge is pressed gently into the cork, and the borer twisted (always in the same direction) under gentle pressure until it emerges at the other side. It should *not* be pressed up against a hard object, as this will blunt the borer. Well-sharpened borers can also be used for indiarubber stoppers. In this case they are moistened either with alcohol or glycerine, and pressed through more slowly.

To bend a piece of Glass Tubing.—Take a piece of $\frac{3}{16}$-inch soft tubing, and hold it horizontally in the upper part of an ordinary gas flame, with its length in the plane of the flame. Turn the tubing slowly round and round so as to heat it uniformly. When it begins to soften remove it from the flame and bend it slowly and carefully to the required shape. Allow it to cool, and *then* remove the coating of soot from the bend.

To cut narrow Glass Tubing with a File.—Take a piece of glass tubing and lay it on a table. Taking hold of it with the finger and thumb of the left hand near the point where it is to be cut, draw one edge of a sharp triangular file *once* across it, from heel to point. The tube can now be broken by forcibly attempting to bend it away from the file-scratch, and at the same time trying to pull it apart. Round off the sharp edges by holding the tube nearly vertically in the Bunsen flame and gently rotating it, until the flame is coloured strongly yellow by the sodium of the glass

Use of Spatula.—It is often necessary to take a small quantity of some solid substance out of a bottle. For this purpose the spatula—an instrument very like a small table-knife—is used. A small bone or ivory paper-cutter answers the purpose very well. The blade of a penknife is sometimes used, but the use of iron or steel is objectionable. A platinum spatula is the best.

QUESTIONS—CHAPTER I.

1 Briefly explain what you understand to be the *method of scientific inquiry.*

2. To what chief causes were the mistakes of the early chemists due ?

3. What do you consider to be the field of inquiry for the chemist ?

4. Describe an experiment illustrating the apparent transmutation of one metal into another.

5. Explain the difference between a *physical* and a *chemical* change.

CHAPTER II.

THE NATURE AND ACTION OF AIR.

6. Use of the Desiccator.—Now let us make further inquiry into the results comprised under Exp. 4 in the previous chapter, with the view especially of learning the significance of the changes in mass which have there been recorded.

The operations of weighing must now be performed in such a manner as to exclude the complications arising from causes really external to the experiment. Vessels, and especially finely-divided substances, if left about, take up moisture from the surrounding air, and become heavier, sometimes in a marked degree. We shall simplify our labours if we proceed in such a manner as to prevent this occurring.

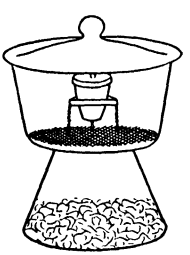


Fig. 4

This we can do by providing a dry air chamber in which to keep the vessel and substance while it is cooling, for, as already pointed out, it must never be weighed until it is quite cold. The piece of apparatus shown in Fig. 4 is termed a *desiccator*.

It is divided into two compartments communicating with one another. A circular piece of perforated zinc is placed at the bottom of the upper compartment, and on this stands a pipe-clay triangle with the wires bent down to form legs; crucibles, etc., can be supported on the triangle while cooling. The lower compartment contains granulated

calcium chloride or pumice stone soaked with strong sulphuric acid, by means of which the air in the desiccator is kept dry.[1]

Exp. 7.—Take a small porcelain crucible and half fill it with finely powdered sand or dried soil. Heat it over the Bunsen burner for say fifteen minutes, till it is red-hot throughout. Now remove it at once, while still hot, to the desiccator, and allow it to cool. Weigh it as quickly as possible. Leave it in the air of the room for a day, and then weigh it again. Note the increase in weight.

We shall henceforward take it for granted that wherever accuracy is desired such precautions will be adopted in order to exclude moisture.

7. Effect of the Presence of Air.—

Exp. 8.—Introduce a small piece of lead into a porcelain crucible and weigh the whole. Heat over the flame of a Bunsen burner. The metal first melts; very soon its bright surface becomes covered with a greyish scum. Scrape this scum to the side of the crucible so as to expose the bright surface of the metal again. A fresh layer of scum forms and should be scraped off as before. By repeating this process the whole of the metal may be ultimately converted into a greyish powdery substance which on continued heating becomes yellow.[2] Cool and weigh. You will note that there is an increase in weight.

Exp. 9.—Introduce lead into a crucible as before, and then fill up with clean white sand[3]; weigh; heat as before without disturbing the crucible or the sand overlying the lead. After say half an hour allow it to cool, and weigh.

[1] Leave a fragment of calcium chloride on a watch-glass in the air of the room, and note how in the course of the day it becomes moist and increases in weight.

[2] If the temperature is sufficiently high the powder melts, forming a red liquid which forms a yellow scaly solid on cooling.

[3] The sand should have been previously strongly heated and allowed to cool in the desiccator.

Note that there is no change in weight. Now throw out the sand and examine the lead at the bottom of the crucible. You will find that it has undergone no change except that it has melted and solidified again. Also examine the sand and note that its appearance has not changed.

A similar pair of experiments may be made using magnesium, tin, copper, or iron instead of the lead. In each case you will find that under the conditions of Exp. 8 the metal undergoes a permanent change in character and increases in weight, whereas under the conditions of Exp. 9 there is no permanent alteration in character and no change in weight.

Exp. 10.—Introduce a piece of charcoal into an open crucible and weigh. Now heat the crucible and observe that soon the charcoal glows and gradually burns away, leaving only a minute quantity of white ash.

Exp. 11.—Repeat the experiment, as with the lead, covering the charcoal with a thick layer of sand. Satisfy yourself that heating, even if continued for a considerable time, fails to bring about any material alteration in the weight.

Now allow the crucible to cool and turn out the contents. You will find that neither the charcoal nor the sand has undergone any change.

8. Review of the Experimental Results.—From these experiments it appears that the transformation of lead into a yellow substance, differing in mass and in properties from lead, takes place under the conditions of Exp. 8, but not under those of Exp. 9. Likewise that charcoal burns away under the conditions of Exp. 10, and not under those of Exp. 11.

In what do these conditions differ? Chemists in the seventeenth century were fully aware of these changes, and were even aware of the fact that they were accompanied by a gain (or *apparently* in some cases a loss) of mass.

The increment of substance was, however, regarded for long as of small importance, and attributed to particles derived from the flame.

In these experiments the flame and the heat are provided under both sets of conditions, and the sole difference that can be detected is that in one case there is free access of air, whilst in the other the substance is imprisoned beneath the sand and shut off from the air.

9. Action of Air during the Heating Operation.—Before we proceed to examine how and why the air effects such a change, let us satisfy ourselves that the lead, however unlikely it may appear to be so, is still contained in the yellowish residue from Exp. 8.

Exp. 12.—Scrape out of the crucible some of this residue, powder it very fine, and introduce it into a fresh crucible. Now take about a gram of finely-powdered charcoal, and mix it (by stirring with a thin glass rod) intimately with the yellowish powder. By gently tapping the crucible shake the contents well together, and cover the surface with a layer of powdered charcoal. Put a lid on the crucible. [Why?] Heat over the flame for an hour without disturbance. Allow to cool, and then carefully shake out the charcoal and see what lies under it.

Examine the substance, press it in a mortar, and satisfy yourself that it corresponds to the metal which was taken in Exp. 8.

The suggestion which these experiments give rise to, that air plays an important part in the changes observed, is one that must be tested with great care, and further experiments must be devised in order more fully to appreciate the nature of the changes. For the present you will be satisfied to note that, while heating in air transformed the lead into a yellow powder with increase in mass, the heating of this yellow powder with charcoal has brought it back to metallic lead again.

10. The changes which Air may effect at Ordinary Temperatures.—Rusting of Iron.—Our next investigations will be made upon *iron*, a substance which possesses the advantages of being familiar to us, not only in itself but in the changes which it undergoes, and also in respect of the fact that such changes take place at ordinary temperatures.

Exp. 13.—Obtain some bright iron or steel filings,[1] sprinkle a thin layer of them on a watch-glass; weigh; place in the desiccator, and leave them there for two or three days, after which again weigh. You will find that the weight remains unaltered. Examine the filings with a lens; they present the same appearance as at first.

Exp. 14.—Perform the same operations with the difference that the filings are left under a bell-jar, the inner surface of which is well moistened with water. This time you will find that there is an increase in weight and that the filings have become covered more or less completely with a reddish-yellow powdery-looking substance.[2]

The change which has taken place in the one case, and of which evidence is wanting in the other, is one that you must frequently have observed in iron utensils, railway lines, etc. It is termed "rusting," and the reddish-yellow powder formed is called "rust." So far you find it to be associated with an increase in weight and apparently due in some way to the moisture, for in dry air it did not take place. Let us now try to find out whether rusting will take place in the presence of *moisture alone*.

Exp. 15.—Fit a round-bottomed flask of about a litre capacity with a rubber cork, through which passes a short length of rather wide glass tubing to which is attached an

[1] Such filings are usually contaminated with oil, and this should be removed by shaking them with a little *ether*, pouring off the liquid, and then leaving them a few minutes in a dry, warm place —in a steam bath or in a gently warmed basin.

[2] Reserve these rusty filings for a later experiment.

inch or two of indiarubber tubing. Introduce about 300 c.c. of hot water, and drop into this some yards of bright iron wire wrapped into small compass by winding it round a pencil.

Now boil the water, not too violently, but so that the steam issues freely from the end of the rubber tubing (Fig. 5). Continue the boiling for at least a quarter of an hour, and then slip over the rubber tubing a strong brass clip, being careful, *just the instant before doing so*, to remove the burner. During the boiling the steam will have displaced the air almost completely from the flask. By turning the flask arrange that part of the wire is exposed to the space occupied by water vapour. Leave it so for some days, and note that the wire keeps quite untarnished. After that let in air, and notice how after some hours reddish-yellow rust forms on the wire.

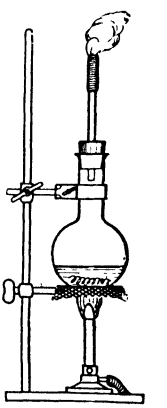


Fig. 5.

The rusting of the iron therefore takes place only in presence of air and moisture, and does not occur either in *dry* air or in water or water vapour alone.

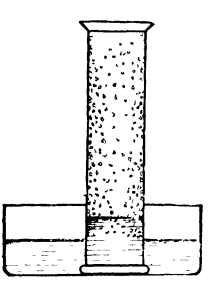


Fig. 6.

11. Does all the Air take part in the process of Rusting?—

Exp. 16.—Take a tall, narrow gas jar, moisten its inner surface with water (by filling it with water and then emptying the water out) and then sprinkle bright iron filings freely over the moistened surface. Fill a small earthenware or glass trough half full of water and stand the jar in the trough mouth downwards (Fig. 6). No air should be allowed to escape from the jar during this

process, and this is secured by keeping the jar vertical while lowering it into the trough.

After two or three hours examine the tube again; you will note that the water has risen in it.[1]

Leave for two or three days, examining from time to time. You will find that after a time the water ceases to rise.[2] Mark the level of the water inside the jar carefully by means of a piece of gummed paper. Now remove the jar, fill it completely with water, and measure the volume by pouring it into a graduated cylinder. Now fill the jar with water up to the piece of gummed paper. The larger volume (say v_1) gives the volume of air contained in the jar at the commencement of the experiment; the difference between the two volumes (say $v_1 - v_2$) represents the quantity of air which has disappeared. You will find that the ratio $(v_1 - v_2) : v_1$ is approximately 1 : 5, *i.e.* one-fifth of the air has disappeared.[3]

Obviously then only about one-fifth of the air takes part in the process of rusting, for some of the filings remain bright after this quantity has been removed.

12. What has become of the Air which has disappeared?—Recalling the fact demonstrated in Exp. 14 that the rusting of iron is accompanied by an increase in weight,[4] we are justified in concluding that the air which

[1] If it has not done so the reason is that the rim of the jar fits so exactly on to the bottom of the trough that water cannot pass in from the trough. In this case raise the jar very slightly, when the level of water will at once rise in it.

[2] The air in the jar is now under reduced pressure and it might be restored to atmospheric pressure by pouring water into the trough till the levels are the same inside and outside the jar. The change in volume produced would, however, be so small in this case as to be negligible; so the correction need not be made.

[3] *Note.*—If the ratio $(v_1 - v_2) : v_1$ is found to be less than one-fifth you will most probably find that none of the iron filings remain bright after the water has ceased to rise. This shows that an insufficient quantity of filings was used, and the experiment should be repeated, using a larger quantity.

[4] It is assumed that the student is acquainted with the fact that *air has weight.*

has disappeared has become in some way fixed or added on to the iron, and that the result of this fixation is the conversion of the iron into reddish-yellow rust.

13. The Nature of the Change which takes place when Metals are heated in Air.—We have seen in Exps. 4 and 8 that when metals are heated in air they increase in weight and become changed into earthy-looking powders (which the early chemists called "calces" [sing "calx"] of the metals). Can we explain these changes as we did the rusting of iron? If so, then they should be accompanied by the disappearance of a certain amount of air. Let us test this by burning magnesium (for example) in an enclosed volume of air.

Exp. 17.—Arrange a bell-jar in a trough which is not too shallow,[1] and half fill with water (see Fig. 7). The bell-jar should not be too narrow nor too large. Mark the level of the water in the jar by means of a piece of gummed paper. Attach a piece of magnesium ribbon to a cork which fits the bell-jar well. Ignite the magnesium, and *as quickly as possible* place it in the bell-jar, pushing in the cork tight. After burning brightly a short time the magnesium goes out. The water rises rapidly inside the jar. When it ceases to rise further mark the level of the water again with gummed paper.[2] Now proceed, as in Exp. 16, to measure the volume up to each gummed mark. You will find that, as in Exp. 16, about one-fifth of the air has disappeared.

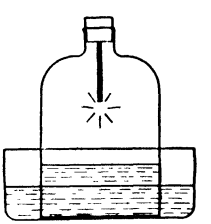


Fig. 7.

[1] If the trough is very shallow it will be necessary to have a thin rubber disc at the bottom on which to press the jar during the burning and so prevent any escape of air through expansion by the heat evolved. In this case you must see that the jar is ground at the base in order that it may not cut the rubber

[2] See footnote marked [2] on p. 20.

Similar results would be obtained by heating other metals in an enclosed volume of air, so that we may safely conclude that the change in appearance and properties and the increase in weight which the metals undergo is due to the fixation of air on them.

Exp. 18.—Allow some iron filings to rust in a test-tube, as in Exp. 16, till the level of water ceases to rise. Cover the mouth of the tube with your hand, turn it the right way up, remove your hand, and introduce a lighted taper into the tube. The taper is extinguished. Next burn magnesium in a bell-jar, as in Exp. 17. Remove the stopper and introduce a lighted taper. It is again extinguished.

From this similarity in behaviour, and from the fact that in both Exps. 16 and 17 about one-fifth of the air was removed, we may suppose that ordinary air consists of two gases in the proportion of 4 : 1 by volume, and that iron on rusting and magnesium on burning have removed the constituent present in smaller quantity. This we may term the *active constituent*, and that present in larger quantity the *inactive constituent*. The latter has been named *Nitrogen*, and we shall in future call it by that name.

14. Burning of Non-Metallic Substances.—So far our investigation upon atmospheric air has been mainly concerned with the behaviour of *metals* towards it under certain conditions. There are, however, a large number of bodies which are not metals (termed non-metallic) which undergo a change when heated sufficiently in air. Among these we may mention such substances as candle, wood, phosphorus, sulphur.

The student will be familiar with the behaviour of the first two substances on burning—namely, that a candle burns with a white flame, and appears to burn completely away, and that wood burns away, leaving a small quantity of ash.

Let us now see what happens when sulphur and phosphorus are burnt in air.

Exp. 19.—Place a small quantity of flowers of sulphur in a deflagrating spoon (Fig. 8). Warm gently in a Bunsen burner. Note that the sulphur first melts to a reddish liquid and then takes fire, burning with a pale blue flame and giving off white fumes having the well known disagreeable smell of burning sulphur. At this stage plunge the spoon into a gas-jar and press the brass plate down tightly. The jar becomes filled with white fumes. When the action ceases pour a little water into the jar, cover the mouth with a greased glass plate, and shake up. The white fumes disappear, and you will find that some difficulty is experienced in removing the glass plate, which appears to be pressed down tightly on to the jar. Now drop a piece of blue litmus paper[1] into the jar: the litmus is turned red, proving the presence of an acid. [Burn off all the sulphur remaining on the spoon before doing the next experiment.]

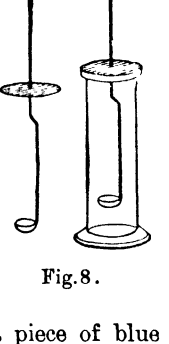


Fig. 8.

We may explain the results just obtained by assuming that when sulphur burns in air a gas is formed which has a pungent odour, and dissolves readily in water[2] to form an acid. The gas is called *sulphur dioxide*.

[1] *Litmus* is a colouring matter which occurs in certain lichens such as *Rocella* and *Variolaria*, and is very sensitive to the action of many chemical substances. It turns red in acids, and substances which turn it red are said to have an *acid reaction*; it turns blue in alkalies, or in substances having an *alkaline reaction*; and it is unaffected by water and many other substances which have a *neutral reaction*. *Blue litmus paper* is prepared by dipping unglazed paper in a solution of litmus (obtained by boiling commercial litmus with water and filtering). *Red litmus paper* is prepared by adding just sufficient acid to a solution of litmus to turn it red and then dipping unglazed paper in the liquid and drying it.

[2] Hence the difficulty in removing the cover from the cylinder. There is a reduction of pressure in the jar when the gas dissolves, and consequently the atmosphere outside presses the cover firmly on to the jar.

Exp. 20.—Cut off from some yellow phosphorus, *held below water*, a piece not larger than a pea, and transfer it on the point of a knife to a deflagrating spoon. Dry it by touching it with a bit of filter paper and watch it for a few seconds. White fumes with a peculiar odour are given off: the phosphorus is already reacting with the air.

Touch the phosphorus with a warm glass rod, plunge it into a gas-jar and press the brass plate of the spoon down tightly on the jar. The phosphorus burns with a brilliant white flame, evolving dense fumes which ultimately settle down as a white powder. These fumes are very irritating. When they have settled, remove the deflagrating spoon. [If any phosphorus remains on it (as shown by the formation of fumes), burn it away in a fume cupboard. *It must not be wiped off with a cloth*, or the latter will presently take fire.] You will notice that the white powder soon gives place to colourless drops of liquid. Test these with blue litmus paper. The litmus becomes red, showing that an acid has been formed.

Evidently the white solid formed when phosphorus burns in air (called *phosphoric oxide*) dissolves readily in water with formation of an acid.

Let us now proceed to investigate the burning of non-metallic substances *in a confined volume of air*, in order to find out whether the same portion is removed as when metals burn or iron rusts.

Exp. 21.—Stand a small porcelain crucible containing some red phosphorus on a broad flat cork and float on water in a deep trough which is half full of water [1] (Fig. 9). Place over the crucible a large bell-jar with the stopper removed. Mark the level of the water in the jar with gummed paper. Now ignite the phosphorus by

[1] If a deep trough is not available you may use a shallow one, but in that case a rubber pad must be employed, as in Exp. 17 (footnote).

touching it with a hot wire and close the bell-jar *at once*[1] by means of the stopper (or a cork).

The phosphorus will burn brightly at first, and the heat evolved will expand the gas and depress the water inside the jar. After a little while the combustion will cease, and the water will ultimately rise above its original level. The fine white powder which is formed during the combustion (consisting of phosphoric oxide) will gradually settle down and dissolve in the water. When the water has ceased to rise within the jar, again mark the level of the water in it.[2] You will find (using the method of Exp. 16) that *one-fifth of the air* has disappeared. Test the residual gas as in Exp. 18. It is nitrogen.

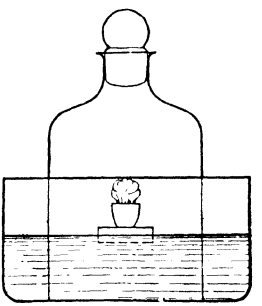


Fig. 9.

Note.—Burn away all the remains of phosphorus in the crucible in a fume cupboard.

The experiment may be repeated with sulphur; again about one-fifth of the air is removed, and the remaining gas extinguishes a lighted taper.

Now this is exactly what happened in the case of metals; one-fifth of the air was removed and the remainder extinguished a lighted taper. We are therefore justified in concluding that when non-metallic substances burn in air they *combine with the oxygen* and leave the nitrogen.

[1] If the stopper is not placed in the bell-jar immediately after the burning substance is covered by it, some air will escape owing to expansion by heat, and, as it does not return, the water rises more than one-fifth.

[2] See footnote marked [2] on p. 20.

15. Preparation of Nitrogen from the Air.—We have seen in Exps. 16-19 how a quantity of nitrogen can be obtained, but these methods are not very convenient. A better one, which does not, however, differ from them in principle, will now be investigated. If you will refer back to Exp. 4 you will see that when the metal copper is heated in air it gains in weight and becomes coated with a greyish-black scale. Now in the light of our later experiments we should say that in all probability the copper has combined with the active constituent of air, forming a calx of copper (the greyish-black scale) and leaving the nitrogen. Let us examine this further.

Exp. 22.—Almost fill with clean copper turnings a piece of hard-glass or "combustion" tubing about 25 cm. long and 1·5 cm. in diameter. Fit each end with a cork, through

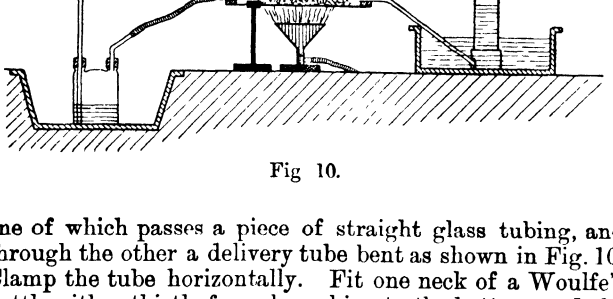


Fig 10.

one of which passes a piece of straight glass tubing, and through the other a delivery tube bent as shown in Fig. 10. Clamp the tube horizontally. Fit one neck of a Woulfe's bottle with a thistle funnel reaching to the bottom, and the other with a piece of glass tube bent at an obtuse angle and just penetrating the cork. (A large flask with a two-holed cork may be used instead.) Connect the bottle and combustion tube by means of rubber tubing.

Next take a small trough, place in it a bee-hive shelf (Fig. 11), and arrange so that the end of the delivery tube passes under the arch of the shelf. Pour sufficient

water into the trough to cover the shelf by at least half an inch. Next fill a small gas-jar completely with water, cover it with a ground glass plate, invert it, place it under the water in the trough, remove the cover, and stand it down. (Take care not to let any air enter the jar during this process.) In a similar way fill three or four other gas-jars with water and stand them inverted in the trough.

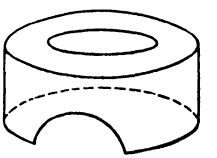


Fig. 11.

Next heat the tube by means of a spreading Bunsen flame. Place the Woulfe's bottle in the sink and when the copper has become red-hot allow water to drip into the funnel. As the bottle fills with water air is slowly driven from it through the heated tube. Now stand one of the gas-jars which you have filled with water on the bee-hive shelf. You will observe that bubbles of gas rise through the water in the jar and collect above it. When the jar is full of gas stand it down in the trough and replace it in succession by the other jars which you have filled with water.

Now disconnect the Woulfe's bottle and tube and turn off the gas. Place a ground glass plate over the mouth of one of the jars of gas, keeping the mouth under water, stand the jar upright, remove the cover and introduce a lighted taper. The taper is extinguished.

The gas you have collected must therefore be *nitrogen*, the inactive constituent of air, showing that the copper has combined with the active constituent as we anticipated. Thus the method of Exp. 22 affords a convenient process for the preparation of nitrogen from the air. We have collected the gas by the "**displacement of water,**" a method generally employed for collecting gases not too soluble in water.

16. Properties of Nitrogen.—Since this is the first gas that we have prepared, it may be worth while to indicate what are the properties of gases which the chemist is usually interested to learn. They are naturally those

which distinguish the gas in question from other gases he may have to deal with. These properties may be divided into (*a*) physical, (*b*) chemical: but only those physical properties which are not common to all gases are usually considered. Briefly, we may set out our plan of investigation as follows:—

I. *Physical.* Determination of colour, taste, smell, solubility in water, and density.

II. *Chemical.* (*a*) Behaviour when a lighted taper is applied; (*b*) behaviour towards water (test liquid afterwards with blue and red litmus paper).

It is a good plan always to take the properties of a gas in some definite order, such as is here indicated.

Let us apply this scheme to the investigation of the properties of nitrogen.

I. *Physical properties.*—

Exp. 23.—Examine a jar of the gas collected in Exp. 20 and notice that it is colourless, tasteless, and odourless. Now invert this jar in a trough of water and leave it standing for some time. Examine again and note that there is no appreciable rise of water in the jar, showing that nitrogen is either insoluble or only slightly soluble in water. [It is in fact very slightly soluble.]

Exp. 24.—Leave a jar of nitrogen open to the air, and test it from time to time with a lighted taper. You will find that it is some time before the taper will burn in the jar, showing that the nitrogen has only slowly escaped and given place to air. It follows that, if nitrogen is lighter than air, it cannot be much lighter.

Now support a jar of nitrogen mouth downwards in the air by means of a retort stand and clamp. Introduce a lighted taper into the jar occasionally. You will again find that it is some time before the taper will burn in the jar, *i.e.* air has only slowly replaced the nitrogen.

From this experiment we should gather that nitrogen has a density not very different from that of air [It is rather lighter than air.]

II. *Chemical properties.*—

(*a*) In your previous experiments you have already noticed that a taper does not burn when introduced into a jar of nitrogen, *i.e.* nitrogen is *not* a *supporter of combustion.* Further, you will have observed that the gas does not take fire when the taper is brought in contact with it, *i.e.* nitrogen is not inflammable.

(*b*) **Exp. 25.**—Introduce a little water into a cylinder of nitrogen. Put the cover on the cylinder and shake up vigorously. Test the liquid with blue litmus paper. There is no result, *i.e.* nitrogen does not impart to water either an acid or an alkaline reaction.

It will be noticed that nitrogen is remarkable for its negative rather than for its positive characteristics: it has *no* colour, taste, or odour; does *not* support combustion; and so on.

17. The Active Constituent of Air (Oxygen).—We must now inquire whether it is possible to recover the active constituent of the air from the calx of a metal.

We choose for our first experiment a calx of mercury known as mercuric oxide or "red precipitate," and which can be obtained by heating mercury for a long time at a certain temperature in contact with air.*

Exp. 26.—Into a hard-glass tube introduce sufficient crystalline red precipitate to cover a threepenny-piece, and hold it in a Bunsen flame. Notice that the colour of the powder changes from scarlet to black—it looks "*burnt.*" Take the tube from the flame, let it cool, and notice what happens. The scarlet colour is recovered. Evidently the change is not due to *burning.*

Have by you a splinter of wood long enough to reach down to the bottom of the tube. Now heat the latter in the hottest part of the flame (*i.e.* near the tip). You will observe a mirror gradually forming on the sides of the tube. Ignite the splinter, blow out the flame, and thrust the glowing end down the tube. Observe that the glowing

splinter bursts into flame, and burns more brightly than in common air.

Now scrape off the mirror formed in the tube with the clean end of the splint. You obtain a liquid metallic globule of "quicksilver" or *mercury*.[1]

If, then, mercury is heated in air to a certain temperature, we obtain the calx of the metal; and we have just found that, by heating the calx to a *higher temperature* (for the temperature of the hottest part of the Bunsen flame is much higher than that at which mercury is converted into red precipitate), the calx has been broken up again into mercury and a gas which is more active than ordinary air. This gas must, therefore, be the active constituent of air. It is called *oxygen*.

Exp. 27.—Now repeat Exp. 24, using red lead. Here, again, you obtain oxygen; *but the residue in the tube is not metallic lead:* it is a yellow solid, litharge, which is the *yellow* calx of lead, that is, the substance obtained in Exp. 8 by heating lead in air. [Red lead is also obtained by heating lead in air, but a lower temperature must be used than in the preparation of litharge.]

Heat in a similar way the residues you obtained from magnesium and copper in Exp. 4, and the rusty iron filings formed in Exp. 14. None of these gives off any oxygen.

It is clear, therefore, that the oxygen is not recoverable from *all* the bodies obtained by heating metals in the air or simply exposing them to the air, as in the case of iron rust—at any rate, not by simple heating.

18. Elements and Compounds.—Red precipitate contains, then, at least two substances—mercury and oxygen—which are joined together in some mysterious way, so that the product is an entirely different substance from either of its constituents. This kind of union is termed *chemical combination*, and both the formation of this

[1] Mercuric oxide is usually prepared by quite a different method, and is a substance which may be easily procured from the chemist.

substance by heating mercury in air and its subsequent decomposition by heat are excellent examples of *chemical changes*. Red precipitate is an instance of a *chemical compound*; so also are red lead, iron rust, and the calces of the metals in general.

Chemical compounds, then, are evidently substances which may be split up into two (or more) new substances. Now neither mercury nor oxygen has, so far, by any means in the chemist's power, been decomposed into anything simpler. Substances like mercury and oxygen, which have up to the present resisted all attempts to break them up into simpler bodies, are termed **elements.** Nitrogen is also an element, as are all the pure metals, as well as sulphur, carbon, and a great many substances. In all about 75 elements are known; but some of them are very rare, and only obtained with great difficulty.

A chemical compound containing oxygen and some other element is termed an *oxide*: red precipitate, for instance, is *oxide of mercury*; red lead and litharge are *oxides of lead*; iron rust is an *oxide of iron*.[1]

19. Preparation of Oxygen in Quantity.—We have seen that it is not easy to obtain supplies of pure oxygen, unmixed with other gases, from the atmosphere; nor are there naturally occurring substances which readily yield the gas in quantity. "Nitre," which is found in quantity in Chili, and "pyrolusite" (manganese dioxide) will, when *strongly* heated, give up oxygen, and were used by the earlier chemists as sources of the gas.

There are, however, substances which have been specially prepared by the chemist more convenient for the purpose than red precipitate, or red lead, or any of these naturally occurring bodies. One of these is "chlorate of potash," the nature of which you will more fully appreciate at a later stage. We shall use it at present merely as a means of obtaining oxygen free from other gases.

[1] It is not, however, pure oxide of iron; in addition it contains other iron compounds.

Exp. 28.—Heat a small quantity of potassium chlorate in a test-tube. Notice that it first crackles, then melts, and at last seems to boil. At this stage test the issuing gas with a glowing splinter. It will be found to be oxygen. Now heat some more potassium chlorate, first grinding it up in a mortar with a little manganese dioxide, till the substances are thoroughly mixed. Observe that the mixture gives off oxygen much more readily than potassium chlorate alone.

It is a remarkable fact that the manganese dioxide is unchanged at the end of the operation, the oxygen appearing to have come from the chlorate only. It is, however, very likely that the manganese dioxide does take some part in the reaction, but we cannot stop to discuss the question here.

The mixture just described is the one generally used to prepare oxygen in large quantities, and is often called the "oxygen mixture."

Exp. 29.—Procure a small, round-bottomed flask and fit it with a cork and delivery tube, bent as shown in Fig. 12. Pour sufficient water into a pneumatic trough to cover its shelf well. Fill one large gas-jar and several smaller ones with water and invert them in the trough. Have ready some ground-glass covers to be placed over the mouths of the jars when filled with gas.

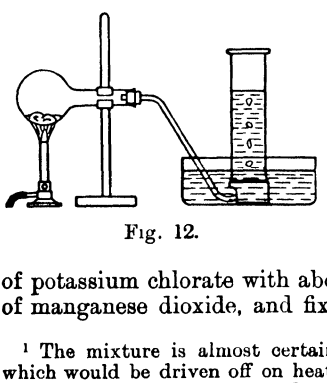


Fig. 12.

Fill the flask about one-quarter full with a mixture of potassium chlorate with about one-quarter of its weight of manganese dioxide, and fix it as shown in the figure.[1]

[1] The mixture is almost certain to contain adhering moisture which would be driven off on heating and condense in the neck of the flask. If, therefore, the flask is supported in a vertical position there is a danger that this moisture would run down on to the hot part of the flask and crack it.

so that the delivery tube just dips under the shelf of the trough. Use a small flame to heat the mixture, and move it to and fro to avoid getting too high a temperature. Oxygen soon comes off rapidly, and after allowing a short time for the air in the flask to be driven out, place a jar in position on the shelf, and, when filled, quickly cover its mouth while still under water with a glass plate, and replace it with a second jar, and so on.

Note on Manganese Dioxide.—Before using a fresh sample of this compound for the production of oxygen, it should be tested for carbonaceous matter (soot, etc.), as such material is apt to cause explosion when heated with potassium chlorate. To do this, mix it with some of the chlorate and heat gently in an open crucible. If the action is violent, reject the sample of dioxide.

20. Properties of Oxygen and Comparison with Ordinary Air.—

Exp. 30.—You will already have noticed that oxygen is colourless like ordinary air. Remove the cover from a small jar of the gas and inhale a little of it. You will find that it is odourless and tasteless,[1] but that it produces a feeling of exhilaration as though it were ordinary air *intensified*.

Invert the jar in water and leave for a time. You will find that there is no appreciable rise of water in the jar, so that if the gas is soluble at all the solubility is quite small. [The gas is slightly soluble.]

Exp. 31.—Proceed on the lines of Exp. 24 to investigate the density of oxygen. You will find that it does not differ greatly from that of air. [It is slightly heavier.]

Exp. 32.—Bring a lighted taper to the mouth of a jar of oxygen; the gas does not take fire, showing that it is not inflammable. Now push the taper into the jar; it burns more brightly.

[1] Generally, however, oxygen made from potassium chlorate and manganese dioxide contains rather too much chlorate to be quite odourless or tasteless.

Exp. 33.—Repeat Exps. 19, 20, using small jars of oxygen instead of jars of air. Notice that the result is the same, except that the burning is more vigorous.

Exp. 34.—Attach a piece of magnesium ribbon to a deflagrating spoon, ignite the end of the ribbon and plunge into a jar of air. Note that the magnesium burns with a very bright flame and formation of white fumes, which settle down as a white powder on the walls of the jar. Repeat the experiment with a small cylinder of oxygen. You will observe that the result is similar but that the burning is much more vigorous, the flames being intensely bright.

Exp. 35.—Introduce through a funnel sufficient sand to cover the bottom of the large jar of oxygen which you collected, to a depth of about half-an-inch. Roll 8 or 10 inches of thin iron wire round a glass rod to form a spiral, and fasten a bit of match stalk to one end. Attach the other end to a deflagrating spoon. Light the match and plunge the wire into the jar. The iron wire burns and small black globules fall on to the sand. Repeat this experiment, using a cylinder of air; the wire does not burn.

It is quite obvious from the foregoing experiments that oxygen possesses the properties of ordinary air in an intensified degree, or, in other words, that air behaves as though it were diluted oxygen. We shall experience no difficulty in understanding this when we recall the fact that only one-fifth of the air is oxygen, the remainder consisting of the inactive gas nitrogen.

QUESTIONS.—CHAPTER II.

1. Describe a *desiccator* and explain its use.
2. Describe two experiments illustrating the part played by air in chemical changes.
3. What conditions are necessary for the rusting of iron? Describe experiments in support of your answer.

4 What do you suppose takes place when magnesium burns in air? Describe the experiments you would perform to verify your statement.

5 What is red precipitate? What happens when it is heated? What other red powder behaves somewhat similarly? In what respects do they differ?

6. Distinguish between "element" and "compound." Give as many examples as you can of substances belonging to each of these classes of bodies.

7. How would you prepare oxygen gas in quantity? Sketch the apparatus you would use. Describe in detail the experiments you would perform to show that when substances are burnt in oxygen the products are the same as when the same substances are burnt in air.

8. Describe as carefully as you can how you would prove that when phosphorus burns in air in a confined space one-fifth of the air disappears. What has become of this portion?

CHAPTER III.

THE NATURE AND ACTION OF WATER.

21. Behaviour of Substances towards Water.—We will commence our study of water in a manner similar to that which we followed in the case of air, *i.e.* by investigating the changes which familiar substances undergo in contact with water. Let us take *nitre* or *saltpetre* (potassium nitrate) as our first substance.

Exp. 36.—In a test-tube containing a little cold water place a few crystals of nitre. Notice that they gradually get less and less in bulk, and finally disappear *from sight*. We say the nitre has dissolved, and that it is *soluble* in water. What we have in the test-tube now is a *solution of nitre in water*. The water is termed the *solvent*. The term *solute* is used for the substance (in this case nitre) that has dissolved.

Now add more nitre, and shake; probably that will dissolve also. At length, however, if we continue to add the solid, a point will be reached at which some will remain undissolved in that quantity of water.

We have now a *saturated solution* of nitre in *cold* water.

If we wish to cause the still undissolved portion to pass into solution there is one very obvious way, viz. by adding more water. A second possibility suggests itself, namely, that at a different temperature (higher or lower) the water may be able to take up more nitre. Let us put this to the test of experiment.

Exp. 37.—Warm the test-tube containing the saturated nitre solution obtained in Exp. 36. You will find that the undissolved nitre soon disappears, showing that at a higher temperature water can take up more nitre.

Now add more nitre and heat again. This will probably also dissolve, but if the addition of nitre is continued a point will be reached when some nitre remains undissolved even on heating.

We now have a saturated solution of nitre in *hot* water. The question naturally arises as to what will happen if this solution is allowed to cool. Let us investigate this.

Exp. 38.—Allow the hot solution of nitre obtained in Exp. 37 to stand for some time. You will observe that a large part of the dissolved nitre reappears.

This is what might be expected, for we have already seen in Exp. 37 that hot water can hold more nitre in solution than cold water. The nitre which has separated out is the excess above that required to saturate the water when cold.

We see then that we may have saturated solutions at different temperatures, and that the quantity of solid necessary to produce such a solution depends upon two things at least—(1) the quantity of water present; (2) the temperature of the water.

22. Crystallisation.—

Exp. 39.—Pour off the liquid from the solid nitre which separated out from the hot saturated solution in Exp. 38. Now turn out the solid on to a piece of blotting-paper and examine it. You will find that it is made up of a number of small lumps having flat faces and a similar geometrical form.

These small lumps of definite shape are called *crystals*, and it is a rule of very general application that when solids separate out from solution they do so in the form of crystals, which have a definite (though not necessarily different) shape for each substance.

Exp. 40.—Procure some alum, Demerara sugar, and blue vitriol, pick out well-formed crystals of each, and draw them.

When crystals are formed by the slow evaporation of hot saturated solutions as in Exp. 38 (or by the slow evaporation of cold saturated solutions), they are usually large and well-formed. If on the other hand the cooling is rapid the crystals separate quickly and are generally small.

Exp. 41.—Prepare a hot saturated solution of nitre and pour some of it into a clock-glass. You will notice that the crystals formed are small—much smaller than those obtained in Exp. 38. This is because the large surface exposed causes rapid cooling.

If a well-formed crystal of any substance be suspended by a very fine thread in a saturated solution of the same substance, it will grow at the expense of the solution, but will usually retain its shape. In this way very large and almost perfect crystals of some substances may be obtained. Alum is a good substance to experiment with in this way.

Exp. 42.—Prepare a cold saturated solution of alum and suspend a well-formed crystal of alum in it. Leave for some time, and note the result.

23. Water of Crystallisation.—

Exp. 43.—Introduce a few crystals of copper sulphate into a test-tube and warm gently by means of a Bunsen burner. The crystals decrepitate and fall to a bluish-white powder, which, on further heating, becomes quite white. At the same time a colourless liquid which looks like water condenses in the upper part of the tube. Test the liquid as follows, to prove that it is water:—(1) Taste it: it is tasteless. (2) Introduce pieces of red and blue litmus into it: they are unaffected. (3) Apply a light to it: it is non-inflammable. (4) Evaporate a few drops to dryness: there is no residue If larger quantities of the

liquid were obtained and the freezing and boiling points taken they would be found to be 0° C. and 100° C. respectively, proving conclusively that the liquid is water.

When the test-tube is cold drop a little water on the white powder and note the return of the blue colour. [This serves as a delicate test for the presence of water.] Now add hot water a little at a time in just sufficient quantity to dissolve the blue solid completely. Allow the solution to cool: crystals of blue vitriol separate out.

We have now succeeded in removing water from blue vitriol with formation of a white powder, and we have obtained the crystals from the powder again by the addition of water. It is clear then that copper sulphate is a compound of the white powder and water. The white powder is called *anhydrous* copper sulphate, to indicate that it contains no water.[1]

Many other crystalline substances behave like copper sulphate when heated, *i.e.* they give off water and fall to a powder, so that it appears that water is essential to the formation of crystals of these substances. Such water is termed *water of crystallisation.* Washing soda, alum, and borax are substances which contain a large proportion of water of crystallisation.

Amorphous substances are those which do not possess a crystalline form. Examples of this class are chalk, charcoal, and starch.

24. Recovery of the Solute of a Solution.—When the solute is a solid (we shall see later that it need not necessarily be a solid) it may be recovered by allowing it to evaporate into the air at ordinary temperature or more rapidly by applying heat to assist the evaporation.

The first part of the evaporation may be carried out by supporting the containing vessel on wire gauze or a sand-bath (*i.e.* a tin tray containing sand) and heating by means of a Bunsen burner. If, however, the evaporation were carried to dryness under these conditions there would be

[1] *Anhydrous* being derived from a Greek word meaning *without water.*

great danger of loss by spirting. It is therefore advisable to use an arrangement to moderate the rate of evaporation. A convenient form of apparatus for this purpose is a *water-bath*.

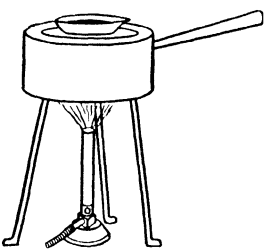


Fig 13.

A suitable form of water-bath consists of a tin saucepan which is partially closed by concentric rings of decreasing size. The largest ring fits on to the rim of the saucepan and the other rings fit into each other, the number being so arranged that the vessel containing the liquid to be evaporated rests comfortably on the edges of the innermost one (see Fig. 13). Water is boiled in the saucepan and the steam escapes between the vessel and the ring in contact with it.

Exp. 44.—Prepare a solution of nitre as in Exp. 36. Pour part of it into a porcelain dish and evaporate off the water by heating the dish first on a sand-bath and finally (when most of the water has disappeared) on the water-bath. The nitre (the solute in this case) remains behind.

25. Recovery of the Solvent of a Solution.—Distillation.—If we wish to recover the *solvent* of a solution we must make suitable arrangements to condense it. This is best done by using a *Liebig condenser*, which consists of a glass tube surrounded by a wider tube, through which cold water is made to circulate as indicated in Fig. 14.

* **Exp. 45.**—Pour the remainder of the nitre solution prepared in Exp. 44 into a flask and connect with a condenser, as shown in Fig. 14. Boil the liquid in the flask. The steam passes through the inner tube of the condenser, where it becomes liquid, and flows down into the flask placed to receive it. Do not boil off all the water or the flask may crack. Evaporate to dryness a little of

* See Preface as to Experiments marked by an asterisk.

the condensed liquid. There is no residue, showing that only the water has passed over.

The process of boiling a liquid and condensing and collecting the vapour as you have done in Exp. 45 is known as *distillation.*

Water which is produced by boiling ordinary tap water and condensing the steam by a suitable cooling apparatus

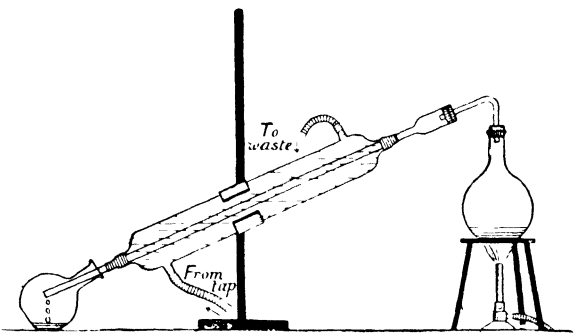


Fig. 14

(a Liebig condenser may be used on the small scale) is known as *distilled water.* Its use is essential in many chemical experiments because it contains no dissolved solids, whereas tap water does.

Exp. 46.—Evaporate a few drops of tap water to dryness on a watch-glass held in the hot air rising from a Bunsen flame. Notice that a white residue remains.

26. Solubility Curves.—Let us now investigate the solubility of nitre quantitatively at different temperatures.

*** Exp. 47.**—Introduce about 100 c.c. of water into a small flask, add some finely powdered[1] nitre, and shake

[1] Solution takes place more rapidly and effectively if the substance is finely powdered.

well. If the powder all dissolves add more and shake again. Repeat the addition of nitre, if necessary, till some remains undissolved after vigorous shaking, *i.e.* the solution is *saturated.* Allow the mixture to settle, take the temperature of the liquid with a thermometer (say 10° C.), and then pour off about 10 c.c. of the clear liquid into a weighed porcelain dish, after carefully wiping the inside of the neck of the flask on which there may be some solid nitre or water unsaturated with nitre. Weigh again. The difference gives the weight of the solution (w gm. say).

Now evaporate to dryness on the water-bath, wipe the moisture off the bottom of the dish, and weigh. The difference between this and the weight of the empty basin gives the weight of nitre dissolved.

Suppose this is w_1 gm., then we have w_1 gm. of nitre dissolved in $w - w_1$ gm. of water. Therefore at 10° C. the weight of nitre which would dissolve in 100 gm. of water would be $\frac{w_1}{w - w_1} \times 100$ gm. This is the *solubility of nitre at* 10° C. *expressed as a percentage.*

Now warm the water in the flask to about 20° C. and find the solubility as before. Repeat at 30°, 40°, and 50° C.

Next take a piece of squared paper and draw two lines (axes) at right angles, one horizontal along the bottom of the paper, the other vertical along the left-hand side.

Mark off along the horizontal axis lengths proportional to the temperatures taken, and on the vertical axis lengths proportional to the solubilities. Now from each point representing a solubility draw a horizontal line till it cuts a vertical line from the corresponding temperature. Make a cross at the point of intersection. Join the centres of the crosses by a line, drawing the line so that it forms a smooth curve (see Fig. 15). This is called the *solubility curve* of nitre.

By means of this curve you can at once find the solubility of nitre at any temperature between 0° C. and 50° C. All you have to do is to follow the vertical line corresponding to the required temperature till it cuts the curve; then

follow the horizontal line from this point till it cuts the vertical axis and read off the solubility.

Other examples of soluble substances are common salt, sugar, Epsom salts, bicarbonate of soda, alum and borax. You might construct solubility curves for them as you did for nitre. You would find that the solubilities of these

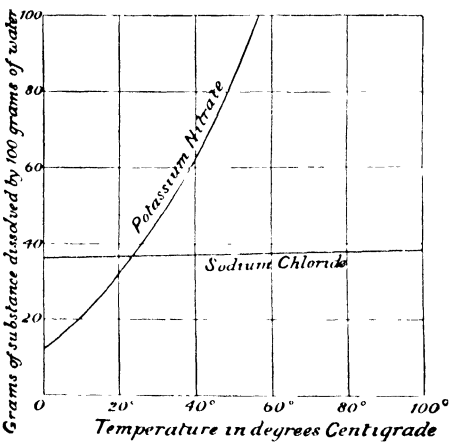


Fig 15.

substances vary greatly; also that whilst in some cases, *e g.* nitre, the solubility increases very rapidly with rise in temperature, in other cases, *e g.* common salt, the increase is very slight indeed.

27. Other Solvents.—It is important for the student to remember that water is not the only substance which possesses the property of dissolving solids. *All* liquids possess this power, in a greater or less degree, though any given liquid does not necessarily dissolve the same substances as another liquid.

Some substances that will not dissolve in water dissolve readily in other liquids. Sulphur, for example, is very soluble in a liquid called *carbon bisulphide*, and resin in *alcohol* or *methylated spirit*.[1]

Exp. 48.—Powder a small piece of roll sulphur, introduce it into a little carbon bisulphide in a test-tube a little at a time, and shake till completely dissolved. Then pour on to a clock-glass and allow the liquid to evaporate slowly (in a fume closet). Note the yellow crystals of sulphur which form.

28. Insoluble Substances.—Decantation.—Filtration.—

Behaviour of Chalk towards Water.—

Exp. 49.—Shake up some chalk with distilled water in a test-tube and allow the mixture to stand for a considerable time; the chalk settles down to the bottom, and leaves a clear liquid above. Carefully pour off (*decant*) some of this clear liquid on to a watch-glass without allowing any chalk to be carried with it. Evaporate the liquid to dryness by holding the watch-glass in the hot air rising from a small Bunsen flame. No residue remains, showing that none of the chalk has dissolved, *i.e.* chalk is *insoluble* in water.

The process we have just employed for separating water from an insoluble substance such as chalk is known as *separation by decantation*. The greater the density of the substance the sooner will it subside, so the more easily can the separation be effected; red lead, for example, settles much quicker than chalk.

There is, however, a process by which the separation can be effected more rapidly and completely, namely, *filtration*, and we will now investigate this.

[1] These liquids are **very volatile and inflammable**, and should not be boiled in the open air, but in a distillation apparatus, on a water-bath. They may, however, be allowed to evaporate slowly in the open air, without the application of heat.

Exp. 50.—Take a circle of filter paper about 15 cm. in diameter and fold it in half along a diameter; now fold it in half again at right angles to the diameter in such a way as to make a quarter of a circle. On looking at the

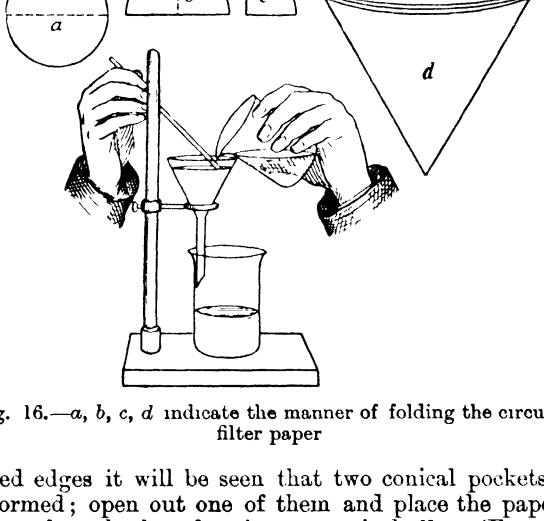


Fig. 16.—*a*, *b*, *c*, *d* indicate the manner of folding the circular filter paper

curved edges it will be seen that two conical pockets can be formed; open out one of them and place the paper in a glass funnel, thus forming a conical *filter* (Fig. 16). moisten the paper with water to make it adhere to the funnel. Support the funnel by means of a retort stand and ring, and place a beaker underneath it to receive anything which runs through the filter. The neck of the funnel should be in contact with the beaker to prevent splashing.

Now shake up some chalk with distilled water in a test-tube or beaker and, without letting it settle, pour it carefully on to the filter, guiding it down without splashing by means of a glass rod with rounded end in the manner indicated in Fig. 16. Do not pour so much liquid on to the filter at one time that the liquid extends above the filter paper.

You will notice that a clear liquid (the *filtrate*) runs through the filter and that the chalk (the *residue*) is retained on it. If any chalk passes through it must be in solution. Test whether this is the case by evaporating a little of the liquid to dryness on a watch-glass. There will be no residue (as you would expect from Exp. 49, in which it was found that chalk is insoluble in water).

Since the chalk is retained by the filter paper, it is evident that the pores of the paper are too small to allow the chalk particles to get through, but they cannot prevent the water passing through. The residue on the filter paper may be dried by heating at some distance over a small Bunsen flame, or in a steam oven,[1] and by this means recovered in its original form.

Substances which do not dissolve in water, but which when mixed with it, even in small quantity, can still be seen, are said to be *suspended* or *in suspension*. *Suspended matter* can always be *completely removed by filtration*, provided the filter paper is fine enough. Sulphur, sand, and charcoal may be mentioned as other examples of bodies which are insoluble in water.

Let us now see whether it is possible to separate a solid from a liquid in which it is *dissolved* by means of filtration.

Exp. 51.—Make a solution of nitre and pour it on to a filter fitted up as in Exp 49. The liquid runs through completely, leaving no residue on the filter, and if you evaporate a portion of the filtrate to dryness you will obtain a residue of nitre.

Dissolved matter then *cannot be removed by filtration*, the pores of the filter paper are evidently larger than the particles of the dissolved substance.

29. Separation of Mixtures.—It will not be difficult now for the student to see how we could effect a separation of two substances when one is soluble in some liquid and the other is not. It is only necessary to warm the mixture

[1] *I.e.* an oven heated by steam.

gently with an excess of the solvent, and filter. The insoluble portion remains on the filter, the soluble portion runs through and may be recovered as described already (by evaporation of the solvent).

Before we proceed to illustrate the process of separation by experiment we must fit up a piece of apparatus which will be required, namely a *wash-bottle*.

30. To fit up a Wash-bottle.—

* **Exp. 52.**—Procure a flask of about 500 c.c. capacity and fit it with a two-holed cork, through which pass a short tube bent at an obtuse angle and a long tube reaching nearly to the bottom of the flask and bent at an acute angle near the upper end (Fig. 17).

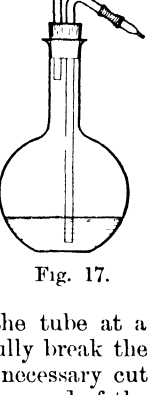
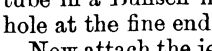


Fig. 17.

Now prepare a jet as follows:—Take a short piece of tubing, about $\frac{1}{2}$ cm. in diameter, and heat the middle portion in a small blowpipe flame, supporting each end of the tube with the fingers, and continually turning it round so as to heat all sides equally; when the tube is quite soft, remove it from the flame and slowly draw it out (Fig. 18). The more slowly it is drawn out, the more gradually will the tube taper towards the centre.


Fig. 18.

Then with a file make a fine scratch on the drawn-out part of the tube at a suitable point and carefully break the tube at this point. If necessary cut off a piece from the other end of the tube so as to bring the total length down to about 3 cm. Finally round off each end of the tube in a Bunsen flame, being careful not to seal up the hole at the fine end.

Now attach the jet to the long delivery tube of the wash-bottle by means of a short piece of rubber tubing as shown in Fig. 17. The object of the jet is to enable water to be driven out of the wash-bottle in a fine stream by blowing through A.

31. Separation of Chalk and Nitre.—

Exp. 53.—Grind up some chalk and nitre together in a mortar. Shake up the mixture in a beaker with hot water and pour on to a filter, collecting the filtrate in a beaker. When you have transferred as much as possible of the mixture on to the filter, shake up the residue in the beaker with a little hot water and pour on to the filter, first allowing the liquid to run through completely. When the liquid has again run through you have the chalk on the filter and a solution of the nitre in the beaker, but the chalk is contaminated with a little nitre solution, which must be removed by repeated washing with hot water. This is best carried out by means of the wash-bottle you have set up in Exp. 52.

Heat some water in the wash-bottle, hold it with a duster, shake it round several times,[1] and then blow *gently* through A.

First direct the jet on to the upper edge of the filter paper and move it round so that the whole of this is washed. Then gradually work downwards, thus driving the chalk into the apex. When the filter is about two-thirds full of wash-water discontinue the blowing and allow the liquid to run through *completely*. Now fill up the filter again with wash-water and once more allow the water to completely[2] run through. The washing must be repeated till on collecting a drop of the liquid running through on a watch-glass and evaporating it to dryness no residue remains (or till the liquid running through ceases to taste of nitre).

Now transfer the funnel to a steam oven and leave it till the chalk is dry, and evaporate the nitre solution to dryness on the sand-bath and finally on the water-bath.

[1] The object of this is to bring about condensation of the steam contained in the wash-bottle; otherwise there is a danger that you would scald your mouth on blowing through A.

[2] If you do not let the wash-water run through completely before repeating the washing the addition of more water dilutes the wash-water already present, and so prolongs the process of washing and wastes water.

32. Separation and Isolation of the Constituents of Gunpowder.—Using the knowledge already gained concerning soluble and insoluble substances, the student will find this also an instructive exercise. Gunpowder contains three ingredients—nitre, sulphur, and charcoal. Of these nitre is soluble in water; sulphur and charcoal are insoluble, but sulphur dissolves in carbon bisulphide.

* **Exp. 54.**—To separate them we proceed as follows:—Shake the gunpowder with water, warm gently, and filter: the filtrate contains the nitre, which can be recovered by evaporation of the water, wash the residue on the filter with hot water till free from nitre and then dry it carefully in the steam oven; scrape it off the paper into a beaker and add carbon bisulphide. Shake and allow to stand; filter off the liquid from the black charcoal and let it evaporate slowly in a fume cupboard [or boil it off in a distillation apparatus if the quantity is large]. The sulphur is thus recovered. The charcoal remains behind on the filter. It should be washed with a little carbon bisulphide to free it from adhering sulphur, and then dried.

33. Water as a Solvent for Liquids.—

* **Exp. 55.**—Take three test-tubes and about half-fill each with water. Now carefully pour down the side of one tube a little alcohol, pour into the second tube a little carbon bisulphide, and into the third some turpentine. You will notice that the alcohol and turpentine float on the surface of the water whilst the carbon bisulphide sinks. This shows that alcohol and turpentine are lighter than water, whilst carbon bisulphide is heavier. Now shake up each tube and allow the liquids to settle. The turpentine and carbon bisulphide separate out and form layers at the top and bottom of the water respectively, but no separation takes place in the case of the alcohol.

Alcohol then mixes completely with water and is an example of a liquid which is *soluble in water* (or we may say with equal truth that the *water* dissolves in the *alcohol*). *Turpentine* and *carbon bisulphide* on the other hand are

examples of liquids which are *insoluble in water*. This property is characteristic of *oils* in general, and they either float on water or sink according as their density is less or greater than that of water. Ether is an example of a liquid which is only slightly soluble in water; so that some would dissolve while the remainder would float on the water.

In the case of liquids which are insoluble in water partial separation may be effected by decantation; but for more complete separation we must have recourse to special apparatus (such as the separating funnel). Liquids which are soluble in water can be easily separated from it by distillation, if their boiling points are either much higher or much lower than that of water. In the former case the mixture is heated to the boiling point of water, and the water passes over into the receiver, leaving the other liquid behind; in the latter case the mixture is heated to the boiling point of the other liquid, which passes over, leaving the water behind

When, however, the boiling point of the liquid does not differ very greatly from that of water (*e.g.* alcohol) the process of separation by distillation becomes much more complicated, because the two liquids pass over together, though in different proportions. The further consideration of this process is beyond the scope of this work.

34. Water as a Solvent for Gases.—When a bottle of soda water is opened, bubbles are seen to rise in large quantities to the surface. When these bubbles have ceased coming off the liquid can be made to effervesce again by shaking the bottle. When shaking no longer produces effervescence a further supply of bubbles can be liberated by warming the liquid. All this effervescence is due to the escape of *a gas that was dissolved in the water*. By means of a suitable arrangement this gas, which is called *carbon dioxide*, can be collected.

Again, ordinary tap water contains gas dissolved in it. This gas consists of air and carbon dioxide;[1] it may be

[1] Tap water always contains a considerable quantity of carbon dioxide derived from subterranean sources.

partially expelled on warming the water, and may be completely expelled on heating to the boiling point. Unlike solids, *gases dissolve better in cold water than hot.* The quantity of a gas dissolved in water will depend upon the pressure exerted by the gas upon the water, as well as upon the temperature of the water. The gas in soda water is forced in under pressure; when the pressure is relieved by taking out the stopper some of the gas escapes.

One litre of ordinary water at 15° is able to dissolve at the ordinary pressure about 16 c.c. of air.

Aquatic animals (fishes, etc.) obtain the air they breathe from that which is dissolved in the water in which they live.

The following is a convenient method of collecting the small quantity of air dissolved in water:—

* **Exp. 56.**—Procure a flask of about a litre capacity, and provide it with a well-fitting one-holed rubber cork and a delivery tube. Fill the flask completely with tap water. Push the upper end of the delivery tube into the cork till it is *just level*[1] with the base of the latter, and then fill the tube completely with water by immersing it in a trough of water. Now close the lower end of the tube by the thumb, lift the tube out carefully, insert the cork in the flask, then remove the thumb from the delivery tube, and place the lower end of the tube underneath a solution of caustic soda contained in a small trough (Fig. 19).

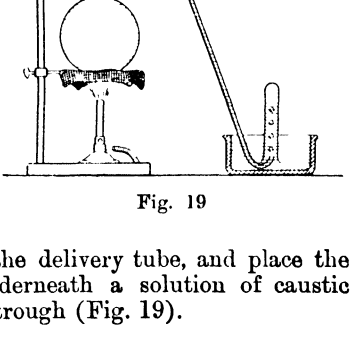


Fig. 19

[1] If the tube extends *below* the cork, some of the air collects in the neck of the flask when heat is applied, instead of passing over into the test-tube.

Fill a test-tube with caustic soda[1] solution and invert it over the end of the delivery tube; support by a clamp (not shown in the diagram). Now heat the flask, when bubbles of gas will slowly rise up through the water and pass over into the test-tube. When the volume of gas in the test-tube ceases to increase, close the end of the tube with the thumb, remove it from the trough, and invert it. Show that a match will burn in the gas as in ordinary air, but more brightly, because dissolved air contains a higher percentage of oxygen than ordinary air—in fact sufficient oxygen is present for the gas to cause a glowing splint to burst into flame. Test this.

Just as in the case of solids and liquids, some gases dissolve more readily than others. It is especially important to remember in some of the experiments that follow that water is able to take up gases if brought in contact with them.

QUESTIONS.—CHAPTER III.

1 Explain the terms *solvent, solution, water of crystallisation, saturated solution.* How would you separate and recover the ingredients in a mixture of powdered sulphur and common salt?

2. Describe carefully how you would proceed to ascertain whether a given white powder was soluble in water or not. How would you expect the following substances to behave when added to water:—Epsom salts, powdered charcoal, carbonate of soda?

3. Describe in detail how you would proceed to obtain pure water and pure nitre from a solution of nitre in water. Sketch the apparatus you would employ.

[1] The object of the caustic soda is to absorb the carbon dioxide which is evolved along with the air. Refer back to footnote on page 50.

4. What do you understand by the term *solubility curve*? How would you proceed experimentally to obtain the solubility curve of washing soda between 15° C. and 70° C.?

5. How would you proceed to prove that alum is more soluble in hot than in cold water?

6. Explain what is meant by *distillation*, and describe an experiment to illustrate its use.

7. Describe how you would proceed to investigate the action of heat on blue vitriol. State and explain what you would observe.

8. If you were provided with a mixture of chalk and powdered borax, how would you proceed to obtain a pure dry specimen of each constituent?

CHAPTER IV.

THE NATURE AND ACTION OF WATER (*Continued*).

35. Action of Water on Metals.—Production of Hydrogen.—

(*a*) *Sodium.—*

Exp. 57.—Take a piece of sodium about the size of a pea (*not larger*) and drop it into a small quantity of water contained in a beaker. Watch the behaviour of the metal through the *side* of the vessel, not over it, as the hissing globule sometimes explodes. The metal floats on the surface of the water and a thin heavy stream may be seen falling from it as it disappears. Is the metal simply dissolving in the water? It was angular when cast on the water; it is now globular: the solid has become liquid. Had the metal been placed upon a floating filter paper, the temperature would have risen sufficiently to produce a flame. Chemical action between the metal and the water may therefore be suspected.

Fill a test-tube with water and invert it in a trough. Cut off a piece of sodium about the same size as the first, wrap it up in tinfoil or thin sheet lead perforated with a few pinholes, and place it under the gas-jar. Bubbles of gas are now seen to rise apparently from the metal. When bubbles cease to rise cover the mouth of the tube with the thumb, remove it from the trough, and take it some distance away, turn it upright, bring a lighted match to the

mouth, and then take away the thumb. The gas ignites, probably with a slight "pop" or explosion,[1] and burns at the *mouth* out of the tube (*i.e.* where it has access to the air) with a yellow flame.[2]

Now prepare another tube of the gas in the same way. Remove it, keeping the mouth covered as before, turn it right side up, place over it a second *dry* test-tube of the same size (or preferably rather smaller) and remove the thumb. After a few seconds apply a light to each tube. The gas in the *upper* tube burns with a slight explosion, but that in the lower tube does not take fire. This shows that the inflammable gas has taken the place of the air in the upper tube, *i.e.* it is *lighter than air.* You will further observe that the sides of the upper tube become *misty*; we shall return to this point later.

Now rub the liquid in the beaker between your fingers: it is soapy. Taste it: it is *caustic.* Test it with red litmus paper: the colour changes to blue, *i.e.* the solution is *alkaline.* Evaporate the liquid to dryness in a porcelain dish. The residue is not sodium, which we should expect to find if the metal had merely dissolved in the water. The white solid is *caustic soda* (it is also called *sodium hydroxide*), and is the same substance as that from which the solution labelled "caustic soda" or "sodium hydroxide" is made. Dilute a few drops of this liquid with water and apply the tests to it mentioned above.

We have seen, then, that sodium reacts with water at ordinary temperature with liberation of an inflammable gas, which is lighter than air, and formation of a white solid, caustic soda, which possesses caustic properties and when dissolved in water produces an alkaline solution.

[1] This is because the gas forms an *explosive mixture with air.* For this reason *you must be very careful to keep flames at a distance* when experimenting with this gas. *Serious accidents* have often been caused through neglect of this precaution. You will now understand why you were directed to take the test-tube well away from the trough before applying a light.

[2] The yellow colour of the flame is due to the sodium.

(*b*) *Magnesium.*—

Exp. 58.—Take a piece of magnesium about 20 cm. long, scrape it if necessary so that the surface is bright, bend it into a zigzag shape, and fit it into a small test-tube. Fill the test-tube completely with water, invert it in a dish of water and leave for a few hours. Now examine again. You will notice a number of gas bubbles adhering to the metal; and some gas has collected at the top of the tube. Further, the metal has lost its brightness and become covered with a white coating.

Test the gas with a lighted match as in Exp. 57; it ignites with a slight explosion.[1] Test the liquid with red litmus paper; the colour changes to blue, showing it is alkaline.

We see then that the action of magnesium on water at ordinary temperature resembles that of sodium in two points, (1) an inflammable gas is formed, (2) the liquid becomes alkaline. The possibility naturally suggests itself that the gas produced in the two cases is the same. The action in the case of magnesium is, however, very slow at ordinary temperature, and in order to pursue the investigation further we require some means of making it more rapid. It is found that warm water acts more readily than cold water, and if the magnesium is intimately mixed with mercury the action is quicker still.

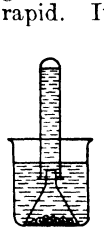


Fig. 20.

Exp. 59.—Place about a teaspoonful of magnesium powder in a mortar and add to it a drop of mercury. Rub them well together. Now place the mixture in a beaker filled with water, and insert a funnel with a short stem, upside down, in such a way as to cover the metal Fill a test-tube with water and invert it over the end of the funnel, as in Fig. 20. Warm the beaker and watch the test-tube. When the bubbles of gas have filled the tube, close the end with your thumb,

[1] Since the quantity of gas collected is small you may not see the flame.

remove the tube from the water, and apply a light to the mouth of the tube, at the same time removing your thumb.

The gas ignites with a slight explosion, and burns at the mouth of the tube with a pale blue practically non-luminous flame. Now prepare another tube of the gas and proceed, as in Exp. 57, to test whether it is lighter than air. You will find that this is so. Also notice the white powder which floats about in the water and ultimately settles down on the bottom of the beaker. This powder closely resembles that formed when magnesium burns in air or oxygen (Exp. 34). Test the liquid with red litmus paper; it is alkaline.

Let us now investigate a second way in which the action between magnesium and water may be caused to take place rapidly.

* **Exp. 60.**—Take a piece of thin-walled hard glass ("combustion") tubing about 10 cm long, fitted with a cork bored with one hole. Through this cork pass one end of a piece of glass tubing bent nearly at right angles, the other end of which is passed through the cork of a small flask containing water (Fig. 21). In the tube place some magnesium powder. Heat the flask carefully until the water begins to boil, then heat the tube and powder to prevent the condensation of water from the steam When hot, light the magnesium at the open end of the tube and continue boiling the water. Note any changes in the magnesium and in the steam.

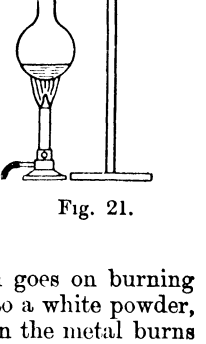


Fig. 21.

You will observe that the magnesium goes on burning in the steam until it is all converted into a white powder, which closely resembles that formed when the metal burns in air or oxygen (Exp. 34). At the same time the inflammable gas which is set free burns at the mouth of the tube.

From the results of Exps. 58-60 we may conclude that when magnesium reacts with water or steam it forms the same inflammable gas as that produced when sodium reacts with water and the same white powder (oxide of magnesium) as that formed when magnesium burns in air or oxygen.[1]

(*c*) *Iron.*—

We have seen in Exp. 15 that water alone has no action on iron even at the boiling point. Let us now try whether there is any action at a higher temperature, namely at a red heat.

* **Exp. 61.**—Fit up and arrange the apparatus shown in Fig. 22. It consists of an iron tube a foot or more in length and a little over half-an-inch in diameter, partly

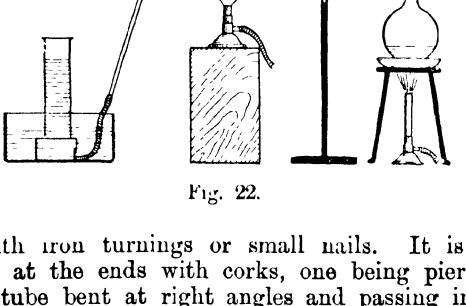


Fig. 22.

filled with iron turnings or small nails. It is fitted properly at the ends with corks, one being pierced by a glass tube bent at right angles and passing into the flask containing a little water, while through the other projects the delivery tube, cut off as shown above the surface of the water in the pneumatic trough. A piece of

[1] The alkalinity of the liquid in Exps. 58-60 is due to the fact that oxide of magnesium slowly combines with water to form a compound called hydroxide of magnesium, and this substance is very slightly soluble in water, forming an alkaline solution.

rubber tube is slipped over it sufficiently long to reach under the arch of the beehive shelf.

Boil the water briskly in the flask, which should rest on a sand-bath. Air will be expelled from the apparatus, and will rise in bubbles through the water.

Soon steam will begin to escape from the delivery tube and will condense with a series of sharp noises. When no more bubbles rise through the liquid, showing that all the air has apparently been expelled from the apparatus, invert a jar full of water on the beehive-shelf. No gas will collect in it unless some air was still present in the apparatus. In this case wait till the volume of air in the jar ceases to increase; then fill the jar with water again completely.

Now heat the iron tube strongly by means of a flat-flame Bunsen burner. Bubbles of gas will soon begin to rise in the jar. When the jar is full of gas, stand it down in the trough and put in its place a second jar full of water. When this is also full of gas, detach the rubber tube from the glass delivery tube, holding it with a duster and taking care that the steam escaping from the delivery tube does not scald you: next remove the Bunsen with spreading flame, and lastly, when the iron tube is no longer red-hot, the Bunsen underneath the flask.

Note.—The water in the flask must be kept *boiling briskly while the iron tube is being heated*, or water may be sucked back into it and cause a slight explosion. If it should cease to boil, at once remove the rubber portion of the delivery tube.

Now place a greased cover over the mouth of one of the jars, remove it from the trough, and stand it the right way up. Light a match, bring it to the mouth of the jar, and slide off the cover. The gas ignites, probably with a slight explosion, and burns at the top of the jar with a pale blue almost non-luminous flame. Remove the second jar in the same way and invert it. Place over it, mouth downwards, a second jar of the same size (or preferably slightly smaller) and remove the cover of the first jar. In a few seconds apply a light to each jar:

the gas in the upper jar burns and the jar becomes misty, but the gas in the lower jar does not burn. This shows that the inflammable gas has been transferred from the lower to the upper jar, *i.e.* it is lighter than air. It is in fact the same gas as that formed in Exps. 57-61, and is called *hydrogen.*

Now turn out the residue[1] in the tube and examine it. The turnings or nails now resemble in appearance the black substance produced when we burnt iron in oxygen (Exp. 35). They are, in fact, coated with the same substance—oxide of iron, and this compound is also formed when iron is heated strongly in air (the so-called "smithy scales" which form on the blacksmith's anvil also consist of it).

We see then that the action of iron on steam closely resembles that of magnesium. In each case *hydrogen* and an *oxide of the metal* are formed.

(*d*) *Copper.*—

Exp. 62.—Repeat Exp. 58, using copper instead of magnesium. You will find that the copper is not tarnished.

Now repeat Exp. 61, using copper turnings and a porcelain or hard glass tube. No gas will be evolved (after the air has been driven out of the apparatus), and on examining the residue in the tube you will find that the copper has undergone no change.

Copper then is not acted upon by water, either in the cold or at a red heat.

The student might continue the experiments with other metals. He would find, for example, that potassium would behave like sodium, zinc like iron, tin like copper, and so on.

36. Composition of Water.—We have seen in Exps. 60 and 61 that iron and magnesium react with steam with liberation of hydrogen and formation of the same substances which are obtained when these metals are burnt in oxygen, *i.e.* the oxides of iron and magnesium. These

[1] Reserve this residue for a later experiment.

results can readily be explained if we assume that *water is a compound of hydrogen and oxygen*, for the changes which have taken place can then be represented thus:—

Water (composed of **hydrogen** and **oxygen**) acted on by a **metal** yields **hydrogen** and the **oxide of the metal** (composed of the **metal** and **oxygen**).

If this is the true explanation, then we should be able to obtain water by the combination of hydrogen and oxygen.

Before attempting to do this, we will investigate a more convenient method for the preparation of hydrogen in quantity, and will study its properties more fully.

37. Preparation of Hydrogen.—

Exp. 63.—Introduce into a half-litre flask, fitted with safety funnel and delivery tube as shown in Fig. 23, 10 gm. of zinc, and add 180 c.c. of dilute sulphuric acid.[1] Bubbles of gas will be observed to rise at the zinc, and the gas passing out of the delivery tube may be collected in gas jars by displacement of water as shown

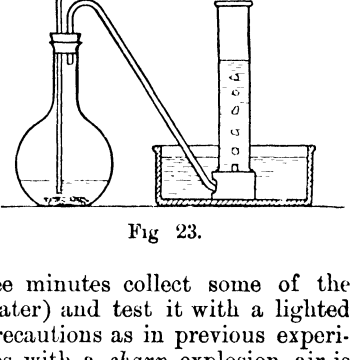


Fig 23.

The first bubbles of gas, however, which rise from the delivery tube consist of air which must be allowed to escape. After two or three minutes collect some of the gas in a test-tube (over water) and test it with a lighted match (taking the same precautions as in previous experiments). If the gas ignites with a *sharp* explosion, air is still mixed with the hydrogen. Wait a short time, collect

[1] Made by pouring sulphuric acid ("oil of vitriol") slowly with gentle agitation into eight or ten times its volume of cold water. The acid is said to be "diluted" with water.

another tube of the gas, and test again. When the gas ignites quite quietly, or with only a slight "pop," you may proceed to fill the jars. *This precaution is very important* owing to the *very explosive nature of a mixture of hydrogen and air.*

38. Properties of Hydrogen.—Let us first show that the gas *is hydrogen* by applying the tests we have already used in previous experiments.

Exp. 64.—Proceed to test two cylinders of the gas as you did in Exp. 61. You will find that the results are the same, namely (1) the gas burns with a pale blue nearly non-luminous flame and the burning takes place only at the mouth of the jar, *i.e.* where it has access to air; (2) the gas is lighter than air; (3) a dry jar becomes misty; (4) moisture is formed when the gas burns in it: the gas is therefore *hydrogen*

Let us now proceed to further investigate the properties of hydrogen.

Exp. 65.—Examine a jar of the gas for colour, taste, and smell.

Hydrogen when pure is colourless, odourless, and tasteless, but when ordinary zinc is used in its preparation it has an unpleasant smell. This is due to presence of small quantities of compounds of hydrogen and carbon in the gas, the carbon being present as impurity in the zinc.

Exp. 66.—Plunge a lighted taper into a jar of the gas, keeping it mouth downwards. The gas burns, but the taper is extinguished. Withdraw the taper; it relights as it passes through the flame of the burning hydrogen. Repeat the experiment with a long splint of wood; the result is similar.

We see then that hydrogen is a *non-supporter of the burning of ordinary combustibles.*

Exp. 67.—Invert a cylinder about two-thirds full of hydrogen (the rest being water) in a trough of water. Mark the level of the liquid in the cylinder. After some time examine it again. There is no appreciable change in level, showing that if hydrogen dissolves in water at all its solubility is only very small

39. Formation of Water by burning Hydrogen in Air.—

Exp. 68.—Take the hydrogen apparatus used above, replacing the long delivery tube by a shorter one leading to one arm of a U-tube containing calcium chloride.

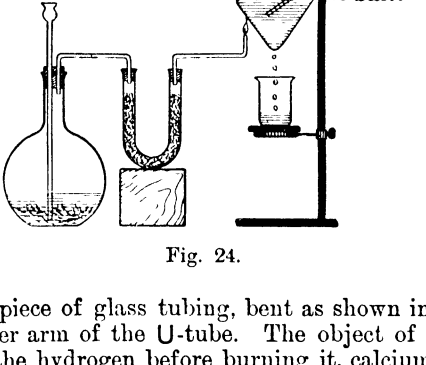


Fig. 24.

Attach a piece of glass tubing, bent as shown in Fig. 24, to the other arm of the U-tube. The object of this tube is to dry the hydrogen before burning it, calcium chloride being a substance which very readily absorbs moisture.[1] Place some granulated zinc (about 10 grams) in the flask, and add a little dilute sulphuric acid. A gentle effervescence of hydrogen will take place, and the air will be driven out. Before we light the hydrogen we must be sure that all the air has been expelled from the apparatus.

[1] It is obvious that the hydrogen must be *dry*, or the experiment does not prove that the water which collects in the beaker has been produced by the burning of the hydrogen.

After the action has proceeded for a few minutes push a small test-tube as far as possible over the end of the delivery tube and keep it there for half a minute. Now remove it, and keeping it mouth downwards at once place your thumb over the mouth, bring the tube to the flame of a Bunsen burner, and remove the thumb. If the gas ignites with more than a slight "pop" you must repeat the test till it is satisfactory.

While you are waiting for the air to be driven out of the apparatus, fit up a flask with two delivery tubes, one reaching to the bottom of the flask, the other just below the cork, and support it by means of a retort-stand and clamp as shown in the diagram. Connect the delivery tube which reaches to the bottom of the flask to a tap by means of rubber tubing; also attach a piece of rubber tubing to the short delivery tube and allow the loose end of it to dip into a sink. Turn on the tap; water will flow into the flask, fill it, and then overflow into the sink. Leave the tap turned on slightly so that a slow stream of water flows through the flask.

When you have lighted the hydrogen jet place the flask in position over it as shown in Fig. 24; also place a beaker in the position indicated. Almost immediately moisture appears to be forming on the bottom of the flask, and soon drops of liquid trickle down and fall into the beaker. [The reason for keeping a stream of cold water running through the flask will now be obvious. It keeps the flask cool and aids the condensation of the liquid formed by the burning of the hydrogen.]

What is this liquid? It looks like water. Examine its properties and you will find that (1) it is colourless; (2) it has no smell; (3) it has no taste; (4) it does not burn; (5) it leaves no residue on evaporation; (6) it has no action on litmus papers; (7) it restores the blue colour to anhydrous copper sulphate. Hence you may conclude that it is *water*.

The density, freezing point, and boiling point of the liquid might be determined as further evidence. It would be found that 1 c.c. of liquid weighs 1 gram, *i.e.* the

[1] Strictly speaking this is only true at 4° C.

density is 1, and that the freezing and boiling points are 0° C. and 100° C. respectively; these agree with the values for water.

When hydrogen, then, burns in ordinary air it forms water; it was called *hydrogen* (water-former) on this account. The hydrogen must have combined with either the oxygen or the nitrogen of the air or with both. From our previous experiments (see § 36), we know that it must be with the oxygen *only*. The anticipation made in § 36 that we should be able to obtain water by the combination of hydrogen and oxygen has therefore been realised. We can now understand why the vessels in which hydrogen was burnt in Exps. 57, etc., became *misty*; it was because the moisture formed during the combustion was deposited on them.

The experiment described in the following paragraph shows how the combination of hydrogen and oxygen may be brought about in a different way.

40. Formation of Water by the Action of Hydrogen on Oxides.—

* **Exp. 69.**—Take a piece of infusible glass tubing about 12 inches long, and half an inch bore, and put into it a

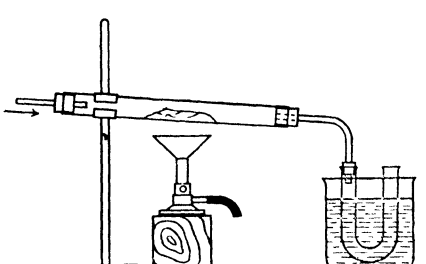


Fig. 25.

layer of dry copper oxide. Support the tube in a slightly inclined position as shown in Fig. 25, and connect the

higher end with a supply of dry hydrogen (prepared and dried as in Exp. 68). Connect the other end with a U-tube partly immersed in a beaker of water. First the oxide is not heated and there is no apparent change; then it is heated[1] strongly, using a flat-flame burner, when it changes gradually into red metallic copper and a liquid collects in the U-tube which can be proved to be water by the usual tests.

When the experiment is finished allow the tube to cool before discontinuing the current of hydrogen (to prevent an explosion).

* **Exp. 70.**—Now repeat Exp. 69, replacing the copper oxide by the oxidised iron nails which you obtained in Exp. 61. Again water collects in the U-tube. When no more comes over allow the tube to cool, disconnect from the hydrogen apparatus, and turn out the contents. The nails have regained the appearance of metallic iron; in fact they have been reconverted into iron.

The experiment may be repeated, using litharge (oxide of lead) or red precipitate (oxide of mercury). In the former case beads of metallic lead collect in the tube and in the latter a mirror of mercury is produced, whilst in both water collects in the U-tube.

We see, then, that when hydrogen is passed over some heated metallic oxides it takes up oxygen, forming water, and leaves behind the metal.

41. Reversibility of Chemical Action.—If you compare Exps. 61 and 70 you will see that the action which takes place in the latter is just the reverse of that which takes place in the former. In Exp 61 we have

Water (as steam) reacts with **iron** to form **hydrogen** and **oxide of iron,**

[1] The same precautions are necessary here as when the hydrogen was caused to burn as a jet; that is, the issuing gas must be tested to see if it is free from air before the tube is heated. The apparatus, too, should be made *air-tight*. This latter precaution is *very important*.

whilst in Exp. 70 we have

Hydrogen reacts with **oxide of iron** to form **water** and **iron.**

This is an example of a very common type of chemical action, namely, a *reversible chemical action, i.e.* a change which under certain conditions proceeds in one direction and under other conditions proceeds in the opposite direction. The condition which decides the course of the reaction in the particular case under consideration is the relative proportions of steam and hydrogen present.

In Exp. 61 steam is in large excess of hydrogen, and so the iron is converted into oxide of iron; the hydrogen as it is formed is at once swept away by the current of steam, and so steam remains in excess, and ultimately all the iron is changed into oxide of iron. In Exp. 70, on the other hand, hydrogen is in large excess of steam, and consequently the oxide of iron is converted into iron; the steam formed is carried away at once by the current of hydrogen, and so hydrogen remains in excess, and ultimately all the oxide of iron is changed into iron.

42. Oxidation and Reduction. — The *addition of oxygen* to a substance is called *oxidation.*[1] Thus when hydrogen burns in air, when iron rusts, or when lead is heated in air, oxygen is taken up and the hydrogen, iron, and lead undergo oxidation.

On the other hand the *removal of oxygen* from a substance is called *reduction.*[1] The removal of oxygen from heated metallic oxides by hydrogen as in Exps. 69, 70 is an example of reduction, the hydrogen *reducing* the oxide to the metal. But the hydrogen has taken up the oxygen of the oxide, and has therefore undergone *oxidation,* i.e. the processes of reduction and oxidation have taken place *simultaneously,* and we may look upon changes such as these from two points of view: (1) as the reduction of the metallic oxide by hydrogen, and (2) as the oxidation of the hydrogen by the metallic oxide.

[1] Extended meanings are, however, associated with these terms which will be discussed later.

If you refer back to Exp. 12 you will see that charcoal also is able to effect reduction or removal of oxygen, and you will understand the use of coal or coke in the smelting of tin, copper, or other metals from their ores. Hydrogen and carbon are spoken of as *reducing agents.*

43. Decomposition of Water by the Electric Current—Composition of Water by Volume.—Let us now investigate an entirely different method of determining the constituents of water

It will be instructive to examine first a peculiar phenomenon which appears when metals are placed in dilute acid.

* **Exp. 71.** *To produce an Electric Current.*—For this purpose you will require thin clean plates of copper and zinc,[1] say about 15 cm. long and 10 cm. wide. Dip these separately for a moment into a beaker containing dilute sulphuric acid, and note that the copper plate is unaffected, but the bubbles of gas rise from the zinc plate. Now withdraw the zinc plate, and dipping it in still weaker acid, rub the surface with a little mercury until it shows a bright lustre. The upper part of the plate which stood above the level of the acid in the beaker need not be covered with mercury. Now again dip both the plates in the beaker containing acid: nothing happens at either plate. Bring the upper edges of the two plates together: bubbles of gas rise from the *copper* plate. Separate the plates and bring them together again several times: the action ceases on separation but commences again immediately the plates touch.

Now connect copper wires by binding screws to the upper edges of the two plates.

Observe (1) that when you keep the wires apart there is no evidence of action going on in the beaker, but that when you bring the ends of the wires together the action is set up just as it was when the edges of the plates were brought together, and that now a small spark appears when the wires touch. (2) That if you bring a small compass-needle just below the wire, and then bring the

[1] Plates of other metals may be also tried in the same way.

ends into contact, the needle will be turned aside each time you make contact.

If you try to do either of these things simply with two pieces of copper wire, you will then be convinced that there is something present in the wires owing to their attachment to the metal plates in the acid. Metal plates so arranged are called a *voltaic cell*. By fitting up several of them, and joining the zinc in one cell to the copper in the next by copper wire, and finally attaching two lengths of copper wire, one to the copper in the first cell, and the other to the zinc in the last cell, you may fit up a *voltaic battery*, and produce stronger effects than you can do with one cell.

There is a *third* effect that may be shown to accompany the passage of the electric current along the wires.

* **Exp. 72.**—Procure two pieces of platinum foil about 5 cm. long and 2 cm. broad. Prick a row of holes down the middle of each and thread the terminal ends of the wires through them. Take now a small beaker of distilled water and dip into it the two platinum plates (they are called *electrodes*): nothing happens. Add a few drops of dilute sulphuric acid to the water: bubbles of gas rise freely from both electrodes.

The current of electricity is unable to pass through pure water and make itself felt, but it can pass through acidulated water. By a suitable arrangement the gases evolved may be collected and examined.

* **Exp. 73.**—Take a large wide-mouthed bottle and paste a thin strip of paper round the side of it about half-way up, arranging so that the two ends meet and form a circle round the bottle. With a sharp file scratch a line just above the strip of paper (which enables you to keep the line straight). When the scratch forms a complete circle take a glass rod, heat the end red-hot in a Bunsen flame, and touch the scratch with it. The bottle will break into two halves. Take the upper half and rub the rough edge with coarse emery paper till it is smooth.

Now take two pieces of platinum wire about 15 cm. long and attach them to two pieces of platinum foil of the size mentioned in Exp. 72 (in the way described there). Fuse the wires into pieces of narrow glass tubing about 8 cm. long, as shown in Fig. 26. Procure a two-holed rubber cork which fits the bottle, push the glass tubes into it, and insert the cork (see diagram).

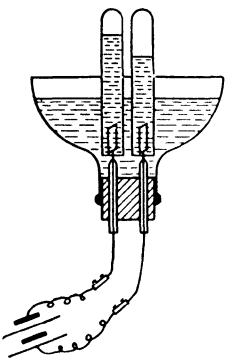


Fig. 26.

Now pour water, to which a little dilute sulphuric acid has been added, into the bottle till the electrodes are covered; also fill two test-tubes with the same liquid and invert them over the electrodes. Connect the wires by binding screws with the leads from a battery of 3 or 4 Grove's cells. As soon as the connection is made gas is seen to rise from the electrodes and collect in the tubes. Further, the volume of gas collecting over the electrode connected with the zinc plate of the battery (called the *negative pole*) will be found to be twice that collecting over the electrode connected with the platinum plate (which corresponds to the copper plate of our simple cell and is called the *positive pole*). Examine the gases with a lighted splint of wood: you will find that the gas collected in larger quantity is *hydrogen*, that in smaller quantity *oxygen*.

Subject to the possibility that it is something in the sulphuric acid with which we are at present insufficiently acquainted that gives us the hydrogen and oxygen, we should conclude that water yields by its decomposition hydrogen and oxygen, and further that it is composed of these two elements *in the proportion of two to one by volume*.

* **Exp. 74.**—Repeat Exp. 73, using first hydrochloric acid and then sodium sulphate in place of sulphuric acid:

you will find that in both these cases hydrogen and oxygen collect in the proportion of two to one by volume, *i.e.* the result is the same as when sulphuric acid was used. Now the only substance present *in all three cases* was *water*, so that we are justified in saying that it is from the water itself that the hydrogen and oxygen are derived.

We may, however, completely remove all doubt which is thrown on the conclusions we have drawn from the results of Exps. 73, 74, owing to the presence of substances other than water, by using a different method for determining the composition of water. In this method measured volumes of hydrogen and oxygen are confined in a closed tube, an electric spark is passed through the mixture which causes combination to take place with formation of water, and then the volume of the residual gas is measured and its nature determined.

† **Exp. 75.**—Take a U-shaped graduated tube called a *eudiometer*, with one end closed and with two platinum wires sealed into the closed end. Fill the tube with water. Take a piece of indiarubber tube a few inches longer than one limb of the U-tube and attach to one end the delivery tube of an apparatus giving off hydrogen. When all air has been expelled from the hydrogen apparatus and rubber tube (test as usual) lower the tube into the open limb until about 10 c.c. of the gas has passed round the bend into the closed limb (Fig. 27). Remove the rubber tube, level the water in the two limbs by pouring water out of the open limb and then adding a little more if necessary, and measure the volume of hydrogen which is now at atmospheric pressure; let us assume that it measures 10 c.c.

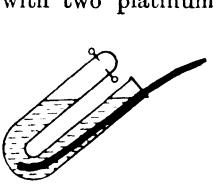


Fig. 27.

Now repeat the process, using oxygen instead of hydrogen, and run the gas in until about twice the hydrogen

† See Preface as to Experiments marked by this symbol (†).

volume has been added. Level and read the volume as before (say it measures 28 c.c.). Fill the open tube with water to within about 2 cm. of the top, and either cork it tightly or hold it with the thumb firmly pressed on the open end. By means of a battery and induction coil or an electric gas-lighter pass a spark between the platinum wires, keeping the thumb pressed on the open end or the cork. After the explosion, remove the thumb or cork carefully, level the columns, and measure the residue again (say it measures 13 c.c.). Fill the open limb with water again, close it with the thumb, decant the residual gas into the open tube, and test it with a glowing splint.

We note that the residue consists of oxygen, so that the total loss of volume (or contraction) is equal to the volume of the hydrogen (which has all been used up) together with the volume of that part of the oxygen which has been used. Thus:—

Hydrogen used = 10 c.c.

Oxygen used = contraction − volume of hydrogen
= (28 − 13) c.c. − 10 c.c.
= 5 c.c

That is 10 c.c. of hydrogen have combined with 5 c.c of oxygen to form water, or the ratio of hydrogen to oxygen by volume is 2 : 1.

44. Analysis and Synthesis.—We have now determined the quantitative composition of water in two ways: in Exps. 73, 74 by *decomposing* it into its constituent elements, and in Exp 75 by *combining* the constituent elements. The first process is an example of the *analytical* method of determining the composition of a chemical compound, *i.e.* of *analysis*, whilst the second is an example of the *synthetical* method, *i.e.* of *synthesis*. These terms may be defined as follows:—

Analysis is the determination of the composition of a chemical compound by breaking it up into its constituents.

Synthesis is the determination of the composition of a compound by building it up from its constituents

QUESTIONS.—CHAPTER IV.

1. What happens when dilute sulphuric acid is poured upon zinc? How would you collect the gas given off? Sketch the apparatus you would use. Describe experiments to show that it is a very light substance.

2. How would you prove conclusively that when hydrogen burns in air water is formed?

3 Describe all that you may see when a piece of sodium is thrown on water in a dish. How does the water differ, after the sodium has disappeared, from pure water?

4. What metals are known to you capable of decomposing water? How do they act respectively? Sketch the apparatus that would be required to collect the hydrogen evolved by the use of any one of these metals

5. How has the composition of water by volume been established analytically and synthetically?

6 Describe how you would proceed to prepare water from a metallic oxide by the action of hydrogen. Sketch the necessary apparatus.

7. What do you understand by the terms *oxidation* and *reduction*? Give examples of these processes.

8. What do you understand by *reversibility of chemical action*? Describe an experiment which illustrates the phenomenon.

CHAPTER V.

CHALK—CARBON DIOXIDE—LIME.

45. Properties of Chalk.—We shall now carry out an investigation on a naturally occurring substance with which every one is familiar, namely, *chalk*. You know that it is a fairly soft substance, for it can be scratched with the finger-nail and will even soil the hands Also, we have learnt (Exp 49) that it is practically insoluble in water.

Let us now proceed to examine the effect of heat on it.

Action of Heat on Chalk.—

* **Exp. 76.**—Place a little powdered chalk in a crucible and weigh the whole. Now heat strongly with a blowpipe flame[1] for quite a long time. Allow to cool, and weigh again: it will now weigh less than before. Repeat the heating and weighing till there is no change in weight. Be careful to direct the flame against the bottom of the crucible.

Since there is a loss of weight, it follows that the residual substance cannot be the same as the original chalk, though it very closely resembles it in appearance. Something must have been lost. Let us see if we can discover what it is.

[1] Use a gas blowpipe and foot-blower. A gas blowpipe consists of two tubes—one within the other. Through the inner tube air is forced by the blower, whilst gas is admitted to the annular space. Light the gas before starting the current of air.

*** Exp. 77.**—Place some chalk in a hard glass test-tube and heat it over a blowpipe flame, keeping the thumb loosely on the open end. When the chalk is red-hot dip a glass rod or quill tube in clear lime-water and lower it into the tube without touching the sides (Fig. 28).

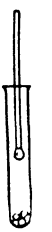


Fig 28.

The lime-water becomes milky, showing that a gas is present in the tube which was not there before, and it must have been the loss of this gas from chalk which caused the reduction in weight in Exp. 76. The gas is *carbon dioxide*, *i.e.* it is the same gas as that contained in soda water; the formation of a milkiness with lime-water forms a characteristic test for carbon dioxide.

Let us now examine the residue remaining in the crucible.

*** Exp. 78.**—Pour a few drops of water on to a portion of the residue in the crucible. The water disappears and the crucible becomes hot; also probably a little steam will be formed. Now pour a little water on some chalk: nothing happens. Next touch the powder in the crucible with a piece of moist red litmus paper. The colour changes to blue, showing that an alkali is present. Repeat the experiment with chalk: again nothing happens

Now break off a small piece from a lump of freshly prepared quicklime such as is used by builders, powder it, and repeat the above experiments with it. The results are the same as when the residue in the crucible was used. This residue is, in fact, *quicklime* (calcium oxide).

Chalk is, then, composed of two substances—a colourless gas, carbon dioxide, and a white solid, quicklime; when chalk is strongly heated the carbon dioxide is evolved and the quicklime remains.

This explains the manufacture of lime, and also the poisonous nature of the fumes which escape from lime kilns; for the presence of much carbon dioxide in the air is fatal to animals. Vast quantities of this gas are poured into the air in volcanic districts, being derived from the limestone rock similarly decomposed by the hot lava. Since it

is a heavy gas, on its escape through the cracks and joints of rock it lies in hollows and flows along the surface of the ground until dissipated by the wind or the slower process of diffusion (see § 79). Certain neighbourhoods are thus rendered unhealthy, and some even deadly, like the far-famed Guevo Upas or Poison Valley of Java. The Grotto del Cane (Dog's Grotto) near Naples owes its fame to the same cause. A dog entering the grotto is suffocated, while a man, being taller, escapes.

Limestone, chalk, and marble, egg and other shells are all made of the same chemical compound (the chemical name for which is *calcium carbonate*), and all break up in a similar manner on heating.

46. Action of Acids on Chalk.—

Exp. 79.—Into a test-tube put a small quantity of chalk and pour on it a little dilute hydrochloric acid. A brisk effervescence at once takes place, showing that a gas is escaping. Introduce a drop of lime-water into the tube on the end of a glass rod: the lime-water immediately becomes milky, showing that the gas is carbon dioxide. Repeat the experiment, using other dilute acids, *e.g.* sulphuric and nitric; also use limestone in place of chalk: the result is in all cases the same.

* **Exp. 80.** *Action of Acids on Lime.*—Now add a little dilute hydrochloric acid to the remainder of the residue obtained in Exp. 76. If the experiment was performed properly, the residue will dissolve in the acid, but *without effervescence*, showing that all the chalk has been decomposed and that lime does not yield carbon dioxide when treated with an acid.

47. Preparation of Carbon Dioxide.—The action of acids on chalk, limestone or, better still, marble affords a ready method of preparing carbon dioxide in quantity. Let us use it for this purpose, and then proceed to examine the properties of the gas more fully.

Exp. 81.—Put some lumps of limestone or chalk into a flask of suitable capacity—say half a litre. Fit with a thistle funnel reaching nearly to the bottom, and a delivery tube bent twice at right angles. Connect this with a Woulfe's bottle containing a little water so that the tube dips well into the liquid The water will dissolve any hydrochloric acid (which is itself a very soluble gas) that may accompany the dioxide (see Fig. 29). Convey the "washed" gas to the bottom of the collecting jars; while filling cover their mouths with a piece of cardboard in which a slot has been cut to enable it to slide over the tube (Fig. 30). Pour in sufficient water to cover the limestone; then add through the funnel some strong hydrochloric acid. Collect several jars of the gas and allow the rest to bubble through a little distilled water.

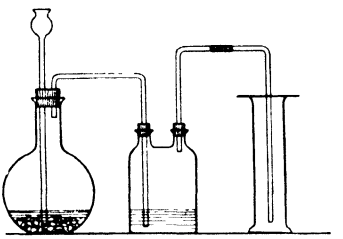


Fig. 29.

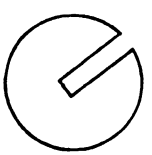


Fig. 30.

To see when each jar is full, hold a lighted match near its mouth, when the heavy overflowing gas will extinguish the flame.

The method of collecting a gas which we have just used and which depends on its density is known as *collection by displacement*. If we look at the matter from the point of view of the upward movement of the air, we may call it upward displacement, but if from that of the downward movement of the gas, then it may be called downward displacement: it is called *collection by downward displacement* by the majority of chemists.

48. Properties of Carbon Dioxide.—

Exp. 82.—Remove the cover from a jar of the gas, note that it has a slightly pungent smell and taste reminding one of soda-water. You will already have observed that the gas is colourless.

Exp. 83.—Stand a beaker on one scale-pan of a rough balance and counterpoise it by placing weights in the other scale-pan. Take a jar of carbon dioxide, remove the cover, and hold the jar as though you were pouring a liquid out of the jar into the beaker. The pan containing the beaker falls.

This shows that carbon dioxide is *heavier than air* and has been *poured into the* beaker, displacing the air. The high density of the gas may also be shown by the following experiment.

Exp. 84.—Set a wide bell-jar in an inverted position. Sprinkle a small handful of powdered chalk or "whiting" in the bottom and pour upon it some dilute hydrochloric acid. A considerable amount of the gas is quickly evolved, and an ordinary soap-bubble dropped into the jar will float where the gas and air meet.

Exp. 85.—Invert a jar of the gas in a trough of water and remove the cover. The water gradually rises in the jar and ultimately fills it. Invert another jar in a solution of caustic soda. The water rises *rapidly* in the jar and very soon fills it.

From this experiment we infer that carbon dioxide is soluble in water, but much more so in a solution of caustic soda.

Exp. 86.—Introduce a lighted wood splint into a jar of the gas. It is extinguished and the gas does not burn.

49. Composition of Carbon Dioxide.—

Exp. 87.—Wire a bit of charcoal to the end of a deflagrating spoon. Make it red-hot, then remove it from the flame and watch it. It soon ceases to glow. Now

make it red-hot again and introduce it into a small jar of oxygen. It continues to glow and gradually disappears, just as it did in air when the external heating was kept up as in Exp. 10.

Now pour a little lime-water into the jar and shake up The lime-water becomes milky, showing that carbon dioxide has been formed. Also burn charcoal in air as described in Exp. 10. Prove that carbon dioxide is being evolved by holding a glass rod with a drop of lime-water on the end in the mouth of the crucible.

We may conclude from this experiment that charcoal burns more readily in oxygen than in air, but that in both cases the charcoal has combined with oxygen to form carbon dioxide. Now charcoal has been proved to be an element and its chemical name is *carbon*, so that carbon dioxide is a *chemical compound of the elements carbon and oxygen*. This being the case it should be possible to recover the carbon from the gas if we can find a substance which has a stronger attraction for oxygen than carbon. Such a substance is metallic magnesium.

Exp. 88. *To extract the carbon from the dioxide.*—Ignite a strip of magnesium ribbon tied to a deflagrating spoon, and plunge it into the gas. The metal continues to burn, and, on examination of the solid formed, white oxide of magnesium will be found together with black specks of carbon.

Now pour a little dilute hydrochloric acid into the jar. The oxide of magnesium dissolves, but the black specks remain floating in the liquid. They should be filtered off, dried, and then heated in a crucible as in Exp. 10, when they will be found to burn away just as charcoal did.

On the other hand most metals have less attraction for oxygen than carbon. We have had an example of this in Exp. 12, where carbon removed oxygen from litharge, forming carbon dioxide and leaving metallic lead.

We have now proved the composition of carbon dioxide, both by *synthesis* and *analysis*, for in Exp. 87 we obtained it by the combination of its constituent elements, and in

Exp. 88 we broke it up into its elements (one of which, however—the oxygen—at once combined with magnesium, for which it has a great attraction).

50. Formation of Carbon Dioxide by burning Wood, Coal, etc.—Carbon dioxide is also formed when substances such as wood, coal, paraffin, etc., which contain carbon in large quantities, are burnt.

Exp. 89.—Fasten a match on to a piece of wire, ignite it, and lower it into a small gas-jar. When the flame goes out prove the presence of carbon dioxide in the jar by means of lime-water. Similar experiments may be performed with a piece of candle, etc.

51. Formation of Carbon Dioxide by Living Organisms.—

Animals —The food material of animals—such as meat, vegetable tissue, sugar, etc. — contains a considerable quantity of carbon. As the food undergoes decomposition in an animal's body, much of the carbon unites with oxygen in its blood derived from the air through the medium of its lungs. Carbon dioxide is thus formed, and is returned to the air through the same medium Its presence may be readily detected in expired breath

Exp. 90.—Introduce a little lime-water into a beaker, and blow through a glass tube[1] dipping into the liquid. The lime-water soon becomes milky.

Plants.—(1) *Respiration* in plants is a similar, but slower, oxidation process. The stored starch is broken up, and carbon dioxide is expelled into the air as a result. This process is not confined to the green parts of plants, and it goes on by night as well as by day; but it is only under certain special conditions that the process can be detected easily. Germinating seeds, however, show it well.

[1] The end of the tube which you place in your mouth should have been heated in a Bunsen burner till the edges of the glass soften. They will then be smooth when cold.

* **Exp. 91.**—Suspend a thermometer with its bulb in some wheat, oats, peas, etc., placed in a funnel and kept damp. They presently germinate or "sprout," and will be found to be at a higher temperature than the surrounding air.

The rise in temperature is evidence that chemical change is taking place.

* **Exp. 92.**—Place a small vessel containing lime-water amongst some of the germinating seeds when transferred to a beaker. Cover the beaker with a glass plate. The lime-water speedily becomes milky.

This experiment proves that during the chemical change carbon dioxide is formed.

(2) In *fermentation* such as occurs in breweries, minute unicellular plants which form the yeast contain in their cells a substance which decomposes dissolved sugar. The break up of the sugar gives rise to large quantities of carbon dioxide as well as alcohol.

Exp. 93.—Half fill a large flask with water moderately sweetened with common brown sugar. Add some brewer's yeast; then fit the flask with a cork and a delivery tube leading into some lime-water, and stand it in a warm place. Carbon dioxide will be slowly expelled and give its characteristic reaction.

52. Further experiments with Lime.—

Exp. 94.—Weigh a lump of quicklime in a porcelain dish. Pour water on it a little at a time. The lump gradually falls to a white powder which, if you do not add too much water, remains quite dry; note the increase in *bulk*. Reweigh, and note that there is also an increase in *weight*.

The lime has combined chemically with the water to form **slaked lime**; this explains the increase in weight.

Exp. 95.—Shake up the slaked lime with water in a bottle provided with a stopper. Allow the mixture to stand till the liquid above the solid is *quite* clear. Carefully pour off a portion of the clear liquid into an evaporating basin. Test it with litmus: it is alkaline. Evaporate it to dryness: a small white residue remains.

Slaked lime is, then, somewhat soluble in water, forming an alkaline solution. The solution is known as *lime-water.*

Exp. 96.—Pass carbon dioxide (prepared as in Exp. 81) into some lime-water. A white precipitate is formed Filter, remove the precipitate to a test-tube, and add a little dilute hydrochloric acid. The precipitate dissolves with effervescence, and you can show in the ordinary way (namely, by the lime-water test) that the gas evolved is carbon dioxide.

The precipitate is calcium carbonate, so that you have now not only succeeded in decomposing calcium carbonate (chalk) into its constituents, quicklime and carbon dioxide, but have also built it up again from them, though not directly, for the quicklime was first combined with water to form slaked lime.

You will naturally ask yourself whether quicklime and carbon dioxide will combine directly to form calcium carbonate. Let us try to answer the question by means of an experiment.

Exp. 97.—Place a little powdered quicklime in the bottom of a gas-jar and fill it with carbon dioxide prepared as in Exp. 81. Cover the jar with a glass plate and leave for a day.

Now transfer the powder to a test-tube and pour a little dilute hydrochloric acid on to it. A gas is evolved with effervescence, and you can prove in the usual way that it is carbon dioxide.

This shows that the lime and carbon dioxide have united (at any rate in part) with formation of calcium carbonate.

QUESTIONS.—CHAPTER V.

1. Describe how you would prepare and collect a few jars of carbon dioxide. Sketch the apparatus you would use, and explain the use of each part. What experiments would you perform in order to illustrate the chief properties of the gas?

2. In what different ways can carbon dioxide be obtained?

3. Describe how you would proceed to investigate the action of heat on chalk.

4. Describe an experiment by which you could obtain free carbon from carbon dioxide.

5. When chalk is strongly heated it is converted into lime What experiments would you make to show that this change has taken place?

6. State exactly what you would observe on gradually adding (1) dilute hydrochloric acid, (2) water, to chalk and quicklime respectively. Explain the changes which take place as far as you can.

7. Describe how you would proceed to prove by experiment that the white powder formed when carbon dioxide is passed into lime-water is chemically identical with chalk.

CHAPTER VI.

ACIDS, SALTS, BASES

53. Properties of Acids.—

(*a*) *Sourness.—*

Exp. 98.—Introduce *one drop* of dilute[1] hydrochloric acid (*spirit of salt*) and one drop of dilute sulphuric acid respectively into clean test-tubes and nearly fill the tubes with water. Shake up and then taste the liquids. They are sour.

Vinegar also is sour. *Sourness* is a characteristic property of a large class of bodies called *acids*.

(*b*) *Action on Litmus.—*

Exp. 99.—Pour a little dilute hydrochloric acid and a little dilute sulphuric acid into separate beakers and dip pieces of blue litmus paper into them. The colour changes to *bright red*.

(*c*) *Action on Metals.—*

Exp. 100.—Fill a test-tube about one-third full of dilute sulphuric acid and introduce some small pieces of magnesium ribbon. You will notice that there is a violent effervescence of gas, accompanied by the gradual disappearance of the metal, and that the tube soon becomes warm.

[1] "Dilute" hydrochloric acid is obtained by adding two or three volumes of water to one volume of the strong acid.

After a short time apply a light to the mouth of the tube. The gas ignites with a slight explosion and burns with an almost non-luminous flame. It is *hydrogen*.

If the effervescence ceases before all the metal has dissolved add a little more acid. When solution is complete allow the liquid to stand for some time. (Filter it if it is not clear.) Colourless crystals may separate out. If they do not, evaporate the liquid to small bulk in a porcelain dish and allow to cool, when crystals will form.

Exp. 101.—Now repeat Exp. 100, using first granulated zinc and then iron filings. The results will be quite similar to those obtained in the case of magnesium. You will find, however, that the gas evolved in both cases has a rather unpleasant odour, and that some small black particles remain floating about in the liquid after the metal has disappeared and ultimately settle down. In the case of iron the black particles consist of carbon, present as impurity in the metal; the unpleasant odour of the gas is due (chiefly) to the presence of compounds of carbon and hydrogen produced by the combination of carbon derived from the metal with a portion of the hydrogen generated. The black insoluble particles remaining when zinc is used consist of a mixture of carbon and lead. The explanation of the unpleasant smell is the same as that given in the case of iron.

You will also observe one other difference when iron is the metal used, namely that the crystals which form are *pale green*, not colourless.

Exp. 102.—Now repeat Exps. 100, 101, using dilute hydrochloric acid in place of dilute sulphuric acid. The results will be similar, except that it is much more difficult to obtain crystals, and in the case of the zinc only a thick white treacly mass remains.

We see then from Exps. 100-102 that acids have a third characteristic, namely that they act upon certain metals such as magnesium, zinc, and iron with liberation of hydrogen and formation of crystalline substances.

54. Neutralisation of Acids by Metals.—

Exp. 103.—Introduce a little sulphuric acid into a porcelain dish and add some magnesium ribbon. If all the ribbon dissolves add a little more so that some does remain undissolved when the action has ceased. Now test the solution which remains with (1) blue litmus paper, (2) red litmus paper; neither is affected, *i.e.* the liquid is now neutral to litmus. Repeat the experiment, using hydrochloric acid in place of sulphuric; the result is the same

Similar experiments, using other acids, *e.g.* nitric and acetic, give similar results.

We see therefore that when the metal magnesium acts on an acid it removes one of the characteristic properties of the acid, namely that of turning blue litmus red: the metal is said to have *neutralised* the acid, since the resulting liquid is *neutral to litmus.*

A few other metals, *e.g.* sodium and calcium, are able to neutralise[1] acids completely, but in the majority of cases (*e g.* when zinc or iron is the metal used) the neutralisation is only partial, the liquid being still able to turn blue litmus paper red, even when excess of the metal has been added and all action has ceased. The explanation of this is given later.

55. Salts.—The crystalline substances produced by the action of metals on acids are termed *salts.* We must now investigate their nature more closely.

Exp. 104.—Introduce about 5 grams of iron filings into a small flask, and add dilute sulphuric acid a little at a time till they are dissolved. Filter the liquid (if any crystals have separated, warm the flask to redissolve them before filtering), and collect the filtrate in an evaporating dish. Evaporate to small bulk and allow to crystallise.

[1] In the case of metals such as sodium and calcium, however, the liquid turns red litmus blue if excess of the metal is added, since the metal decomposes water with formation of an alkali (see Exp. 57).

Pour off the liquid from the green crystals which separate, dry them between blotting-paper, and introduce them into a porcelain crucible. Heat the crucible gently at first, then more strongly by means of a Bunsen burner in a *fume cupboard*. The crystals soon begin to lose water (of crystallisation), and a white residue is formed. As the heating is continued pungent acid fumes are evolved, and the residue becomes first yellow and then red. When no more acid fumes are produced, even when the crucible becomes red-hot, discontinue the heating

Crush up the powdery residue when cold, introduce it into a piece of hard glass tubing, and proceed to heat it in a current of hydrogen as in Exp. 69. The powder will turn grey, and water (test as usual) will collect in the U-tube. When the change appears to be complete allow the tube to cool, and then turn out the residue and examine it. Bring a magnet near it. What do you observe? Introduce a little of it into a test-tube, and add dilute sulphuric acid. What is the result? The appearance of the powder, and the facts that it is attracted by a magnet and effervesces with dilute sulphuric acid tell you that it is metallic iron. [The fact that water was also formed shows that the red powder was an *oxide of iron* which has been reduced to the metal by hydrogen.]

We have succeeded then in recovering metallic iron from the green crystals which were produced by the action of iron on dilute sulphuric acid, and we have consequently traced what became of the metal. The metals can also be recovered from other salts, though not always as easily as in the case we have investigated. We may therefore conclude that when an acid acts on a metal the *metal* forms *part of the crystalline salt* produced

56. Nature of Acids.—We must now inquire what it is which imparts to an acid its characteristic properties, *e.g.* its action on litmus. Now we have seen that when a metal is acted on by an acid hydrogen is evolved and a crystalline compound (a salt) is formed which contains the metal and which often fails to turn blue litmus red when in solution.

These results are readily explained if we make the following assumptions:—

(1) An acid is a chemical compound containing hydrogen united with one or more other elements, and it is the presence of the hydrogen which imparts to the acid its characteristic properties, *e.g.* its action on litmus.

(2) When a metal acts on an acid the metal takes the place of the hydrogen of the acid.

Making these assumptions it follows that the *salt* produced when an acid acts on a metal contains the *metal combined with the element or elements other than hydrogen of which the acid is composed.* The neutrality[1] of salts to litmus is explained by the fact that the hydrogen of the acids from which they are derived has disappeared, and with it the characteristic properties of an acid.

The explanation of the results of our investigation of the action of acids on metals given above is not the only possible one, but that it is the correct one has been conclusively proved by a large number of other experiments.

57. Nomenclature of Salts.—The salts derived from an acid take their scientific names partly from the metal and partly from the acid, though they frequently have popular names as well Thus the salts derived from sulphuric acid are called *sulphates*; those from hydrochloric acid, *chlorides*; those from nitric acid, *nitrates*; and so on. Further, the salts produced by the action of the metals magnesium, zinc, and iron on sulphuric acid are called respectively *magnesium sulphate, zinc sulphate,* and *ferrous*[2] *sulphate.* The popular names for these salts are, however, *Epsom salts, white vitriol,* and *green vitriol.*

58. Alkalis.—We have already learnt (Exp. 57) to recognise this class of substances by the use of litmus solution. They possess the property of restoring the colour to litmus which has been reddened by the addition of acid.

[1] There are, however, a great many salts which are not neutral to litmus. This point will be further discussed later.

[2] Lat. *ferrum* = iron.

One of the most important substances belonging to this class of bodies is that known as *caustic soda* or *sodium hydroxide*. It is a substance of considerable interest and importance, and is manufactured in large quantities for various purposes, but especially for soap-making. We met with it when describing the behaviour of sodium towards water.

Exp. 105.—Examine a piece of caustic soda and observe that—

(*a*) It is a white solid, but does not seem to be crystalline.

(*b*) If left exposed to the air, it becomes moist, that is, it *deliquesces*. It would, if left long enough, run down to a liquid. It absorbs moisture from the air Such bodies are termed *hygroscopic* or *deliquescent*

(*c*) It dissolves very readily, as do most deliquescent bodies, in water, and considerable heat is developed during solution. The liquid thus formed has a soapy feeling.

(*d*) This solution turns reddened litmus blue.

(*e*) When a little olive oil or linseed oil is shaken up with the solution it dissolves (it is converted into *soap*)

Caustic Potash, Potassium Hydroxide, may be examined in the same way as was caustic soda. It is an exactly similar body, and could not be distinguished from it by ordinary means. It can be obtained by the action of the metal potassium on water just as in Exp. 57 we obtained caustic soda by the action of sodium on water.

59. Action of Acids on Alkalis.—Since acids, as you know, turn blue litmus paper red, and alkalis turn red litmus paper blue, it is possible that a mixture of the two in certain proportions would have no effect on either kind of litmus paper.

Exp. 106. *To make Common Salt* (*Sodium Chloride*).—To about 5 c.c. of dilute hydrochloric acid add caustic soda solution a little at a time. Test the liquid with blue litmus paper after each addition. After a time a point will be reached when the litmus is not turned red, and, further, when a red litmus paper is not turned blue, *i.e* the solution is *neutral* to litmus; the alkali is said to have *neutralised* the acid.[1] If too much caustic soda has been added (in which case a red litmus paper will be turned blue), add a little very dilute hydrochloric till the neutralisation point is exactly reached.

Now evaporate the solution to dryness. Notice that the white solid which remains is not like caustic soda. Taste it: you will recognise it as *common salt.*

Exp. 107. *To make Saltpetre* (*Potassium Nitrate*).—Add dilute nitric acid to about 5 c.c. of caustic potash solution contained in an evaporating dish, till the liquid is just neutral, *i.e.* the *acid* has *neutralised the alkali.* Evaporate till the solution begins to crystallise. Allow to cool: colourless crystals separate out. Pour off the liquid, dry the crystals between blotting-paper, and examine them. They resemble ordinary *saltpetre*—in fact they consist of this substance.

Exp. 108. *To make Glauber's Salt* (*Sodium Sulphate*).—Proceed as in Exp. 107, using dilute sulphuric acid in place of nitric acid, and caustic soda instead of caustic potash. Colourless crystals will separate; these consist of *Glauber's salt.*

Whether, then, we use hydrochloric, nitric, or sulphuric acid, the effect of neutralising the acid with an alkali is to produce a *salt.* If the experiment were repeated with other acids the results would be similar, and we may make the general statement that *when an acid is neutralised by an alkali a salt is formed.* It can be shown, however, that

[1] Because we added the *alkali* to the *acid.* Of course at the same time the *acid* has *neutralised* the *alkali* added to it, the action being mutual.

besides the salt another substance is formed, namely *water*, so that we have—

Acid neutralised by **Alkali** yields **Salt** and **Water.**

Now all acids contain hydrogen, whilst alkalis (with certain exceptions) contain a metal, and when an alkali neutralises an acid, the metal of the alkali takes the place of the hydrogen of the acid and a salt is formed; at the same time the displaced hydrogen combines with the remaining constituents (hydrogen and oxygen) of the alkali to form water.

60. Quantitative Experiments in Neutralisation. —Titration.— Before we can make accurate quantitative experiments in neutralisation we must provide ourselves

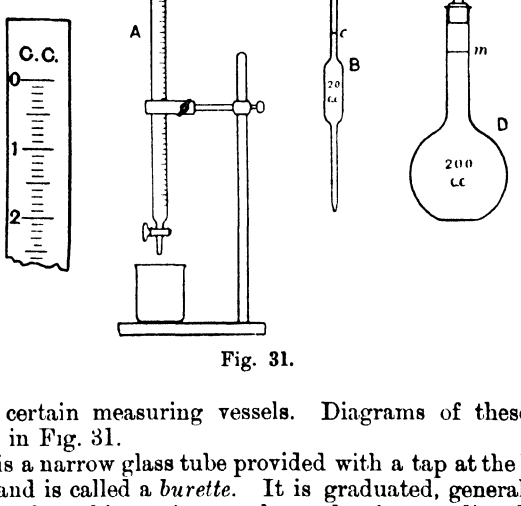


Fig. 31.

with certain measuring vessels. Diagrams of these are given in Fig. 31.

A is a narrow glass tube provided with a tap at the lower end, and is called a *burette*. It is graduated, generally in tenths of a cubic centimetre, the graduations reading downwards (see enlargement of the upper part of the burette

on the left of the diagram), so that the volume of liquid run out can be measured by reading the level of the liquid at the start and at the end of the operation. The burette is supported in a vertical position by a wooden or iron stand, as shown.

B (Fig. 31) is called a *pipette*, and is a glass vessel by means of which a known small volume of a liquid may be withdrawn from one vessel and transferred to another. The pipette is filled by suction[1] up to a mark (*c*) near the top, and then will deliver exactly 20 c.c. of liquid. (Pipettes for measuring out other volumes, 50, 25, 10, or 5 c c , are also made.)

To prevent the liquid running out during transference, the upper end of the pipette must be held between the thumb and fingers, the open end being closed by the first finger. The liquid is then delivered into a beaker or flask as required.

D (Fig. 31) represents a *measuring flask*. When filled up to the mark *m* it contains a definite volume of liquid (200 c.c. in this particular case). Measuring flasks are usually provided with ground glass stoppers.

Note.—Readings of measuring vessels should not be hurriedly done as the liquid requires a little time to drain down from the walls. The reading, especially of the burette, is liable to parallax error To avoid this, place the eye level with the surface. The surface is slightly curved ; it is usual to read from the bottom of the curve.

Suppose now we wish to find what volume of a given acid solution is required to neutralise 20 c.c. of a given solution of an alkali. 20 c.c. of the alkaline solution are measured out into a beaker or flask by means of a pipette, and two or three drops of litmus solution are added. The acid solution is then gradually run in from a burette till the blue colour of the litmus is *just* changed to red. The volume of liquid run out is the required volume of acid.

The operation is called *titration*, and the coloured substance (litmus in this case) that is used to indicate when the neutralisation is exact is called the *indicator*.

[1] Be careful to avoid sucking the liquid into your mouth.

It should be noted that, as solutions are of the same strength throughout if properly mixed, the *weight* of dissolved substance used in a titration is proportional to the *volume* of solution which is used.

Exp. 109. *To compare the quantities of acid required to neutralise equal weights of caustic potash and caustic soda.*— Two solutions are provided, one containing 10 grams of caustic soda in a litre of water, and the other containing 10 grams of caustic potash in a litre.

Rinse a 20 c.c. pipette with the caustic soda solution. Suck up the liquid carefully into the pipette till it is slightly above the mark, close by the finger as directed above, and then by slightly removing the finger bring the surface of the liquid exactly to the mark. Now let the liquid run out into a clean beaker or flask, allowing the last drops to run out with the end of the pipette held against the moist side of the beaker or flask for a few seconds; do not *blow through* the pipette.

Fill the burette with the given solution of hydrochloric acid (after first rinsing it out with the solution), and adjust until the lower part of the meniscus is on the zero graduation mark. Take care that no air bubbles are contained in the tap or jet.

Add a few drops of litmus solution to the caustic soda in the flask, and run in the acid gradually, shaking the liquid round from time to time, until the colour is just turned bright red.

Read the level of the acid in the burette (the bottom of the meniscus as before). Repeat the whole process and take the mean of the readings, provided they do not differ by more than 1 per cent. Enter your results in the following manner:—

For 20 c.c. of caustic solution,

	(1)	(2)
1st reading	0·0 c.c.	15·1 c.c.
2nd ,,	15·1 c.c.	30·3 c.c.
Vol. of acid used	15·1 c.c.	15·2 c.c.

Average = 15·15 c.c. of the acid solution.

Now repeat the whole process, using caustic potash solution instead of caustic soda.

Suppose that the following results were obtained:—

For the 20 c.c. of caustic potash solution,

	(1)	(2)
1st reading	0 0 c.c.	10 9 c.c.
2nd „	10 9 c.c.	21·9 c.c.
Vol. of acid used	10 9 c.c.	11 0 c.c.

Average = 10·95 c.c. of the acid solution

The quantities of acid required to neutralise equal weights of caustic soda and caustic potash are therefore in the ratio 15·15 : 10 95 or 1·38 : 1 (since equal volumes of the solutions contain equal weights of the alkalis).

61. The Use of Standard Solutions.—Careful experiments show that it requires 1·4 grams of caustic potash to neutralise the same amount of acid as is neutralised by 1 gram of caustic soda. These amounts of the two alkalis and the amount of the acid required to neutralise them are said to be *equivalent* to each other.

It has been found that 40 grams of caustic soda are required to neutralise 36·5 grams of pure hydrochloric acid.[1] From this fact you will be able to calculate the strength of the acid solution you used, *i e.* to find the weight of hydrochloric acid contained in one litre of it.

Thus taking the results obtained in Exp. 26 we have

20 c.c. of the caustic soda solution neutralised 15 15 c.c. of the acid solution.

∴ 1000 c.c. or 1 litre of the caustic soda solution would neutralise $\frac{1000}{20} \times 15{\cdot}15$ c.c. of the acid solution.

But 1 litre of the caustic soda solution contains 10 grams of caustic soda;

∴ 10 grams of caustic soda would neutralise

$\frac{1000}{20} \times 15{\cdot}15$ c.c. of the acid solution;

[1] Strictly speaking we should say "hydrogen chloride" or "hydrochloric acid *gas*," but in practice the term "hydrochloric acid" is used.

$\therefore$ 40 grams of caustic soda would neutralise

$\frac{40}{10} \times \frac{1000}{20} \times 15{\cdot}15$ c.c. of the acid solution

But 36·5 grams of hydrochloric acid are required to neutralise 40 grams of caustic soda.

Hence 36·5 grams of hydrochloric acid are contained in

$\frac{40}{10} \times \frac{1000}{20} \times 15{\cdot}15$ c.c. of the acid solution;

$\therefore 36{\cdot}5 \times 1000 \div (\frac{40}{10} \times \frac{1000}{20} \times 15{\cdot}15)$ or 12·05 grams of hydrochloric acid are contained in 1000 c.c. or 1 litre of the acid solution.

Exp. 110. Volumetric Analysis.—*To find the strength of the caustic soda solution in the reagent bottle.*—

You know the strength of your hydrochloric acid solution, and also the weight of caustic soda that neutralises 1 gram of hydrochloric acid; hence by performing a titration you will be able to find the strength of any solution of caustic soda.

The solution in the reagent bottle is so much stronger than the caustic soda solution used in Exp 109 that 20 c.c. of it will require far more than a burette-full of the acid. To avoid filling the burette several times, the caustic soda solution is first diluted in an aliquot manner. By means of a 10 c.c. pipette transfer 10 c.c. of the solution from the bottle to a 200 c.c. flask, make up to the mark with water, shake well, and take 20 c.c. of this diluted solution for the titration.

Repeat the titration until the results agree to within 1 per cent., then calculate the weight of caustic soda in one litre of the solution in the bottle.

Suppose you found that on the average 14·7 c.c. of your acid solution were required to neutralise 20 c.c. of the diluted caustic soda solution.

Then $14{\cdot}7 \times \frac{200}{20}$ or 147 c.c. of the acid solution would neutralise 200 c.c. of the diluted caustic soda solution or 10 c.c. of the solution in the reagent bottle.

$\therefore 147 \times \frac{1000}{10}$ or 14700 c.c. of the acid solution would neutralise 1000 c.c. or 1 litre of the solution in the reagent bottle.

Now 1 litre of the acid solution contains 12·05 grams of hydrochloric acid,

$\therefore$ 14700 c.c. will contain $\frac{12\cdot05 \times 14700}{1000}$ grams of hydrochloric acid.

But 36·5 grams of hydrochloric acid are equivalent to 40 grams of caustic soda.

$\therefore$ $\frac{12\cdot05 \times 14700}{1000}$ grams of hydrochloric acid are equivalent to $\frac{12\cdot05 \times 14700}{1000} \times \frac{40}{36\cdot5}$ or 194 grams of caustic soda;

i.e. the solution in the reagent bottle contains 194 grams of caustic soda per litre.

Solutions that contain a known weight of substance in a known volume of water are called **standard solutions.** They are very useful in chemical analysis, for by means of them the strength of other solutions can be determined without the continual aid of a balance. This saves much time, since a titration can be performed far more quickly than an evaporation and a weighing.

62. Action of Water on Oxides of the Metals.—

Exp. 111.—Introduce a piece of sodium about the size of a pea into a deflagrating spoon, heat in a Bunsen flame until the metal ignites and then lower into a jar. The metal continues to burn with a bright yellow flame, forming a dirty-white solid—oxide of sodium.[1] Pour in some water: the substance dissolves. Test with red litmus paper: the colour changes to blue, *i.e.* the solution is *alkaline.*

Here we have an oxide of a metal dissolving in water to form an alkali—the substance in solution is in fact *caustic soda,* and is formed by the combination of the oxide of sodium with water.

Oxide of potassium behaves in a similar way; it dissolves in water, forming *caustic potash.*

[1] Or more correctly a mixture of two oxides.

Exp. 112.—Moisten several pieces of red litmus paper and place on them small quantities of the following metallic oxides (finely powdered): quicklime, litharge, magnesia, red precipitate, black oxide of copper, red oxide of iron (rouge). You will find that quicklime, litharge, magnesia, and red precipitate all turn the litmus blue to a greater or less extent, while the oxides of copper and iron do not affect it.

Now shake up some of each of these oxides with water, filter and evaporate the filtrates to dryness. You will find that only in the case of lime is there any appreciable residue, *i.e.* only lime is soluble in water to any great extent. The other oxides which change the colour of the litmus can, however, be shown to be slightly soluble in water.

Oxides of metals, then, if they dissolve in water at all, give rise to alkalis, if not they behave as neutral bodies.

63. Action of Metallic Oxides on Acids.—Bases.—

Exp. 113.—Add finely-powdered black oxide of copper gradually to a little dilute sulphuric acid, shaking up after each addition. The oxide dissolves at first, forming a blue solution, and if you test the liquid from time to time with blue litmus paper you will find that the red colour formed becomes gradually less vivid,[1] showing that the acid is being gradually neutralised. After a time no more oxide dissolves, and if the liquid is filtered and the filtrate evaporated down somewhat and then allowed to stand, blue crystals separate out.

The crystals obtained in Exp. 113 consist of *copper sulphate*, a salt derived from sulphuric acid by the replacement of the hydrogen by the copper of the copper oxide. At the same time the hydrogen of the acid and the oxygen of the copper oxide unite to form water.

[1] The colour never disappears entirely, however, because a solution of copper sulphate alone turns blue litmus paper red

Exp. 114.—Repeat Exp. 113, using (1) magnesia (oxide of magnesium) and sulphuric acid, (2) litharge (yellow oxide of lead) and nitric acid in place of oxide of copper and sulphuric acid. In the first case you will obtain colourless crystals and in the second white crystals.

The colourless crystals consist of *magnesium sulphate* (the same salt as you obtained in Exp. 100 by the action of sulphuric acid on metallic magnesium) and the white crystals of *lead nitrate*. It can further be shown that water is also formed in each case.

Most metallic oxides will be found to behave in a similar way towards acids. Further, if the salts formed are strongly heated in air they very frequently undergo decomposition; acid fumes are produced, and a residue of metallic oxide remains. We met with an example of such decomposition when we heated green vitriol in Exp. 104; the residue consisted of oxide of iron. It was on this account that metallic oxides were called "bases" by the early chemists, the oxide being the *base of the salt, i.e.* the residue remaining when the salt was strongly heated. The term is still applied to metallic oxides, which are also called *basic oxides*; it is also applied to compounds of metals with hydrogen and oxygen, *i.e.* to metallic *hydroxides* (caustic soda and caustic potash are examples). The terms acid, base, and salt are concisely connected together in the following statement:—

Acid + Base yield **Salt + Water,**

the sign "+" standing for "added to" or "treated with."

A few bases which dissolve in water, forming solutions which turn red litmus blue (*e.g.* caustic soda), are called *alkalis*, so that an alkali is a particularly active kind of base.

64. Action of Water on Oxides of Non-metallic Elements or Non-metals.—When sulphur, phosphorus, and carbon are burnt in oxygen and the oxides formed—sulphur dioxide, phosphoric oxide, and carbon dioxide—are dissolved in water *acids* are formed. The oxide combines with part of the water, and the acid formed then

dissolves in the excess of water. Oxides which behave in this way are called *acid-forming oxides* or *acidic oxides*. Most oxides of non-metals are acidic oxides; a few, however, when dissolved in water form *neutral* solutions, *i.e.* they are *neutral oxides*. Such oxides are only *slightly* soluble in water; examples are nitric oxide and carbon monoxide. Neutral oxides of non-metals differ from neutral metallic oxides in that they are unacted upon by acids.

QUESTIONS.—CHAPTER VI.

1. What is a *salt*? How would you prepare the following:—(1) potassium chloride from caustic potash, (2) copper sulphate from black oxide of copper?

2. What are the distinguishing characters of *acids*? Describe the experiments you would perform in order to illustrate them.

3. Describe the properties of any common alkali known to you. Mention also two other examples of alkalis.

4. Describe how you would proceed to investigate the action of water on the following oxides:—sulphur dioxide, quicklime, phosphoric oxide, black oxide of copper, litharge. State the results you would obtain. Into what classes would you be led to divide oxides as a result of your investigations?

5 Describe some experiments to illustrate the chief properties of any *common alkali* known to you.

6. A solution of caustic soda is gradually added to a little hydrochloric acid to which a little litmus solution has been added. State and explain the colour-changes which take place.

7. Explain why the early chemists called the oxides of the metals *bases*. Describe an experiment to illustrate the action of an acid on a base.

8. A few small pieces of metallic sodium are added gradually to a little water, and when the metal has disappeared the liquid which remains is evaporated till its bulk ceases to diminish, and then allowed to cool. What is the appearance of the residue and what are its chief properties? Also what is it called and to what class of bodies does it belong?

9. Describe how you would proceed to prepare a pure specimen of sodium nitrate if you were provided with some caustic soda and some nitric acid.

10. Explain the meaning of the terms *titration*, *indicator*, *standard solution*.

11. Describe in detail how you would proceed to determine the strength of a given solution of sulphuric acid if you were provided with a solution of caustic potash of known strength. [49 grams of sulphuric acid are equivalent to 56 grams of caustic potash.]

12. How would you proceed to find the strength of an unknown solution of caustic potash, given a solution of caustic soda of known strength and some sulphuric acid? Sketch the apparatus you would employ. [40 grams of caustic soda are equivalent to 56 grams of caustic potash.]

CHAPTER VII.

CONSERVATION OF MATTER—LAWS OF CONSTANT AND MULTIPLE PROPORTIONS.

65. The Conservation of Matter.—With the aid of the chemical balance we are now in a position to approach a question of very great importance which as yet has not been touched upon. During the changes which are continually being observed by chemists, is there any reason to suppose that matter may be actually destroyed or created?

Let us investigate the problem by experiment.

* **Exp. 115.**—Take a clean, dry litre flask, and fit it with a good cork. Cut off from a stick of ordinary phosphorus a piece *not larger than a pea*,[1] taking care to perform this operation under water. Dry the piece of phosphorus with filter paper, place it in the flask, fit in the cork, and weigh the whole. Now ignite the phosphorus by dipping the flask into hot water. The flask will soon be filled with white fumes of oxide of phosphorus. When the flask is cool, wipe it dry and weigh again. The weight will be found to be the same as before.

Exp. 116.—Take two small beakers. Pour into one a little copper sulphate solution and into the other a little caustic potash solution. Weigh the two beakers together. Now pour the caustic potash into the copper sulphate, taking care not to lose any liquid. A bulky precipitate forms. Evidently chemical change has taken place. Weigh the two beakers again together. The weight is the same as before.

[1] Too large a piece is dangerous.

It is clear that in these two experiments there has been no creation or destruction of matter but merely a redistribution. A vast number of experiments conducted on similar lines have led chemists to the conclusion that *in the course of chemical operations matter is neither destroyed nor created.* This statement is called the *Principle of The Conservation of Matter*, and is one of the fundamental principles of the science of chemistry.

66. Mixtures and Compounds.—We may bring together sand and sugar, or common salt and soot, etc., *in any proportions we please*, and the first mixture will be the sweeter, and will dissolve in water the more freely the greater the proportion of the sugar is; the latter, with a predominance of soot, will be very dark in colour, and with a predominance of salt may be only faintly grey. An infinitely large number of mixtures could be made, all slightly differing in taste and appearance, and also in respect of the extent to which the mixture will dissolve in water. In any of the mixtures you might, however, by very simple means recognise the sand and the sugar, or the soot and the salt, and it is also an easy matter to separate them, *e.g.* by shaking up with water and filtering, when the sugar or salt dissolves and passes through the filter, whilst the sand or soot remains on the filter (compare Exp. 53).

Exp. 117.—Mix together intimately seven parts by weight of finely-powdered iron and four parts of flowers of sulphur. Heat one-half of the mixture over a Bunsen burner in a small porcelain crucible for a few minutes with the lid on. Allow to cool, and powder some of the product very finely. Compare with the rest of the mixture: you will notice a difference in colour. Draw a magnet through each of the powders. You will find that iron is extracted from the mixture which has not been heated, and a residue of sulphur remains. No iron can, however, be extracted from the substance formed on heating by means of a magnet; a *chemical compound* has been formed. Shake up a little of each of the powders with carbon sulphide; filter; allow the filtrate to evaporate. In the

case of the mixture a residue of iron remains, but there is no residue[1] in the case of the compound.

Drop a little of each of the powders into some dilute sulphuric acid contained in separate test-tubes. Note that in the case of the mixture hydrogen is evolved and a residue of sulphur remains, whilst in the case of the compound an evil-smelling gas (sulphuretted hydrogen) is evolved, and no residue[1] remains.

In the mixture of iron and sulphur, then, the two elements retain their individual properties, iron its magnetic properties and its solubility in dilute acid with evolution of hydrogen, sulphur its solubility in carbon bisulphide and insolubility in acid; in the compounds, on the other hand, these individual properties of the two elements are completely lost. The constituents of the mixture can readily be separated by making use of their individual properties, but the constituents of the compound cannot be separated in this way.

Similar experiments with other substances lead to similar results, and we may define a *chemical compound* as *a substance produced by the union of two or more simpler substances in such a way that the individual properties of the constituents have disappeared.* We shall now investigate a very important property of chemical compounds.

67. Law of Constant Proportion.—

Exp. 118. *Composition of Magnesium Oxide.*—Heat a porcelain crucible with its lid; allow to cool in a desiccator, then weigh. Measure off 12 cm. of *bright* magnesium ribbon (scrape the ribbon with a knife if it is not bright), roll it up *loosely* and place in the crucible; then weigh the whole. Fix securely on a pipeclay triangle and tripod. Heat the closed crucible sufficiently to cause the metal to burn when the lid is slightly raised. Do not let any white fumes escape. When the burning has nearly ceased remove the lid, but continue to heat for a few

[1] There may be a slight residue of sulphur owing to the incomplete combination of the iron and sulphur.

minutes longer. Cool in the desiccator and weigh the whole again. Now reheat for a short time, cool, and reweigh. If the weight has changed, you must repeat the heating, cooling, and weighing till two consecutive weighings are the same, showing that the change is complete.

Tabulate your results like this:—

	grams
Weight of crucible, lid, and magnesium ...	=
,, crucible and lid	=
,, magnesium	=
,, crucible, lid, and magnesium oxide (1)	=
,, crucible, lid, and magnesium oxide (2) and (3) (constant —suppose)	=
,, magnesium oxide	=
Increase in weight of metal, *i.e.* weight of oxygen	=

Weight of oxygen combined with one gram of magnesium, *i.e.*

$$\frac{\text{Weight of oxygen}}{\text{Weight of magnesium}} =$$

Now repeat the whole experiment, using a different weight of magnesium.

You will find that, however many times you perform the experiment, you will always obtain the same result on calculating out the weight of oxygen which combines with one part by weight of magnesium.

Let us now prepare oxide of magnesium from magnesium in another way and see whether the proportions of oxygen and magnesium are the same as before.

Exp. 119.—Again heat a crucible and lid; allow to cool in a desiccator, then weigh. Roll up a piece of magnesium ribbon about the same length as you used in the previous experiment, introduce into the crucible and reweigh. Remove to a fume cupboard, pour on the metal two or three drops of water, followed by a *few* drops of strong nitric

acid. *At once* nearly cover the crucible with the lid. The metal dissolves with copious evolution of brown fumes. If necessary add more acid to complete the solution of the metal. Gently evaporate down to dryness on a sand-bath, taking care that there is no loss by spirting (the lid should still nearly cover the crucible). The white residue is *magnesium nitrate.*

Support the crucible on a pipe-clay triangle and heat (again with the lid nearly covering the crucible) until evolution of brown fumes ceases. A white residue of *magnesium oxide* remains. Now remove the lid, taking care not to lose any white residue which may adhere to it as a result of spirting earlier in the experiment. Heat the crucible for a short time without the lid, and at the same time heat the lid, having placed it upside down on a pipe-clay triangle. Now transfer crucible and lid to a desiccator, allow to cool, and weigh. Heat them again for a short time, cool and reweigh, repeating the process till the weight is constant.

Enter your results as in Exp. 118.

You will find that the result (expressed as the weight of oxygen combined with one gram of magnesium) is the same as in Exp. 118, *i.e.* whether magnesium oxide is made as in Exp. 118 or in Exp. 119 its composition is the same.

* **Exp. 120.** *Composition of Chalk.*—Carefully weigh a small poreclain crucible (without lid), introduce about half a gram of dry powdered chalk (calcium carbonate), and reweigh. Now heat the crucible strongly over the blowpipe for fifteen minutes; cool and weigh. Reheat and reweigh. If the weight has altered, repeat the operation till it is constant. The residue in the crucible is calcium oxide (quicklime), and you should find its weight to be about 56 per cent. of that of the calcium carbonate. The 44 per cent. loss in weight represents the weight of carbon dioxide which was united with the quicklime to form calcium carbonate.

Now moisten the contents of the crucible with a strong solution of ammonium carbonate, leave the crucible and

contents for an hour in a steam oven, cool, and weigh. The quicklime will be reconverted into the carbonate, the weight of which should be *equal to that of the original calcium carbonate*, the excess of ammonium carbonate being readily volatilised.

Your results should be entered on the lines of the previous experiment.

From this experiment we learn that chalk is composed of quicklime and carbon dioxide *combined in fixed proportions.*

* **Exp. 121.** *Composition of Water.*—Take a hard glass tube about 20 cm. long and 1·5 cm. wide, and fit it with corks. Push into the tube a loose plug of asbestos (which has been previously ignited and allowed to cool in a desiccator) so that it is about a quarter of the way up the tube (A, Fig. 32).

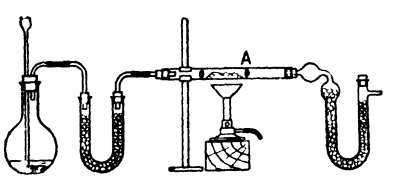


Fig. 32.

Weigh out, approximately, 5 grams of finely-powdered black oxide of copper,[1] and introduce it into the tube at the end remote from the asbestos, by means of a small funnel. Now introduce a second plug of asbestos (ignited as before), carefully pushing it up the tube so that it sweeps along all particles of oxide. The distance between the two asbestos plugs should be about 6 cm. Place the tube horizontal and tap it so that the oxide forms an even layer with a free air space all along the tube. Carefully wipe off any oxide from the outside of the tube.

Next weigh the tube and copper oxide accurately. Also weigh a U-tube containing granular calcium chloride, and united with a horizontal bulb as shown in the diagram

[1] This should be previously heated to redness in air (to get rid of moisture, etc., attached to it), and, whilst still warm, introduced into the tube just before commencing the experiment.

Attach the U-tube and bulb to the straight tube as shown (arranging that the tube which passes through the cork *does not reach beyond it*).[1] Connect the other end of the tube to a supply of hydrogen prepared by the action of dilute sulphuric acid on zinc, and dried by passing through a U-tube filled with granular calcium chloride. Allow the hydrogen to pass through the tube for a few minutes in order to displace the air. (Test if the air has been removed in the usual way.) Then heat the oxide of copper by means of a flat-flame burner.

The colour of the oxide will slowly change to a dark red, and water will condense in the further end of the tube and the horizontal bulb. The heating must be continued and the stream of hydrogen passed until no more traces of

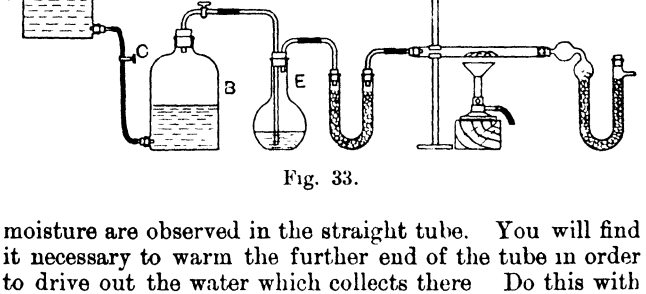


Fig. 33.

moisture are observed in the straight tube. You will find it necessary to warm the further end of the tube in order to drive out the water which collects there Do this with an ordinary Bunsen burner, taking care that the tube does not become so hot as to affect the cork. Most of the moisture will now collect in the horizontal bulb, and the rest will be absorbed by the calcium chloride.

Now allow the apparatus to cool, still passing a slow current of hydrogen. When cold disconnect the hydrogen generating flask, leaving the calcium chloride tube in place. Now pass a slow current of dry air through the apparatus

[1] If it did you would be unable subsequently to drive all the water out of the tube.

by means of the arrangement shown in Fig. 33.[1] The upper bottle A is filled with water, which flows down into B when the tap D and screw-clip C are open, and forces the air out through the exit-tube. The air is first passed through a small sulphuric acid wash-bottle E, which serves to indicate the rate of flow and also partially dries it. It then traverses the remainder of the apparatus (being further dried by the calcium chloride in the U-tube), and sweeps out the hydrogen.[2] The current of air is regulated by the tap and screw-clip, and should be maintained for about five minutes.

Reweigh the tube (+ copper) and the U-tube and bulb. We now have all the data necessary for calculating the ratio of hydrogen to oxygen in water.

Enter your results thus.—

	grams.
Weight of heating tube + copper oxide	$= x$
,, ,, ,, + copper ...	$= y$
,, oxygen which has been converted into water	$= x-y$
,, U-tube and bulb before experiment	$= a$
,, U-tube and bulb after experiment	$= b$
,, hydrogen in the water formed	$= b-a-(x-y)$

Hence—

Weight of oxygen united with 1 gram of hydrogen is

$$\frac{x-y}{b-a-(x-y)}.$$

You should find this to be about 8 grams.

Repeat the experiment and show that you get the *same result.* Now try another oxide in place of copper oxide—say litharge; again the result will be the same.

[1] A simpler way is to use a "*scent bottle*" *bellows*

[2] If you weigh with hydrogen in the tubes instead of air, you will introduce errors; for the previous weighings were made with air in the tube, and hydrogen is much lighter than air.

A very large number of experiments have been made similar to those you have just performed, and all have led to similar results, which may be generalised in the following statement known as the *Law of Constant Proportion*:—

The same compound always contains the same elements combined in the same fixed proportion by weight.

Here, then, we have a very important characteristic of a *chemical compound*, for in a *mixture* the constituents may be present in *any proportions*.

68. Law of Multiple Proportion.—Many elements, however, are capable of combining together to form more than one compound. Let us now perform some experiments with a view to finding out whether in two compounds of the same elements there is any simple relation between the relative proportions of these elements.

* **Exp. 122.**—Weigh accurately into a small porcelain boat (*a*, Fig. 34) about a gram of lead peroxide (brown oxide of lead). Push the boat into a hard glass tube of

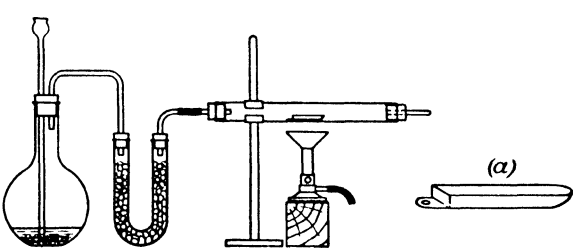


Fig. 34.

about the same size as that used in Exp. 121. Fit the tube with corks, carrying short pieces of glass tubing. Now connect one end of the tube with an apparatus for preparing dry hydrogen. Allow the hydrogen to pass through the tube for a few minutes to displace the air (test as usual). Then heat the boat gently by means of a

flat-flame burner. The powder gradually changes colour, while *steam* passes out of the tube along with the unused hydrogen. When the cloud ceases and the powder has become quite black (*i.e.* changed into metallic lead) raise the boat to red heat for a few seconds to fuse the lead, while the current of hydrogen still passes. Cool, stop the current of hydrogen, withdraw the boat by means of a copper wire from the end of the tube attached to the hydrogen apparatus (because there will probably be some drops of water at the other end) and reweigh it.

Enter your results thus:—

		grams
Weight of boat + lead peroxide	=	x
,, boat	=	y
,, boat + lead	=	a
,, lead in oxide taken	=	$a - y$
,, oxygen in oxide taken	=	$x - a$

Therefore the weight of lead combined with one part by weight of oxygen in lead peroxide is $\frac{a-y}{x-a}$ grams.

Your result should work out at about 6·45 grams.

Now repeat the experiment, using litharge (yellow oxide of lead) instead of lead peroxide, and again calculate out the weight of lead which was in combination with one gram of oxygen. The weight found should be about 12·9 grams.

Now $12{\cdot}9 : 6{\cdot}45 = 2 : 1$, *i.e.* the weights of lead which unite with 1 gram of oxygen to form litharge and lead peroxide respectively are in the ratio 2 : 1.

There is then a very simple relation between the relative weights of oxygen which combine with a fixed weight of lead to form these two oxides of lead.

* **Exp. 123.**—Clean and heat a porcelain crucible and lid, and allow them to cool. Place in the crucible about 1 gram of well-powdered recrystallised copper sulphate crystals, and accurately weigh the whole. Heat, with the

lid off, for half an hour in an air oven (Fig. 35) kept at a temperature of 135° C. to 140° C. Stir the powder occasionally with a platinum wire. When properly heated it should appear whitish all through. Allow the crucible to cool with its lid on, and weigh again. The difference in weight gives the weight of water lost.

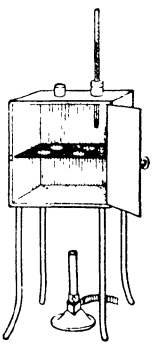


Fig. 35.

Next support the crucible on a pipeclay triangle, and heat it very carefully (without the lid), using a small flame, which is not allowed to touch the crucible.[1] Cool with the lid on, and weigh. The heating and cooling should be repeated until practically a constant weight is obtained, when all water will have to be expelled. The difference between this weight and the former shows the loss of water due to the raised temperature. It should be just one quarter of the first loss.

The results obtained by a student were as follows :—

	grams
Weight of crucible, lid, and powdered crystals ...	13·727
,, crucible, lid, and powdered crystals after heating to 140° C.	13·440
,, water expelled at lower temperature...	0·287
,, crucible, lid, and anhydrous copper sulphate	13·367
,, water expelled at higher temperature	0·073
Total weight of water in the crystals	0·360

Thus the proportion of water in the crystals to that in the first product was found to be 0·360 : 0·073, or 5 : 1, or, in other words, the weights of water which unite with a fixed weight of copper sulphate to form two different compounds bear to one another the simple ratio 5 : 1.

[1] Or heat in the oven at 220° C.

Similar experiments with other substances have led to similar results. Thus:—

12 gm. of carbon combine with 16 gm. of oxygen to form carbon monoxide.

12 gm. of carbon combine with 32 gm. of oxygen to form carbon dioxide.

Ratio between the weights of oxygen combining with the same weight of carbon is 1 : 2.

32 gm. of sulphur combine with 32 gm. of oxygen to form sulphur dioxide.

32 gm. of sulphur combine with 48 gm. of oxygen to form sulphur trioxide.

Ratio between the weights of oxygen combining with the same weight of sulphur is 2 : 3.

These and all similar cases may be summed up in the following statement, which is known as the *Law of Multiple Proportion:—When one element combines with another in more than one proportion the different quantities of the one element which unite with a fixed quantity of the other element bear a simple ratio to one another.*

69. Dalton's Atomic Theory.—Over a century ago Dalton propounded the theory that there is a limit to the masses of the ultimate particles of matter capable of taking part in chemical change. That, for instance, when oxygen is attached to an element or transferred from one element to another, the amount so transferred is not indefinitely or infinitely small, but that the transfer takes place *step by step* in masses of definite dimensions. These ultimate particles he regarded as being incapable of further division, and hence termed them *atoms*.[1] His theory is thus known as the *Atomic Theory*.

The Law of Multiple Proportion (see § 68), which was first established by Dalton, is the foundation on which the Atomic Theory mainly rests.

[1] From the Greek *ἀ*, not; *τέμνω*, I cut.

It is important that the student should realise that atoms are excessively small, and we can never hope to see them even with microscopes many times more powerful than the best that are in use at the present time.

Small as the atoms are, their *relative weights* have been determined, and some of these will be found in the table in § 86, hydrogen being taken as unity. Further, very approximate determinations of the *absolute* weight of atoms have recently been made.

QUESTIONS—CHAPTER VII

1. Describe two experiments to illustrate the truth of the statement that matter can neither be created nor destroyed.

2. In what respects does a chemical compound differ from a mixture? Describe experiments to illustrate your answer.

3. State the *Law of Constant Proportion*, and describe how you would proceed to demonstrate its truth by experiment.

4. What is the *Law of Multiple Proportion*? Describe experiments which illustrate it.

5. Show that the following numbers illustrate the Law of Multiple Proportion:—Red oxide of copper contains 88·8 per cent. of copper and 11·2 per cent. of oxygen. Black oxide of copper contains 79·87 per cent. of copper and 20·13 per cent. of oxygen

6. Show that the following numbers illustrate the Law of Constant Proportions:—2·4 grams of oxide of iron on complete reduction by hydrogen yielded 1·68 grams of iron; 2·9 grams of the oxide yielded on similar treatment 2·03 grams of iron.

7. What do you understand by the *Principle of the Conservation of Matter*? Describe how you would proceed to illustrate the truth of this principle by experiment.

8. You are provided with a powder containing copper and sulphur in the proportions of 63 : 32. Describe how you would proceed to find out whether it is a mixture or a compound of the two elements.

9. What do you understand by the *Atomic Theory*? Give evidence in support of its truth.

10. In an experiment 0·98 gram of magnesium on heating in air yielded 1·62 grams of magnesium oxide. In a second experiment 1·12 grams of magnesium yielded 1·85 grams of the oxide by solution of the metal in dilute sulphuric acid, precipitation by sodium carbonate, and ignition of the carbonate. Show that these results illustrate the Law of Constant Proportion.

11. In two determinations of the composition of water by the reduction of copper oxide by hydrogen, the following results were obtained:—

	Exp. 1. grams	Exp. 2. grams
Weight of copper oxide tube before the reduction	= 14·82	15·17
Weight of copper oxide tube after the reduction	= 13·85	14·13
Weight of absorption apparatus before the reduction ...	= 16·21	17·36
Weight of absorption apparatus after the reduction	= 17·30	18·53

Show that these numbers illustrate the Law of Constant Proportion.

12. Iron forms two sulphides, *ferrous sulphide* and *iron pyrites*. When these are strongly heated in a current of hydrogen they are completely reduced to the

metal. In two experiments the following numbers were obtained :—

Exp. 1.—

Weight of ferrous sulphide taken ... = 1·21 gm.
„ iron remaining after reduction = 0·77 „

Exp. 2.—

Weight of iron pyrites taken ... ... = 1·35 gm.
„ iron remaining after reduction = 0 63 „

Show that these results illustrate the Law of Multiple Proportion.

CHAPTER VIII.

PHYSICAL PROPERTIES OF GASES.

70. Effect of Temperature on the Volume of a Gas.—You have already observed (Exp. 6) that air expands when heated and contracts when cooled, and you would find a similar result with other gases. Let us now examine this phenomenon quantitatively by experiment.

* **Exp. 124.** *Relation of volume of air to temperature.*—Take a 250 c.c. flask and tightly-fitting indiarubber cork, through which passes a piece of glass tubing of very narrow bore (capillary tubing), bent twice at right angles as shown in Fig. 36. Immerse the flask up to the level of the cork in a beaker or tin vessel of hot water, clamping it in position so that there is, say, half an inch of water between the bottom of the flask and the beaker. Boil the water and keep it boiling for five or ten minutes.



Fig. 36.

Now place a beaker filled with cold water so that the outlet of the capillary tube dips deeply into it. Raise the flask out of the hot water, keeping the outlet all the while dipping beneath the water in the beaker, and let it cool by standing in the air. Notice that water is driven from the beaker into the flask. Plunge the flask overhead into a mixture of water and ice, still keeping the outlet under water, and let it remain so long as water drips back into it through the capillary tube.

Take now a cylindrical measure graduated into cubic centimetres, and pour the water from the flask into it so as to ascertain how many cubic centimetres have flowed back into the flask. Call this v. Then measure how much water is needed to fill the flask up to the level of the lower surface of the cork. Call this V. Then V represents the volume of air which just fills the flask at 100° C. and $(V - v)$ the volume which this air occupies at 0° C., the temperature of ice-cold water. Therefore $(V - v)$ c.c. of air at 0° C. expand v c.c. on heating to 100° C.

The amount of expansion for 1° C. rise in temperature is $\frac{v}{100}$ c.c.; therefore the expansion for 1° is $v \div (V - v)$ 100 of the whole. Calculate out from your results the value of this expression, and see how near it agrees with the number $\frac{1}{273}$.

John Dalton, who in 1801 made this determination, and found that oxygen, hydrogen, and carbonic acid gas behaved in the same manner as air, obtained the result $\frac{1}{275}$. He concluded "that all elastic fluids under the same pressure expand equally by heat."

This generalisation is, however, usually known as *Charles's Law*, which is expressed thus :—

Equal volumes of all gases under the same pressure expand equally for equal increments of temperature.

Experiments in which precautions were taken to secure great accuracy yield the result that gases at 0° C. expand $\frac{1}{273}$ part of their volume for each increment of 1° C.

Thus 273 volumes of gas at 0° C. become 274 vols. at 1° C.,
" " " 275 vols. at 2° C.,
" " " 276 vols. at 3° C.,
and so on.

For temperatures below zero, we should have—

273 volumes of gas at 0° C. become 272 vols. at — 1° C.,
" " " 271 vols. at — 2° C.,
" " " 270 vols. at — 3° C.,
and so on.

If the behaviour of gases remained the same at *very low* temperatures, we should find that 273 vols. at 0° C. would become *nil* at — 273° C. But, long before such a low temperature is reached, most gases condense to liquids, and many even to solids.

In dealing with gases in practice, however, the chemist has usually only to concern himself with temperatures above zero and a few degrees below zero; and hence you will find it convenient to notice that *under the same pressure the volume of a gas is proportional to the temperature as reckoned, not from* 0° C., *as is generally done, but from* — 273° C., termed *absolute zero.* We have thus:—

Temperature.	Absolute Temperature.	Volume.
0° C	273	273
10° C.	283	283
— 10° C.	263	263

and so on.

71. Effect of Pressure on the Volume of a Gas.—A simple experiment with a pop-gun will convince you that the volume of space taken up by a gas depends also on its pressure. The effect can be investigated quantitatively by means of the following experiment.

* **Exp. 125.**—Procure a *good* 50 c.c. burette fitted with a stopcock (which should be well greased). Since the burette is not graduated right up to the end the volume from the 50 c.c. graduation to the end must be determined. For this purpose pour mercury[1] into the burette by means of a small funnel till it stands at the 50 c.c. graduation. Run this mercury into a weighed beaker and reweigh. The difference between the two weighings is equal to the weight of the mercury, and this divided by 13·6 (the specific gravity of mercury) gives the volume.

[1] Water might of course be used, but it would take a considerable time to dry the burette again.

Suppose you obtained the following results:—

Wt. of beaker	=	10·02 grams.
„ „ + mercury	=	80·65 „
Wt. of mercury	=	70 63 „

$$\text{Vol. of mercury} = \frac{70{\cdot}63}{13{\cdot}6} \text{ or } 5{\cdot}2 \text{ c c.}$$

Then 5 2 c.c. is the volume of the burette from the closed end to the 50 c.c. graduation. Write this volume down on a small piece of gummed paper and fasten it on to the burette below the 50 c.c. graduation.

Next thoroughly dry the burette by attaching a piece of rubber tubing to it and blowing air through by means of a foot-bellows, at the same time warming the burette in the hot air rising from a Bunsen flame. When the burette is quite dry close the open end with a well-fitting rubber cork carrying a short piece of glass tubing.

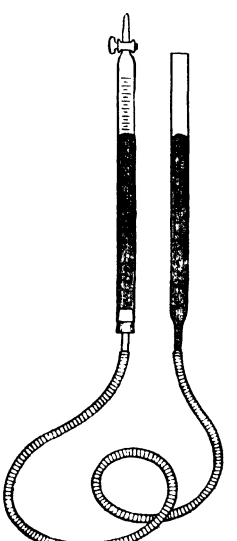


Fig. 37.

Now obtain a glass tube of about the same diameter and length as the burette and narrowed at one end. Take about $1\frac{1}{2}$ metres of thick-walled tubing ("pump-tubing") and wire the ends firmly on to the short glass tube of the burette and the narrow end of the other tube (which we will call the *pressure tube*). Support the burette and pressure tube close together in a vertical position (Fig. 37) by means of a retort stand and clamps, and fix vertically behind them a metre scale.

Open the stop-cock of the burette, raise the pressure tube about 60 centimetres, and carefully pour mercury into it till the burette is just full. Next attach a long calcium

chloride tube to the burette beyond the stop-cock (by rubber tubing), and then very *gradually* lower the pressure tube so that air dried by the calcium chloride is slowly drawn into the burette. When this is about one-third full of air clamp the pressure tube, and close the stop-cock of the burette as soon as the mercury is quite steady. Now read the level of the mercury in the burette. (This must, of course, be done *upside down*, but no difficulty should be experienced in doing this.) Suppose the reading is 34·6 c.c. Then the volume of air in the burette is given by

$$5{\cdot}2 + 50 - 34{\cdot}6 \text{ or } 20\ 6 \text{ c c.}$$

Also, since the mercury level is the same in the two limbs, the pressure of the air is equal to that of the atmosphere, which should be found by reading the barometer. Suppose it is equal to that of 746 mm of mercury. Then we have in the burette 20·6 c.c of air at 746 mm. pressure.

Let us now see what pressure is required to reduce the volume to *one-half*, *i.e.* to 10·3 c.c. If we call the reading of the burette x c.c. when the volume is 10·3 c.c. we have

$$5{\cdot}2 + 50 - x = 10\ 3 \text{ c.c.}$$

$$\therefore \quad x = 44{\cdot}9 \text{ c.c.}$$

Raise the pressure tube till the mercury in the burette, *when steady*,[1] stands at the reading 44·9 c.c. Now by means of the metre scale (the position of which must be adjusted as required) read the difference between the levels of the mercury in the burette and in the pressure tube. Suppose this is 74 8 cm., *i.e.* 748 mm. Then the total pressure on the gas is equal to that due to a column of mercury 748 mm. high, together with the atmospheric pressure, viz. 746 mm. of mercury. But

[1] Allow the tubes to stand for a few minutes. The level may gradually change at first after apparently becoming steady owing to the gas having become somewhat hotter as a result of compression. When this change in level ceases, showing that the gas is again at atmospheric temperature, readjust till the reading is exactly 44·9 c.c.

these two numbers are equal within the limits of error of the experiment, so that it has been necessary to *double* the pressure in order to *halve* the volume.

Next let us double the volume and see what change is necessary in the pressure. If we let y represent the reading of the mercury in the burette when the volume is doubled, *i.e.* when it becomes $2 \times 20\cdot6$ or $41\cdot2$ c.c., we have

$$5\cdot2 + 50 - y = 41\cdot2 \text{ c.c.}$$
$$\therefore \quad y = 14 \text{ c.c.}$$

Lower the pressure tube therefore till the mercury in the burette, when steady,[1] reads 14 c.c.

Read the difference between the mercury levels as before; suppose it is $37\cdot4$ cm., *i.e.* 374 mm. Since the mercury level in the pressure tube is now *below* that in the burette the pressure of the gas is equal to that of a column of mercury $746 - 374$, or 372 mm. high. But 372 is *one half* of 746 within the limits of experimental error, so that in order to *double* the volume it has been necessary to *halve* the pressure.

These results are in agreement with the following statement, which is known as *Boyle's Law*:—

When the temperature remains constant the volume occupied by a given quantity of a gas varies inversely as the pressure.

Note also that this being the case the product of the volume and the pressure will be constant. Thus taking the numbers given above we have

$$20\cdot6 \times 746 = 10\cdot3 \times (748 + 746) = 41\cdot2 \times 372$$

within the limits of experimental error.

Representing pressure by P and volume by V we have then

$$PV = \text{a constant}$$

as a concise expression of Boyle's Law.

[1] Wait a few minutes and readjust if necessary, since a gas is cooled by expansion.

72. Liquefaction of Gases.—The above description is only true for a perfect gas under moderate pressure and temperature. No perfect gas exists in reality, for though very many gases show a close agreement at such pressures and temperatures as occur in general practice, yet under extreme conditions even hydrogen, nitrogen, and those gases which behave most nearly like perfect gases, fail to show agreement, and at sufficiently low temperature and high pressure they change their condition and become liquid.

The following table gives the temperatures and pressures at which some of the commoner gases become liquids:—

Carbon dioxide at −	80° C.	and	1	atmosphere	pressure.
or at −	20° C.	,,	23	,,	,,
or at +	20° C.	,,	58	,,	,,
Sulphur dioxide at −	10° C.	,,	1	,,	,,
or at +	10° C.	,,	2·3	,,	,,
or at +	30° C.	,,	5·3	,,	,,
Nitrogen at −	195° C.	,,	1	,,	,,
or at −	160° C.	,,	14	,,	,,
or at −	146° C.	,,	35	,,	,,
Air at −	194·4° C	,,	1	,,	,,
or at −	140° C.	,,	39	,,	,,
Chlorine at −	34° C.	,,	1	,,	,,
or at	0° C.	,,	6	,,	,,
Ethylene at −	102·5° C.	,,	1	,,	,,
Nitrous oxide at	0° C.	,,	30	,,	,,

A gas cannot always be liquefied by pressure alone. There is, in fact, a temperature peculiar to each gas *above* which the gas cannot be liquefied by any pressure whatever. Thus Andrews has shown that at temperatures above 31° C. it is impossible to liquefy carbon dioxide by pressure.

This temperature is called the *critical temperature* of the gas, so that the critical temperature of carbon dioxide is 31° C. The pressure which a gas exerts at its critical temperature is called the *critical pressure*. The

following table gives these two constants for a number of gases :—

	Critical temperature.	Critical pressure.
Nitrogen	— 146° C.	35 atmospheres.
Oxygen	— 118·8° C.	50·8 ,,
Nitric oxide	— 93·5° C.	71·2 ,,
Marsh gas	— 95·5° C.	50 ,,
Carbon monoxide	— 141° C.	36 ,,
Hydrogen	— 242° C.	15 ,,
Sulphur dioxide	+ 155° C.	79 ,,
Carbon dioxide	+ 31° C.	72·6 ,,
Ethylene	+ 9° C.	58 ,,

It will be noticed that the six gases in the table have very low critical temperatures; these gases were until recently called *permanent gases*, because until 1879 all attempts to liquefy them had failed owing to the temperatures employed being above the critical point.

Various methods have been employed in liquefying gases. Faraday was able to liquefy a large number of gases by means of their own pressure in glass tubes. To liquefy chlorine in this way a quantity of the yellow crystals of chlorine hydrate (a compound of chlorine and water) are brought into a glass tube of about 1 cm. in diameter, and closed at one end. The tube is then bent at right angles at about its middle point, and sealed. If now the sealed end be placed in a freezing mixture, whilst the other end containing the hydrate be gently warmed, a comparatively large volume of chlorine is liberated, and the pressure of the accumulated gas together with the low temperature employed is sufficient to bring about its liquefaction.

If silver chloride be saturated with ammonia gas, a compound of the two is formed, and this body treated in the same way evolves ammonia in such a quantity as to liquefy by its own pressure.

With many gases a much lower temperature is required than can be obtained by using an ordinary freezing mixture. Thus Pictet liquefied oxygen by submitting it to a very high pressure in a copper tube at — 140° C.

73. To measure the Volume of Carbon Dioxide evolved from one gram of Chalk.—

Method I.—

Exp. 126.—Take a large bottle (a Winchester quart) and fit it with a cork carrying two delivery tubes bent at right angles, one long enough to reach nearly to the bottom of the bottle, the other quite short (see Fig. 38). The longer delivery tube should be attached to another similar tube by a piece of rubber tubing on which a clip is placed. Nearly fill the bottle with water and pour on the top a few cubic centimetres of paraffin oil. Introduce the cork, blow through the short delivery tube till water runs out of the long delivery tube which constitutes a siphon tube; then tighten the clip. Now procure a small wide-mouthed flask and fit it with a cork and short delivery tube bent at right angles. Weigh the flask, introduce about a gram of chalk, and weigh again. The difference between the two weighings gives you the weight of chalk taken

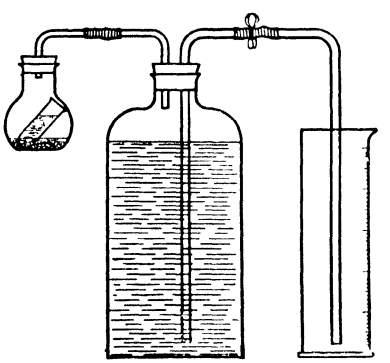


Fig 38.

Now add a little water, and then carefully introduce a small tube nearly filled with strong hydrochloric acid, leaning it up against the side of the flask. Insert the cork, and connect the delivery tubes of the flask and the bottle by a short piece of rubber tubing.[1] Place the free arm of the siphon in a tall graduated cylinder. Open the

[1] By this arrangement the pressure of the air in the apparatus at the commencement of the experiment is atmospheric.

clip A few drops of water escape and then the flow should cease; if it does not do so then air is finding its way into the apparatus, *i.e.* the corks are not tight. Close the clip, push all the corks well home and test again.

When the apparatus is gas-tight[1] incline the flask until a little of the liquid runs over on to the chalk, repeating the operation from time to time so long as effervescence continues. The carbon dioxide evolved pushes air over into the bottle, and this in its turn displaces water, which passes over into the cylinder. In time carbon dioxide reaches the bottle but is prevented from dissolving in the water by the layer of oil. At the end of the experiment allow the apparatus to remain for a few minutes in order that it may regain atmospheric temperature. Gently agitate the liquid in the flask occasionally.

Next make the levels of the liquids in the cylinder and bottle the same by raising or lowering the cylinder (so making the pressure in the apparatus atmospheric), close the clip, remove the siphon tube from the cylinder, and read the volume of water in the latter. This represents the volume of gas which has passed into the bottle, and so the volume of carbon dioxide evolved from the chalk taken, measured at the temperature and pressure of the atmosphere.

Suppose in an experiment the following results were obtained —

Weight of flask + chalk	=	10·364	gm.
„ „ alone	=	9·134	„
„ chalk taken	=	1·230	„

Volume of water collected = 287 c.c.

Then we have—

1·23 grams of chalk yield 287 c.c. of carbon dioxide.

Therefore—

1 gram of chalk would yield $\frac{287}{1{\cdot}23}$ or 233 c.c. of carbon dioxide measured at the temperature and pressure of the atmosphere.

[1] If a measurable quantity of water has collected in the cylinder you must read off the volume and subtract it from the final volume.

Now we have seen that the volume of a given quantity of gas varies with both the pressure and the temperature. But the temperature of the laboratory and the pressure of the surrounding atmosphere vary from day to day and from place to place, so that some one else working with quite as great accuracy might obtain a volume of gas somewhat different from yours. In order therefore that results may be compared together, we must all agree to state our results as they would be if they were all performed under the same conditions as to temperature and pressure, and it has been agreed that the temperature for such reference shall be the freezing-point of water (0° C.), and the normal or average pressure of the atmosphere, equal to that of a column of mercury 760 millimetres in height. These *standard conditions* are referred to as "Normal temperature and pressure," and the expression is often abbreviated to the letters "N.T.P."

Suppose that when you performed your experiment the temperature of the atmosphere was 15° C. and the pressure 775 millimetres of mercury. Let us reduce the volume of gas evolved to standard conditions. We have—

$$0° \text{ C.} = 273° \text{ absolute.}$$

$$15° \text{ C.} = 273 + 15 \text{ or } 288° \text{ absolute.}$$

Therefore by Charles' Law the volume will be decreased in the ratio $\frac{273}{288}$ when reduced to 0° C.

Again by Boyle's Law the volume will be increased in the ratio $\frac{775}{760}$ when reduced to 760 millimetres pressure.

Applying both corrections we have for the volume at 0° C. and 760 millimetres pressure—

$$233 \times \frac{273}{288} \times \frac{775}{760} \text{ or } 225 \text{ c.c.}$$

Method II.—

* **Exp. 127.**—The apparatus used in Exp. 125 is required for this experiment.

The burette must be *completely* filled with water by pouring the liquid into the pressure tube (which should be

raised about 60 cm.) till it just reaches the stopcock The stopcock is then closed, and the pressure tube lowered and clamped. Now weigh out into a flask similar to that you used in Exp. 126 about 0·15 gm. of chalk Cover this with a little water and introduce a tube of fairly strong hydrochloric acid. Close the flask with a cork carrying a short delivery tube bent at right angles and connect this up to the burette by means of a short piece of rubber tubing (Fig. 39).

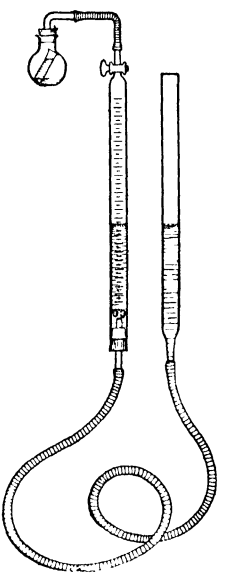


Fig. 39.

Next open the stopcock and upset the acid on to the chalk a little at a time. Gas collects in the burette which consists chiefly of air driven out by the carbon dioxide, though a little carbon dioxide[1] may also pass over. When the chalk has all disappeared allow the apparatus to stand till the water level in the burette ceases to *rise*, showing that the apparatus has regained the atmospheric temperature, and then adjust the pressure tube till the water level is the same as that in the burette. Now read the burette.

Suppose the reading is 15·3 c.c. Then the volume of gas collected is (see Exp. 125)

$$5{\cdot}2 + 50 - 15{\cdot}3 \quad \text{or} \quad 39{\cdot}9 \text{ c.c.}$$

Suppose that the weight of chalk taken was 0 17 gm. Then

0·17 gm. of chalk yields 39·9 c.c of carbon dioxide.

$\therefore$ 1 gm. of chalk would yield $\frac{39\,9}{0\,17}$ or 235 c.c.

[1] The slight error introduced owing to the solubility of carbon dioxide in water may be avoided by using mercury in the apparatus.

This is of course at the temperature and pressure of the atmosphere; it can be reduced to standard conditions as explained above.

Forms of apparatus similar to those described in Exps. 126, 127[1] may be employed for finding the volume of hydrogen evolved when metals such as zinc and magnesium are treated with sulphuric or hydrochloric acid. The layer of oil used in Exp. 126 is not required when the gas evolved is hydrogen, for this gas is practically insoluble in water.

74. To measure the Mass of Carbon Dioxide evolved from one gram of Chalk.—

Exp. 128.—Take a small wide-mouthed flask and fit it with a rubber cork carrying a drying tube filled with granulated calcium chloride and a glass tube reaching nearly to the bottom of the bottle (see Fig. 40). Accurately weigh out into the flask about 1 gram of chalk. Pour water into the flask till the chalk is well covered. (Do not add too much water.) Next tie a piece of cotton underneath the rim of a small test-tube, nearly fill the tube with strong hydrochloric acid, and lower it into the bottle. Now without leaving hold of the cotton insert the cork, so arranging that when the cotton is held tight by the cork the tube is in the position shown in the figure. See that the end of the straight tube dips in the liquid.

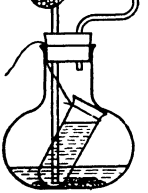


Fig. 40.

Now carefully weigh the whole. Then manipulate the flask so that a *little* acid escapes from the small tube on to the chalk. Carbon dioxide is evolved, and first drives air out of the flask through the calcium chloride tube (its only exit); after a time the gas itself passes out. Any

[1] If a pair of *Hempel's gas burettes* is available this is the most convenient arrangement of all. For a description of this piece of apparatus a work on *Gas Analysis* must be consulted.

moisture carried away by the escaping gases is retained by the calcium chloride, and so loss in weight is prevented. (If, however, the action is allowed to proceed *too rapidly* the drying will not be carried out effectively.) When the action slackens upset a little more acid, and continue to do this from time to time till all the chalk has disappeared.

The flask is now full of carbon dioxide, and, further, some of the gas is dissolved in the liquid. Warm the flask carefully till it is so hot that you can barely hold it. (*Do not boil the liquid.*) Now attach a piece of rubber tubing to the calcium chloride tube and suck *gently* till the pungent taste of carbon dioxide ceases to be noticed. The flask is now full of air again. Allow it to stand till it becomes quite cold, and then reweigh.

Suppose the following results were obtained —

Weight of flask + chalk	=	10 321 gm.
„ „ alone	=	9·136 „
„ chalk taken	=	1 185 „

Weight of apparatus before the reaction	=	35 614 gm.
„ „ after „ „	=	35 087 „
„ carbon dioxide evolved	=	0·527 „

We have then—

0·527 gram of carbon dioxide is evolved from 1 185 grams of chalk.

Therefore—

$\frac{0\ 527}{1·185}$ or 0 445 gram of carbon dioxide is evolved from 1 gram of chalk.

75. Density of Gases.—By the *density* of a gas we mean the *mass of it which occupies unit volume.* The most convenient volume to take as the unit is 1 *litre.*

Since hydrogen is the least dense of all gases it is very common to state the *relative density* (or specific gravity) of a gas in terms of hydrogen as unity, instead of stating the density as defined above. The *relative density* of a gas (in terms of hydrogen as unity) may be defined as the *weight*

of a given volume of the gas divided by the weight of an equal volume of hydrogen under the same conditions of temperature and pressure.

Sometimes relative densities are given in terms of *air* as unity.

76. Density of Air.—The density of air may be determined approximately in the following manner:—

* **Exp. 129.**—Fit a strong flask, holding about 300 c.c., with a cork through which passes a short length of glass tubing. Attach to it a piece of rubber tubing carrying a clip. Place about 30 c.c. of water in the flask, open the clip, and boil the water for ten minutes. The steam drives out all the air. Close the clip, remove the flame at once, allow to cool, and weigh the flask and its contents (w_1).

Now open the clip carefully so as to allow air to enter gradually. [Why does air enter?] When no more air enters weigh again (w_2), and measure the volume of water that remains (v_1). Finally, fill the flask with water to the level of the cork, and measure the volume of this water (v_2).

Let $t°$ be the temperature of the air.

Let H be the barometric height in millimetres of mercury.

$(v_2 - v_1)$ c.c. is the volume of air at $t°$ and H millimetres that (together with the v_1 c.c. of water) filled the flask.

$(w_2 - w_1)$ grams is the weight of this air.

The volume at N.T.P. is

$$(v_2 - v_1) \times \frac{H}{760} \times \frac{273}{273 + t} = v \text{ say.}$$

Therefore the mass of 1 litre at N.T.P. is

$$\left(\frac{w_2 - w_1}{v} \times 1000\right) \text{gm.}$$

Calculate out your result and see how nearly it agrees with the value 1·293 grams, which accurate measurements have shown to be the correct density of dry air.

[Your result cannot be quite correct because the air filling the flask is *moist*, not *dry*; but at this stage you had better not trouble about the correction.]

77. Density of Carbon Dioxide.—You can calculate this roughly from the results of Exps. 126, 128, for in Exp. 126 you have found the *volume* of carbon dioxide evolved from 1 gram of chalk, and in Exp. 128 the *mass* of the gas evolved from 1 gram of chalk.

By Exp. 126—

1 gram of chalk gave 225 c.c. of carbon dioxide measured at N.T.P.

By Exp. 128—

1 gram of chalk gave 0·445 gram of carbon dioxide.

∴ 225 c.c. of carbon dioxide measured at N.T.P. weigh 0·445 gram.

∴ 1000 c.c. or 1 litre of carbon dioxide measured at N.T.P. weigh $1000 \times \frac{0{\cdot}445}{225}$ or 2 gm.

Now 1 litre of hydrogen has been found to weigh 0·09 gram; therefore the density of carbon dioxide relative to hydrogen is about $\frac{2}{0{\cdot}09}$ or 22.

78. Density of Oxygen.—We can determine the density of oxygen by a method somewhat similar to that which we have used in the case of carbon dioxide, namely by finding (*a*) the mass, (*b*) the volume of oxygen evolved on heating 1 gram of potassium chlorate.

(*a*) *To estimate the mass of oxygen evolved on heating 1 gram of potassium chlorate.*—

Exp. 130.—Weigh a small hard glass tube, place in it about 1 gram of potassium chlorate and weigh again. Heat carefully, holding the tube in a slanting position and rotating it constantly. The salt melts and then appears to boil. After a time the liquid gets thick, and when the gas evolution ceases a white and solid mass (potassium chloride) remains in the tube.

Weigh the tube again when cool, and calculate the weight of oxygen which would be evolved from 1 gram of potassium chlorate. The result should be about 0·39 gram.

In a similar way the weight of oxygen evolved from 1 gram of nitre or red lead may be found.

(*b*) *To estimate the volume of oxygen evolved on heating 1 gram of potassium chlorate.*—

Exp. 131.—Fit up an apparatus similar to that described in Exp. 126,[1] but replace the small bottle by a hard glass tube containing about 1 gram of potassium chlorate (accurately weighed out). After filling the siphon tube as described in Exp. 126, attach the hard glass tube and test if the apparatus is air-tight. When it is so, heat the potassium chlorate. The oxygen evolved displaces the water from the bottle, and the water runs into the cylinder. When the level of water in the latter ceases to rise, allow the tube to cool to the temperature of the air. This will have happened when the level of water in the cylinder ceases to *fall*. Now make the levels of water in the cylinder and bottle the same, close the clip and remove the siphon tube. Read the volume of liquid in the cylinder: this is the volume of oxygen evolved from the weight of potassium chlorate taken measured at the pressure and temperature of the atmosphere.

From your result calculate the volume of oxygen at N.T.P. which would be evolved from 1 gram of potassium chlorate. It should be about 270 c.c.

From the results of Exps. 130, 131, calculate the density of oxygen just as you did that of carbon dioxide. You should find that a litre of oxygen weighs about 1·4 grams.

79. Diffusion of Gases.—

Exp. 132.—Pour a little "liquor ammonia"[2] (an aqueous solution of the gas ammonia) into a basin, and leave it

[1] The apparatus described in Exp. 127 might be used instead.

[2] Also called "liquid ammonia." Be careful not to inhale much of the vapour rising from the liquid, as it is injurious.

standing in the middle of the room. Very soon you will find that the smell has permeated to all parts of the room.

Exp. 133.—Procure a tall narrow gas jar and pass into it some carbon dioxide, letting the delivery tube reach quite to the bottom of the jar. If you first burn a little brown paper in the jar you will be able to see how the heavier carbon dioxide collects in the bottom of the cylinder, almost as a liquid would, pushing the air out above it. Fill the jar in this way about one-third and then lift out the delivery tube, pinching it so that no gas may pass into the upper part of the jar while you are raising it. Cover the mouth of the jar with a glass plate and set it aside for an hour. After this interval plunge a lighted taper into the jar and lower it until you reach a level where it is extinguished.

Mark the level and compare it with that at which the carbon dioxide originally stood. You will find that the level has risen.

Now by means of a syringe withdraw some of the gas from the bottom of the jar. Fill a test-tube with caustic soda solution, invert it in a trough of water and support it by means of a clamp. Place the syringe in the water and force gas out of it into the test-tube till the latter is about two-thirds full. Next place your thumb over the mouth of the tube, remove it from the trough and shake up vigorously. Invert the tube in the water again and remove your thumb. The water rises but does not completely fill the tube, showing that the gas was not all carbon dioxide.

Test the unabsorbed gas with a lighted taper. The taper continues to burn: the gas is air.

If the jar were left long enough it would be found that the air and carbon dioxide had become uniformly mixed throughout.

Exps. 132, 133 illustrate a general property of gases, namely, that they ultimately spread—or *diffuse*—to the boundaries of any closed space into which they are introduced, however large the space. The spreading or *diffusion* of a gas takes place independently of the presence of

other gases, and consequently, however many different gases are introduced into a closed space, ultimately they will all be distributed homogeneously throughout that space.

The phenomenon of gaseous diffusion is in apparent contradiction to the law of gravitation, for if, as in Exp. 133, we start with the heavier of two gases (carbon dioxide) below and the lighter (air) above the heavier gas passes *upwards* and the lighter *downwards*.

The explanation of the phenomenon is that the very small particles of which gases are composed are in constant rapid motion in directions which are continually changing, owing to collisions with other particles, or with the walls of the containing vessel. [It is the bombardment of the particles on the walls of the vessel which gives rise to gaseous pressure.] It will now be seen that gaseous diffusion does not really contradict the law of gravitation, for, to return to Exp. 133, at any given instant some particles of carbon dioxide are moving upward in opposition to gravity just as a cricket-ball does when thrown up into the air.

It is this property of gaseous diffusion which explains the fact that mixtures of gases of different density do not separate into layers with the heaviest gas at the bottom and the lighter ones above in order of decreasing density. Air, for example, is a homogeneous mixture of oxygen and nitrogen; it does not separate into two layers, oxygen, the heavier gas, below, and nitrogen, the lighter gas, above.

80. Graham's Law of Gaseous Diffusion.—Let us now try to discover whether all gases diffuse at equal rates or whether on the other hand there is (as we might rather expect) some relation between the density of a gas and the rate at which it diffuses.

* **Exp. 134.**—A porous cell, such as is used in voltaic batteries, is fitted with an indiarubber stopper, and a glass tube about half a metre long, furnished with a bulb, is passed through the stopper; this is bent and drawn out

into a jet as shown in Fig. 41. Before inserting the cork fill the bulb and lower part of the tube with water. Now place a beaker filled with hydrogen over the porous cell, and the water will be immediately depressed and driven out of the jet in a fine stream.

This is evidence that the light gas hydrogen passes through the walls into the porous cell quicker than the air is able to pass out of it. A greater volume of gas collects within the space of the cell and tube and forces the water out before it.

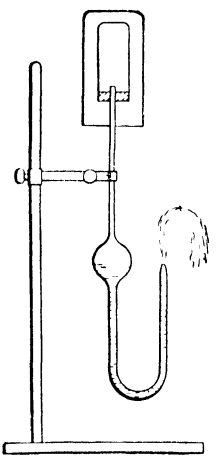


Fig. 41.

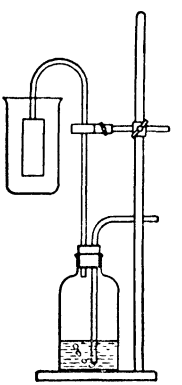


Fig. 42.

Now let us perform a similar experiment, using in place of hydrogen a gas heavier than air—say carbon dioxide.

* **Exp. 135.**—Fit up the apparatus shown in Fig. 42. In this case the glass tube carrying the porous cell is bent round so that a beaker containing the carbon dioxide may be in an upright position when placed over the cell. The bottle contains a little water. When the beaker is placed in position bubbles of air pass up through the liquid in the bottle.

The explanation is that air diffuses out of the cell quicker than the heavier gas, carbon dioxide, passes into it. This tends to produce a partial vacuum, and air enters through the delivery tube dipping into the liquid to take its place.

The relative densities of the gases employed in the above experiments are—

Hydrogen, 1. Air, 14·4. Carbon dioxide, 22.

We see then that the smaller the density of a gas the more rapidly it diffuses. By measuring the amount of different gases which diffused through a porous plug in a given time, under like conditions, Graham found that *the relative rates of diffusion of gases are inversely proportional to the square root of their densities.* This statement is known as *Graham's Law of Gaseous Diffusion.*

Thus in relation to air :—

		$\frac{1}{\sqrt{\text{density}}}$	Velocity of diffusion observed
Density of hydrogen	= 0·0695	= 3·792	3·830
„ carbon dioxide	= 1·5180	= 0·812	0·812

QUESTIONS.—CHAPTER VIII.

1. State Charles's Law, and describe how you would prove it experimentally.

2. What do you understand by *absolute zero* and *absolute temperature*?

3. Enunciate Boyle's Law. Describe an experiment which illustrates it.

4. How would you proceed to find the density of carbon dioxide?

5. Describe how you would proceed to measure the volume of hydrogen evolved from half a gram of magnesium by the action of sulphuric acid.

6. How would you proceed to estimate (1) the mass, (2) the volume of oxygen evolved on heating 1 gram of red lead till decomposition was complete?

7. Describe experiments to illustrate the phenomenon of *diffusion of gases.*

8. Describe how you would proceed to find out whether a given gas diffuses more or less rapidly than air. State the law which relates to the relative rates of diffusion of gases.

CHAPTER IX.

GAY-LUSSAC'S LAW AND AVOGADRO'S HYPOTHESIS.

81. Gay-Lussac's Law.—Experiments have been described in § 43 which show that the volumes of hydrogen and oxygen which combine to form water are in the ratio 2 : 1.

If we modify the synthetic experiment (Exp. 75) in such a way that the water produced remains in the form of steam (by surrounding the eudiometer with a jacket filled with the vapour of a liquid boiling at a temperature considerably above 100° C., the boiling-point of water), we find that the volume of steam produced is equal to that of the hydrogen it contains. (The gases before combination are of course measured at the same temperature as the steam.)

There is then a *simple relation* between the volumes of hydrogen and oxygen which combine together and the volume of steam they produce.

Experiments with other substances have been found to yield similar results (as we shall see in the sequel). For example:—

1 vol. of hydrogen and 1 vol. of chlorine combine to form 2 vol. of hydrochloric acid gas.

2 vol. of carbon monoxide and 1 vol. of oxygen combine to form 2 vol. of carbon dioxide.

1 vol. of nitrogen and 3 vol. of hydrogen combine to form 2 vol. of ammonia.

2 vol. of nitric oxide and 1 vol. of oxygen unite to form 2 vol. of nitrogen peroxide.

Gay-Lussac performed a number of experiments like those referred to, at the beginning of the last century, and generalised the results in the following statement, known as *Gay-Lussac's Law of Volumes*:—

When gases combine together they do so in volumes which bear a simple ratio to one another and to that of the product (if a gas).

82. Avogadro's Hypothesis.—Gay-Lussac announced the Law of Volumes a short time after Dalton had put forward his Atomic Theory, and an attempt was soon made to harmonise the two. To this end the hypothesis that *equal volumes of all gases contain the same number of atoms* was advanced.[1]

It was soon found, however, that this hypothesis was untenable. The following example will illustrate the kind of argument which led to this conclusion.

Consider the combination of hydrogen and chlorine to form hydrochloric acid gas. *One* volume of hydrogen combines with one volume of chlorine to form *two* volumes of hydrochloric acid gas. Let x = number of atoms[2] of hydrochloric acid gas in *two* volumes; then by the hypothesis *one* volume of hydrogen will contain $x/2$ atoms of hydrogen and *one* volume of chlorine $x/2$ atoms of chlorine. Now let us take as two volumes such a volume that $x = 1$ (since we can, of course, take any volume we like). Then $x/2 = \frac{1}{2}$. In other words, one atom of hydrochloric acid gas (contained in two volumes) is produced by the union of half an atom of hydrogen (contained in one volume) and half an atom of chlorine (contained in one volume). But, according to Dalton's theory, an atom cannot be divided; hence the hypothesis is incorrect.

The problem was solved by the Italian physicist Avogadro, who recognised two kinds of ultimate particles—

(*a*) The ultimate particle which can exist in the free state, as, for instance, the smallest particle of hydrochloric acid gas or of hydrogen. This he termed the *molecule*.

(*b*) The ultimate particle which is capable of taking part in a chemical change or capable of being transferred from one chemical compound to another, as, for instance, the

[1] It should be noted that the term "atom" was used loosely here, because both elementary and compound gases were included, and it is obviously a contradiction in terms to speak of an *atom* of a *compound*, since a compound can be broken up into elements. By an "atom" of a compound was meant the smallest particle of the compound which can exist.

[2] Atom being used here in the loose sense already explained

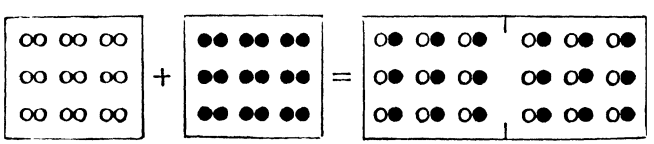
hydrogen or the chlorine contained in the molecule of hydrochloric acid gas. This he termed the *atom*.

A molecule of a compound must necessarily contain at least two atoms. A molecule of an element may contain two or more atoms, or it may consist of one atom only.

Avogadro then restated the hypothesis which had been shown to be untenable, as follows:—*Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules.*

Let us return to the above example, namely, the combination of hydrogen and chlorine to form hydrochloric acid gas, and reconsider it in the light of Avogadro's hypothesis. We will make the assumption that the molecules of hydrogen and chlorine are each composed of two atoms,[1] and that a molecule of hydrochloric acid gas is composed of one atom of hydrogen and one atom of chlorine. Further, we will consider the combination of *nine* molecules of each gas (any other number would do equally well). Then, assuming Avogadro's hypothesis, the combination may be represented as below, where

o	represents	an atom of hydrogen.
oo	„	a molecule of „
●	„	an atom of chlorine.
●●	„	a molecule of „



Nine molecules or 1 volume. | Nine molecules or 1 volume | Eighteen molecules or 2 volumes.

But this agrees with the results of experiment: *i.e.* Avogadro's hypothesis harmonises Gay-Lussac's Law and Dalton's Atomic Theory as far as the combination of hydrogen and chlorine is concerned. By means of similar

[1] There are very good grounds for this assumption, but we cannot stop to consider them here.

diagrams it can be shown that the hypothesis affords a satisfactory explanation of the volumetric relations of the other gases considered in this chapter; in fact its applicability has been found to be perfectly general, and we may consider that its truth is thoroughly well established.

83. The Molecular Weight of Gases.—By combining the definition of relative density given in § 75 with Avogadro's Law, we can easily establish a *simple numerical relation* between the *molecular weight* of a gas (*i.e.* the weight of a molecule of it) and its *relative density*. For consider a given volume of a gas and an equal volume of hydrogen under the same conditions of temperature and pressure. Let n be the number of molecules of the gas present in the given volume; then, by Avogadro's Law, n will also be the number of molecules of hydrogen in the same volume.

Now—

$$\frac{\text{Wt. of given vol. of a gas}}{\text{Wt. of equal vol. of hydrogen}} = \left\{ \begin{array}{l} \text{Relative density} \\ \text{of the gas.} \end{array} \right.$$

$$\therefore \frac{\text{Wt. of } n \text{ molecules of the gas}}{\text{Wt. of } n \text{ molecules of hydrogen}} = \quad ,, \quad ,, \quad ,,$$

Or, putting $n = 1$,

$$\frac{\text{Wt. of 1 molecule of the gas}}{\text{Wt. of 1 molecule of hydrogen}} = \quad ,, \quad ,, \quad ,,$$

But it can be proved that the molecule of hydrogen contains two atoms, and therefore, adopting the *atom* of hydrogen as the unit of mass, the weight of a molecule of hydrogen will be 2.

It follows that

$$\frac{\text{Wt. of 1 molecule of a gas}}{2} = \left\{ \begin{array}{l} \text{Relative density of the} \\ \text{gas.} \end{array} \right.$$

Or,

$$\text{Molecular weight of a gas} = \left\{ \begin{array}{l} 2 \times \text{relative density of} \\ \text{the gas.} \end{array} \right.$$

This relation enables us to find the molecular weight of a gas by determining its density relative to hydrogen. In the following table the relative densities and molecular weights of some common gases are placed side by side:—

Gas.	Relative density.	Molecular weight.
Hydrogen	1·0	2·0
Nitrogen	14·0	28 0
Oxygen	16·0	32 0
Hydrogen chloride	18 25	36 5
Ammonia	8·5	17·0
Carbon dioxide ...	22 0	44 0

84. Symbols and Formulae.—In order to represent an *atom* of an element we use a *symbol* which is an abbreviation of the name of the element. In many cases the initial letter of the name of an element is used as the symbol: *e.g.* an atom of hydrogen is represented by H and an atom of oxygen by O. When the names of two or more elements commence with the same letter, two significant letters are used—the first and one other; one of the elements may, however, be represented by the initial letter only. For example, the names of four elements commence with B—barium, bismuth, boron, and bromine; the symbols for the atoms of these elements are Ba, Bi, B, and Br respectively. Some chemical symbols are derived from the Latin names of the elements they represent; thus an atom of copper is represented by Cu (Lat., *cuprum*) and an atom of iron by Fe (Lat., *ferrum*).

Now the weights of the elements represented by the symbols for their atoms will of course be the weights of the atoms. These are expressed in terms of the weight of an atom of hydrogen as unity, so that the symbols H and O stand for unit weight of hydrogen and 16 units of weight of oxygen respectively (the atomic weight of oxygen being 16).

When the number of atoms in a molecule of an element is known, the *molecule* is represented by placing a small number below and to the right of the symbol for the element. For example, a molecule of oxygen is represented by O_2, since the molecule of oxygen contains two atoms; O_2 further represents 2×16 or 32 units of weight of oxygen. If the molecule of the element only contains *one* atom, the suffix is omitted, *e.g.* the molecule of mercury is represented by Hg.

When we wish to represent the composition of compounds we use *formulae*.[1] The formula for a molecule of a compound is built up by placing the symbols for the atoms of the elements of which it is composed in juxtaposition, and adding suffixes to indicate the number of atoms of each element present. A molecule of water, for example, is represented by the formula H_2O, which implies that two atoms of hydrogen or two units of weight are combined with one atom of oxygen or 16 units of weight, to form one molecule of water weighing 18 units (*i.e.* the *molecular weight* of water is 18 units).

When we do not know the *absolute* number of atoms of each element in a molecule of the compound, as is usually the case when the substance is not in the gaseous state, we write the simplest possible formula which represents the *relative* number of atoms of each element. Thus the number of atoms of copper and oxygen contained in a molecule of black oxide of copper is unknown, but we do know that for every atom of copper there is one of oxygen, so we write the formula for the oxide CuO.

85. Equations.—A *chemical equation* is an equation which represents the nature and relative amounts of the bodies concerned in a chemical change by means of symbols.

Certain chemical substances being brought together under suitable conditions, a chemical change takes place by which one or more of the constituents is set free or

[1] The term *formula* is also frequently applied to the symbol for a *molecule* of an *element*.

transferred, the state before and after the change being separated by the sign $=$.

As instances of such equations we may give the action of hydrogen at red heat on black oxide of copper—

$$\underset{\text{Hydrogen}}{H_2} + \underset{\text{Black oxide of copper}}{CuO} = \underset{\text{Water}}{H_2O} + \underset{\text{Copper}}{Cu}$$

and the action of zinc on dilute sulphuric acid—

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

Such equations may be interpreted quantitatively according to the table of atomic weights given in § 122. Thus—

2×1 or 2 units of weight of hydrogen will effect the reduction of $63{\cdot}5 + 16$ or $79{\cdot}5$ units of weight of black oxide of copper, yielding $2 \times 1 + 16$ or 18 units of weight of water and $63{\cdot}5$ units of weight of copper.

In the second case

$65{\cdot}5$ units of weight of zinc acting upon $2 \times 1 + 32 + 4 \times 16$ or 98 units of weight of sulphuric acid yield $65{\cdot}5 + 32 + 4 \times 16$ or $161{\cdot}5$ units of weight of zinc sulphate and 2 units of weight of hydrogen.

It is obvious, from a consideration of the Law of Conservation of Matter, that the quantity of each element and the total quantity of the elements on each side of the equation must be the same. Thus in the first equation discussed above there are on each side two atoms of hydrogen or 2 units of weight, one atom of copper or $63{\cdot}5$ units of weight, and one atom of oxygen or 16 units of weight. The total weight of the elements on each side of the equation is $2 + 63{\cdot}5 + 16$ or $81{\cdot}5$ units.

In writing equations to express chemical reactions, regard must be paid to the state in which the bodies concerned exist. If in the *solid* condition (and often also if in the *liquid* condition), the molecular composition of a substance is usually undefined, and a mere empirical statement of the quantity of the substance entering into the reaction must be made. If in the *gaseous* condition, the molecular composition is known and must be indicated.

2S and S_2 both represent 64 units of weight of sulphur. The first is the form used for expressing a certain weight of solid sulphur; the second expresses the same weight of sulphur in the form of vapour at a high temperature, it being known that the molecule of sulphur at high temperature is composed of two atoms.

Again, the equation

$$H_2 + O = H_2O,$$

though it indicates that hydrogen and oxygen unite to form water in the proportion of 2×1 units of weight of hydrogen to 16 units of weight of oxygen (which agrees with the result of Exp. 121), is not a correct representation of the combination of these gases; for O represents an atom of oxygen which cannot exist in the free state, but immediately unites with another atom to form a molecule. The equation must therefore be doubled thus—

$$2H_2 + O_2 = 2H_2O.$$

It will be noticed that in doubling the equation we have written $2H_2$, not H_4; this is because the molecule of hydrogen contains 2, not 4, atoms. $2H_2$ represents two molecules of hydrogen each composed of two atoms; H_4 would represent one molecule containing 4 atoms.

Avogadro's hypothesis enables us to give a volumetric meaning to equations when they represent the interaction of gases, for since equal volumes of all gases contain the same number of molecules, it follows that the volume occupied by one molecule[1] of any gas (elementary or compound) is the same. It is usual, for the sake of convenience, to arbitrarily fix the volume of one molecule of a gas as *two volumes*.

Consider again the last equation given above. It may be read thus:—2 molecules or 4 volumes of hydrogen unite with 1 molecule or 2 volumes of oxygen to form 2 molecules or 4 volumes of steam; *i.e.* hydrogen unites

[1] By the expression "volume occupied by one molecule" we mean the volume occupied by the molecule and also its share of the free space between the molecules.

with half its volume of oxygen to form its own volume of steam, which agrees with the result of experiment.

Again, the equation

$$H_2 + Cl_2 = 2HCl,$$

which represents the combination of hydrogen and chlorine, may be interpreted thus:—1 molecule or 2 volumes of hydrogen combines with 1 molecule or 2 volumes of chlorine to form 2 molecules or 4 volumes of hydrogen chloride; *i.e.* hydrogen chloride contains half its volume of hydrogen and half its volume of chlorine, which agrees with the results of experiment.

Below are given the equations for a few of the reactions we investigated in Chapter VII and their quantitative interpretations. You will find that these are in agreement with the results of the experiments.

Formation of Magnesium Oxide.—

$2Mg$	$+$	O_2	$=$	$2MgO,$
$2 \times 24{\cdot}5$ or 49 units of weight of magnesium		2×16 or 32 units of weight of oxygen		$2 \times (24{\cdot}5 + 16)$ or 81 units of weight of magnesium oxide

i.e. 1 gram of magnesium combines with 32/49 or 0·65 gram of oxygen. Compare this with Exps. 118, 119.

Decomposition of Chalk.—

$CaCO_3$	$=$	CaO	$+$	$CO_2.$
$40 + 12 + 3 \times 16$ or 100 units of weight of calcium carbonate (chalk)		$40 + 16$ or 56 units of weight of calcium oxide (lime)		$12 + 2 \times 16$ or 44 units of weight of carbon dioxide

Compare this with Exp. 120.

Reduction of the Oxides of Lead by Hydrogen.—

PbO_2	$+$	$2H_2$	$=$	Pb	$+$	$2H_2O,$
Lead peroxide $207 + 2 \times 16$ or 239 units of weight		Hydrogen 2×2 or 4 units of weight		Lead 207 units of weight		Water $2(2 \times 1 + 16)$ or 36 units of weight

PbO	$+$	H_2	$=$	Pb	$+$	$H_2O.$
Yellow oxide of lead $207 + 16$ or 223 units of weight		Hydrogen 2×1 or 2 units of weight		Lead 207 units of weight		Water $2 \times 1 + 16$ or 18 units of weight

Compare these numbers with the results obtained in Exp. 122.

Action of Heat on Copper Sulphate Crystals.—Copper sulphate crystals are represented by the formula $CuSO_4$, $5H_2O$, which means that a molecule of copper sulphate, $CuSO_4$, is loosely combined with 5 molecules of water of crystallisation. The equations representing the decomposition of the crystals are as follows:—

At 140° C.,

$$CuSO_4,5H_2O = CuSO_4,H_2O + 4H_2O.$$

At 220° C.,

$$CuSO_4,H_2O = CuSO_4 + H_2O.$$

These equations agree with the results of Exp. 123, for they represent that four-fifths of the water of crystallisation (four molecules out of five) is given up at 140°, the remaining fifth being driven off only at 220° C.

86. The chief Elements, the symbols representing them, and their atomic weights (in round numbers) in relation to hydrogen as unity are given in the table below. Non-metals are printed in italics.

Aluminium	Al	27	Lead	Pb	207
Antimony	Sb	120	Lithium	Li	7
Argon	A	40	Magnesium	Mg	24·5
Arsenic	As	75	Manganese	Mn	55
Barium	Ba	137	Mercury	Hg	200
Bismuth	Bi	208	Molybdenum	Mo	96
Boron	B	11	Nickel	Ni	59
Bromine	Br	80	*Nitrogen*	N	14
Cadmium	Cd	112	*Oxygen*	O	16
Calcium	Ca	40	*Phosphorus*	P	31
Carbon	C	12	Platinum	Pt	195
Chlorine	Cl	35·5	Potassium	K	39
Chromium	Cr	52	*Silicon*	Si	28·5
Cobalt	Co	59	Silver	Ag	108
Copper	Cu	63·5	Sodium	Na	23
Fluorine	F	19	Strontium	Sr	87·5
Gold	Au	197	*Sulphur*	S	32
Helium	He	4	Tin	Sn	119
Hydrogen	H	1·0	Titanium	Ti	48
Iodine	I	127	Zinc	Zn	65
Iron	Fe	56			

QUESTIONS.—CHAPTER IX.

1. State *Gay-Lussac's Law of Combination of Gases by Volume*, and illustrate it by examples.

2. What is *Avogadro's Hypothesis*? Indicate the nature of the evidence on which it is based.

3. State the relation which exists between the molecular weight of a gas and its relative density referred to hydrogen as unity, and show how this result is deduced.

4. Explain *fully* what the formulae O_2 and CO_2 represent.

5. State all that is implied by the chemical equation

$$2H_2 + O_2 = 2H_2O.$$

6. Write the equations representing (1) the reduction of brown oxide of lead by hydrogen, (2) the decomposition of ammonia by electric sparks, (3) the combination of carbon monoxide with oxygen

CHAPTER X.

CHEMICAL EQUIVALENTS. VALENCY.

87. Chemical Equivalents.—We must now consider a quantity which is very closely related to the atomic weight of an element, namely, its *chemical equivalent* (*or combining weight*).

The *chemical equivalent* of an element is defined as the *weight of that element which combines with or displaces unit weight of hydrogen.*

We saw in Exp. 121 that approximately 8 grams of oxygen combine 1 gram of hydrogen. Hence the chemical equivalent of oxygen is about 8. Again, when sodium acts on water 23 grams of sodium take the place of 1 gram of hydrogen; therefore the chemical equivalent of sodium is 23.

Let us now investigate some of the methods used for the determination of equivalents of metals.

88. Determination of the Equivalent of a Metal by measuring the Volume of Hydrogen evolved.—The method which we shall use in the following experiment for finding the equivalent of a metal consists in treating a known weight (say x grams) of the metal with dilute acid, measuring the volume of hydrogen evolved, and calculating the weight (say y grams) from the volume. Then the equivalent of the metal is $\frac{x}{y}$. A convenient metal to use is magnesium.

Exp. 136.—Take a long measuring tube closed at one end and graduated in cubic centimetres. One graduated up to 100 c.c. is preferable. Take a narrow beaker, pour in about half a litre of water, and add about 30 c.c. of concentrated sulphuric acid, stirring briskly. When cool fill up the tube completely with the acid, taking care that no air bubbles are allowed to enter; close the open end by means of the thumb, and invert in the beaker, which contains the greater portion of the diluted acid. Fix the tube in a small clamp stand.

Now procure a small tube about 4 cm. long and of such a diameter that it will slide comfortably into the graduated tube. Next scrape a piece of magnesium ribbon to remove all oxide, and weigh out a piece of about 0·1 gram (it should not be more). Drop the coiled ribbon into the small tube and fill up with water, shaking well if necessary, to disengage any air bubbles. Close the end by means of the thumb, and bring it under the mouth of the graduated tube (which is still under the dilute acid). Force the small tube up into the wider one, and lower the latter until it almost touches the bottom of the beaker and completely encloses the other (see Fig. 43). Remove your hand and rinse off the acid.

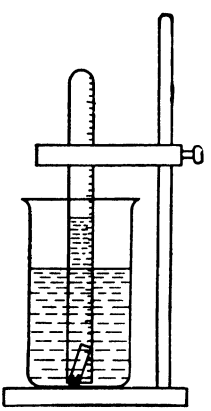


Fig. 43.

Soon the heavier acid will diffuse to the magnesium and begin to dissolve it. Hydrogen will be evolved, and will be collected in the tube. When the magnesium has completely dissolved, adjust the tube so that the liquid inside is level with that outside, more water being poured into the beaker if necessary. Do not touch the tube with your hand, but let it remain in the clamp, upon which hang a thermometer close to the tube in order to read the temperature of the air in the neighbourhood of the gas.

In a few minutes read the volume of gas, the temperature,

and the barometric pressure; and from these calculate the volume at 0° C. and 760 mm. pressure, making allowance for the fact that the gas is not dry, but is saturated with aqueous vapour.[1] In making the correction, use the table given in Appendix I. Knowing that a litre of hydrogen under these conditions weighs 0·09 gram, find the weight of the hydrogen collected.

Then—

$$\frac{\text{Weight of Magnesium}}{\text{Weight of Hydrogen}} = \text{Equivalent of Magnesium.}$$

A similar method may be used for determining the equivalents of the metals zinc, iron, and aluminium, but in the case of the last, dilute *hydrochloric* acid must replace dilute sulphuric acid, which is without action on the metal. Also in place of the apparatus you have just been using that described in Exp. 127 may be employed for the determination of equivalents by this method.

89. Determination of Equivalents by Deposition of Metal.—Another method by which the equivalent may be determined is applicable in some cases where the foregoing cannot be used. This is the deposition of a metal from a solution of one of its salts by placing in it another metal. For instance, if metallic zinc or iron be introduced into a solution of silver nitrate or copper sulphate, etc., finely divided silver or copper will be thrown down, and the amounts deposited under like conditions are proportional to the equivalents of the metals in question.

* **Exp. 137.** *Equivalent of copper.*—Take a rather deep porcelain crucible of about 50 c.c. content. Into this bring about 35 c.c. of a solution containing not less than 3·5 grams of copper sulphate, and then about 0·4 gram of clean zinc foil, the exact weight of which has been determined. Warm *gently*. The zinc will slowly disappear, and

[1] This aqueous vapour exerts a pressure, and for a *given temperature* this pressure has a *definite value* if the gas contains as much aqueous vapour as possible, *i e.* is *saturated* with it.

a heavy powder will be precipitated to the bottom of the vessel. When on stirring with a glass rod there is no longer any sign of the foil, the reaction is complete. The zinc has replaced the copper in the salt originally taken, and we have now in the vessel metallic copper and a solution containing zinc sulphate and excess of copper sulphate.

In the meantime fold a filter paper and fit it into a funnel. Remove it, roll it up, and introduce it into a wide test-tube, the upper half of which has been cut off. Place the tube in an air oven (Fig. 35) and regulate the temperature to about 110° C. After about half an hour allow the tube to cool in a desiccator and weigh. Heat up again, allow to cool, and reweigh. Repeat this process till the weight is constant.

Now place the filter paper in the funnel, filter off the precipitate of copper and wash with hot water till a drop of the wash water gives no blue coloration with ammonia. Wash with alcohol two or three times and dry in the air oven. Next roll up the filter paper with the precipitate inside, place it in the tube, and weigh. Repeat the drying and reweigh. If the weight is not constant repeat until it is. The increase in weight gives the amount of copper precipitated.

We now have (*a*) the weight of zinc used, (*b*) the equivalent weight of copper which this zinc has displaced, and if the experiment has been carried out with due care these weights will be found to show the relation 32·5 : 31·8. Thus, if 32·5 be accepted as the equivalent of zinc, 31·8 must be taken as that of copper.

Similarly, if a solution of silver nitrate be substituted for that of copper sulphate, the equivalent of silver may be determined. Experiments of the same kind may be performed with pure samples of iron and copper sulphate or silver nitrate and with magnesium and silver nitrate.

90. Determination of the Equivalent of a Metal by Conversion into the Oxide.—In many cases the most convenient method of finding the equivalent of a

metal consists in converting a weighed quantity of it into its oxide, and weighing the oxide produced. From the results obtained we calculate the weight of the metal which combines with 8 grams of oxygen (say x grams). Then, since 8 grams of oxygen are equivalent to 1 gram of hydrogen (see § 87), x grams of the metal are also equivalent to 1 gram of hydrogen, *i.e.* x is the equivalent of the metal.

Sometimes, as in the case of magnesium, the metal is readily converted into its oxide by heating in air. Usually it is best to first convert the metal into the nitrate, and then break this up by ignition, when a residue of oxide remains.

Equivalent of Magnesium.—From the results of Exps. 118, 119, you can calculate two independent values of the equivalent of magnesium.

Thus suppose the following results were obtained in Exps. 118, 119 (fill in your own numbers in place of x, y, etc.) :—

	Exp. 118.	Exp. 119.
Wt. of magnesium used ...	$= x$ gm.	y gm.
„ „ oxygen taken up by the magnesium	$= z$ gm.	w gm.
Wt. of magnesium which would combine with 8 gm. of oxygen	$= \frac{x}{z} \times 8$	$\frac{y}{w} \times 8$

i.e. the values for the equivalent of magnesium obtained in these two experiments are $\frac{x}{z} \times 8$ and $\frac{y}{w} \times 8$ respectively.

The correct value is 12·25.

Equivalent of Copper.—**Exp. 138.**—Proceed as in Exp. 119, using about 0·5 gram of pure copper wire in place of the magnesium ribbon. When you have evaporated to dryness after the solution of the metal a green residue of *copper nitrate* remains. This should be heated on a pipeclay triangle till it is completely changed into black copper oxide. (Follow the details of Exp. 119 exactly.)

Work out the equivalent of copper as you did that of magnesium above. Its correct value is 31·75.

Equivalent of Lead.—* **Exp. 139.**—Find the weight of oxygen which combines with 1 gram of lead, and deduce the equivalent of lead. Using *lead foil*, proceed exactly as in Exp. 119, producing first lead nitrate, then yellow lead oxide; but do not heat to fusion. The equivalent of lead in this oxide is 103·5.

Equivalent of Tin.—* **Exp. 140.**—Using moderately strong nitric acid with about 1 gram of pure tin, find the weight of oxygen which combines with the metal, and hence deduce its equivalent. In this case the acid converts the metal into the oxide instead of the nitrate. The oxide separates out as a white powder. After evaporating to dryness the product should be finally heated over the blowpipe flame till it becomes practically white. A brown colour indicates insufficient heating. The equivalent of tin in this oxide is 29·7.

The last three metals do become more or less oxidised when heated in the air, but the process is slow and imperfect.

91. Valency.—The best way to approach the subject of valency is to consider the composition of a number of stable compounds of hydrogen and another element. The formulae of ten such compounds are given below—

HF,	HCl,	HBr,	HI,
Hydrogen fluoride.	Hydrogen chloride.	Hydrogen bromide	Hydrogen iodide
	H_2O,	H_2S,	
	Water.	Sulphuretted hydrogen.	
	H_3N,	H_3P,	
	Ammonia.	Phosphoretted hydrogen	
	H_4C,	H_4Si,	
	Marsh gas.	Silicon hydride.	

We cannot study the metals in a similar manner so satisfactorily because many of them do not form stable compounds with hydrogen. Let us instead compare the

formulae of a series of compounds (salts) derived from some acid, say hydrochloric acid (HCl), by the replacement of the hydrogen by metals. We have—

(1) NaCl, KCl.

(2) $CuCl_2$, $MgCl_2$, $CaCl_2$, $ZnCl_2$, $BaCl_2$.

(3) $AlCl_3$, $FeCl_3$, $CrCl_3$.

The compounds in Group (1) are obviously derived from one molecule of hydrochloric acid, those in Group (2) from two molecules, and those in Group (3) from three molecules, because they contain respectively one, two, and three atoms of chlorine. It follows that—

(1) One atom of sodium or potassium replaces *one atom* of hydrogen.

(2) One atom of copper, magnesium, etc., replaces *two atoms* of hydrogen.

(3) One atom of aluminium, iron, or chromium replaces *three atoms* of hydrogen.

In other words, one atom of sodium or potassium possesses the same power of combining with the non-metal chlorine as one atom of hydrogen; one atom of copper, magnesium, etc., has the same combining capacity as two atoms of hydrogen; and one atom of aluminium, iron, or chromium as three atoms of hydrogen.

An examination of the compounds derived in a similar manner from other acids, *e.g.* sulphuric, nitric, and phosphoric acids, leads to like conclusions; we find, for instance, that one atom of sodium replaces one atom of hydrogen, and one atom of aluminium replaces three atoms of hydrogen, whichever acid is used.

Taking the atom of hydrogen as the standard, and calling its capacity to combine with other elements, or its *valency* (*i.e.* worth), unity, a number can be assigned to each element which expresses its combining capacity or valency in terms of this unit. Thus, since one atom of chlorine unites with *one* atom of hydrogen, the valency of chlorine is the same as that of hydrogen, viz. 1. One atom of oxygen unites with *two* atoms of hydrogen; consequently the valency of oxygen is 2. Similarly the

valencies of nitrogen and carbon are 3 and 4 respectively. Again, one atom of sodium or of potassium possesses the same combining capacity as one atom of hydrogen; sodium and potassium have, therefore, a valency 1. Similarly the valency of copper, magnesium, etc., is 2, and of aluminium, etc., 3.

An element with a valency 1 is said to be *monovalent*, and the corresponding terms *divalent*, *trivalent*, etc., are applied to elements whose valencies are respectively 2, 3, etc. Thus hydrogen, chlorine, and potassium are monovalent, oxygen and copper are divalent, nitrogen and aluminium are trivalent, and carbon is tetravalent.

It must be added that certain metals, such as iron and tin, form two series of salts in which they show different valency. For instance, in $FeCl_2$ (ferrous chloride) one atom of iron replaces *two* atoms of hydrogen, *i.e.* iron is *divalent*, whilst in $FeCl_3$ (ferric chloride) one atom of iron replaces *three* atoms of hydrogen, *i.e.* iron is *trivalent*; in the same way we have *stannous* and *stannic* chlorides ($SnCl_2$ and $SnCl_4$) in which the valency of tin is *two* and *four* respectively.

The valencies of the majority of the elements, both metals and non-metals, can be found from a study of their *oxides* if we assume that oxygen is divalent. Let us examine the formulae of a number of oxides—

Na_2O, K_2O, Cl_2O.
CuO, MgO, CaO, ZnO, BaO, PbO, FeO.
Al_2O_3, B_2O_3.
CO_2, SO_2, SiO_2.
N_2O_5, I_2O_5.
SO_3.

We conclude that in these compounds Na, K, Cl are monovalent; Cu, Mg, Ca, etc., are divalent; Al, B are trivalent; C, S (in SO_2), and Si are tetravalent; N (in N_2O_5), P (in P_2O_5), I (in I_2O_5) are pentavalent; S (in SO_3) is hexavalent.

It will be observed that several of the non-metals, *e.g.* iodine, nitrogen, and sulphur, are capable of exerting a

higher valency towards oxygen than towards hydrogen; thus iodine is *monovalent* in HI and *pentavalent* in I_2O_5, nitrogen is *trivalent* in NH_3 and *pentavalent* in N_2O_5, sulphur is *divalent* in H_2S and *tetravalent* and *hexavalent* in SO_2 and SO_3 respectively. In general an element which is hexavalent may, in some of its compounds, be tetravalent or divalent, and one which is pentavalent may be trivalent. It should be mentioned, however, that many elements exhibit both an odd and an even valency, contrary to the belief of the earlier chemists.

The valencies of a number of common elements are given in the following table:—

Monovalent.	Divalent.	Trivalent.	Tetravalent	Pentavalent.	Hexavalent
H	Ba	Al	Sn (ic)	P (in PCl_5, etc.)	S (in SO_3, etc.)
Na	Sr	Cr	C	N (in N_2O_5, etc.)	Cr (in CrO_3)
K	Ca	Fe (ic)	Si	As (ic)	
Ag	Mg	Co (ic)	S (in SO_2, etc.)	Sb (ic)	
F	Zn	As (ous)	Pb (in PbO_2, etc.)		
Cl	Cd	Sb (ous)			
Br	Co	Bi			
I	Ni	B			
	Pb	P (in PCl_3, etc.)			
	Hg	N (in NH_3, etc.)			
	Cu				
	Fe (ous)				
	Mn (ous)				
	Sn (ous)				
	O				
	S (in H_2S, etc.)				

92. Relation between Equivalent and Atomic Weight.—Suppose we wish to find the valencies of the three elements sodium, magnesium, and aluminium, being given their atomic weights. The first thing to be done is to find their equivalents, *i.e.* the weight of each of them which replaces unit weight of hydrogen (see § 87). Experiment shows that these are respectively 23, 12, and 9,

The atomic weights are Na = 23, Mg = 24·5, and Al = 27. Also H = 1.

We have then,

23 units of weight of sodium replace unit weight of hydrogen, *i.e.* 1 atom of sodium replaces *one* atom of hydrogen.

12·25 units of weight of magnesium replace unit weight of hydrogen. ∴ 2 × 12·25 = 24·5 units of weight of magnesium replace 2 units of weight of hydrogen, *i.e.* 1 atom of magnesium replaces *two* atoms of hydrogen.

9 units of weight of aluminium replace unit weight of hydrogen. ∴ 3 × 9 = 27 units of weight of aluminium replace 3 units of weight of hydrogen, *i.e.* 1 atom of aluminium replaces *three* atoms of hydrogen.

The valencies of sodium, magnesium, and aluminium are therefore 1, 2, and 3 respectively. It will be seen that in order to obtain the valency of an element, all we have to do is to divide the atomic weight of the element by its equivalent.

$$\text{Valency of sodium} = \frac{23}{23} = 1$$

$$\text{,, magnesium} = \frac{24{\cdot}5}{12{\cdot}25} = 2$$

$$\text{,, aluminium} = \frac{27}{9} = 3$$

The following general relation between the atomic weight of an element and its equivalent may then be stated—

$$\text{Valency} = \frac{\text{Atomic Weight}}{\text{Equivalent}}.$$

Where an element has two equivalents and consequently two valencies, the equivalent and valency used in the above formula must both apply to the same compound. Thus, considering the case of iron, its equivalent in ferrous chlordie, $FeCl_2$, is 28 and its valency 2; in ferric chloride, $FeCl_3$, its equivalent is $18\frac{2}{3}$ and its valency 3. Both these sets of values should give the same atomic weight for iron on applying the formula—

(1) *Ferrous iron*—

$$2 = \frac{\text{Atomic Weight}}{28}.$$

$$\therefore \text{Atomic Weight} = 2 \times 28 = 56.$$

(2) *Ferric iron*—

$$3 = \frac{\text{Atomic Weight}}{18\frac{2}{3}}.$$

$$\therefore \text{Atomic Weight} = 3 \times 18\tfrac{2}{3} = 56.$$

93. Nomenclature of Compounds.—Compounds may be divided into two classes, those composed of *two elements* (called "binary" compounds), and those composed of *three or more elements*.

Binary compounds may be designated according to the number of atoms of the elements they contain, the number being usually stated only for the more non-metallic element, the termination of the name being *-ide*—

H_2O_2, hydrogen diox*ide*.
I_2O_5, iodine pentox*ide*.
PCl_3, phosphorus trichlor*ide*.
PCl_5, phosphorus pentachlor*ide*.

Where only two compounds of the same elements exist, the termination *-ous* may be applied to the one with the smaller proportion of the more non-metallic element (the "lower" oxide, iodide, etc.), and the termination *-ic* to the other—

HgI, mercur*ous* iodide; HgI_2, mercur*ic* iodide.
Cu_2O, cupr*ous* oxide; CuO, cupr*ic* oxide.

Oxides which when dissolved in water form acids are termed "anhydrides," and these, together with the acids they give rise to, receive the terminations *ous* and *ic* in the same sense as before—

N_2O_3, nitr*ous* anhydride or nitrogen trioxide; HNO_2, nitr*ous* acid.

N_2O_5, nitr*ic* anhydride or nitrogen pentoxide; HNO_3, nitr*ic* acid.

CO_2, carbon*ic* anhydride or carbon dioxide; H_2CO_3, carbon*ic* acid.

Salts take the termination *ite* or *ate* according as they are derived from *ous* or *ic* acids respectively—

H_2SO_3, sulphur*ous* acid;	Na_2SO_3, sodium sulph*ite*.
H_2SO_4, sulphur*ic* acid,	Na_2SO_4, sodium sulph*ate*.
HNO_2, nitr*ous* acid;	$NaNO_2$, sodium nitr*ite*.
HNO_3, nitr*ic* acid;	$NaNO_3$, sodium nitr*ate*.

Where more than two compounds of the same element exist further discrimination is necessary, and in the case of acids and salts the prefix *hypo* is applied to the lowest and *per* to the highest.

HClO, *hypo*chlorous acid;	KClO, potassium *hypo*chlor*ite*.
$HClO_2$, chlor*ous* acid;	$KClO_2$, potassium chlor*ite*.
$HClO_3$, chlor*ic* acid;	$KClO_3$, potassium chlor*ate*.
$HClO_4$, *per*chloric acid;	$KClO_4$, potassium *per*chlor*ate*.

QUESTIONS.—CHAPTER X.

1. What do you understand by the *chemical equivalent* of an element? Describe two methods by which the equivalent of magnesium can be determined.

2. Describe in detail how you would proceed to find the chemical equivalent of copper by deposition of the metal, assuming the equivalent of zinc known.

3. How would you proceed to determine the equivalent of aluminium, given a supply of the material, some strong hydrochloric acid, and some water?

4. Explain the term *valency*, illustrating your answer by examples.

5. Give examples of elements which exhibit more than one valency, and illustrate the way in which the composition of their compounds changes with the change in valency.

6. What is the relation between the atomic weight, the equivalent, and the valency of an element? Give examples to illustrate your answer.

7. Explain the term *binary compound*, and give three examples of binary compounds.

SECTION II.—SYSTEMATIC TREATMENT OF THE NON-METALS.

CHAPTER XI.

HYDROGEN, H_2.

94. Occurrence.—Hydrogen occurs in the free state as an incandescent gas in the sun, but in the earth it is always found in combination with other elements. Water is a compound of hydrogen and oxygen, H_2O; many oils consist of hydrogen and carbon, and these elements, together with oxygen, form the chief constituents of animal and vegetable tissue, and of organic compounds in general

95. Methods of Preparation.—The more important of these have already been described in Chapter IV. and only require brief recapitulation here; some other methods will, however, also be mentioned.

(1) **Direct decomposition of water by heat.**—On heating water to a high temperature, it undergoes partial decomposition. Grove effected this by passing steam through a strongly heated porcelain tube.

(2) **Decomposition of water by the electric current.**—This process is described in Exp. 73.

(3) **Decomposition of water by metals at ordinary temperature.**—Refer back to § 35 for an experiment illustrating this method of obtaining hydrogen. The metals which will decompose water without the application of heat are comparatively few in number; they comprise the alkali metals (sodium, potassium, lithium, etc.), the metals of the alkaline earths (calcium, strontium, barium),

and magnesium (very slowly). Only half the hydrogen is liberated, the equation representing the reaction in the case of sodium being—

$$\underset{\text{Sodium}}{2Na} + \underset{\text{Water}}{2H_2O} = \underset{\text{Caustic soda}}{2NaOH} + \underset{\text{Hydrogen}}{H_2}.$$

Caustic soda (NaOH) is formed and dissolves in the water, rendering it alkaline, as may be shown by pouring red litmus solution into the liquid.

Some metals which by themselves cannot decompose water at ordinary temperatures are able to do so when in contact with certain other metals. Thus if zinc be coated with a thin layer of copper—forming a so-called *zinc-copper-couple*[1]—it slowly liberates hydrogen from the water in which it is immersed without the application of heat. On warming, hydrogen is rapidly evolved; this provides a convenient method of preparing the pure gas. The zinc alone takes part in the reaction; it is converted into zinc hydroxide, $Zn(OH)_2$—

$$Zn + 2H_2O = Zn(OH)_2 + H_2.$$

Again, the metals zinc and magnesium will decompose water readily at ordinary temperature if they are in contact with platinum. A discussion of the explanation of these contact decompositions is beyond the scope of this work.

(4) **Decomposition of water by metals on the application of heat.**—This method of preparing hydrogen was studied in Exps. 59-61.

When heated metals decompose steam, as in Exps. 60, 61, they displace the whole of the hydrogen, and are converted into oxides—

$$3Fe + 4H_2O = \underset{\substack{\text{Magnetic oxide}\\ \text{of iron}}}{Fe_3O_4} + 4H_2.$$

$$Mg + H_2O = \underset{\substack{\text{Magnesium oxide}\\ \text{of magnesia}}}{MgO} + H_2.$$

[1] The *zinc-copper-couple* is prepared by immersing granulated zinc in a dilute solution of copper sulphate for a short time, and then removing the product and washing it well with water to remove adhering salts.

Most metals will decompose water provided the temperature is sufficiently high; copper, silver, and gold are notable exceptions.

(5) **Action of acids on metals.**—Many metals act on dilute hydrochloric acid or dilute sulphuric acid with evolution of hydrogen. The common laboratory method of preparing the gas is to act on granulated zinc with dilute sulphuric acid, as described in Exp. 63.

The equation representing the reaction is—

$$\underset{}{Zn} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + H_2.$$

(6) Action of alkalis on metals.—A few metals, notably zinc and aluminium, are acted upon by a boiling solution of caustic potash (KOH) or caustic soda (NaOH) with liberation of hydrogen. If zinc and caustic potash are used, the reaction which takes place is represented by the equation—

$$\underset{}{Zn} + 2KOH = \underset{\text{Potassium zincate}^1}{Zn(OK)_2} + H_2.$$

96. Preparation of Pure Dry Hydrogen.—The gas obtained by the common laboratory method (Method 5) is

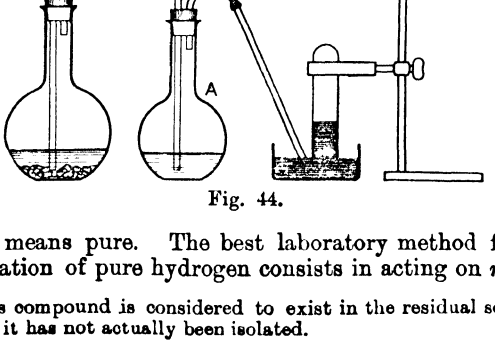


Fig. 44.

by no means pure. The best laboratory method for the preparation of pure hydrogen consists in acting on *magne-*

[1] This compound is considered to exist in the residual solution, though it has not actually been isolated.

sium with dilute sulphuric acid. If the gas is required dry it should be passed through a small flask containing strong sulphuric acid[1] (A, Fig. 44) and collected at the pneumatic trough over mercury (water obviously being inadmissible).

97. Properties.—Hydrogen is a colourless, odourless gas, only very slightly soluble in water, 1 c.c. of which dissolves about 0·02 c.c. of the gas at ordinary temperatures. It is the lightest substance known, its *absolute density*, i.e. the weight of one cubic centimetre of it under standard conditions of temperature and pressure, being only 0·00009 gram. The density of air under the same conditions is about 14·4 times that of hydrogen.

The extreme lightness of hydrogen as compared with air is shown by the fact that hydrogen can be poured *upwards* from one vessel into another, or can be collected by upward displacement. If a beaker is suspended upside down from a balance and counterpoised, and hydrogen is then poured upwards into it so as to displace the air, the beaker will show a decrease of weight. Again, if a gas-jar of hydrogen stands mouth upwards, and a light is applied, the whole of the gas burns in one or two seconds, owing to the rapidity with which the hydrogen rises through the denser air; in an inverted gas-jar, on the other hand, the gas burns far more slowly, as it does not then mix with the air.

Hydrogen burns in air or oxygen with a blue non-luminous flame, which is very hot. A solid infusible substance placed in the flame becomes white hot, and emits a brilliant light. This is the principle of the *lime-light*, in which a jet of hydrogen (or coal-gas) burning in oxygen impinges on a cylinder of quicklime and raises it to a white heat.

In burning, hydrogen combines with oxygen, forming water—

$$2H_2 + O_2 = 2H_2O.$$

[1] The drying is rendered more complete by the use of two sulphuric acid flasks.

A mixture of hydrogen with oxygen or air is violently explosive, as the combustion is practically instantaneous. Hence care has to be taken in experiments with hydrogen not to apply a light to the gas or to heat any part of the apparatus till the air has been expelled.

Hydrogen will not support the combustion of those substances which burn in air. Thus a lighted taper is extinguished on being pushed up into an inverted gas-jar of hydrogen; the gas of course takes fire and burns at the mouth of the jar.

98. Hydrides.—Hydrogen forms compounds with most of the non-metals (either directly or indirectly) and with many of the metals; these compounds are called *hydrides*. The hydrides of the non-metals are, as a whole, stable compounds, but those of the metals are unstable. Examples of non-metallic hydrides are hydrogen chloride, HCl, water, H_2O, ammonia, NH_3, and marsh gas, CH_4; examples of hydrides of the metals are potassium hydride, KH, sodium hydride, NaH, and copper hydride, Cu_2H_2.

99. Reducing Agents.—We have seen in Exp. 69 that hydrogen is able to remove the oxygen from many hot metallic oxides with formation of water. As stated in § 43 the hydrogen is said to *reduce* the oxide to the metal in such reactions, and hydrogen is spoken of as a *reducing agent*.

The original criterion of a *reducing agent* was its *power of removing oxygen from a compound*, but the term has now acquired an extended meaning. For example, the conversion of mercuric chloride ($HgCl_2$) into mercurous chloride (Hg_2Cl_2) by the action of metallic mercury is spoken of as the reduction of mercuric chloride to mercurous chloride.

$$HgCl_2 + Hg = Hg_2Cl_2.$$

The term may now be defined as follows:—

A *reducing agent* is *a substance which is able to bring about a decrease in the ratio of the non-metallic to the metallic part of another substance.*

Returning to the example given above we see that the ratio of the non-metal chlorine to the metal mercury is smaller in mercurous chloride than in mercuric chloride, and *mercury*, which brings about the decrease in ratio, acts as a *reducing agent*.

QUESTIONS.—CHAPTER XI.

1. Name some natural substances which contain hydrogen as an essential constituent. Is hydrogen known to occur in the free state?
2. How may water be decomposed without the application of chemical reagents?
3. What metals decompose water—
   (*a*) at ordinary temperature,
   (*b*) at red heat?

   Give equations showing the nature of the reaction in each case.
4. If you desire to obtain hydrogen in as pure a condition as possible, what method would you adopt?
5. If you desire to prepare moderately pure hydrogen in large quantities, what method would you adopt?
6. Write down equations showing the action of iron and magnesium respectively on dilute sulphuric acid.
7. Devise three experiments suitable for illustrating in a striking manner the extreme lightness of hydrogen.
8. State the chief properties of hydrogen, dividing them into (*a*) physical properties and (*b*) chemical properties.
9. Name three metallic and three non-metallic hydrides, and give their formulae.
10. Explain what is meant by a *reducing agent*. Describe an experiment you would carry out to illustrate the process of reduction; sketch the apparatus you would use.

CHAPTER XII.

OXYGEN AND OZONE.

Oxygen, O_2.

100. Occurrence.—Oxygen is the most widely distributed of the elements; it constitutes about one-half of the earth's crust. Air contains about 20 per cent. of oxygen, water nearly 90 per cent., and the great majority of minerals consist largely of this element.

101. Methods of Preparation.—(1) We have seen in Exp. 28 that oxygen can be obtained by strongly heating potassium chlorate. The course of the reaction is somewhat complex. Decomposition commences at about 370° C., the changes represented in the two following equations taking place simultaneously:—

$$4KClO_3 = 3KClO_4 + KCl$$
$$2KClO_3 = 2KCl + 3O_2.$$

At higher temperature the perchlorate is decomposed thus:—

$$KClO_4 = KCl + 2O_2.$$

It is found that if the potassium chlorate is intimately mixed with certain substances in a fine state of division the decomposition takes place at a much lower temperature (considerably below the melting point of the salt) and can be more easily regulated. Examples of such substances are manganese dioxide, cupric oxide, and finely divided platinum. They are found to be unaltered at the termination of the process, and are called *catalytic agents*, the phenomenon being termed *catalysis*.

In practice manganese dioxide is the substance commonly used, and the laboratory method for the preparation of oxygen which is not required particularly pure consists in heating an intimate mixture of potassium chlorate with about one-quarter of its weight of manganese dioxide.

The oxygen evolved is, however, mixed with a little chlorine, so that if the *pure* gas is required potassium chlorate *alone* must be used or else the gas must be passed through a wash-bottle containing caustic soda, which absorbs the chlorine.

If the gas is required *dry* it should be passed through a small flask containing strong sulphuric acid and collected over mercury.

The change which takes place when manganese dioxide is used may be represented by the equation—

$$2KClO_3 = 2KCl + 3O_2,$$

though this only represents the initial and final states, there being a series of intermediate changes, the discussion of which is outside the scope of this work. It should be mentioned, however, that no potassium perchlorate is formed when a catalytic agent is used in the decomposition of potassium chlorate.

(2) Many oxides on heating evolve oxygen. Two of these—mercuric oxide, HgO, and red lead, Pb_3O_4—have already been used to prepare the gas. The equations representing their decomposition on heating are—

$$2HgO = 2Hg + O_2.$$

$$2Pb_3O_4 = 6PbO + O_2.$$

It was by the action of heat on these two oxides that Priestley and Scheele (independently) first isolated oxygen gas towards the end of the eighteenth century. Priestley's method of procedure was as follows:—He introduced some mercuric oxide into a suitable glass vessel which he then filled completely with mercury and inverted in a trough of mercury. He then heated the substance by concentrating the sun's rays on it with a burning glass. Oxygen gradually collected over the mercury.

Other oxides which lose oxygen on heating are silver

oxide, Ag_2O, lead peroxide, PbO_2, barium dioxide, BaO_2, and manganese dioxide, MnO_2—

$$2Ag_2O = 4Ag + O_2.$$
$$2PbO_2 = 2PbO + O_2.$$
$$2BaO_2 = 2BaO + O_2.$$
$$3MnO_2 = Mn_3O_4 + O_2.$$

In the case of manganese dioxide the temperature required is much higher than that used in the preparation of oxygen from potassium chlorate and manganese dioxide.

(3) Certain metallic oxides containing a high percentage of oxygen, such as manganese dioxide and lead peroxide, yield oxygen on heating with strong sulphuric acid.

$$\underset{\text{Manganese dioxide}}{2MnO_2} + 2H_2SO_4 = \underset{\text{Manganese sulphate}}{2MnSO_4} + 2H_2O + O_2.$$

$$\underset{\text{Lead peroxide}}{2PbO_2} + 2H_2SO_4 = \underset{\text{Lead sulphate}}{2PbSO_4} + 2H_2O + O_2.$$

(4) Many salts which contain a large percentage of oxygen are decomposed on heating, either alone or in some cases with strong sulphuric acid, with evolution of oxygen. We have already discussed the action of heat on one such salt—potassium chlorate. Another example is potassium nitrate (KNO_3), which on heating loses oxygen and becomes converted into potassium nitrite (KNO_2)—

$$2KNO_3 = 2KNO_2 + O_2.$$

As illustrations of salts which evolve oxygen on heating with strong sulphuric acid we may take potassium permanganate ($KMnO_4$) and potassium bichromate ($K_2Cr_2O_7$)—

$$4KMnO_4 + 8H_2SO_4 = 4KHSO_4 + 4MnSO_4 + 6H_2O + 5O_2.$$

$$2K_2Cr_2O_7 + 10H_2SO_4 = 4KHSO_4 + 2Cr_2(SO_4)_3 + 8H_2O + 3O_2.$$

(5) If bleaching powder is mixed with certain oxides such as cobalt oxide (CoO), or cupric oxide (CuO), and the mixture made into a paste with water, a ready supply

of oxygen is obtained on gently heating.[1] Here again the oxide plays the part of a catalytic agent.

Bleaching powder consists of a substance, $CaOCl_2$, loosely combined with slaked lime, $Ca(OH)_2$. On treating as above described the following decomposition occurs :—

$$2CaOCl_2 = 2CaCl_2 + O_2.$$

102. Manufacture of Oxygen.—At the present time oxygen is manufactured by liquefying air and then distilling off the more volatile nitrogen (§ 72). Until recently, however, a process known as Brin's process was used. This depends upon the fact that when baryta (BaO) is heated to *dull redness* in air it takes up oxygen and is converted into the dioxide—

$$2BaO + O_2 = 2BaO_2.$$

The dioxide at a *bright red heat* loses the oxygen which it had taken up, and is transformed again into baryta—

$$2BaO_2 = 2BaO + O_2.$$

The original proposition of Boussingault to prepare oxygen on the large scale in this way failed owing to certain difficulties. These were, however, finally overcome by the Brin process. In this process the same reaction was made use of, but it was found that in order to make the process a continuous one the following conditions must be attended to :—

(*a*) The air must be freed from carbon dioxide and excessive moisture.

(*b*) The baryta must be so prepared as to obtain it in a firm and yet porous condition. It is obtained in the best condition by heating barium nitrate.

(*c*) The temperatures employed in the oxidation of the baryta and its subsequent deoxidation must be kept as low as possible.

An important modification of the original process has also been made under which it is no longer necessary to work

[1] In practice a little cobalt nitrate ($Co(NO_3)_2$) is added to the bleaching powder paste ; the two substances react with formation of cobaltic oxide, Co_2O_3.

alternately at higher and lower temperatures. By means of a force-pump the air is brought into contact with the heated baryta under a pressure of about 15 lb. to the square inch. When sufficient time has elapsed to allow of conversion into barium peroxide connection is made with an exhaust pump, and the pressure reduced to about one-tenth of an atmosphere. Under so low a pressure the barium peroxide is decomposed at the same temperature which under higher pressures sufficed to form it. Instead, therefore, of varying the temperatures it is only necessary to establish high and low pressure alternately, the periods of operation being about a quarter of an hour.

The baryta is contained in a number of iron cylinders connected together by pipes and placed vertically in a furnace and heated by "producer gas." The working is practically continuous and only needs to be interrupted about every six months for the purpose of breaking up the baryta and adding a little fresh material.

103. Properties.—Oxygen is a colourless, odourless gas only slightly soluble in water, 1 c.c. of which dissolves 0·0489 c.c. of the gas at 0° C. and 0·034 c.c. at ordinary temperatures. The weight of 1 c.c. of oxygen under standard conditions of temperature and pressure, *i.e.* its absolute density, is 0·001429 gram. Since 1 c.c. of hydrogen weighs 0·00009 gram under standard conditions, the relative density of oxygen taking hydrogen as unity is $\frac{0{\cdot}001429}{0{\cdot}00009} = 15{\cdot}88$. Taking air as unity, the relative density of oxygen is $\frac{0{\cdot}001429}{0{\cdot}0012935} = 1{\cdot}106$ (for 1 c.c. of air under standard conditions weighs 0·0012935 gram), *i.e.* oxygen is slightly heavier than air.

The distinguishing feature of oxygen is that it combines readily with nearly all the elements, and often with such energy that the union is accompanied by manifestation of light and heat. This phenomenon is termed "combustion," and oxygen is consequently *a powerful supporter of combustion*. A glowing splinter of wood, if plunged into oxygen,

immediately bursts into flame, a property which is only shown by one other gas, nitrous oxide.

Experiments have already been described in Chapter II. illustrating the properties of oxygen, and the student should refer back to them. The chemical changes which take place when sulphur, phosphorus, magnesium, and iron burn in oxygen are represented by the following equations:—

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

$$P_4 + 5O_2 = \underset{\text{Phosphoric oxide}}{P_4O_{10}}.$$

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

$$3Fe + 2O_2 = \underset{\text{Magnetic oxide of iron, or triferric tetroxide}}{Fe_3O_4}.$$

We have also seen, however, that oxidation can go on at ordinary temperatures. Thus, iron rusts in moist air forming ferric oxide, Fe_2O_3, combined with some water; phosphorus fumes and gives out a faint luminosity in air forming phosphorous oxide, P_4O_6, and other compounds. Organic matter and some mineral substances, such as iron pyrites, also undergo oxidation in the air at ordinary temperatures. This phenomenon of oxidation without the application of heat is often termed *slow combustion*, though the usual manifestations of combustion, viz. the production of light and sensible heat, are, as a rule, absent. As a matter of fact, heat is being given out during these reactions, but so slowly that its production is not apparent.

Oxygen plays an important part in vital processes, both in the animal and vegetable organisms, transforming carbonaceous substances ultimately into carbon dioxide and hydrogenous substances into water. This accounts for the fact that exhaled breath always contains carbon dioxide and water vapour. It is the heat evolved during these processes which maintains the body of an animal at the necessary temperature.

104. Oxidising Agents.—An *oxidising agent* is primarily, as the name implies, *a substance which is able to give up oxygen to other substances.* Oxygen itself is therefore the oxidising agent *par excellence.* But the term has acquired an extended meaning similar to that associated with "reducing agent" (see § 99) and may be defined as follows:—

An *oxidising agent* is *a substance which is able to bring about an increase in the ratio of the non-metallic to the metallic part of a substance.*

For example, the conversion of stannous chloride ($SnCl_2$) into stannic chloride ($SnCl_4$) by chlorine is spoken of as the oxidation of stannous chloride to stannic chloride, chlorine acting as the oxidising agent—

$$SnCl_2 + Cl_2 = SnCl_4.$$

As already mentioned in § 42, the processes of oxidation and reduction usually go on together, the oxidising agent being reduced and the reducing agent oxidised. Thus when nitric acid, which is an oxidising agent, acts on metallic tin, which is a reducing agent, the acid is reduced to various oxides of nitrogen, and the tin is oxidised to stannic oxide (SnO_2).

Again, consider the action of stannous chloride on ferric chloride as represented in the equation

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2.$$

From the point of view of the change which takes place in the ferric chloride the action is one of *reduction,* the ferric chloride being reduced to ferrous chloride by the reducing agent stannous chloride; but from the point of view of the change which takes place in the stannous chloride the action is one of *oxidation,* the stannous chloride being oxidised to stannic chloride.

105. The Oxides.—All elements combine with oxygen to form *oxides,* with the exception of fluorine and bromine, and a small group of which argon is the chief. Oxides may be conveniently divided into four classes:—

(1) Acidic oxides. (2) Basic oxides.
(3) Peroxides. (4) Neutral oxides.

106. Acidic Oxides.—It was Lavoisier who first showed that the oxides of certain elements (viz. the non-metals), when dissolved in water, form acids. The following equations represent the reactions which take place when some of these oxides, called *acidic oxides*, combine with water :—

$$\underset{\text{Sulphur dioxide}}{SO_2} + H_2O = \underset{\text{Sulphurous acid}}{H_2SO_3}.$$

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

$$\underset{\text{Phosphoric oxide}}{P_4O_{10}} + 2H_2O = \underset{\text{Metaphosphoric acid}}{2H_2P_2O_6}.$$

$$\underset{\text{Carbon dioxide}}{CO_2} + H_2O = \underset{\text{Carbonic acid}}{H_2CO_3}.$$

$$\underset{\text{Nitrogen pentoxide}}{N_2O_5} + H_2O = \underset{\text{Nitric acid}}{2HNO_3}.$$

107. Basic Oxides.—These are the oxides of the metals which on treatment with acids yield salts and water *only* (cf. peroxides). A few of them are soluble in water, combining with it to form hydroxides. Such are potassium monoxide, K_2O, calcium monoxide or quicklime, CaO, and barium monoxide, BaO. With water these form, respectively, potassium hydroxide or caustic potash, KOH, calcium hydroxide or slaked lime, $Ca(OH)_2$, and barium hydroxide, $Ba(OH)_2$.

$$K_2O + H_2O = 2KOH.$$

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

$$BaO + H_2O = Ba(OH)_2.$$

The majority of the metallic oxides are, however, insoluble in water, and their hydroxides can only be obtained indirectly. Examples of insoluble oxides are zinc oxide, ZnO, mercuric oxide, HgO, and ferric oxide, Fe_2O_3.

108. Oxides which are both Acidic and Basic.—There are some oxides which at one time play the part of basic oxides and at another of acidic oxides, and it is only by considering the nature of the salt in which they occur that we can say in which capacity they are acting.

For instance, sodium stannate, Na_2SnO_3, is formed from soda and oxide of tin, the oxide of tin being the acid constituent, whilst in stannic sulphate, $Sn(SO_4)_2$, the oxide of tin is the basic constituent.

109. Peroxides.—

Exp. 141.—Introduce a little manganese dioxide into a test-tube, cover with strong sulphuric acid, shake up and warm gently.[1] You will observe that a gas is evolved with effervescence. Prove by the glowing splint test that oxygen is evolved. Repeat the experiment, using lead peroxide in place of manganese dioxide; again oxygen is evolved.

Manganese dioxide (also called *manganese peroxide*) and *lead peroxide* are examples of a class of metallic oxides known as *peroxides.*

These are oxides containing a high percentage of oxygen and are chiefly derived from metals. When a metallic peroxide is heated with concentrated sulphuric acid part of its oxygen is evolved in the free state and at the same time the sulphate corresponding to[2] a lower oxide of the metal is formed.

Thus manganese dioxide forms manganous sulphate ($MnSO_4$) corresponding to the oxide MnO, and lead peroxide forms lead sulphate ($PbSO_4$) corresponding to PbO.

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$

We shall have occasion to further investigate the properties of metallic peroxides later on,[3] and shall find

[1] Do not overheat, otherwise so much sulphuric acid vapour comes off that the glowing splint is extinguished, not relit.

[2] When a salt is formed from an acid and the only other product is water (or in other words when the valency of the metal in the salt is the same as its valency in the oxide) the salt is said to *correspond* to the oxide.

[3] See §§ 150, 151, 165.

that they may be divided into two classes which differ considerably in properties.

Nitrogen peroxide (NO_2) is an example of a *non-metallic* peroxide. The name was given to it because it was found to contain more oxygen than nitric oxide (NO); it does not give up oxygen when warmed with concentrated sulphuric, as metallic peroxides do. *Hydrogen peroxide*, so called because it contains a higher percentage of oxygen than water, possesses very distinctive properties which will be studied in due course.

110. Neutral Oxides.—This term is conveniently applied to two non-metallic oxides, nitric oxide (NO) and carbon monoxide (CO), which do not form acids with water (in which they are but slightly soluble).

Ozone, O_3.

111. Under certain conditions oxygen is found to possess a peculiar odour similar to that observed in the neighbourhood of an electrical machine during electrical discharge; and it differs from ordinary oxygen in its physical and chemical properties. This modified form of oxygen is termed *ozone*.

† **Exp. 142.** *Preparation and Properties of Ozone.*—Ozone occurs in the oxygen produced during the electrolysis of water, and is produced in small quantity during the slow oxidation of phosphorus (see § 103), but it is most conveniently obtained by passing "a silent discharge" from two Grove's cells and an induction coil[1] through dry oxygen. For this purpose the apparatus shown (Fig. 45) may be used. An outer tube A B ending below in a narrower portion bent into a U-tube, is provided with two stopcocks, and an inner tube of somewhat smaller diameter,

[1] The exact nature of this electrical phenomenon (produced by the apparatus described below) is not understood; it appears to be doubtful whether any true electric current passes through the oxygen or not.

closed at the bottom, and sealed in at A. The outer tube is surrounded throughout its whole length by a coil of platinum wire, and the inner tube is filled with dilute sulphuric acid, and another platinum wire dips into this.

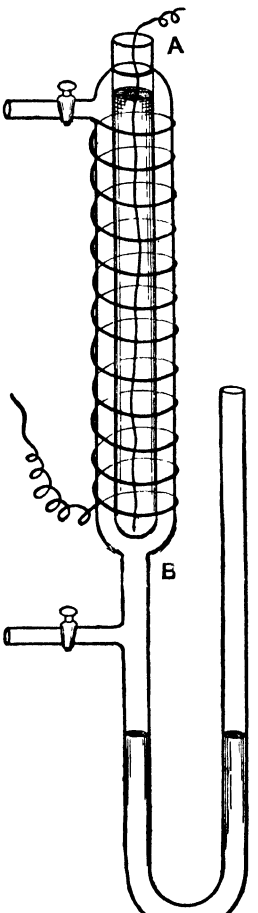


Fig. 45.

The stopcocks are opened, and concentrated sulphuric acid is poured into the U-tube, which serves as a gauge, and dry oxygen passed through the annular space till the air is swept out. The stopcocks are now closed and the two platinum wires connected to the terminals of the induction coil. The temperature of the apparatus should be kept constant during the experiment, and this may easily be effected by surrounding it with water at the same temperature as the room.

After passing the silent discharge for a little while some of the oxygen contained in the space between the tubes will have been converted into ozone, and the following observations may be made:

(1) The volume of gas in the annular space diminishes, as will be indicated by the sulphuric acid in the gauge. By determining beforehand the relative volume of the space in which the oxygen is confined, and that of a given length of the U-tube, an approximate estimate may be made of the amount of contraction.

(2) Attach a tube at the upper stopcock, open both stopcocks, and drive out some of the ozonised oxygen at

the lower one, holding a paper dipped in solution of potassium iodide near the outlet. The paper will turn brown from the liberation of iodine, the ozone being transformed into ordinary oxygen.

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

(3) Bleach indigo or moist litmus in a similar way.

(4) Note the odour of the ozone.

(5) Put a globule or two of mercury in a small flask and pass ozonised oxygen into the flask. On shaking, the mercury is superficially oxidised, loses its convexity of surface, and spreads out in a film on the walls of the flask.

(6) Expel the ozonised oxygen from the lower stopcock through a glass tube about 20 cm. long, heating the tube to dull redness; at 250° C. ozone is transformed into oxygen, and, after heating, a test made as in (2) should give no liberation of iodine.

The above observations show the great chemical activity of ozone, and the features by which it is distinguished from oxygen, for ordinary oxygen does not bleach, nor does it oxidise mercury or liberate iodine from potassium iodide at ordinary temperatures; ozone also readily attacks rubber tubing, and rubber connections should therefore be avoided in making experiments with the gas. It may be added that ozone is readily taken up by turpentine and certain other essential oils.

By using the method described above, not more than 8 or at most 10 per cent. of the oxygen can be transformed into ozone. If, however, ozonised oxygen is passed through a tube surrounded by liquid oxygen, the ozone condenses to a blue liquid, which boils at −110° C. with formation of a blue explosive gas.

112. Composition of Ozone.—The density of pure ozone prepared in this way has been shown by Ladenburg to be 24 (H = 1). Its molecular weight, therefore, is $2 \times 24 = 48$. Now since the atomic weight of oxygen is 16, a molecule of ozone must consist of three atoms of

oxygen, for $3 \times 16 = 48$. This explains why there is a diminution of volume when oxygen is converted into ozone, for *three* molecules of oxygen (O_2) give rise to only *two* molecules of ozone (O_3)—

$$3O_2 = 2O_3.$$

Applying Avogadro's hypothesis, it follows that three volumes of oxygen should give rise to two volumes of ozone. This may be proved experimentally in the following manner :—

The contraction in volume on ozonising a known volume of oxygen is measured. The ozone is then absorbed by turpentine, and the further diminution in volume noted. Thus suppose in an experiment 100 vols. of oxygen contracted to 97 vols. on being ozonised, and absorption with turpentine caused a further diminution of volume to 91 vols. Then we have—

Volume of ozone ... ... = (97—91 vols) = 6 vols.
" " oxygen from which it was formed = (100—91 vols.) = 9 vols.

The ozone was therefore formed by the condensation of 9 volumes of oxygen into the space of 6 volumes, or 3 volumes of oxygen condense to produce 2 volumes of ozone.

113. Allotropy.—Oxygen and ozone afford the first example of a phenomenon exhibited by several elements, namely, of existing in two or more forms with different physical and to some extent chemical properties. The different forms of an element are said to be *allotropes* of that element; thus ozone and ordinary oxygen are allotropes of the element oxygen. When one allotropic modification of an element is converted into another, heat is invariably either evolved or absorbed; if there are two modifications of an element A and B, and if heat is evolved when A is converted into B, it will be absorbed when B is converted into A.

Now oxygen is changed into ozone with absorption of heat. It is a general rule that bodies produced with absorption of heat are decomposed very easily, giving out the heat absorbed in their formation. This explains

the greater activity of ozone as compared with oxygen. The molecule of ozone readily breaks down into a molecule of oxygen and a free atom of oxygen, with evolution of heat—

$$O_3 = O_2 + O.$$

This free atom of oxygen immediately attacks any oxidisable substance within reach, such as mercury, potassium iodide, etc., and if no such substance is present the free oxygen atoms unite to form stable molecules of oxygen.

The reason that a free atom of oxygen is so much more active than a molecule of oxygen is that before the latter can enter into a chemical reaction it must be broken down into two atoms of oxygen, and it requires the expenditure of a considerable amount of energy to bring this about.

114. Nascent state.—An element when just liberated from a compound is said to be *nascent* (*nascor*, I am born), and in general it shows special activity when in this state. This will be understood from what has just been said with regard to oxygen, for an element is always in the atomic condition when just set free from combination.

QUESTIONS.—CHAPTER XII.

1. Describe the laboratory method of preparing oxygen, and sketch the apparatus used.
2. Give a list of oxides which evolve oxygen on heating, and represent the decompositions which they undergo by equations.
3. Express by equations the changes which take place when the following substances are heated: (1) a mixture of manganese dioxide and strong sulphuric acid, (2) potassium nitrate, (3) a mixture of potassium permanganate and strong sulphuric acid.
4. How may oxygen be obtained from bleaching powder?
5. State how baryta may be used as a means of obtaining oxygen from the atmosphere.

6. Give instances of the formation of oxides by the action of oxygen on elementary substances, (*a*) where such action takes place at ordinary temperatures, (*b*) where heat must be applied in order to start the reaction.

7. What takes place when the products of combustion of carbon, sulphur, and phosphorus are respectively brought into contact with water?

8. What is meant by *slow combustion*?

9. Explain the term *oxidising agent*. Describe an experiment which illustrates the process of oxidation.

10. What is an *oxide*? Give instances of oxides of the metals which are soluble in water, and of oxides which are insoluble in water.

11. How do acid-forming oxides (anhydrides) differ from basic oxides? What is usually the effect of bringing together solutions of these two classes of oxides?

12. How do the peroxides differ (*a*) in composition, (*b*) in their chemical deportment, from ordinary metallic oxides?

13. How would you prove that lime contains oxygen?

14. Give a classification of oxides, and explain the principles on which your classification is based.

15. Give two methods by which ozone may be produced.

16. How may ozonised oxygen be distinguished from ordinary oxygen (*a*) without the application of reagents, (*b*) by means of chemical tests?

17. What experiments tend to show that ozone is a more active oxidising agent than oxygen?

18. The molecule of oxygen being represented by O_2, that of ozone is found to be O_3; how has this been established?

19. Explain the meaning of the term *allotropy*.

20. What do you understand by the term *nascent state*?

CHAPTER XIII.

ACIDS—BASES—SALTS—TYPES OF CHEMICAL CHANGE.

115. Acids.—A brief historical sketch of the use of the term "acid" will be of value before we consider the meaning assigned to it at the present time. The properties originally associated with an "acid" were—

(1) Sourness (Gk. ὀξύς, L. *acidus*, sour).

(2) Solubility in water.

(3) Power of removing the alkaline properties of such substances as caustic soda and caustic potash.

(4) Power of changing the colour of certain blue vegetable substances (such as litmus) to red.

It was found, however, that certain substances not included under the head of acids possessed all these properties. Thus alum has a sour taste, is soluble in water, deprives caustic soda of its alkaline properties, and turns blue litmus red.

After Lavoisier's discovery that the compounds produced by burning certain elements in oxygen yield acids with water, it was assumed that *oxygen was the essential constituent of an acid.* This view was overthrown when it was proved that certain acids such as hydrochloric acid (HCl) and sulphuretted hydrogen (H_2S) do not contain oxygen at all. A distinction was then made between acids which do contain oxygen and those which do not. The former were (and still are) called *oxyacids* and the latter *hydracids.*

It was Davy who first showed that *hydrogen* and not oxygen is the essential constituent of an acid. He was led to this conclusion by the discovery that iodic anhydride (I_2O_5), which contains oxygen but no hydrogen, is not an

acid, but on treating it with water (*i.e.* with a compound of hydrogen and oxygen) it acquires acid properties About the same time Dulong arrived at a similar conclusion as a result of studying the action of metallic oxides on oxalic acid. He considered that when an acid was treated with a metallic oxide the metal of the oxide replaced the hydrogen of the acid with formation of a *salt.*

At the present time an *acid* may be defined as *a substance containing hydrogen, part or all of which it exchanges for potassium* (*or sodium*) *when brought into contact with caustic potash* (*or caustic soda*).

It will be noticed that this definition excludes such substances as alum.

116. Salts.—A *salt* may be defined as *a substance produced by the replacement of part or all of the hydrogen of an acid by a metal or group of elements* (*such as* NH_4) *which takes the place of a metal.*

Thus when zinc dissolves in hydrochloric acid the zinc replaces the hydrogen of the acid forming the salt zinc chloride, $ZnCl_2$—

$$\underset{\text{Acid}}{Zn + 2HCl} = \underset{\text{Salt}}{ZnCl_2} + H_2.$$

Again, when one molecule of caustic soda, NaOH, reacts with one molecule of sulphuric acid, H_2SO_4, part of the hydrogen of the acid is replaced by the metal sodium forming the salt sodium hydrogen sulphate, $NaHSO_4$—

$$\underset{\text{Acid}}{NaOH + H_2SO_4} = \underset{\text{Salt}}{NaHSO_4} + H_2O.$$

117. Bases.—A *base* may be defined as a *substance which with an acid produces a salt and water only.* The substances included as bases adopting this definition are basic oxides and hydroxides of the metals or of a group of elements equivalent to a metal (*e.g.* NH_4). Thus, hydrochloric acid reacts with the base calcium oxide, to produce the salt calcium chloride and water—

$$\underset{\text{Base}}{CaO} + \underset{\text{Acid}}{2HCl} = \underset{\text{Salt}}{CaCl_2} + \underset{\text{Water}}{H_2O}.$$

Again, sulphuric acid reacts with the base zinc hydroxide, to produce the salt zinc sulphate and water—

$$\underset{\text{Base}}{Zn(OH)_2} + \underset{\text{Acid}}{H_2SO_4} = \underset{\text{Salt}}{ZnSO_4} + \underset{\text{Water}}{2H_2O}.$$

Once again, nitric acid reacts with the base ammonium hydroxide, to produce the salt ammonium nitrate, and water—

$$\underset{\text{Base}}{NH_4OH} + \underset{\text{Acid}}{HNO_3} = \underset{\text{Salt}}{NH_4NO_3} + \underset{\text{Water}}{H_2O}.$$

Usually, certain substances are, for convenience, called bases which do not conform to the above definition. These are ammonia (NH_3), and its numerous derivatives (such as aniline) which are met with amongst the compounds of carbon. These substances form salts with acids, but without the production of water. Thus ammonia with hydrochloric acid gives the salt ammonium chloride—

$$\underset{}{NH_3} + \underset{\text{Acid}}{HCl} = \underset{\text{Salt}}{NH_4Cl}.$$

It is unfortunate that a separate name has not been adopted for these substances.

118. Alkalis.—Those bases which are soluble in water, such as caustic soda and lime, are called *alkalis*; they possess special properties, which were illustrated by Exp. 105, and may be summarised as follows:—

(1) Their solutions in water restore the blue colour to litmus which has been reddened by an acid;

(2) They are capable of removing from an acid its characteristic properties, *i.e.* can *neutralise* an acid;

(3) Their solutions have usually a soapy feel;

(4) Their solutions convert oils such as olive oil into soaps.

119. Basicity of Acids.—Some acids can only produce one salt by interaction with a given base, whereas others can form two, three, or even four different salts. This may be studied by experiment.

Exp. 143.—Measure out 50 c.c. of dilute hydrochloric acid into an evaporating basin, and gradually add dilute caustic potash to it from a burette until the solution is neutral to litmus. Note the volume of caustic potash used. Now measure out another 50 c.c. of the acid into a second evaporating basin, and add to it half the quantity of caustic potash required to neutralise it. Evaporate the two solutions down to small bulk, and allow to cool. Crystals will separate out from each; drain away the mother liquor from them, and dry between blotting-paper. Examine the two lots of crystals. You will notice that they are quite similar in appearance.

Exp. 144.—Proceed exactly as in the last experiment, but use dilute sulphuric acid instead of hydrochloric acid. Again examine the two sets of crystals. This time they differ in appearance.

From these two experiments we learn that hydrochloric acid only gives one salt with potash, whereas sulphuric acid gives two salts. On comparing the formulae of these acids—HCl, H_2SO_4—it will be noticed that whilst the former only contains one atom of hydrogen in its molecule the latter has two. When we neutralised hydrochloric acid with caustic potash, we replaced the hydrogen atom of each of the molecules of acid by potassium according to the equation—

$$KOH + HCl = KCl + H_2O,$$

and when we only added half the quantity of potash required for neutralisation, we replaced the hydrogen atoms of half the HCl molecules by potassium according to the same equation. The other half of the HCl molecules remained unattacked.

On neutralising sulphuric acid with caustic potash, the two hydrogen atoms of each molecule of the acid were replaced by potassium according to the equation—

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

When, however, only half the quantity of potash was used

only one atom of hydrogen in each molecule of the acid was replaced by potassium, the equation being—

$$KOH + H_2SO_4 = KHSO_4 + H_2O.$$

No acid remained unacted upon here, as was the case with hydrochloric acid. If we had gone further and used only one-third the quantity of potash required to neutralise the sulphuric acid, we should not have obtained another new salt. The reaction would have proceeded as in the last equation, and some of the acid would have remained unacted upon.

Phosphoric acid contains three atoms of hydrogen, and gives rise to three classes of salts according as one, two, or all of these atoms are replaced by a metal—

$$H_3PO_4 + NaOH = NaH_2PO_4 + H_2O.$$
$$H_3PO_4 + 2NaOH = Na_2HPO_4 + 2H_2O.$$
$$H_3PO_4 + 3NaOH = Na_3PO_4 + 3H_2O.$$

It must not be assumed that all the atoms of hydrogen in an acid are necessarily replaceable by a metal; this is often not the case. For instance, acetic acid has the formula $C_2H_4O_2$, but only one of the four hydrogen atoms can be replaced by a metal. To indicate this we may write the formula $C_2H_3O_2.H$, showing that one hydrogen atom differs in properties from the others. On neutralising acetic acid with caustic soda the following change takes place:—

$$C_2H_3O_2.H + NaOH = C_2H_3O_2.Na + H_2O.$$

The number of atoms of hydrogen replaceable by a metal contained in one molecule of an acid is termed the *basicity* of the acid. Thus the basicity of hydrochloric acid is 1, of sulphuric acid 2, of phosphoric acid 3, and of acetic acid 1; or, in other words, hydrochloric and acetic acids are *monobasic*, sulphuric acid is *dibasic*, and phosphoric acid is *tribasic*.

120. Normal and Acid Salts.—Salts produced by the replacement of the whole of the replaceable hydrogen of an acid by metals are called *normal* salts. Potassium chloride (KCl), normal potassium sulphate (K_2SO_4), trisodium

phosphate, or normal sodium phosphate (Na_3PO_4), and sodium acetate ($C_2H_3O_2.Na$) belong to this class. When only part of the replaceable hydrogen of an acid is replaced by metals, the resulting salts are known as *acid salts*. Such are potassium hydrogen sulphate or acid potassium sulphate ($KHSO_4$), disodium hydrogen phosphate (Na_2HPO_4), and sodium dihydrogen phosphate (NaH_2PO_4).

It should be noticed that normal salts are not by any means always *neutral* to litmus and similar indicators. Many of them show an acid reaction (*e.g.* copper sulphate, $CuSO_4$), whilst others show an alkaline reaction (*e.g.* normal sodium carbonate, Na_2CO_3). Sodium chloride and normal potassium sulphate are examples of normal salts which are neutral.

So, again, though many acid salts are *acid* to litmus, this is not true for all. Disodium hydrogen phosphate, for instance, shows an alkaline reaction.

121. Basic Salts.—On considering the formulae of the bases potassium hydroxide, KOH, lead hydroxide, $Pb(OH)_2$, and bismuth hydroxide, $Bi(OH)_3$, it will be noticed that they differ in the number of hydroxyl (OH) groups which they contain. The question arises whether these OH groups can be successively replaced by the acid group of an acid (*e.g.* NO_3, the acid group of nitric acid) in the same way that the hydrogen atoms of a polybasic acid can be successively replaced by a metal. This is found to be the case very frequently, and, just as the basicity of an acid is determined by the number of replaceable hydrogen atoms its molecule contains, so the *acidity* of a base is determined by the number of hydroxyl groups it contains. (We will leave out of consideration for the present the case of *oxides*, dealing only with *hydroxides*.) Thus KOH is a *monacid* base, $Pb(OH)_2$ is a *diacid* base, and $Bi(OH)_3$ is a *triacid* base.

When only part of the OH groups of a base are replaced by an acid group, the salt formed is termed a *basic salt*. Thus $Pb(OH)_2$ gives basic lead nitrate, $Pb(OH)(NO_3)$, by the replacement of one of its hydroxyl groups by the acidic group NO_3 (from HNO_3). When both hydroxyl groups are replaced, normal lead nitrate, $Pb(NO_3)_2$, is formed.

Basic salts may be made in three ways—

(1) By treating the base with insufficient acid to convert the whole of the base into the normal salt.

Thus, on treating a molecule of bismuth hydroxide with one of nitric acid, only one of the OH groups of the base is replaced by NO_3—

$$Bi(OH)_3 + HNO_3 = Bi(OH)_2NO_3 + H_2O.$$

(2) By treating the normal salt with excess of water.

Normal bismuth nitrate is converted by the action of water into the same basic salt that was obtained in (1)—

$$Bi(NO_3)_3 + 2H_2O = Bi(OH)_2NO_3 + 2HNO_3.$$

(3) By mixing the normal salt and the free base.

Thus, on mixing normal lead acetate and lead hydroxide, basic lead acetate is produced—

$$Pb(C_2H_3O_2)_2 + Pb(OH)_2 = 2Pb(OH)(C_2H_3O_2).$$

Basic salts can be derived from *oxides* as well as from hydroxides. One atom of oxygen is equivalent in combining capacity to two hydroxyl (OH) groups. Thus, CaO (quicklime), on treatment with water, forms $Ca(OH)_2$, slaked lime. Hence a basic oxide having the formula MO, where M is a metal, will be a *diacid* base; for it will be able to neutralise as much acid as a basic hydroxide which contains *two* hydroxyl groups. Thus quicklime, CaO, and slaked lime, $Ca(OH)_2$, both neutralise two molecules of nitric acid—

$$CaO + 2HNO_3 = Ca(NO_3)_2 + H_2O.$$
$$Ca(OH)_2 + 2HNO_3 = Ca(NO_3)_2 + 2H_2O.$$

An example of a basic salt derived from an oxide is bismuth oxychloride, BiOCl. This may be obtained by the action of excess of water on bismuth trichloride—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

It should be pointed out that all basic salts can be considered as compounds of normal salts with the free base, and in many cases this is the most convenient way of treating them; thus white lead, or basic lead carbonate, is formulated $2PbCO_3 + Pb(OH)_2$, basic mercuric sulphate

is $HgSO_4 + 2HgO$. Reverting to the examples given above, we may write their formulae out again on the plan just mentioned, and show as below that the two sets of formulae are equivalent—

Basic lead nitrate $= Pb(OH)_2 + Pb(NO_3)_2 = Pb_2(OH)_2(NO_3)_2$
$= 2Pb(OH)(NO_3)$.

Basic bismuth nitrate $= 2Bi(OH)_3 + Bi(NO_3)_3 = Bi_3(OH)_6(NO_3)_3$
$= 3Bi(OH)_2NO_3$.

Basic lead acetate $= Pb(OH)_2 + Pb(C_2H_3O_2)_2 = Pb_2(OH)_2(C_2H_3O_2)_2$
$= 2Pb(OH)(C_2H_3O_2)$

Bismuth oxychloride $= Bi_2O_3 + BiCl_3 = Bi_3O_3Cl_3 = 3BiOCl$

Basic salts are usually less soluble in water than the corresponding normal salts, but there are exceptions.

122. Types of Chemical Change.—In the foregoing chapters we have met with several different kinds of chemical change, and it will be well before going further to classify these under a few main headings.

(1) **Direct Combination.**—This consists in the union of two or more simpler molecules (either elementary or compound) to form a more complex molecule. For example, the two elements iron and sulphur combine on heating to form ferrous sulphide; the two compounds quicklime and water unite to form slaked lime; and the element chlorine unites with the compound carbon monoxide to form phosgene gas—

Fe	+	S	=	FeS.
Iron		Sulphur		Ferrous sulphide
CaO	+	H_2O	=	CaH_2O_2.
Quicklime		Water		Slaked lime
Cl_2	+	CO	=	$COCl_2$.
Chlorine		Carbon monoxide		Phosgene gas

(2) **Simple Decomposition.**—This term is applied to the breaking up of a complex molecule into simpler molecules (either elementary or compound). For example, mercuric oxide on heating decomposes into mercury and oxygen, chalk on heating breaks up into quicklime and

carbon dioxide, and potassium nitrate on heating yields oxygen and potassium nitrite—

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

$$\underset{\text{Chalk}}{CaCO_3} = \underset{\text{Quicklime}}{CaO} + \underset{\text{Carbon dioxide}}{CO_2}.$$

$$\underset{\text{Potassium nitrate}}{2KNO_3} = \underset{\text{Potassium nitrite}}{2KNO_2} + \underset{\text{Oxygen}}{O_2}.$$

(3) **Simple Replacement.**—When an element acts on a compound by replacing another element the change may be termed "simple replacement." Zinc, for example, acts on sulphuric acid and replaces the hydrogen—

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

Similarly, iron reacts with copper sulphate and replaces the copper—

$$\underset{\text{Iron}}{Fe} + \underset{\text{Copper sulphate}}{CuSO_4} = \underset{\text{Ferrous sulphate}}{FeSO_4} + \underset{\text{Copper}}{Cu}.$$

(4) **Double Decomposition.**—In this kind of change two compounds react and undergo a mutual exchange of constituents. For example, silver nitrate reacts with sodium chloride to produce silver chloride and sodium nitrate—

$$\underset{\text{Silver nitrate}}{AgNO_3} + \underset{\text{Sodium chloride}}{NaCl} = \underset{\text{Sodium nitrate}}{NaNO_3} + \underset{\text{Silver chloride}}{AgCl}.$$

Again, copper oxide and sulphuric acid (or hydrogen sulphate) react to form copper sulphate and water (or hydrogen oxide)—

$$\underset{\text{Copper oxide}}{CuO} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Copper sulphate}}{CuSO_4} + \underset{\text{Water.}}{H_2O}.$$

QUESTIONS.—CHAPTER XIII.

1. Write a short history of the term *acid.*
2. Define the terms *acid, salt, base,* and *alkali,* and give examples of each class of compounds.
3. What is meant by the *basicity* of an acid? Illustrate your answer by examples.
4. Describe an experiment which proves that sulphuric acid is a dibasic acid.
5. What is the basicity of the following acids:—(1) acetic, (2) phosphoric, (3) hydrochloric?
6. Explain the terms *normal salt* and *acid salt,* and give examples of each class of compounds.
7. What is a *basic salt*? By what methods can basic salts be prepared?
8. State the principal types of chemical change, and give examples of each.

CHAPTER XIV.

COMPOUNDS OF HYDROGEN AND OXYGEN.

123. Hydrogen and oxygen combine together in two proportions, forming water, H_2O, and hydrogen peroxide, H_2O_2; the latter contains twice as much oxygen in relation to hydrogen as the former.

WATER, H_2O.

124. We shall commence the study of water by investigating its composition by volume and by weight more completely than we have done in Section I.

Composition of Water by Volume—Synthetic Method.—The composition of water was first proved by Cavendish at the end of the eighteenth century. He introduced a mixture of two volumes of hydrogen and one of oxygen into a strong glass vessel fitted with two wires which passed into the inside of the vessel so as nearly to touch one another. The electric spark was passed by means of the wires, and the gases exploded. By repeating the experiment many times he was able to show that oxygen combines with twice its volume of hydrogen and that the liquid resulting from the combination was water.

The method employed at the present day to prove the volumetric composition of water is similar in principle to that employed by Cavendish but capable of greater accuracy, and moreover it is applicable to gases in general; it was first introduced by Bunsen.

A tube of even bore, about 70 centimetres in length, is used. This is furnished with platinum wires to enable the gases to be "sparked," and millimetre divisions are

etched on the tube. The "eudiometer," as such a tube is called,[1] is filled with mercury and inverted in a trough containing mercury (see Fig. 46).

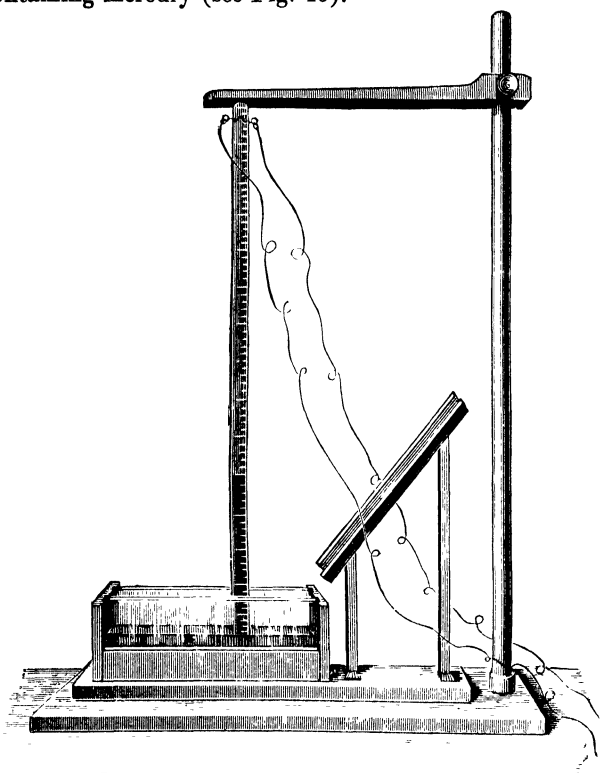


Fig. 46.

Pure oxygen sufficient to occupy about one-tenth of the volume of the eudiometer is now passed in, and the exact

[1] You have already used a eudiometer in Exp. 75, but in that case the tube was U-shaped; such a eudiometer is termed a *bent eudiometer*.

level of the mercury in the eudiometer and in the trough is read. Hydrogen is then added equal to about six or seven times the volume of the oxygen, and the levels of the mercury again read. The temperature and pressure existing at the time must also be noted. The eudiometer is now closed by pressing it down firmly on an indiarubber cushion at the bottom of the trough, and the spark is passed by connecting the platinum wires with an induction coil actuated by a battery.

Under these circumstances the whole of the oxygen enters into combination with hydrogen, and as the water which forms condenses a partial vacuum is formed inside the tube, and on gently raising it from the cushion the mercury is seen to rise. After allowing sufficient time for the gas to regain the temperature of the room (much heat having been generated by the combination which has taken place) the levels of the mercury in the eudiometer and trough are again read.

We have now the whole of the data necessary for ascertaining the relative volumes of hydrogen and oxygen which have united to form water. The volumes occupied by the gases are all reduced so as to represent standard conditions. When this has been done, let us suppose—

Oxygen taken occupied 12 volumes.
Hydrogen added ,, 80 ,,
Residual hydrogen ,, 56 ,,

It is evident that 12 volumes of oxygen have entered into combination with $80 - 56 = 24$ volumes of hydrogen to form water.

This method is the same in principle as that used in Exp. 75, but is more accurate.

125. Correction for Pressure of Aqueous Vapour.—There is one correction in the above description which has been omitted. A small quantity of water vapour is produced on the combination of hydrogen and oxygen, and this vapour exerts a pressure (see § 131), so that the pressure exerted by the residual hydrogen is rather less than that measured as above, which is the total pressure

of hydrogen plus water vapour. The amount of water vapour produced is however too small to *saturate* the residual hydrogen, so the vapour pressure cannot be found by reference to the tables referred to in § 131. How then are we to make the necessary correction? The method adopted is to ensure that the residual gas is saturated with aqueous vapour by moistening the eudiometer with a few drops of water before introducing the mercury at the commencement of the experiment.

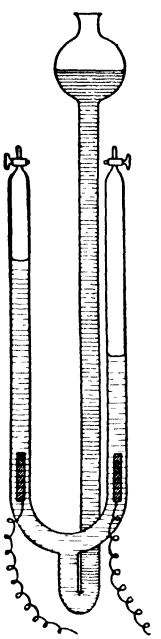


Fig. 47.

Of course, all the other volumes of gas measured will also be saturated with aqueous vapour, and the pressure which each volume exerts can be found by noting the temperature of the gas and referring to the tables. If, then, the pressure of any of the volumes of gas as previously measured was found to be P and the saturation pressure of water vapour at the temperature of the gas is p, then the corrected pressure is $P - p$.

126. Composition of Water by Volume—Analytical Method.—We have already determined the volumetric composition of water analytically in Exp. 73. The apparatus used in that experiment is called a *voltameter*. A more accurate form of voltameter is shown in Fig. 47. It consists of a three-limbed glass tube: the centre limb is longer than the others and terminates in a funnel at the open end; the two side limbs are provided with stopcocks and are graduated.

Two pieces of platinum bearing strips of platinum foil are fused into the lower ends of the side tubes: these constitute the electrodes.

The apparatus is filled with water containing a little sulphuric acid by opening the stopcocks and pouring the

acid into the funnel till the side tubes are quite full, *i.e.* the liquid reaches up into the narrow parts of the tubes above the stopcocks. The electrodes are now connected by copper wires with the poles of a battery of four Bunsen's or Grove's cells. Hydrogen rises from the negative electrode and oxygen from the positive. Now though these gases are only slightly soluble in water they do dissolve to a small extent, and of the two oxygen is the more soluble.

If therefore the gases were allowed to collect in the tubes at once and then measured the volume of oxygen would be relatively rather too small, for a greater amount of it would have dissolved as it passed up through the liquid. In order to correct this error the stopcocks are opened occasionally for say the first 20 minutes or so and the gases allowed to escape; in this way the liquids in the side tubes become *saturated* with hydrogen and oxygen. The side tubes are now filled completely with liquid and the current is allowed to pass till a considerable volume of each gas has collected; then the battery is disconnected and the volume of each gas read off. It will be found that the volume of hydrogen collected is twice[1] that of oxygen. The identity of the two gases may be shown by applying the usual tests.

127. Volumetric Composition of Steam.—In order to find out the relation between the volumes of hydrogen and oxygen which combine, and that of the steam produced from them, we must so arrange the experiment that the temperature of the gases is maintained above the boiling-point of water. The steam produced will not, under these conditions, condense to water.

The apparatus shown in Fig. 48 may conveniently be used for this experiment. A U-tube, one limb of which is closed and graduated, is fitted with platinum wires for

[1] Strictly speaking the volume of hydrogen is rather greater than twice the volume of oxygen, because a little of the latter is liberated in the form of ozone. The formation of ozone may be minimised by adding caustic potash to the water, to render it a conductor, instead of sulphuric acid.

"sparking," as in the Bunsen eudiometer. The tube is filled with mercury. The closed limb is then surrounded by a wider tube through which the vapour of a liquid boiling at about 130° C. (*e.g.* amyl alcohol) is passed.

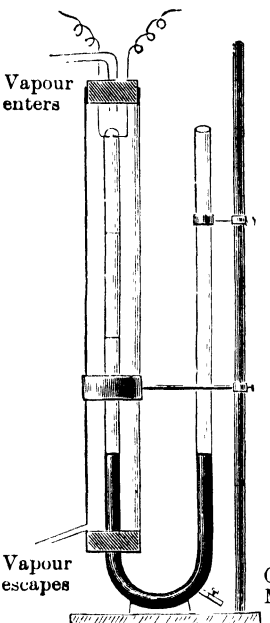


Fig. 48.

A mixture of hydrogen and oxygen in the proportion of 2 : 1 by volume (obtained by the electrolysis of water) is now passed into the closed limb by rubber tubing reaching round the bend through the mercury, and the displaced mercury is allowed to run out through the stopcock. When the closed limb is about two-thirds full of gas, the supply is cut off and the rubber tubing removed. The mixture is allowed to attain the temperature of the jacket, the mercury is adjusted to the same level in each limb, and the volume of mixed gases read off. The open end of the tube is closed with a cork (to prevent the explosion from expelling the mercury) and a spark is passed. The gases combine, and on bringing the mercury in each limb to the same level by pouring mercury into the open limb, it will be seen that the volume of steam occupies two-thirds that of the mixed gases.

If the tube is now allowed to cool down to the ordinary temperature, the mercury will rise almost to the top of the closed limb—not quite owing to the small vapour

pressure which water exerts at ordinary temperature; this shows that there is no hydrogen or oxygen remaining uncombined. From this experiment it follows that steam contains its own volume of hydrogen and half its volume of oxygen, and this agrees with the equation—

$$\underset{4\text{ vol.}}{2H_2} + \underset{2\text{ vol.}}{O_2} = \underset{4\text{ vol.}}{2H_2O}.$$

128. Composition of Water by Weight.—A fairly accurate method of determining the composition of water by weight has already been given in Exp. 121. In order

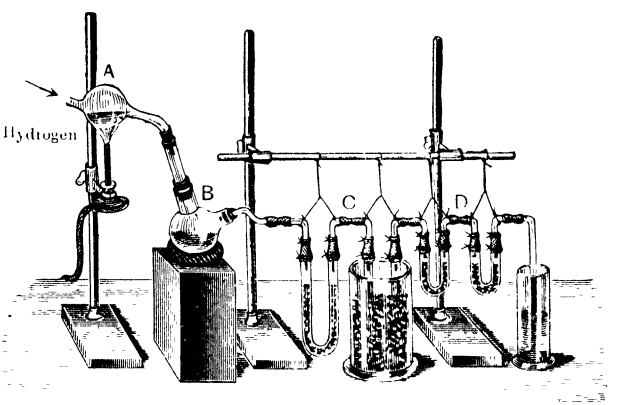


Fig 49.

to obtain more accurate results, however, the hydrogen must be purified more completely, and the method of collecting the water formed must be more effective.

Dumas and Stas in their classical determination of the composition of water by weight in 1843 adopted the principle of the method used in Exp. 121 introducing the requirements just mentioned. They purified the hydrogen (which was prepared by the action of dilute sulphuric acid on zinc) by passing it through a series of U-tubes con-

taining various absorbents.[1] The oxide of copper was placed in a bulb A (Fig. 49),[2] the weight of both being determined. The greater part of the water condensed in the bulb B, and the rest was absorbed in U-tubes containing solid caustic potash C and phosphorus pentoxide D.

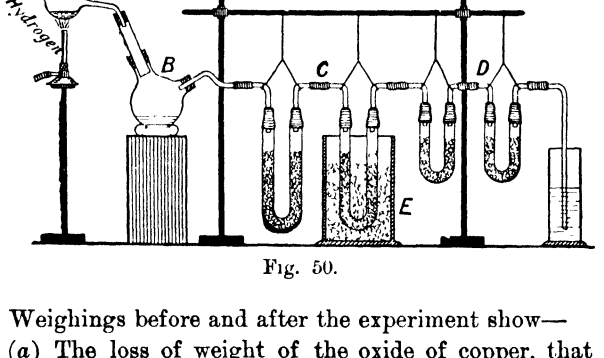


Fig. 50.

Weighings before and after the experiment show—

(*a*) The loss of weight of the oxide of copper, that is the amount of oxygen used.

(*b*) The gain in weight of the second bulb B and the U-tubes succeeding it, that is the amount of water formed.

[1] For details the student is referred to *Tutorial Chemistry*, § 68.

[2] In sketching apparatus the student is advised not to attempt *perspective* drawings, which take a long time and are seldom satisfactory. A much better plan is to draw the apparatus *in front elevation*, i.e. as it would be seen by a person looking at it straight in front. When, however, the exact nature of any part of the apparatus can be better explained by drawing it *in section*, i.e. as if it were cut in two through the middle and the front half removed, this method should be adopted for that particular part. To indicate that an object has been cut through, inclined lines are drawn parallel to one another across any part which is sufficiently thick for its two sides to be represented by separate lines (thin glass vessels, for instance, do not admit of this). Fig. 50 is a drawing, partly in front elevation and partly in section, of the apparatus shown in perspective in Fig. 49. For instance, the retort-stands are represented in front elevation in Fig. 50, whilst the vessels B and E are drawn in section.

As the combined result of nineteen determinations, they found that the amount of oxygen used was 840·161 grams and the amount of water formed 945·439 grams. Water consists, therefore, of

840·161 grams of oxygen
and 105 278 „ „ hydrogen;

or one part by weight of hydrogen combines with 7·98 parts of oxygen to form water.

More accurate experiments performed in recent years by E. W. Morley and other chemists have shown that the exact ratio by weight in which hydrogen and oxygen combine is 1 : 7·94.

129. Physical Properties of Water.—When pure, water is a clear and tasteless liquid; under ordinary circumstances it may be regarded as colourless, but in reality it has a faintly bluish tinge which is perceptible when white light is passed through a stratum of about 20 feet in thickness.

Changes which Water undergoes on the addition and removal of Heat.—These changes are of two kinds—

(1) Change of volume.

(2) Change of state.

Suppose heat is continually abstracted from a given mass of water originally at ordinary temperature (say 15° C.). The temperature gradually falls and the volume gradually diminishes till 4° C. is reached, when the volume ceases to diminish and begins to *increase*, though the temperature continues to fall. A given mass of water has less volume at 4° C. than at any other temperature; 4° C. is therefore the temperature of maximum density of water. At this temperature 1 c.c. of water weighs *exactly* 1 gram.

When the temperature falls to 0° C. the water gradually becomes solid (*i.e.* it is converted into ice), the volume increasing more rapidly than before. The temperature remains constant at 0° C. till all the water has been

converted into ice (though heat is being abstracted all the time), when it again begins to fall. This fall in temperature below 0° C. is accompanied by a slow diminution in the volume of the ice.

Now suppose instead of removing heat from the water at 15° C. we continually add heat to it. This causes a rise of temperature accompanied by increase in volume till 100° C. is reached, when the water gradually changes into the gaseous state (*steam*), with great increase in volume. The temperature does not change till all the water has been converted into steam, when it gradually rises, the volume continuing to increase, though much more slowly than during the change from water to steam.

If the preceding processes are reversed, *i e.* if heat is gradually added to ice below 0° C. or removed from steam at high temperature, all the changes above described take place in the inverse order.

130. Evaporation of Water at ordinary temperature.—We have seen that at 100° C. water boils and is converted into vapour. Water, however, gradually evaporates at ordinary temperature, and even ice very slowly passes away as vapour.

Exp. 145.—Leave a little water in a dish for a day or two, and note its gradual disappearance.

131. Pressure of Aqueous Vapour.—It can easily be demonstrated by experiment that water vapour exerts a pressure even at ordinary temperature.

* **Exp. 146.**—Take a eudiometer tube about 85 centimetres long, fill it with mercury, and invert in a trough of mercury. The level of the mercury will fall a little, leaving a vacuum at the top of the tube. Introduce a *few* drops of water into the vacuous space by means of a curved pipette; notice that it rapidly vaporises causing depression of the mercury. This shows that water vapour exerts a pressure, the amount of which is measured by the depression of the mercury. Now introduce a few

more drops of water. This will probably vaporise and produce a further depression of the mercury, but a point will soon be reached when no more water evaporates and no further depression takes place.

The space above the mercury is then said to be *saturated* with water vapour, and if any more water is introduced it merely rests upon the surface of the mercury. If the temperature is raised the space becomes unsaturated again and more water will evaporate, producing a further depression of the mercury. This goes on till the space becomes saturated at the higher temperature, when the depression ceases. For each particular temperature the pressure of *saturated* aqueous vapour has a particular value, which is called the *maximum* or *saturation pressure* of aqueous vapour for that temperature. This saturation pressure is the same whether another gas, *e.g.* air, is present or not.

Tables have been constructed for reference, which give the maximum pressure of aqueous vapour at different temperatures.

132. The boiling-point of Water.—Now consider what happens when water is gradually heated in an open vessel. Evaporation takes place at all temperatures, but more rapidly as the temperature rises, because the saturation pressure increases rapidly with increase of temperature. Finally the liquid boils, *i.e.* bubbles form in its interior, rise to the surface, and burst. This, however, cannot take place till the saturation pressure of aqueous vapour is equal to (or, strictly speaking, slightly greater than) the pressure of the atmosphere; before this is the case a bubble would immediately be squeezed up if it were formed, owing to its inability to withstand the external pressure exerted on it. The boiling-point of water may therefore be defined as *the temperature at which its maximum vapour pressure is equal to the atmospheric pressure.* It follows that the boiling-point of water changes when the atmospheric pressure changes.

By substituting the word *liquid* for *water* the above definition becomes quite general.

133. Water as a Solvent.—Most of the solid substances and gases which we meet with in chemical operations dissolve to an appreciable extent in water: some liquids, such as alcohol and sulphuric acid, associate themselves with water in all proportions; whilst others, such as oils, if shaken up with water separate again, being taken up by the water either only to a slight extent or not at all.

134. Solubility of Solids.—The extent to which solid substances are soluble in water under similar circumstances varies according to the nature of the substance.

Minerals, such as coal, limestone, quartz, and some chemical compounds, such as calcium sulphate, oxide of lead, sulphide of iron, are only very slightly soluble, whilst others, *e.g.* nearly all chlorides and nitrates, are freely soluble. In any case, however, there is a limit to the amount of solid matter which can be dissolved, and when water has taken up as much as it will, we have what is known as a *saturated* solution.

The quantity of a substance required to form a saturated solution is usually greater the higher the temperature, though there is no simple general relation between the temperature and the amount dissolved.

The solubility in parts per 100 of water is given for a few substances in the following table—

	0° C.	20° C.	50° C.	100° C.
Potassium nitrate ...	13·3	31·2	85·0	246·0
Sodium chloride ...	35·5	36·0	37·0	39·6
Potassium chlorate ...	3·3	8·0	19·0	58·0
Sodium chlorate ...	81·9	99·0	136·0	232·6
Mercuric chloride ...	5·7	7·4	11·3	54·0
Potassium sulphate ...	8·3	12·5	17·0	26·0

135. Solubility of Liquids.—This subject has been sufficiently dealt with in § 33.

136. Solubility of Gases.—There is no general connection between the solubility of gases and their chemical composition. The very soluble gases are all, however, acid or alkaline in presence of water. Some gases, such

as nitrogen, hydrogen, and carbon monoxide, are very slightly soluble, whilst others, such as ammonia, sulphur dioxide, and hydrochloric acid, are very freely soluble in water. The solubility, instead of increasing with the temperature, as in case of solids, *decreases*, though in no simple relation. One volume of water at the temperatures stated, and under 760 mm. pressure, dissolves the volumes of the respective gases given in the following table—

	0° C	10° C.	20° C.
Nitrogen	0·020	0·016	0·014
Oxygen	0·049	0 033	0 028
Hydrogen	0 019	0 019	0 019
Carbon dioxide	1·799	1 185	0·901
Sulphuretted hydrogen ...	4 371	3 586	2·905

As instances of much more soluble gases we may take—

Sulphur dioxide	79·8	56·6	39 4
Hydrochloric acid	503 0	475 0	444·0
Ammonia	1049 6	812 8	654 0

137. The influence of Pressure on the solubility of Gases.—*The volume of a gas which dissolves in a liquid is directly proportional to the pressure of the gas.* This relation was discovered by Henry, and is known as *Henry's Law*. The term "volume" in this definition must be understood to mean "volume reduced to standard pressure." Thus 1 c.c. of water at 0° C. dissolves of carbon dioxide—

At 1 atmosphere pressure	1·8 c c.		
,, 2 atmospheres ,,	3·6 ,,	(reduced to 1 atmosphere pressure)	
,, 4 ,, ,,	7 2 ,,	,, ,,	,,
,, ½ atmosphere ,,	0 9 ,,	,, ,,	,,
,, ⅓ ,, ,,	0·6 ,,	,, ,,	,,

Soda-water is water charged with carbon dioxide under a pressure of about 4 atmospheres, and so long as this pressure on the surface of the water is maintained this volume of gas will be retained, but directly the pressure is released an effervescence is observed, and gas escapes from the liquid in proportion to the diminution of pressure.

138. Solution of Mixed Gases.—At 0° C. and standard pressure a litre of water shaken up with oxygen will dissolve 41 c.c. of the gas. If, however, we mix another gas, say nitrogen, with the oxygen, a smaller volume of oxygen will be found to dissolve, a volume indeed proportional to the pressure of oxygen alone (Dalton's Law of Partial Pressures). In the same way the nitrogen will no longer dissolve to the extent of 20 c.c. (see table), but to a smaller extent, in proportion to the pressure due to the nitrogen alone For mixed gases, therefore, solution takes place in accordance with (*a*) the solubility of the gas in question, (*b*) the pressure exerted by it independently of any other gas or gases that may be present in the mixture.

Let us consider the important case of the solution of air (taken as 79 volumes of nitrogen[1] and 21 of oxygen) in water—

The oxygen dissolved by a litre of water from air will, according to this law, be, not 41 c.c , but

$$\frac{41 \times 21}{100}, \text{ or } 8{\cdot}6 \text{ c.c. per litre.}$$

The nitrogen dissolved will be, not 20 c c., but

$$\frac{20 \times 79}{100}, \text{ or } 15{\cdot}8 \text{ c.c. per litre}$$

So that in consequence of its greater solubility the proportion of oxygen to nitrogen dissolved in water is 8 6 : 15·8, and is therefore 35 per cent. of the whole. Air expelled from solution in water by boiling or by exposure to a vacuum is, then, much richer in oxygen than ordinary air (see Exp. 56).

So taking 0·04 as the normal percentage of carbon dioxide in air, this gas will be dissolved, not to the extent of 1,799 c.c. to the litre, but

$$\frac{1{,}799 \times 0{\cdot}04}{100}, \text{ or } 0{\cdot}72 \text{ c.c. per litre.}$$

[1] Argon is here reckoned as nitrogen.

Now 1 litre of water dissolves $8{\cdot}6+15{\cdot}8+0{\cdot}72=25{\cdot}12$ c.c. of oxygen + nitrogen + carbon dioxide from the air. Of this carbon dioxide constitutes $\frac{0{\cdot}72}{25{\cdot}12} \times 100 = 2{\cdot}87$ per cent. Air dissolved in water is, therefore, $\frac{2{\cdot}87}{0{\cdot}04} = 71\frac{3}{4}$ times as rich in carbon dioxide as the original air taken.

139. Natural Waters.—The water which evaporates from the surface of sea and land, and passes as water vapour into the air, is the purest form of natural water, and it retains its purity until it begins to fall as drops from the rain cloud.

Rain Water.—When this is collected at the surface of the earth it has passed through a considerable stratum of air, and dissolved in its passage not only gases normally occurring in the atmosphere, but also such impurities as are found there. Even then the solid matter contained in it does not amount normally to more than 3 or 4 parts per 100,000. In the neighbourhood of towns the impurities taken up are more numerous and in larger quantity; also near the sea, and especially during high winds, much sodium chloride is found in rain water.

River Water.—The composition of this water will of course depend on the nature of the surface and of the strata over which the water passes. For instance, a considerable part of the drainage area of the Thames consists of chalk, and its water contains about 30 parts of dissolved matter in 100,000, two-thirds of this consisting of calcium carbonate and sulphate, whilst the Dee in Scotland, passing over the older strata (principally slate, sandstone, and granite), contains about 5·6 parts of dissolved matter per 100,000, one-fourth of this being calcium salts. Since the water which passes into rivers collects from the surface of the soil, it contains also much more organic matter and carbon dioxide than rain water, arising from contact with plants and decaying vegetable matter.

Spring Water.—The water of springs is rain water which has percolated through soil and rocks. The composition of spring waters varies very considerably according to the depth from which the water rises and the nature of the strata which it has traversed. In some cases the amount of dissolved matter is very large, and such springs, especially when they have a saline taste or medicinal properties, are known as *mineral* springs.

The springs of Epsom and Harrogate contain magnesium sulphate (Epsom salts) and sulphuretted hydrogen respectively, and are known as magnesium and sulphur waters; a spring near Woodhall Spa contains free iodine; many springs contain iron, and are known as *chalybeate* waters.

Mineral springs which rise from great depths are frequently hot, some having a temperature of nearly 100° C.; this is especially the case in volcanic regions, where the earth's temperature rises more rapidly with increase in depth below the surface than elsewhere.

Spring water is bright and sparkling, since it is more fully charged with gases than either rain or river water, and contains less organic matter, this being removed in its passage through beds of soil or gravel. The composition of some typical waters is given in the table further down.

Sea Water.—The matters dissolved or suspended in river or spring water are carried to the sea and remain there, since the water vapour rising from the sea consists of practically pure water; so that, notwithstanding the removal of large quantities of these substances by settling out or by the action of organisms, sea water is very impure. The water from the open ocean contains on the average about 3·5 per cent. of dissolved solids and has a specific gravity of about 1·03; the greater part of this soluble matter, nearly four-fifths, consists of sodium chloride, the remainder being chiefly calcium and magnesium sulphates and calcium chloride. The peculiar taste of sea water is due to the presence of these salts. There are, however, certain land-locked seas where the evaporation is very rapid and the quantity of dissolved solids is much greater than in sea-water; the Dead Sea, for example, contains nearly 23 per cent.

In the following table details are given of the composition of some typical natural waters, the solids in parts per 100,000, the gases in cubic centimetres per litre:—

COMPOSITION OF SOME NATURAL WATERS.

	Solids.					Gases.		
	Total Residue.	Calcium Salts.	Magnesium Salts.	Sodium Chloride.	Organic Matter.	N_2.	O_2	CO_2
Rain Water	3·4	*nil.*	*nil.*	0·5	1·0	13·1	6·4	1·3
River Water (Thames)	29	20	1·8	2·6	3·4	15·0	7·4	30·3
River Water (Dee)	5·6	1·4	0·5	1·0	2·2			
Spring Water	20			2·0	Traces	15·8	8·6	1·0
Mineral Water (Bath)	236	137	23	34	Traces	4·0	2·0	29·0
Sea Water	3,500	140	530	2,650	Traces	12·1	6·0	17·0

The composition of some natural waters should be investigated as follows:—

Exp. 147.—Evaporate 20 c.c. of each of the natural waters, rain water, spring water, sea water, and Selters[1] or Epsom water. Examine the quantity, appearance, and taste of the residues and note the differences.

Exp. 148.—Fit a test-tube with a cork and a tube bent at right angles, fill it with the above natural water in turn, and boil. Pass the gases and steam given off through the lime-water.

The thickness of the precipitate formed will give you some idea of the relative amounts of carbon dioxide present in the different samples.

Exp. 149.—Repeat Exp. 56 with the various waters mentioned above and compare the amounts of dissolved air contained in them.

140. Chemically pure water may be obtained by distillation, the water being boiled and the steam which is given off condensed. The first portion of the water coming over contains the dissolved gases and should be

[1] Incorrectly called "Seltzer water."

rejected. On a small scale the apparatus shown in Fig. 14 may be used. The water is boiled in a flask connected with a condenser, through which a continual stream of cold water passes for the purpose of condensing the steam.

A small quantity of volatile organic matter may be carried over during a first distillation, and soluble matter from the glass condenser and receiver may be present; but on adding a few drops of potassium permanganate solution, and distilling again in platinum apparatus, very pure water is obtained.

141. Drinking Water.—When water is to be used for drinking purposes, it is of the highest importance that it should be clear and colourless, and as free as possible from organic impurity arising from sewage contamination or contact with decaying animal or vegetable matter. Dissolved salts, such as ordinarily occur in natural waters, are of less moment than organic impurity, and even such minute quantities of the latter as 0·3 or 0·4 part per 100,000 may be injurious. The taste of drinking water is also an important factor, and whilst distilled water and rain water are flat and insipid owing to the smaller quantity of dissolved gases which they contain, spring water has a characteristic freshness which renders it most palatable.

142. Hardness of Water.—It is a matter of common experience that the sensation felt when washing the hands differs with waters from different sources. With rain water or the waters derived from sandstone areas a lather quickly forms, whilst with calcareous waters there is a sense of harshness and a good deal of soap is required to produce a lather; we notice further that in the latter case a scum is formed which floats on the surface of the water. Waters that readily form a lather are known as *soft* waters, whilst those that do not are called *hard* waters.

Exp. 150.—Pass carbon dioxide into some lime-water for a considerable time. You will notice that the precipitate of calcium carbonate (chalk) first formed gradually redissolves. This is due to the fact that calcium carbonate

combines with carbon dioxide and water (*i.e.* carbonic acid) to form a soluble salt called *calcium bicarbonate*, which may be considered as the acid calcium salt of carbonic acid, $CaH_2(CO_3)_2$.

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O.$$
$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

Divide this solution into *four* parts for subsequent experiments.

Exp. 151.—Prepare a solution of soap by dissolving a few grams of soap in about 200 c.c. of distilled water. Shake up a little of this solution with (i) distilled water, (ii) a part of the solution of calcium bicarbonate prepared in Exp. 150, (iii) a solution of magnesium sulphate. A lather will appear in (i), but in (ii) and (iii) a scum or precipitate will be formed.

The results of this experiment are explained as follows:—

Soap consists of the sodium or potassium salts of certain complex acids composed of carbon, hydrogen, and oxygen, *e.g.* stearic acid. These salts are soluble in water, and the solution possesses the remarkable property of preventing finely-divided particles of fats from running together in it. Such an intimate mixture of fat particles and water is termed an *emulsion*, and the cleansing properties of soap are due in part to the formation of an emulsion of any particles of grease by the action of the soapy water. Now the calcium and magnesium salts of the acids present in soap are *insoluble* in water, so that on adding soap to water containing salts of these metals in solution, double decomposition immediately takes place between the soap and the salts with precipitation of the insoluble calcium and magnesium salts of the fatty acids.[1]

E g. Calcium bicarbonate + sodium stearate (soap) = Calcium stearate (insoluble) + sodium bicarbonate.

Now when soap is added to water containing these

[1] This is an example of the general rule that when an *insoluble* substance *can be* formed by the interaction of soluble substances, it is formed

dissolved salts none of it is available for cleansing purposes (*i.e.* a soap solution cannot be formed) till all the calcium and magnesium have been removed from the solution by precipitation. This explains the difference in behaviour of *hard* and *soft* waters; for the former contain considerable quantities of dissolved salts, especially bicarbonates and sulphates of calcium and magnesium and chlorides of sodium[1] and magnesium; soft waters, on the other hand, contain practically no dissolved salts. The use of hard waters is therefore wasteful; for the calcium and magnesium salts have first to be precipitated before the cleansing properties come into play.

143. Temporary Hardness and its Removal.—

Exp. 152.—Boil another portion of the calcium bicarbonate solution obtained in Exp. 150 for a few minutes. A precipitate is formed; filter and add soap solution to the filtrate. No precipitate is formed, showing that the hardness has been removed.

What has happened is that on boiling the calcium bicarbonate was decomposed into normal calcium carbonate, water and carbon dioxide.

$$CaH_2(CO_3)_2 = CaCO_3 + H_2O + CO_2.$$

The carbon dioxide passed away as a gas and the calcium carbonate was precipitated. The "fur" which forms on a steam boiler and on a kettle is chiefly calcium carbonate produced during the process of boiling.

Magnesium bicarbonate ($MgH_2(CO_3)_2$) undergoes a similar decomposition on boiling, and these two bicarbonates are the chief causes of what is known as *temporary hardness*, i.e. hardness which can be *removed by boiling*.

There is another way in which temporary hardness can be removed, viz. by the *addition of lime*; this decomposes the bicarbonates with precipitation of normal carbonates.

[1] The hardness produced by sodium chloride is due to a different cause (see § 144).

Calcium bicarbonate, for example, is decomposed in the following manner:—

$$CaH_2(CO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

This is known as *Clark's process.*

Exp. 153.—Gradually add lime-water to a third portion of the calcium bicarbonate solution prepared in Exp. 150. After each addition shake up the liquid and then allow the precipitate to settle. When the further addition of a drop of lime-water ceases to produce any milkiness, pour off the clear liquid, and add soap solution to it. No precipitate is formed, showing that the hardness has been removed.

144. Permanent Hardness and its Removal.—The hardness due to salts other than bicarbonates cannot be removed by boiling, and is called *permanent* hardness. It is chiefly caused by the sulphates of calcium and magnesium and the chlorides of magnesium and sodium.

When permanent hardness is due to salts of magnesium and calcium it can be removed by the addition of washing soda (Na_2CO_3, $10H_2O$), which precipitates the magnesium and calcium as insoluble carbonates:—

$$\underset{\text{Calcium Sulphate}}{CaSO_4} + Na_2CO_3 = \underset{\text{ppt.}}{CaCO_3} + Na_2SO_4$$

$$\underset{\text{Magnesium Chloride}}{MgCl_2} + Na_2CO_3 = \underset{\text{ppt.}}{MgCO_3} + 2NaCl.$$

Washing soda also removes *temporary* hardness. Magnesium bicarbonate, for instance, is decomposed in the following manner:—

$$MgH_2(CO_3)_2 + Na_2CO_3 = 2\,NaHCO_3 + \underset{\text{ppt.}}{MgCO_3}.$$

Exp. 154.—Add a solution of washing soda to solutions of (i) calcium sulphate, (ii) magnesium chloride, (iii) magnesium sulphate, (iv) the remaining portion of the calcium bicarbonate prepared in Exp. 150, till precipitation is complete. Filter. Add soap solution to the filtrate. Note that in each case no precipitate is formed, showing that the hardness has been removed.

Hardness due to *sodium chloride*, being caused by the insolubility of soap in the solution, cannot of course be removed by the addition of washing soda. There are, however, certain soaps which are soluble in brine, such as *marine soap*, and these enable us to get over the difficulty. It should be noted that soap is only insoluble in a solution of sodium chloride when the solution is *fairly strong*, as in sea water.

This explains why washing soda can be used to remove the hardness due to magnesium (or calcium) chloride, although sodium chloride is formed by the double decomposition: the amount of magnesium (or calcium) chloride present is usually small and so there is not sufficient sodium chloride formed to prevent the solution of the soap.

All kinds of hardness can of course be removed by *distillation*.

145. Estimation of Hardness.—The hardness of a sample of water is determined by finding how much of a standard soap solution is required to produce a permanent lather with a known volume of the water. This gives the *total* hardness, *i.e.* the temporary and permanent hardness combined. The *permanent* hardness is found by boiling a known volume of the water for a short time to remove temporary hardness and then adding standard soap solution as before. The difference between the total and permanent hardness gives the *temporary* hardness.

Let us compare the hardnesses of various kinds of waters by performing the following experiment:—

* **Exp. 155.**—Weigh out 10 grams of sodium oleate or green Castile soap and dissolve it in 1 litre of water. If you wish the solution to keep, it is better to use 650 c.c. of water and 350 c.c. of methylated spirit: this is your standard soap solution. Measure 50 c.c. each of distilled water, rain water, well water, and sea water into 6-oz. bottles, and run the soap solution from a burette into each, until a lather is formed by shaking which does not break for five minutes. Note the volume of soap solution required for each. Evaporate 20 c c. of each water

and compare the residues in each case: the water which requires most soap for a permanent lather leaves the largest residue.

It will be found that the order of hardness is (1) sea water, (2) well water, (3) rain water and distilled water (practically equal).

146. Chemical Properties of Water.—Water possesses the power of combining directly with a very great many substances. Sometimes the compounds are very easily broken up again, whilst in other cases they are remarkably stable.

Water of Crystallisation.—Many salts, when they are allowed to crystallise from solution, contain water, which is associated with them in definite proportions, and it cannot be regarded otherwise than as water *in combination* with the salt.

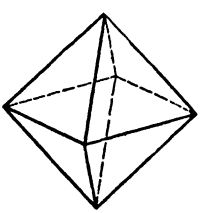
There is, however, very little stability in the combination; for instance, copper sulphate crystallises with the composition $CuSO_4$, $5H_2O$. At 110° C. $4H_2O$ is set free, and the remaining molecule of water requires a temperature of 220° C. to liberate it.

Alum crystallises with $24H_2O$; $10H_2O$ separate at 100° C., a further $9H_2O$ at 120° C., and nearly the whole of the remainder at 280° C. In some cases, indeed, such as crystallised sodium carbonate or washing soda, Na_2CO_3, $10H_2O$, the salt loses water or *effloresces* at ordinary temperatures in a dry atmosphere.

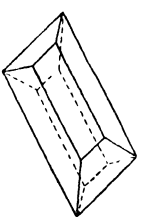
The amount of water of crystallisation which attaches itself to a salt varies according to the temperature at which the crystals form. Thus, from a solution of sodium sulphate, crystals of Na_2SO_4, $7H_2O$ can be obtained at temperatures below 26°, or crystals of Na_2SO_4, $10H_2O$ (Glauber's salt) at temperatures below 34°; while above 34° crystals of Na_2SO_4 are obtained. Epsom salts, $MgSO_4$, $7H_2O$, furnishes another example, passing into $MgSO_4$, $6H_2O$ at 48° C. Frequently, salts which at ordinary temperatures separate from solution in the anhydrous

condition, possess water of crystallisation when crystallised at low temperatures. Thus if a concentrated solution of common salt be allowed to stand at ordinary temperatures crystals of NaCl are obtained, but at — 10° C. crystals of $NaCl, 2H_2O$.

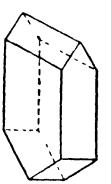
As examples of the crystalline forms assumed by salts containing water of crystallisation we may consider three



Alum.
$K_2SO_4, Al_2(SO_4)_3, 24H_2O$.
Fig. 51.



Washing Soda.
$Na_2CO_3, 10H_2O$.
Fig. 52.



Epsom Salts.
$MgSO_4, 7H_2O$.
Fig. 53.

very common substances, viz. alum, washing soda, and Epsom salts. Figs. 51, 52, and 53 represent crystals of these substances, and it will be noticed how widely the three crystals differ in shape.

147. Compounds of Water with Oxides.—We have seen in discussing acids and bases that many oxides combine directly with water. The products vary in stability, but are as a whole very much more stable than those obtained when salts and water combine.

In many cases great heat is evolved when oxides and water unite, thus demonstrating the vigorous nature of the action.

Exp. 156.—Pour a *little* water on to some quicklime contained in a porcelain dish. Note the clouds of steam formed, showing that much heat is evolved during the combination. Dip a thermometer in the mixture and note the rise of temperature.

Other examples of oxides which evolve much heat on combination with water are baryta, BaO, sulphur trioxide, SO_3, and phosphoric oxide, P_4O_{10}. To bring about the decomposition of the compounds produced a correspondingly large amount of heat must be supplied, *i.e.* a high temperature is necessary.

To explain the greater stability of the compounds of water with oxides as compared with the compounds with salts, it is supposed that in the latter the water is present in *whole molecules* loosely combined with the molecule of the salt, whereas in the former it has completely lost its identity. Thus crystallised copper sulphate may be formulated $CuSO_4$, $5H_2O$ or $CuSO_4 + 5H_2O$, but barium hydroxide must not be represented BaO, H_2O or $BaO + H_2O$, *i.e.* as containing a molecule of BaO and a molecule of water; it must be written $Ba(OH)_2$, *i.e.* it contains two *hydroxyl* (OH) groups united to an atom of barium.

It is supposed that all the compounds of water with oxides contain one or more (OH) groups, and they are consequently called *hydroxides*, whereas the combinations of salts and water are termed *hydrates*.

148. Action of Metals on Water.—This has been fully discussed in § 35, and does not require further treatment here.

149. Tests for Water.—To distinguish water from other colourless liquids the following tests may be applied :—

(1) Add a few drops of the liquid to a small quantity of anhydrous copper sulphate (prepared by igniting some powdered blue vitriol in a crucible till it is perfectly white and allowing it to cool in a desiccator). Water rehydrates it and changes the colour from white to blue.

(2) Add a little of the liquid to some quicklime (see Exp. 156).

(3) Drop a small pellet of sodium or potassium (about the size of a pea) on to a portion of the liquid. If the liquid is water hydrogen will be evolved and will take fire in the case of potassium.

To decide whether water is *pure* or not its physical properties may be utilised. The liquid should

(*a*) be colourless, tasteless, and odourless;

(*b*) freeze at 0° C.;

(*c*) boil at 100° C. under 760 mm. pressure.

Moreover, pure water should give no precipitate or coloration with (1) *silver nitrate* (showing absence of chlorides), (2) *barium chloride* (showing absence of sulphates), *Nessler's solution* (showing absence of ammonia), (4) *lime-water* (showing absence of carbonates).

Hydrogen Peroxide, H_2O_2.

150. Action of Dilute Acids on Peroxides.—

Exp. 157.—Introduce some dilute sulphuric acid into two test-tubes, and add to one a small quantity of barium peroxide and to the other a little manganese dioxide. Shake up each tube and filter. To each filtrate add a little potassium iodide solution, followed by some starch solution (made by boiling starch with water). You will find that a blue coloration is produced in the filtrate from the tube which contained the barium peroxide, but not in the other filtrate.

The formation of a blue colour with starch solution is a characteristic property of *iodine*, which has therefore been liberated from the potassium iodide. Thus liberation must have been brought about by the agency of a substance produced by the action of dilute sulphuric on barium peroxide and which is soluble in water (since it is contained in the liquid passing through on filtration).

This substance is called *hydrogen peroxide*, and it is represented by the formula H_2O_2.

151. Classification of Peroxides.—We have seen in the above experiment that there is a difference in the behaviour of the peroxides, barium peroxide and manganese dioxide, towards dilute sulphuric acid; only the

former gives hydrogen peroxide (the manganese dioxide being unacted upon). If other dilute mineral acids were substituted for sulphuric acid the results would be the same, *i.e.* hydrogen peroxide would be produced only in the case of barium peroxide. Of other peroxides some, *e g.* sodium peroxide, behave like barium peroxide, whilst others, *e.g.* lead peroxide, behave like manganese dioxide. We may therefore divide peroxides into two classes: (1) those which form hydrogen peroxide with dilute mineral acids, (2) those which do not. We shall see later that the two classes have another important difference.

152. Preparation of Hydrogen Peroxide.—Hydrogen peroxide is usually prepared by the action of dilute sulphuric or dilute hydrochloric acid on barium peroxide or sodium peroxide.

* **Exp. 158.**—Add 10 c.c. of concentrated sulphuric acid to 200 c.c. of water contained in a beaker, and allow the mixture to stand till it becomes quite cold; now add little by little, with constant stirring, about 30 grams of barium peroxide. Allow to settle, and decant off the clear liquid. It is a dilute solution of hydrogen peroxide.

The change which has taken place is represented by the equation—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

153. Properties of Hydrogen Peroxide.—

* **Exp. 159.**—Heat some of the hydrogen peroxide solution in a test-tube. Bubbles of gas soon begin to rise rapidly (much more so than if dissolved air alone were being driven out of solution). In order to collect this gas in the tube nearly cover the mouth with your thumb. After a short time introduce a glowing splint into the tube. What do you observe?

We see that when hydrogen peroxide is heated it readily decomposes with liberation of oxygen. The other product

of the decomposition is water and the change is represented by the equation—

$$2H_2O_2 = 2H_2O + O_2.$$

In contact with certain metals such as finely divided platinum the decomposition takes place at *ordinary temperature*, thus affording a striking example of *catalysis*.

154. Oxidising Action of Hydrogen Peroxide.—Since hydrogen peroxide gives up oxygen so readily we might expect it to act as a powerful oxidising agent. That this is the case may be illustrated by the following experiment:—

* **Exp. 160.**—Make a dark stain of sulphide of lead on filter paper by first moistening it with a solution of a lead salt, say the acetate, and then exposing this to sulphuretted hydrogen. Steep the paper in a little of the hydrogen peroxide solution and it will become white.

The explanation of this is that the black sulphide of lead (PbS) has been transformed into white lead sulphate ($PbSO_4$) by oxygen derived from the hydrogen peroxide which is reduced to water.

$$PbS + 4\ H_2O_2 = PbSO_4 + 4\ H_2O.$$

Ordinary molecular oxygen will not bring about this change except on heating. We have, however, seen in discussing ozone that atomic oxygen is more active than molecular oxygen, and it is the atomic oxygen produced when hydrogen peroxide decomposes which acts so readily on the lead sulphide. We may therefore represent the reaction in two stages—

$$4H_2O_2 = 4H_2O + \underset{\text{Atomic}}{4O}.$$

$$PbS + \underset{\text{Atomic}}{4O} = PbSO_4.$$

This reaction is made use of in restoring the colour of old pictures which have been blackened by the action of sulphuretted hydrogen on the lead paint. The hydrogen

peroxide converts the *black* lead sulphide into *white* lead sulphate.

The liberation of iodine from potassium iodide (Exp. 157) is another example of the oxidising action of hydrogen peroxide. In this case the metallic part (potassium) of the potassium iodide is entirely removed.

$$\underset{\text{Potassium iodide}}{2KI} + H_2O_2 = \underset{\text{Caustic potash}}{2KOH} + \underset{\text{Iodine}}{I_2}$$

Again, hydrogen peroxide converts the hydrogen of sulphuretted hydrogen (H_2S) to water, setting free sulphur.

$$H_2S + H_2O_2 = S + 2H_2O.$$

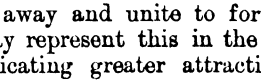
Hydrogen peroxide possesses the power of bleaching many vegetable and animal colours, and is much used for bleaching hair, silk, ivory, etc. It also destroys bacteria and decaying organic matter, and consequently finds application as an antiseptic and disinfectant (it forms the basis of "Sanitas"). All these properties depend upon its oxidising action.

155. Reducing Action of Hydrogen Peroxide.—

***Exp. 161.**—Add silver nitrate to some of your hydrogen peroxide solution, and then caustic soda; a black precipitate will be formed, and almost at once a gas is evolved with effervescence. Show in the usual way that this gas is oxygen.

The explanation is as follows:—Silver nitrate and caustic soda react to form hydrated silver oxide (*i.e.* silver oxide, Ag_2O, combined with water)—the black precipitate.

Now silver oxide and hydrogen peroxide each contain an atom of oxygen which readily splits off, and the attraction of these two atoms for one another is greater than their respective attractions for silver and water. They consequently break away and unite to form a molecule of oxygen. We may represent this in the following way, a thick arrow indicating greater attracting force than a thin arrow—



The silver oxide is therefore reduced to the metal and at the same time the hydrogen peroxide is reduced to water, the reaction being represented by the equation—

$$Ag_2O + H_2O_2 = 2Ag + H_2O + O_2.$$

* **Exp. 162.**—Introduce a few drops of a solution of potassium permanganate ($KMnO_4$) into a test-tube and some dilute sulphuric acid and then some hydrogen peroxide solution. The solution becomes colourless and a gas (oxygen) is evolved with effervescence.

This change resembles the previous one: both the potassium permanganate and hydrogen peroxide have undergone reduction, each compound supplying part of the oxygen evolved.

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = \underset{\text{Potassium sulphate}}{K_2SO_4} + \underset{\text{Manganous sulphate}}{2MnSO_4} + 8H_2O + 5O_2.$$

Other examples of the reducing action of hydrogen peroxide are represented by the following equations:—

$$\underset{\text{Manganese dioxide}}{MnO_2} + H_2O_2 = \underset{\text{Manganous oxide}}{MnO} + H_2O + O_2.$$

$$\underset{\text{Chromium trioxide}}{2CrO_3} + 3H_2O_2 = \underset{\text{Chromic oxide}}{Cr_2O_3} + 3H_2O + 3O_2.$$

$$H_2O_2 + \underset{\text{Ozone}}{O_3} = H_2O + 2O_2.$$

All these actions are explained in the same way as the first, *i.e.* they depend on the fact that both the substance reduced and the hydrogen peroxide contain an oxygen atom which readily splits off; it is in fact a general rule that whenever hydrogen peroxide exercises a reducing action it loses oxygen itself and is changed into water.

156. Pure Hydrogen Peroxide is a thick liquid with a specific gravity of about 1·5; it is colourless in small masses, but in large masses it has a decidedly bluer colour than water.

156a. Catalysis.—This is a convenient point at which to consider in greater detail a phenomenon with which we have already become acquainted to some extent. We have seen that various substances, such as manganese dioxide, cupric oxide, and finely divided platinum, when mixed with potassium chlorate enable oxygen to be obtained from the latter at a lower temperature than when the pure salt is used (§§ 19, 101); that such oxides as cobalt oxide and cupric oxide enable oxygen to be obtained very readily from bleaching powder (§ 101); and that finely divided platinum brings about the decomposition of hydrogen peroxide at ordinary temperature (§ 153).

Now in all these cases a substance has been added to assist in the decomposition of another substance, and this added substance is found to be *chemically unchanged* at the end of the reaction (though it may be changed physically to some extent). These are but a few examples of *catalysis* (Gk. κατά = down, λύω = I loosen), a phenomenon of very common occurrence; in fact, it is probable that all chemical reactions are capable of being assisted more or less by the presence of a suitable substance which does not itself undergo any permanent change. To such a substance the name *catalytic agent* or *catalyst* is given. We may state a formal definition as follows:—

A **catalytic agent** or **catalyst** is a substance which assists a chemical change but is found unchanged among the end products.

Catalysts have been compared to lubricants for machinery; they "oil the wheels," and so enable the change to proceed more easily.

The following are the chief characteristics of catalytic action:—

(1) *The catalyst is not used up during the reaction.* This follows from the definition of the term catalyst.

(2) *A relatively small amount of the catalyst is sufficient to bring about a large amount of chemical change.*

This is readily understood since the catalyst is not used up. It is generally supposed that, in a great many cases at any rate, the catalyst goes through a cycle of changes, being repeatedly converted into a compound which is unstable under the conditions of the reaction, and at once breaks down again, only to be reformed and once more decomposed, and so on.

(3) *A catalyst cannot start a reaction, but only accelerates it.* It is supposed that in cases where the catalyst seems to start a reaction, the reaction is really proceeding in its absence, but only extremely slowly.

(4) *The accelerating action of a catalyst is proportional to the amount of it which is present.*

(5) *If the reaction is a reversible one, the catalyst assists the reverse change to the same extent that it assists the direct change.*

This is true, for example, of the formation of sulphur trioxide from sulphur dioxide and oxygen by heating in contact with such catalysts as finely divided platinum or ferric oxide; the reverse change, *i.e.* the decomposition of sulphur trioxide into the dioxide and oxygen by heat is facilitated to the same extent as the direct change by the catalysts mentioned (see §§ 263, 264)

The most important catalyst of all is *water*, which would appear to be essential to very many reactions if they are to take place other than infinitely slowly. One example will suffice. If electric sparks are passed through a mixture of carbon monoxide and oxygen in the proportions required to form carbon dioxide, which has been thoroughly dried by contact with phosphoric oxide, no explosion takes place. If, however, a trace of moisture is admitted, the passage of a spark brings about immediate combination with explosion (§ 305).

QUESTIONS.—CHAPTER XIV.

1. How would you prove by experiment that steam contains its own volume of hydrogen?

2. Pure hydrogen is passed over heated oxide of copper, and the water which forms is collected; if the loss in weight of the oxide of copper be 4·20 grams, and the weight of the water obtained 4·73 grams, determine the amount of hydrogen and oxygen in 100 grams of water.

3. What amount of potassium nitrate (see table, § 134) would be required to form a saturated solution in 150 grams of water, (*a*) at zero, (*b*) at 50° C.?

4. State Henry's Law. What volume of carbon dioxide will dissolve in 250 c.c. of water under standard pressure, (*a*) at zero, (*b*) at 20° C; and what at these same temperatures when the pressure is that of 76 mm. of mercury, and when it is three atmospheres (the volume being reduced to standard pressure)?

5. A mixture of carbon dioxide and oxygen containing 95 per cent. by volume of the latter gas is shaken up with 500 c.c. of water at S.T.P.: what volume of each gas will be dissolved?

6. State the constituents to which the temporary and permanent hardness of water are respectively due, and explain the methods of removing each kind of hardness.

7. Write down in separate paragraphs (*a*) the physical, (*b*) the chemical properties of water.

8. It is said that hydrogen peroxide behaves both as an oxidising and a reducing agent; explain this statement, and illustrate your remarks by references to reactions.

CHAPTER XV.

THE HALOGENS.

Hydrochloric Acid, HCl, and Chlorine, Cl_2.

157. Action of Sulphuric Acid on Common Salt.—

Exp. 163.—Introduce a small quantity of common salt into a test-tube and then pour in just sufficient concentrated sulphuric acid to cover it. The mixture froths up, showing that a gas is being evolved. You will notice further that the gas is colourless, but forms white fumes at the mouth of the tube, and that it has a very pungent odour. Blow over the mouth of the test-tube: the white fumes become much more visible.

Now place a piece of blue litmus paper in the mouth of the tube. Its colour is at once changed to red, showing that the gas has an *acid reaction.*[1]

When the action slackens warm the tube: the mixture effervesces vigorously again. If you continue the heating you will observe that after a time the salt dissolves completely. When the evolution of gas appears to have ceased allow the tube to cool. The residue will solidify to a white crystalline mass, so that you can invert the tube without anything running out (if you have not used too much acid).

From this experiment we learn that when sulphuric acid acts on common salt a colourless, fuming, pungent-smelling gas is evolved and a white crystalline solid is formed. The

[1] This is really only true *in the presence of water.* The *perfectly dry* gas has no action on *dry* litmus paper.

gas is *hydrogen chloride* (or hydrochloric acid gas), HCl; the solid is sodium hydrogen sulphate, $NaHSO_4$.

Let us now investigate the gas further.

Exp. 164.—Fit a test-tube with a cork through which passes a delivery tube bent as shown in Fig. 54. Introduce a little common salt into the tube, add sufficient concentrated sulphuric acid to just cover it, and insert the cork and delivery tube. Slip over the latter a second test-tube (B) so that the delivery tube reaches nearly to the bottom of this tube. After a short time white fumes will be formed at the mouth of B, showing that the gas produced by the action of the acid on the salt is escaping. When these fumes become very pronounced (warm A if the action slackens) remove B, immediately cover its mouth completely with your thumb and invert it in a trough of water. Then remove the thumb. The water rises *very rapidly* in the tube and *nearly fills it.*

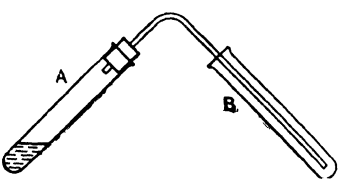


Fig. 54.

The very rapid rise of the water proves that the gas produced by the action of sulphuric acid on common salt is *very soluble in water.* Further, the fact that the water nearly fills the tube shows that nearly all the air had been displaced by the gas, which cannot therefore be much lighter than air and is probably heavier.

Since the gas is very soluble in water it cannot be collected over that liquid, but we have already collected a test-tube of it by downward displacement, and this is the method usually adopted.

158. Preparation of Hydrogen Chloride.—Almost any chloride[1] gives hydrogen chloride when treated with concentrated sulphuric acid. For the preparation of the

[1] The exceptions are silver chloride and mercurous chloride.

gas the commonest chloride, viz. sodium chloride (common salt), is naturally employed and the method is essentially that of Exp. 164. The details are as follows:—

Exp. 165.—Fit up a flask of about ¾ lit. capacity with a thistle funnel and a short glass exit tube bent at right angles. By means of a short piece of rubber tubing attach to the exit tube another glass tube bent at right angles near one end, and long enough to reach nearly to the bottom of a glass cylinder when the apparatus is fitted up as shown in Fig. 55. All the glass apparatus must be *quite dry*.

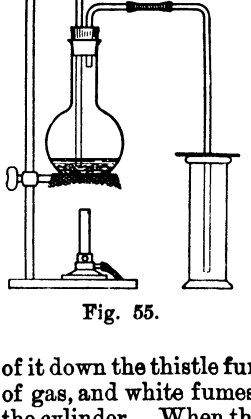


Fig. 55.

Introduce into the flask about 20 grams of common salt,[1] fit in the cork tightly and see that the thistle funnel reaches nearly to the bottom of the flask. Place the free arm of the delivery tube in the cylinder, and cover the mouth of the latter with a piece of cardboard.

Measure out about 25 c.c. of concentrated sulphuric acid into a beaker with a lip, and pour a little of it down the thistle funnel. There is a violent effervescence of gas, and white fumes form in the flask and pass over into the cylinder. When the reaction slackens add a little more acid, and so on till the whole 25 c.c. have been run in.

When the gas fumes strongly at the mouth of the cylinder you may assume that the latter is full of gas. Remove it, cover its mouth with a greased glass plate, and place another dry cylinder in position. In this way collect several cylinders of the gas. It will be necessary to warm the flask *gently* when the first violent action has subsided.

[1] It is best to use lumps of fused common salt, otherwise the reaction is very violent. Or instead of this a somewhat diluted acid (11 vol. of oil of vitriol to 8 vol. of water) may be used along with ordinary common salt; the action can then be readily controlled by heating or removing the Bunsen as required.

The equation representing the change which has taken place is—

$$NaCl + H_2SO_4 = HCl + NaHSO_4.$$

If the gas is required *dry*, it should be passed through a sulphuric acid wash-bottle, and if *pure*, it should be collected over mercury.[1]

159. Properties of Hydrogen Chloride.—We have already seen that hydrogen chloride is a colourless, fuming, pungent-smelling gas, which is very soluble in water. Accurate experiment shows that 1 c.c. of water at 0° C. dissolves 503 c.c. of the gas, and at ordinary temperature about 450 c.c. The solution of the gas is accompanied by a considerable evolution of heat, and there is also an increase in the volume of the liquid.

Let us continue our investigation of the properties of the gas.

* **Exp. 166.**—Fit a fairly large glass flask with a cork, hang it from one arm of a balance and weigh it. Now remove the cork, displace the air from the flask by hydrogen chloride prepared as in Exp. 165, replace the cork, and reweigh. There will be an increase in weight.

This experiment proves that the density of the gas is greater than that of air; it is actually about 1¼ times as great.

Exp. 167.—Introduce a lighted taper into a jar of the gas: the flame is extinguished and the gas does not burn. Try similar experiments with a lighted splint of wood, burning sulphur and phosphorus: these are also extinguished.

Hydrogen chloride then is not combustible, nor is it a supporter of combustion.

[1] A very convenient laboratory method of preparing hydrogen chloride is to drop concentrated sulphuric acid slowly into a concentrated aqueous solution of the gas which is evolved steadily without the application of heat.

160. Action of Hydrogen Chloride on Metals.—

* **Exp. 168.**[1]—Procure a rather wide hard glass tube about 40 cm. long and provided with a bulb near one end. Introduce into the other end of the tube a closely wound spiral of iron wire. Fit the bulb end of the tube with a cork through which passes a short piece of glass tubing bent at right angles. Support the tube by a retort stand and clamp and arrange that the exit tube bends upwards, as shown in Fig. 56.

Now connect the tube with an apparatus for preparing *dry* hydrochloric acid gas. This consists of a generator

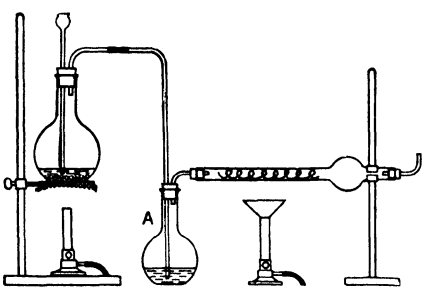


Fig. 56.

similar to that used in Exp. 165, and a small flask A containing concentrated sulphuric acid, which serves to dry the gas. Start the current of gas, and when it begins to fume at the exit tube (showing that the air has been expelled from the apparatus) heat the iron spiral by means of a spreading Bunsen flame. After a time white feathery crystals will begin to collect in the bulb.

Now hold a test-tube over the exit tube for a short time, cover the mouth with your thumb, place the tube under water contained in a trough, and remove the thumb. The water will rise up the tube owing to the absorption of the hydrochloric acid gas, but will only partially fill it, *i.e.* a

[1] This experiment should be performed in a *fume cupboard*.

residue of gas remains undissolved. Now close the tube with your thumb, remove it from the trough, and bring its mouth to a Bunsen flame. The gas will ignite with a slight explosion. It is *hydrogen.*

Heated metallic iron then decomposes hydrogen chloride with liberation of hydrogen; the white crystals formed at the same time consist of ferrous chloride, $FeCl_2$, and the change is represented by the equation—

$$Fe + 2HCl = FeCl_2 + H_2.$$

Most other metals are acted upon by hydrogen chloride in a similar manner, hydrogen and the chloride of the metal being formed. In some cases, *e.g.* that of sodium, the action proceeds readily even at ordinary temperature. Mercury and silver are examples of metals which are not acted upon by hydrogen chloride.

161. Action of Hydrogen Chloride on Metallic Oxides.—

* **Exp. 169.**—Introduce a layer of litharge into a tube similar to that used in Exp. 69. Arrange the tube and accessories as in Fig. 25, but connect it with an apparatus for preparing dry hydrogen chloride (§ 158) instead of hydrogen. Heat the litharge and pass hydrogen chloride through the tube. A liquid collects in the U-tube: test it and show that it is water. When no more water appears to be formed allow the tube to cool and examine the residue: it is a white crystalline solid.

* **Exp. 170.**—Repeat Exp. 169, using lead peroxide in place of litharge. You will observe that the apparatus soon becomes filled with a yellowish green gas which has a suffocating odour.

Hold a piece of moist red litmus paper in the yellow gas as it escapes from the U-tube: the colour is bleached.

You will further notice that water collects in the U-tube, and when the change is complete a white crystalline residue remains similar to that obtained in Exp. 169.

The formation of water in Exps. 169, 170 affords an independent proof of the presence of hydrogen in hydrogen chloride (for litharge and lead peroxide are metallic oxides and contain no hydrogen). The yellowish green gas formed in Exp. 170 is called *chlorine* from its colour. It must be *derived from* the *hydrogen chloride*, since lead peroxide contains only lead and oxygen. We have shown therefore that *hydrogen chloride* contains *hydrogen* and *chlorine*; further, since it can be obtained by the direct union of hydrogen and chlorine (see later), these are the *only* elements it contains.

The white crystalline substance formed in both Exps. 169 and 170 consists of lead chloride, $PbCl_2$, and the complete changes which take place are represented by the equations—

$$PbO + 2HCl = PbCl_2 + H_2O$$
$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

The difference in the behaviour of the two oxides of lead is explained by the fact that one contains more oxygen than the other. The extra oxygen in the peroxide may be supposed to oxidise the hydrogen of some of the hydrogen chloride to water, with liberation of free chlorine. The following way of representing the change will perhaps assist the student to realise the explanation more clearly—

$$\left\{\begin{matrix}PbO\\O\end{matrix}\right. + \left\{\begin{matrix}2HCl\\2HCl\end{matrix}\right. = \begin{matrix}PbCl_2 + H_2O\\H_2O + Cl_2.\end{matrix}$$

Basic oxides in general behave like litharge when heated in hydrogen chloride, *i.e.* they give water and the chloride of the metal. On the other hand, manganese dioxide behaves like lead peroxide in that chlorine is formed in addition to water and the chloride of the metal; both of these oxides are *peroxides*.

162. Preparation of Hydrochloric Acid, *i.e.* an aqueous solution of hydrogen chloride.—A solution of hydrogen chloride in water, commonly called hydrochloric acid (also known as "spirits of salt" and "muriatic acid"), may be conveniently prepared in the following manner:—

* **Exp. 171.**—Remove the long arm from the delivery tube of the apparatus used in Exp. 165 (Fig. 55) and replace it by a shorter tube also bent at right angles near one end. Attach a small glass funnel to the other end by means of rubber tubing, and arrange that the funnel dips *just below*[1] the surface of some water contained in a small beaker (Fig. 57). Now prepare hydrogen chloride as already described. Owing to its great solubility it will be completely absorbed by the water in the beaker.

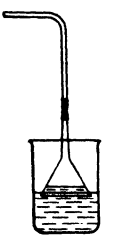


Fig. 57.

The arrangement adopted for the absorption of the gas prevents the possibility of the liquid in the beaker "sucking back" into the generating flask, owing to the great solubility of the gas; for as soon as the solution has risen a little way up the funnel, the level of liquid in the beaker falls to that of the rim of the funnel.

The experiment should be allowed to proceed till the liquid *smells strongly* of the gas; the solution is then *concentrated hydrochloric acid.*

163. Properties of Hydrochloric Acid.—

Exp. 172.—Test the solution you have prepared in Exp. 171 with litmus. Also try its action on a few metals such as zinc, iron, and copper.

Hydrochloric acid is a strongly acid liquid, turning blue litmus bright red; it is very corrosive, being much more active than the gas.

Action on Metals.—Many metals are attacked by hydrochloric acid, some readily by the dilute acid, others only by the hot concentrated acid. In all cases the products are a chloride of the metal and hydrogen. The

[1] An alternative arrangement is to have the rim of the funnel *just above* the surface of the water.

following table gives a *résumé* of the action of the acid on a number of common metals under different conditions.

Metal.	Cold dilute HCl.	Hot conc. HCl.
Zinc	Dissolves readily	Dissolves readily
Magnesium	,, ,,	,, ,,
Iron	,, ,,	,, ,,
Aluminium	,, rather slowly	,, ,,
Tin	,, slowly	,, ,,
Copper	Insoluble[1]	,, slowly
Lead	,,	,, very slowly
Mercury	,,	Insoluble
Silver	,,	,,
Gold	,,	,,
Platinum	,,	,,

164. Test for Hydrochloric Acid.—

Exp. 173.—Add a little *silver nitrate* solution to a small quantity of your acid solution. A white curdy precipitate of silver chloride forms at once.

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

This reaction is used as a *test* for hydrochloric acid, and also for soluble chlorides (*e.g.* common salt) which give the same precipitate.

165. Action of Concentrated Hydrochloric Acid on Peroxides.—

Exp. 174. *Action on Manganese Dioxide.*—Introduce into a test-tube a small quantity of manganese dioxide. Pour in sufficient of your hydrochloric acid to cover it. Warm gently. *Chlorine* is evolved as shown by its colour,

[1] Copper is slowly attacked by dilute hydrochloric acid *in the presence of air*; the same remark applies to lead.

odour, and bleaching action on moist litmus. The manganese dioxide dissolves completely if sufficient acid is present, forming a brown solution (which contains manganous chloride, $MnCl_2$, dissolved in it).

When a similar experiment is tried with barium peroxide —which gives with dilute acids hydrogen peroxide (see *ante*)—chlorine or oxygen or both together are evolved, depending on the conditions.

The changes which have taken place in these reactions are represented by the following equations:—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2,$$
$$2BaO_2 + 4HCl = 2BaCl_2 + 2H_2O + O_2,$$
$$BaO_2 + 4HCl = BaCl_2 + 2H_2O + Cl_2.$$

These results illustrate another important difference between the two classes of peroxides, which we have distinguished in § 151. Those which are unacted upon by dilute mineral acids, such as manganese dioxide and lead peroxide, give *chlorine only* when heated with concentrated hydrochloric acid; whilst those which form hydrogen peroxide with dilute mineral acids, such as barium peroxide and sodium peroxide, yield *oxygen or chlorine or both* when heated with concentrated hydrochloric acid. In the latter case hydrogen peroxide is the first product of the reaction, but as already stated it decomposes readily on heating into water and oxygen, the latter often decomposing some of the hydrochloric acid into water and free chlorine.

166. Action of Hydrochloric Acid on Red Lead.—

Exp. 175.—Repeat Exp. 174, using red lead in place of manganese dioxide. You will find that chlorine is evolved and the red lead dissolves completely, forming a colourless solution if sufficient acid is added. When the solution cools white crystals of lead chloride ($PbCl_2$) separate out.

Red lead (Pb_3O_4) then acts like a peroxide towards hydrochloric acid. It may be considered as a compound of one molecule of lead peroxide (PbO_2) and two molecules of litharge (PbO).

$$2PbO + PbO_2 = Pb_3O_4.$$

In order to arrive at the equation for the action of hydrochloric acid on red lead, let us first consider it composed of the two oxides indicated above and write the equations for the action of the acid on these. Then if we add the left-hand sides of each equation together and also the right-hand sides, we shall arrive at the equation expressing the whole reaction.

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$$
$$2PbO\S + 4HCl = 2PbCl_2 + 2H_2O$$
$$PbO_2.2PbO \text{ or } Pb_3O_4 + 8HCl = 3PbCl_2 + 4H_2O + Cl_2.$$

167. Preparation of Chlorine.—The method we shall adopt for the prepartion of chlorine is that investigated in Exp. 174.

Exp. 176.—Introduce about 20 grams of manganese dioxide, in small lumps, into a fairly large flask, and just cover it with strong hydrochloric acid. Close the mouth of the flask with a cork carrying a thistle funnel and delivery tube. Support the flask on a sand-bath by means of a retort stand, and connect it with a wash-bottle containing a little water. Provide the wash-bottle with a delivery tube reaching to the bottom of a glass cylinder as shown in Fig. 58. Now apply a gentle heat, when chlorine is evolved mixed with hydrochloric acid gas. For a short time both the chlorine and the hydrochloric acid gas are absorbed by the water in the wash-bottle. Soon, however, the solution becomes saturated with chlorine, which then passes on, whilst the

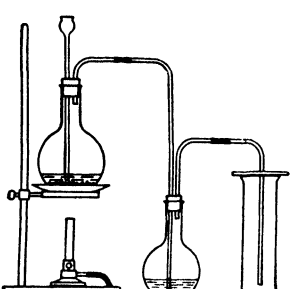


Fig. 58.

§ We must write 2 *molecules* of litharge, i.e. *double the equation throughout*, because red lead contains 2 molecules of litharge.

hydrochloric acid gas, being very much more soluble, continues to be absorbed in the wash-bottle. Collect the chlorine in glass cylinders by displacement of air. Cover each cylinder with a piece of cardboard during the collection. When a lighted match is extinguished at the mouth of the cylinder you may assume that it is full of chlorine; at once cover with a glass plate.

If the gas is required *dry* it should be passed through one or two wash-bottles containing concentrated sulphuric acid before being collected as above.

Instead of using hydrochloric acid in the preparation of chlorine just described, a mixture of common salt and strong sulphuric acid may be employed. The equation representing the reaction which takes place is—

$$MnO_2 + 3H_2SO_4 + 2NaCl = \underset{\text{Manganese sulphate}}{MnSO_4} + 2NaHSO_4 + 2H_2O + Cl_2.$$

Exp. 177.—Warm a little common salt and manganese dioxide with some concentrated sulphuric acid in a test-tube. Note the evolution of chlorine.

The most convenient method of preparing chlorine is to act on bleaching powder with dilute hydrochloric acid. The bleaching powder is used in the form of small lumps, obtained by first pressing it into a cake with a little plaster of Paris and then breaking this cake up. Under these conditions chlorine is evolved at a convenient rate without the application of heat—

$$\underset{\text{Bleaching powder}}{CaOCl_2} + 2HCl = \underset{\text{Calcium chloride}}{CaCl_2} + H_2O + Cl_2.$$

168. Properties of Chlorine.—Chlorine is a greenish-yellow gas which has a very irritating action on the mucous membrane. It is soluble in water, as shown by the fact that the liquid in the wash-bottle in Exp. 176 soon acquires the colour of the gas. Its solubility is further illustrated by the following experiment.

Exp. 178.—Take one of the jars of chlorine which you have prepared, fill it about one-third full of water, at once replace the cover and shake up vigorously. Invert the jar in a trough of water and remove the cover; water rapidly rises in the jar to take the place of the chlorine which has dissolved in the water. Replace the cover, stand the jar upright, and introduce into it a red litmus paper. The solution of the gas bleaches the litmus just as the gas itself did.

It is found that one volume of water takes up about two volumes of the gas at ordinary temperatures. The solubility is not so great as to preclude the possibility of collecting the gas over water, but if this method is adopted a considerable amount of gas is used up in saturating the water; hence the method adopted in Exp. 176 is better.

Chlorine is a heavy gas, its density being about two and a half times that of air.

***Exp. 179.**—Show that the density of chlorine is greater than that of air, using the method adopted in Exp. 166.

All attempts to break up chlorine into simpler substances have proved futile; it is therefore an *element*. Chlorine occurs very abundantly in Nature in combination with metals as *chlorides*, *e.g.* with sodium as *sodium chloride* (common salt), but it is never found free on account of its great activity.

It is in fact one of the most active substances known, for it reacts with a great many elements and compounds at the ordinary temperature, frequently with incandescence.

169. Combination of Chlorine and Hydrogen.—When chlorine and hydrogen are mixed and exposed to direct sunlight they combine with explosion, hydrogen chloride being formed according to the equation—

$$H_2 + Cl_2 = 2HCl.$$

Burning magnesium wire, which gives out light very rich in chemically active rays, also causes the mixture

to explode. In diffused daylight combination takes place gradually, and in the dark hydrogen and chlorine do not unite. By proceeding as described in the following experiment it is possible to burn hydrogen quietly in chlorine.

* **Exp. 180.**—Prepare a jar of chlorine from manganese dioxide and hydrochloric acid as described above, and introduce a lighted jet of hydrogen into it. It continues to burn with the production of fumes of hydrogen chloride.

The affinity of chlorine for hydrogen is so great that it is able to extract it from many compounds, such as turpentine ($C_{10}H_{16}$), sulphuretted hydrogen (H_2S), and water.

Exp. 181.—Introduce a piece of blotting-paper soaked in turpentine into a jar of chlorine. The turpentine takes fire; white fumes of hydrochloric acid are formed and a black deposit of free carbon settles on the sides of the jar.

$$C_{10}H_{16} + 8Cl_2 = 10C + 16HCl.$$

Exp. 182.—Pass chlorine for some minutes through about 50 c.c. of water, and to this add a solution of sulphuretted hydrogen; hydrochloric acid is formed, the liquid becoming turbid owing to the separation of sulphur, according to the equation—

$$Cl_2 + H_2S = 2HCl + S.$$

Exp. 183.—Pass chlorine for some minutes through about 100 c.c. of water. Now take a long narrow glass tube closed at one end and fill it completely with the chlorine solution. Invert it in a dish containing a little water, and expose it to direct sunlight. Bubbles of gas will be seen to rise slowly in the liquid. Leave for some time. When sufficient gas has collected, cover the mouth of the tube with your thumb, turn it mouth upwards and test the glass with a glowing splinter; the splinter bursts into flame, showing that the gas is oxygen. Prove the presence of hydrochloric acid in the liquid by applying the test described in Exp. 173.

The change may be expressed by the equation—

$$2Cl_2 + 2H_2O = 4HCl + O_2,$$

but this is not a complete representation of what happens, as chloric acid ($HClO_3$) is also formed.

Chlorine will, moreover, support the combustion of a candle or of coal gas on account of its affinity for hydrogen. The substances of which candles are composed consist either entirely, or at any rate largely, of carbon and hydrogen, and when a lighted candle is lowered into a jar of chlorine it continues to burn with formation of hydrogen chloride and separation of carbon, just as in the case of turpentine.

Exp. 184.—Fix a piece of candle into a deflagrating spoon, light it, and lower it into a jar of chlorine. The candle continues to burn with a dull red smoky flame, and soot is deposited on the walls of the jar.

Coal gas, again, consists almost entirely of a mixture of free hydrogen and compounds of carbon and hydrogen, and when a jet of lighted coal gas is lowered into a jar of chlorine it continues to burn; but the flame becomes duller and smoky owing to the separation of free carbon.

170. Combination of other Elements with Chlorine.—

Exp. 185.—Into a jar of chlorine bring a piece of phosphorus on a deflagrating spoon: presently the phosphorus will ignite and burn freely with the formation of a liquid substance called phosphorus trichloride (PCl_3).

Antimony, copper, and some other metals in a finely divided condition also take fire spontaneously when plunged into chlorine; if, however, the metals are in mass they require heating before they will ignite.

Exp. 186.—Heat a piece of sodium in a deflagrating spoon until it takes fire, and then plunge it into a jar of chlorine: the sodium burns brilliantly, uniting with the chlorine to form a solid substance—common salt.

171. Oxidising Action of Chlorine.—Chlorine is a strong oxidising agent *in the presence of moisture*, this property depending on its power of combining with the hydrogen of water and liberating *nascent* oxygen. An example of such action is its power of converting sulphurous acid into sulphuric acid.

$$\underset{\text{Sulphurous acid}}{H_2SO_3} + H_2O + Cl_2 = \underset{\text{Sulphuric acid}}{H_2SO_4} + 2HCl.$$

Another example is furnished by the *bleaching* properties of chlorine; vegetable colouring matters, *e.g.* the pigments in the leaves and flowers of plants, are deprived of their colour by moist chlorine, though in the absence of moisture no such action takes place.

Exp. 187.—Prepare a jar of *dry* chlorine (using two sulphuric acid wash-bottles). Place in this a piece of cloth dyed with turkey-red and leave it some minutes with the cover on; no decolorisation will occur, but on moistening the cloth it will be bleached.

172. Action of Chlorine on Organic Substances.—Many organic substances are very readily attacked by chlorine. In some cases (*e.g.* ethylene) the chlorine simply adds itself on to the compound, and *addition products* are formed. In other cases (*e.g.* marsh gas) chlorine replaces one or more atoms of hydrogen, and *substitution products* result: the displaced hydrogen combines with more chlorine forming hydrochloric acid. We shall return to this subject when studying the hydrocarbons.

Chlorine is a very powerful *disinfectant*, as it rapidly kills the minute forms of life known as bacteria, which are the chief cause of the putrefaction of organic matter.

173. Chlorides.—The chlorides of the metals may be produced by the direct union of the metals with chlorine or by the action of hydrochloric acid on the metals (in some cases) or on their oxides, hydroxides, or carbonates. Zinc chloride, $ZnCl_2$, for instance, may be produced by

any of these methods, as shown in the following equations:—

$$Zn + Cl_2 = ZnCl_2.$$
$$Zn + 2HCl = ZnCl_2 + H_2.$$
$$ZnO + 2HCl = ZnCl_2 + H_2O.$$
$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O.$$
$$ZnCO_3 + 2HCl = ZnCl_2 + H_2O + CO_2.$$

When a metal forms an *insoluble* chloride a special method of preparation is applicable, viz. the addition of a solution of a soluble chloride to a solution of a soluble salt of the metal; double decomposition takes place, the insoluble chloride being precipitated. Silver chloride is, for example, precipitated when a solution of silver nitrate, $AgNO_3$, is added to a solution of calcium chloride, $CaCl_2$.

$$CaCl_2 + 2AgNO_3 = Ca(NO_3)_2 + 2AgCl.$$

Calcium nitrate Silver chloride

Most metallic chlorides are easily soluble in water; the only common insoluble ones are mercurous chloride (calomel), Hg_2Cl_2, cuprous chloride, Cu_2Cl_2, and lead chloride, $PbCl_2$ (which is sparingly soluble in cold water and readily in hot), in addition to silver chloride already referred to.

174. Action of Heat on Hydrochloric Acid.—When a strong solution of hydrogen chloride is distilled it at first loses hydrogen chloride much faster than water, *i.e.* it becomes weaker. This goes on till the percentage of HCl is 20·24, when the liquid distils over unchanged in composition. Similarly, if a solution containing less than 20·24 per cent. of hydrogen chloride is distilled it loses water faster than HCl till the percentage of HCl is 20·24, when the liquid again distils unchanged. The boiling-point of hydrochloric acid of this particular strength is 110° C. It must be noted that the acid which distils unchanged only has the composition and boiling-point stated when the *pressure is normal*; for any other pressure the composition and boiling-point of the liquid which distils unchanged have different values, which, however, are constant for each particular pressure.

175. Manufacture of Hydrochloric Acid.—Hydrochloric acid is manufactured in enormous quantities as a by-product in the conversion of common salt into salt-cake (sodium sulphate, Na_2SO_4) by the action of strong sulphuric acid. The first part of the process is performed at a gentle heat and the reaction is the same as that given in § 158. The mixture is then heated to a *much higher* temperature, when the acid sodium sulphate reacts with another molecule of sodium chloride, producing normal sodium sulphate and hydrogen chloride according to the equation—

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

The gas is passed up stone towers filled with lumps of coke, over which a slow stream of water flows; the hydrogen chloride is absorbed, and the aqueous solution runs away from the bottom of the tower into suitable receivers.

Impurities in the Commercial Acid.—The chief impurities found in commercial hydrochloric acid are free chlorine, sulphuric acid, sulphurous acid, arsenious chloride, ferric chloride, and organic matter. The organic matter is the principal cause of the yellow colour usually noticeable in the commercial acid.

176. Uses of Hydrochloric Acid.—The most important use of hydrochloric acid is in the manufacture of chlorine. It is also used in dyeing and calico-printing, in obtaining phosphates from bones, and in manufacturing colours. Its employment in the manufacture of metallic chlorides is also of importance, and it is very extensively used in chemical laboratories for a variety of purposes.

177. Liquid Chlorine and Hydrogen Choride.—Chlorine can readily be liquefied as described in § 72. Liquid chlorine is an orange-yellow substance of specific gravity 1·66; it boils at −33·6° C. It is prepared commercially for use in extracting gold.

Hydrogen chloride condenses to a colourless liquid under a pressure of 40 atmospheres at 10° C.; the liquid boils under ordinary pressure at −83·7° C. Liquid hydrogen chloride is without action on most metals, *e.g.* magnesium and zinc, nor does it act on metallic oxides, such as lime, or on anhydrous carbonates; it is therefore an inactive substance.

178. Composition of Hydrogen Chloride by Volume. —Analytical Method.—We can find the ratio of the volumes of hydrogen and chlorine which combine to form hydrogen chloride by submitting an aqueous solution of the gas to electrolysis (*i.e.* to the action of a current of electricity).

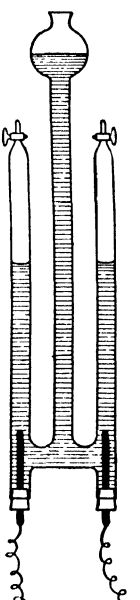


Fig. 59.

* **Exp. 188.**—The experiment is carried out in an apparatus similar to that used for the determination of the composition of water in § 126. The side limbs are, however, open at the lower ends, the openings being closed with corks through which pass two rods of gas-carbon (see Fig. 59). These are connected with the poles of a battery and constitute the electrodes.[1] Concentrated hydrochloric acid is introduced through the funnel till the side tubes are full, and an electric current from three or four Grove's or Bunsen's cells is passed through the liquid with the stopcocks open, till the liquid in the limb containing the positive electrode is saturated with chlorine; the hydrogen liberated in the other limb, being almost insoluble, escapes through the open stopcock. The stopcocks are now closed, and the gases will be found to collect in equal volumes in the two limbs. Their identity may be proved by the usual tests.

[1] Platinum cannot be used for the electrodes (or at any rate for the positive electrode) because it is attacked by chlorine.

We see then from this experiment that hydrogen and chlorine combine in *equal volumes* with formation of hydrogen chloride.

Next we require to find the ratio of the volume of hydrogen chloride to that of the hydrogen (or chlorine) it contains. This we can do by acting on a measured volume of the gas with metallic sodium which extracts the chlorine and leaves the hydrogen, the volume of which can be determined.

The sodium is most conveniently used in the form of a solution in mercury (called *sodium amalgam*), and the experiment may be carried out as described in the following experiment:—

† **Exp. 189.**—About 50 c.c. of hydrogen chloride are introduced into the closed limb of a bent eudiometer tube[1] previously filled with mercury (Fig. 60). The levels of mercury in the two limbs are made equal by running mercury out of the tap or pouring more into the open limb, and the volume of gas is measured. Mercury is now allowed to run out of the tap till very little is left in the open limb, and the latter is completely filled up with liquid sodium amalgam. The open end is then closed by the thumb and the hydrogen chloride transferred to the other limb by inverting and suitably manipulating the apparatus. The eudiometer is now restored to its normal position and then again inverted so as to bring the gas intimately in contact with the amalgam. Finally the gas is transferred back to the closed limb, and liquid is run out through the tap till the levels in the two limbs are equal.

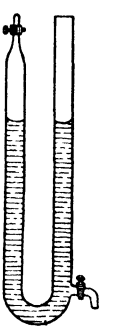


Fig. 60.

The volume of gas which remains will be found to be half that originally taken, and it may be proved to be hydrogen by the usual tests.

[1] The apparatus described in Exp. 125 may be used in place of a bent eudiometer.

Combining the results of Exps. 188, 189 we arrive at the result that *one volume of hydrogen combines with one volume of chlorine to produce two volumes of hydrogen chloride.*

Of course we have assumed that the hydrogen collected in Exp. 188 has come from the *hydrogen chloride*, whereas it *might* have come either entirely or partially from the *water*, so that our analytical proof is *not complete.* That the conclusion arrived at is correct is shown, however, by the synthetical method of determining the composition of the gas a description of which is given in the next paragraph.

179. Composition of Hydrogen Chloride by Volume. —Synthetical Method.—The composition of hydrogen chloride may be investigated synthetically, as described in the following experiment.

† **Exp. 190.**—Hydrochloric acid is electrolysed in the vessel A, Fig. 61 (using gas carbon electrodes), and when

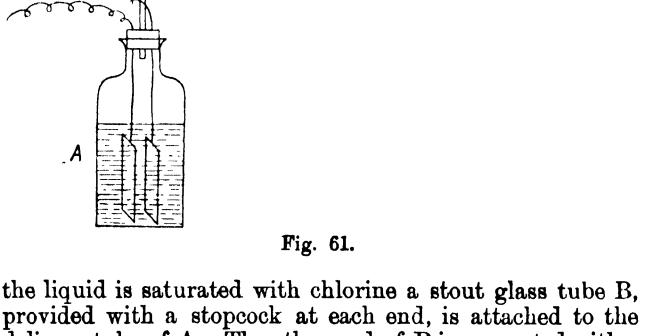


Fig. 61.

the liquid is saturated with chlorine a stout glass tube B, provided with a stopcock at each end, is attached to the delivery tube of A. The other end of B is connected with a bottle containing fragments of pumice stone moistened with caustic soda solution to absorb the chlorine as it escapes. The stopcocks are opened and the mixture of hydrogen and chlorine in equal volumes generated in A is passed through

B for some time so that all the air is driven out.[1] The stopcocks are then closed and the tube disconnected.

On opening one of the stopcocks under a solution of potassium iodide the chlorine reacts with the potassium iodide, liberating iodine, and if the experiment has been conducted properly the liquid will rise just half-way up the tube, showing that the chlorine and hydrogen are present in equal volumes. The tube is now cleaned out and again filled with the electrolytic mixture of hydrogen and chlorine. The stopcocks are again closed and the tube is disconnected and exposed to the action of the rays from burning magnesium wire (the face should be protected by a thick sheet of glass to avoid accident in case the tube explodes). The gases combine with explosion.

The tube is allowed to become quite cold and one of the stopcocks is then opened under mercury. No gas escapes and the mercury does not rise in the tube, showing that the volume of hydrogen chloride is exactly the same as that of the mixed gases from which it was formed. The stopcock is now closed and opened again under water; the water rushes up and fills the whole tube, the hydrogen chloride formed dissolving completely. This shows that the whole of the gases have combined to form hydrogen chloride.

We thus arrive at the same composition for hydrogen chloride by synthesis as by analysis.

180. Formulae of Chlorine and Hydrogen Chloride.—The densities of chlorine and hydrogen chloride relative to hydrogen are 35·5 and 18·25 respectively. Their molecular weights are therefore $2 \times 35{\cdot}5$ or 71 and $2 \times 18{\cdot}25$ or 36·5 (see § 83). These values correspond to the formulae Cl_2 for chlorine and HCl for hydrogen chloride, for

$$Cl_2 = 2 \times 35{\cdot}5 = 71,$$
$$HCl = 1 + 35{\cdot}5 = 36{\cdot}5.$$

[1] This must be done in the dark to prevent combination of the gases.

Bromine, Br_2, and Iodine, I_2.

181. Formation of Hydrogen Bromide and Hydrogen Iodide.—

Exp. 191.—Introduce a little potassium bromide into a test-tube and add some strong sulphuric acid. A pungent fuming gas resembling hydrogen chloride is evolved with effervescence; the gas has, however, a distinctly brown colour.[1] Show that the gas has an acid reaction to litmus.

If this experiment is repeated, using potassium iodide in place of potassium bromide, a similar pungent fuming acid gas is evolved, mixed, however, with violet fumes (of iodine).

It is possible therefore to obtain from potassium bromide and potassium iodide respectively two gases closely resembling hydrogen chloride, in a manner precisely similar to that by which we obtained hydrogen chloride from sodium chloride in Exp. 163. We should consequently expect that these two gases are compounds of hydrogen with two elements resembling chlorine, and that potassium bromide and iodide (which closely resemble sodium chloride in appearance and properties) are compounds of potassium and the same two elements.

If such is the case we ought to be able to obtain these elements from their potassium compounds in a similar manner to that by which we obtained chlorine from sodium chloride in Exp. 177. Let us investigate this point by experiment.

182. Formation of Bromine.—

Exp. 192.—Introduce small quantities of potassium bromide and manganese dioxide into a test-tube, add a little concentrated sulphuric acid, and warm. Dark red fumes are evolved having a *most offensive* smell (do not

[1] The brown colour is due to the presence of bromine vapour, the very objectionable smell of which tends to mask that of the gas evolved.

inhale more of them than you can help, as they are *very injurious*).

Introduce a piece of moist red litmus paper into the mouth of the tube; the colour gradually disappears, showing that the red fumes bleach like chlorine, but more slowly.

183. Formation of Iodine.—

Exp. 193.—Now repeat the experiment, using potassium iodide in place of the bromide. This time violet fumes are evolved and condense in the cool part of the tube, forming a blue-black crystalline solid. Test the fumes with moist red litmus paper; the colour is not bleached.

The brown fumes obtained in Exp. 192 consist of the vapour of a liquid which is called *bromine*. You will have recognised that the violet vapours and blue-black solid produced in Exp. 193 consist of *iodine*. These two substances are the elements combined with potassium in potassium bromide and iodide and with hydrogen in hydrogen bromide and iodide. They are found to resemble chlorine closely in properties and form with it a natural group called the *halogens*.

The primary changes taking place when sulphuric acid acts on potassium bromide and potassium iodide are represented by the equations—

$$\underset{\text{Potassium bromide}}{KBr} + H_2SO_4 = KHSO_4 + \underset{\text{Hydrogen bromide}}{HBr}.$$

$$\underset{\text{Potassium iodide}}{KI} + H_2SO_4 = KHSO_4 + \underset{\text{Hydrogen iodide}}{HI}.$$

They should be compared with the equation representing the action of sulphuric acid on sodium chloride (see § 158), when the similarity will be apparent.

Hydrogen bromide and hydrogen iodide are not, however, nearly so stable as hydrogen chloride, and both of them undergo partial oxidation by the excess of sulphuric acid present with formation of free bromine (hence the brown fumes in Exp. 191) and free iodine respectively,

the sulphuric acid being simultaneously reduced to sulphur dioxide.

$$2HBr + H_2SO_4 = Br_2 + 2H_2O + SO_2.$$
$$2HI + H_2SO_4 = I_2 + 2H_2O + SO_2.$$

This secondary change is specially marked in the case of hydrogen iodide, which is much less stable than hydrogen bromide.

The reactions taking place in Exps. 192, 193 are thus expressed—

$$MnO_2 + 3H_2SO_4 + 2KBr = MnSO_4 + 2KHSO_4 + 2H_2O + \underset{\text{Bromine}}{Br_2}.$$

$$MnO_2 + 3H_2SO_4 + 2KI = MnSO_4 + 2KHSO_4 + 2H_2O + \underset{\text{Iodine}}{I_2}.$$

Compare with these the equation for the action of sulphuric acid and manganese dioxide on sodium chloride (which precedes Exp. 177); again the similarity is obvious.

184. Preparation of Bromine.—The reaction investigated in Exp. 192 is made use of for the preparation of bromine.

* **Exp. 194.**—Introduce into a tubulated retort a mixture of about 20 grams of potassium bromide and 10 grams of manganese dioxide. Cover the mixture with concentrated sulphuric acid poured in through a funnel inserted in the tubulus of the retort. Insert the stopper and place over the open end of the retort a flask resting in a trough of water and covered over with a wet cloth, as shown in the diagram (Fig. 62). On gently heating the mixture bromine distils over and condenses in the cooled receiver, where it collects as a

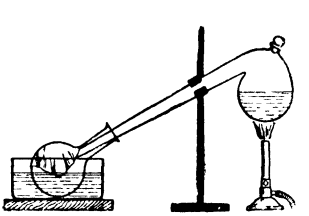


Fig. 62.

dark-red liquid. Since the vapours of bromine are very injurious, the operation *must* be performed in a fume cupboard with a *good draught*.

185. Properties of Bromine.—Bromine is a heavy, mobile, dark-red liquid, possessing a very offensive odour (hence its name from $\beta\rho\hat{\omega}\mu\circ\varsigma$ = a stench). Its action on the mucous membrane is worse even than that of chlorine. Bromine has a specific gravity of about 3·2 (water = 1), and it boils at 59° C., the vapour possessing the same colour as the liquid. At ordinary temperatures bromine rapidly evaporates if exposed in an open vessel.

Bromine is soluble in a number of liquids such as water, carbon disulphide, and chloroform, giving reddish-brown solutions. Its solubility in water is about 3 parts in 100; the solubility in the other liquids mentioned is considerably greater.

* **Exp. 195.**—Test the solubility of bromine in some or all of the above liquids (using the bromine you prepared in the last experiment). By adding the bromine drop by drop to equal volumes of each of the liquids (say 5 c.c.), shaking up after each addition, and noting when further solution ceases (as shown by the bromine remaining undissolved at the bottom of the liquid), a rough comparison of its solubility in the different solvents can be made.

The density of bromine vapour is 80 times that of hydrogen, so that the molecular weight of the gaseous molecule is 160. Now the atomic weight of bromine is 80, so that its gaseous molecule contains two atoms, like that of chlorine, and is represented by the formula Br_2.

As regards its chemical properties, bromine behaves like chlorine, but is generally much less active. Thus, many metals and non-metals combine readily with bromine, some (*e.g.* arsenic) with evolution of so much heat that they take fire. The action of bromine on phosphorus is, indeed, so violent that it is advisable to moderate it by dissolving the bromine in three times its volume of carbon bisulphide.

Bromine and hydrogen do not combine directly at ordinary temperature, but combination can be brought about by the

application of heat, *e.g.* by passing the mixed gases through a red-hot tube. The change is represented by the equation

$$H_2 + Br_2 = 2HBr.$$

A solution of bromine in water (called *bromine water*) gradually decomposes in sunlight with evolution of oxygen and formation of hydrobromic acid.

$$2Br_2 + 2H_2O = 4HBr + O_2.$$

The decomposition is, however, much slower than with chlorine.

As we should expect from what has just been said, bromine water acts as a mild oxidising agent and exhibits feeble bleaching properties (see Exp. 192), its action being explained exactly as in the case of chlorine. It is much used as an oxidising agent in analytical chemistry.

Bromine readily attacks organic substances such as starch and the skin, turning them *yellow*.

Exp. 196.—Add a drop of bromine water to some starch and note the yellow colour developed.

The action of bromine on sulphuretted hydrogen is similar to that of chlorine, hydrogen bromide being formed and sulphur set free.

$$H_2S + Br_2 = 2HBr + S.$$

Bromine is readily displaced from its compounds with metals by the more active element chlorine. The following experiment should be performed to illustrate this.

Exp. 197.—Add some chlorine water to a solution of potassium bromide: note the red colour developed. Shake up the liquid with a little carbon disulphide. The bromine dissolves in it and the red solution collects at the bottom of the vessel.

$$2KBr + Cl_2 = 2KCl + Br_2.$$

Similarly the bromine of hydrogen bromide is displaced by chlorine.

$$2HBr + Cl_2 = 2HCl + Br_2.$$

186. Preparation of Iodine.—In the laboratory iodine is prepared in a similar way to bromine, the reaction used being that which we investigated in Exp. 193.

* **Exp. 198.**—Prepare iodine by following the directions in Exp. 194, using potassium iodide in place of potassium bromide. The same apparatus should be used, but it will not be necessary to cool the receiver by cold water. Some of the iodine will probably condense in the neck of the retort; it can be driven into the receiver by gently warming with a Bunsen burner.

187. Properties of Iodine.—Iodine is a lustrous crystalline black solid of specific gravity about 5. It melts at 113° C., and boils at 184° C., forming a deep violet vapour; at ordinary temperatures, however, iodine slowly undergoes vaporisation. The density of iodine vapour is very high, being about eight and a half times as great as that of air, and 126 times that of hydrogen. This corresponds to a molecular weight of $2 \times 126 = 252$, which is twice the atomic weight of iodine, so that the gaseous molecule of iodine contains two atoms (I_2), just like the gaseous molecules of chlorine and bromine.

Iodine is only slightly soluble in water, 100 grams of which dissolve 0·02 gram of the element, but many other liquids dissolve it in much greater quantity. These solvents may be divided into two classes, according as the colour of the solution they produce is reddish-brown or violet; to the former class belong water, potassium iodide solution, and alcohol; and to the latter, carbon disulphide and chloroform.

* **Exp. 199.**—Introduce a crystal of iodine into about 5 c.c. of each of the liquids mentioned above (as an example of a liquid hydrocarbon you can use benzene). You will notice that in all these liquids, except water, a deeply-coloured solution is rapidly formed; the water is only coloured slightly brown.

Observe that the colours of the different solutions correspond with those stated above.

188. Action of Iodine on other Substances.—Iodine is not nearly such an active substance as the other halogens, but it nevertheless combines directly with many elements, both metals and non-metals, often, indeed, without the application of heat. For example, mercury and iodine will unite on merely rubbing them together.

Exp. 200.—Weigh out fairly accurately 5 grams of mercury and 3 grams of iodine. Rub them together in a mortar. The mercury and iodine disappear and a green powder takes their place.

The green powder is impure[1] mercurous iodide (Hg_2I_2) and has been formed according to the equation—

$$2Hg + I_2 = Hg_2I_2.$$

Exp. 201.—Now weigh out another three grams of iodine, add it to the green powder, and rub them together. The iodine disappears and a scarlet powder takes the place of the green one.

The iodine has combined with the mercurous iodide and converted into scarlet mercuric iodide (HgI_2)—

$$Hg_2I_2 + I_2 = 2HgI_2.$$

If we had used 6 grams of iodine instead of 3 grams in Exp. 200 the scarlet iodide would have been formed at once. [This illustrates a very common phenomenon, namely that the course of a chemical reaction depends on the *relative masses* of the reacting substances.]

Again, on bringing together phosphorus and iodine, the phosphorus first melts and then combination takes place with so much energy that the mixture bursts into flame. When antimony powder is thrown into iodine vapour it takes fire; and on heating potassium and iodine together they unite with explosive violence.

Hydrogen and iodine combine directly with even greater difficulty than hydrogen and bromine, the temperature necessary being much higher; the combination is facilitated

[1] Pure Hg_2I_2 is *yellow*.

by the presence of spongy platinum, which acts as a catalytic agent. The change is represented by the equation—

$$H_2 + I_2 = 2HI.$$

As we should expect from the difficulty with which iodine and hydrogen unite, iodine in the presence of water has no bleaching properties.

Iodine acts on sulphuretted hydrogen in a similar way to chlorine and bromine; hydrogen iodide is formed and sulphur liberated—

$$H_2S + I_2 = 2HI + S.$$

189. Displacement of Iodine from its Compounds.—Just as chlorine displaces bromine from its compounds, illustrating thereby its greater activity, so both chlorine and bromine will displace iodine from its compounds. For example, on treating potassium iodide with either chlorine or bromine, free iodine is liberated—

$$2KI + Cl_2 = 2KCl + I_2.$$
$$2KI + Br_2 = 2KBr + I_2.$$

Exp. 202.—Add a few drops of chlorine water to about 10 c.c. of a solution of potassium iodide. The solution will turn reddish-brown, owing to the liberated iodine dissolving in the excess of potassium iodide. Now shake up with a little carbon bisulphide. This will dissolve out the iodine, forming a violet solution which will collect at the bottom of the vessel.

A similar experiment may be performed using bromine water in place of chlorine water. Again, either chlorine or bromine will set free iodine from hydrogen iodide—

$$2HI + Cl_2 = 2HCl + I_2.$$
$$2HBr + Cl_2 = 2HCl + Br_2.$$

190. The "starch test" for Iodine.—Iodine forms a very characteristic blue compound with starch. On heating the compound is decomposed and the colour disappears, but on cooling recombination takes place and the colour reappears.

Exp. 203.—Shake a very little starch in a test-tube of cold water and boil well; cool and then add a few drops of a solution of iodine in potassium iodide; a blue colour is formed. Boil the blue solution, and the blue colour disappears, reappearing on cooling.

Comparison of the Properties of the Halogens.

191.—That the elements chlorine, bromine, and iodine form a well-defined group is shown in two ways, first by the *resemblance* in properties, and secondly by the *gradual transition* in their properties which proceeds nearly always in the same order, viz. chlorine, bromine, iodine, *i.e.* in the order of their atomic weights. A general survey of the group will bring this out clearly.

Physical Properties of these Elements.—Chlorine is a readily-condensible gas, and has a distinct greenish colour; bromine is a dark-red liquid boiling at 59° C. and solidifying at – 7° C.; whilst iodine is a black crystalline solid which boils at 184° C., its vapour being of a beautiful violet colour.

In the gaseous condition these elements have a very irritant action on the mucous membrane, which is, however, much less marked in the case of iodine than in that of the other three elements. The halogens have an odour resembling that of seaweed if they are in a largely-diluted condition.

Their solubility in water does not exactly follow the order of their atomic weight; chlorine dissolves in about half its volume of water, *i.e.* the solution contains about 0·5 per cent. of the halogen by weight, bromine to the extent of 3 parts by weight in 100 of water, whilst iodine is only very slightly soluble. Bromine is therefore the most soluble of the three halogens, thus occupying an anomalous position.

192. General Chemical Properties.—All the halogens combine directly with hydrogen to form gases having a similar chemical composition, as shown by their formulae—

HCl, HBr, HI.

These hydrides of the halogens are very soluble in water, giving rise to strongly acid solutions (hydrochloric, hydrobromic, and hydriodic acids). The readiness with which combination with hydrogen takes place *decreases* as the atomic weight *increases*. Thus chlorine and hydrogen combine at ordinary temperature, bromine and hydrogen require heating, and iodine and hydrogen require heating strongly. Moreover the stability of the products hydrogen chloride, hydrogen bromide, and hydrogen iodide shows a falling off in the order named; hydrogen iodide is broken up into its elements by gentle heat, hydrogen bromide requires a higher temperature, and hydrogen chloride is only decomposed at very high temperature.

The hydrogen atom of each of these compounds can be replaced by the metals potassium and sodium to form a group of bodies all of which closely resemble *sea-salt*. It is from this that the name *halogens* is derived (ἅλς, sea-salt, and γεννάω, I produce).

A comparison of the silver salts of the halogen acids is very interesting. All three are insoluble in water and in nitric acid and are consequently precipitated when silver nitrate is added to a solution of the corresponding acid or one of its soluble salts. The changes in the case of the acids are represented by the equations—

$$\underset{\text{Hydrochloric acid}}{HCl} + AgNO_3 = HNO_3 + \underset{\text{Silver chloride}}{AgCl},$$

$$\underset{\text{Hydrobromic acid}}{HBr} + AgNO_3 = HNO_3 + \underset{\text{Silver bromide}}{AgBr},$$

$$\underset{\text{Hydriodic acid}}{HI} + AgNO_3 = HNO_3 + \underset{\text{Silver iodide}}{AgI}.$$

So far the resemblance is complete. There is, however, a gradation in the properties of these silver salts shown, for

example, by their colour and by the action of ammonia on them. As regards their colour, silver chloride is *white*, silver bromide *yellowish white*, and silver iodide *lemon yellow*. Their behaviour towards ammonia is as follows:—The chloride is *readily soluble* in *dilute* ammonia, the bromide is *soluble* in *strong* ammonia, whilst the iodide is *insoluble*.

The tendency of the halogens to combine with oxygen *increases* as the atomic weight *increases*. Thus, whilst chlorine can only be made to combine with oxygen indirectly giving rise to unstable oxides, iodine is directly oxidised by nitric acid, and its oxide is much more stable. Bromine occupies an anomalous position here, as no oxide of it is known.

The interaction of the halogens and water affords another example of this gradation in properties as we pass from chlorine to iodine. Chlorine decomposes water slowly in the presence of sun-light with liberation of oxygen; bromine acts similarly but more slowly; whilst iodine has no action on water.

193. Occurrence of the Halogens in Nature.—The halogens are all such active elements that they are never found in the free state in nature. They are, however, found widely distributed in combination with certain metals, chiefly sodium, potassium, magnesium, and calcium, but whereas chlorine compounds occur very abundantly, those of bromine and iodine are only found in small quantities.

Sea water contains compounds of all three elements, sodium chloride being the chief solid constituent, whilst bromides and iodides are only present in small quantity. Metallic compounds of the halogens (chiefly chlorides) are also present in solution in many mineral waters. The enormous salt deposits at Stassfurt in Germany are composed largely of the chlorides of potassium and magnesium; they contain, however, a small percentage of bromides, and it is from this source that the bromine of commerce is obtained. The crude sodium nitrate (caliche), found in such great abundance in Chili and Peru, contains a little

sodium iodate ($NaIO_3$) and this is now the chief source of iodine, though in Scotland some is extracted from sea-weed, which contains small quantities of iodides.

It may be noted that free hydrochloric acid is an essential constituent of the gastric juice.

QUESTIONS.—CHAPTER XV.

1. Describe exactly what you would observe (*a*) on adding strong sulphuric acid to some common salt contained in a test-tube, (*b*) on warming hydrochloric acid gas with red lead. Explain as far as you can the changes which take place.

2. Describe in detail how you would prepare and collect a few cylinders of hydrochloric acid gas. Sketch the apparatus you would employ. What experiments would you perform to illustrate the chief properties of the gas?

3. How would you proceed to prove that hydrochloric acid gas contains hydrogen and chlorine? Sketch the apparatus you would employ.

4. Describe how you would prepare and collect a few jars of chlorine. Sketch the apparatus you would employ. Describe a few experiments to illustrate the most important properties of the gas.

5. How would you proceed to prepare a strong aqueous solution of hydrochloric acid gas? Give a diagram of the necessary apparatus. State exactly what (if anything) you would observe on adding a little of the solution to (*a*) some granulated zinc, (*b*) a solution of silver nitrate, (*c*) metallic mercury, (*d*) iron filings.

6. What would you observe on introducing the following into jars of dry chlorine: (1) phosphorus, (2) a lighted taper, (3) a jet of burning hydrogen, (4) copper powder, (5) dry litmus paper, (6) moist litmus paper? Explain the changes which take place as far as you can.

7. Compare the action of hydrochloric acid on the peroxides of manganese and barium.

8. Describe how you would proceed to investigate the action of hydrochloric acid or *red lead*. What results would you obtain?

9. Describe a synthetical method of proving that hydrogen chloride contains half its volume of hydrogen and half its volume of chlorine.

10. How would you proceed to prove experimentally that hydrogen chloride contains half its volume of hydrogen?

11. Make a comparison of (*a*) the physical, (*b*) the chemical properties of the elements chlorine, bromine, and iodine.

12. Compare the action of concentrated sulphuric acid on the iodide and chloride of potassium.

13. State and explain what you would observe on adding concentrated sulphuric acid to some sodium bromide contained in a test-tube.

14. Describe exactly how you would prepare bromine from potassium bromine, and give a sketch of the apparatus you would employ.

15. Name some liquids which dissolve bromine and iodine, and state the colour of the solution produced in each case. Compare the action of these two halogens on starch.

16. What is the action of chlorine on solutions of sodium bromide, potassium iodide, and sulphuretted hydrogen respectively?

17. Describe the action, if any, which takes place when sulphur, phosphorus, carbon, silicon, and sulphuretted hydrogen are respectively brought into contact with iodine.

18. By what general method can the halogens (except fluorine) be prepared?

19. What is the action (if any) of (*a*) cold dilute, (*b*) hot strong hydrochloric acid on the following metals: (1) zinc, (2) aluminium, (3) gold, (4) lead, (5) copper, (6) tin?

20. State briefly the general methods of preparing metallic chlorides, giving equations.

21. How is hydrochloric acid manufactured? What are the chief impurities in the commercial acid?

22. Enumerate the chief uses of hydrochloric acid.

CHAPTER XVI.

NITROGEN—THE ATMOSPHERE—AMMONIA.

NITROGEN, N_2.

194. Occurrence.—Nitrogen occurs mixed with oxygen in the atmosphere, of which it forms nearly four-fifths the volume.

Although it does not enter to any large extent into the composition of animal and vegetable tissues, it is, notwithstanding, a very constant and essential constituent of such tissues. The nitrogen of plants is obtained chiefly through the medium of the soil, in which small quantities of nitric acid, nitrates, and ammonium salts always occur. Animals cannot assimilate nitrogen directly, and derive their supply from the plants.

195. Preparation.—We have seen in Exps. 16, 17, 21 that air may be deprived of its oxygen by means of iron, magnesium, or phosphorus, and in Exp. 22 we investigated a more convenient method of bringing this about in practice, namely by passing air over heated copper contained in a hard glass tube. The nitrogen so obtained is not pure, for air contains a number of other inert gases, chiefly argon, in addition to nitrogen (see § 206). The best method of preparing pure nitrogen is to heat a solution of ammonium nitrite, NH_4NO_2, when decomposition takes place according to the following equation—

$$NH_4NO_2 = N_2 + 2H_2O.$$

In practice a mixture of ammonium chloride, NH_4Cl, and sodium nitrite, $NaNO_2$, is used instead of ammonium nitrite, since both these salts are quite stable, whereas

NH_4NO_2 is an unstable compound. We may suppose that the ammonium chloride and sodium nitrite undergo double decomposition with formation of ammonium nitrite and sodium chloride thus—

$$NH_4Cl + NaNO_2 = NH_4NO_2 + NaCl,$$

and that the ammonium nitrite is then decomposed according to the equation given above.

Exp. 204.—Introduce about 15 grams of sodium nitrite and 10 grams of ammonium chloride into a small flask, and add about 100 c.c. of water. Fit the flask with a cork carrying a delivery tube. Warm gently and collect the gas over water at the pneumatic trough. Show that it is nitrogen by testing with a lighted taper and lime-water (the latter to prove that it is not carbon dioxide).

If the nitrogen is required dry, it should be passed through a sulphuric acid wash-bottle and collected over mercury.

Nitrogen can also be obtained by the action of chlorine on a concentrated solution of ammonia, taking care to keep a large excess of ammonia present throughout the experiment, thus preventing the formation of the explosive chloride of nitrogen—

$$8NH_3 + 3Cl_2 = N_2 + 6NH_4Cl.$$

This reaction may be represented in two stages—

$$2NH_3 + 3Cl = N_2 + 6HCl.$$
$$6NH_3 + 6HCl = 6NH_4Cl.$$

196. Properties of Nitrogen.—Nitrogen is a colourless, tasteless gas, which is unable to support life or combustion. It does not combine with oxygen under ordinary conditions; but it may be made to do so by passing electric sparks through the mixture of gases, when nitrogen peroxide, NO_2, is formed. Nitrogen is somewhat lighter than air, and is only condensed to the liquid form with great difficulty; it is slightly soluble in water, less so than oxygen (see § 136).

The chief characteristic of nitrogen is its inertness, but at the same time there are some elements with which it readily combines directly, *e.g.* magnesium, calcium, and boron. Nitrogen also combines directly with barium, strontium, lithium, aluminium, silicon, carbon, and hydrogen.

The Atmosphere.

197. The gaseous envelope which surrounds the earth is chiefly composed of nitrogen and oxygen. With these are associated argon, water vapour, carbon dioxide, ammonia, and other gases, the amounts of which vary according to circumstances. From whatever locality the air has been obtained, the relative proportions of nitrogen and oxygen exhibit only slight variations, as the following results show:—

Percentage of Oxygen by Volume.

72	analyses	in different parts of Europe (mean)	20·95
17	„	in the Polar Seas „	20·90
3	„	at elevation of 15,000 ft. or over „	20·94

198. Determination of the Composition of the Atmosphere by Volume.—A rough method of determining the volumetric composition of the atmosphere has already been described in Exp. 21. A better method is to explode a known volume of air with about twice its volume of hydrogen in a eudiometer; two volumes of hydrogen combine with one volume of oxygen to form water vapour, which condenses, and thus *one-third* the diminution in volume represents the volume of oxygen present. This method is not quite accurate, because some of the nitrogen and oxygen combine to form nitrogen peroxide, which dissolves in the water produced with formation of nitric and nitrous acids.

The most accurate method consists in removing the oxygen from an enclosed volume of air, the pressure and temperature of which are known, by heating a spiral of

copper wire in it by means of an electric current. On reducing the temperature to the original value and measuring the pressure of the residual gas the percentage of oxygen present by volume can be calculated by applying Boyle's Law.

The experiment is carried out in Jolly's apparatus which is shown in Fig. 63. A is a glass globe of about 100 c.c. capacity, provided with an exit-tube E, at the end of which is a three-way tap D. This tap is connected with (1) a short tube F, open at the end, and (2) a pressure-gauge consisting of two glass tubes, B and C (of which C is open to the atmosphere), connected by rubber tubing and containing mercury. The tube C can be raised and lowered, and behind it is placed a scale so that the level of the mercury can be read off. By suitably turning the tap D it can be arranged that A is connected with either F or B, or is shut off from both.

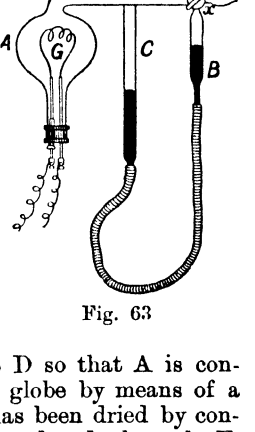


Fig. 63

The first part of the operation consists in filling the globe with dry air; this is done by turning tap D so that A is connected with F, and exhausting the globe by means of a pump connected to F. Air which has been dried by concentrated sulphuric acid is now introduced through F. The globe is next surrounded by a vessel containing melting ice to reduce the temperature of the gas to 0° C. C is now raised till the mercury in B just reaches the top of the tube, *i.e.* the point *x*, the tap being turned so that A is in connection with B only. The height of the mercury in C is then read and also the barometer. The pressure of the gas in A is calculated by combining the difference in mercury levels in B and C with the barometric pressure. (If the level of C is *higher* than the point *x* the difference must be *added* to the pressure of the barometer, if *lower* it must be subtracted from that pressure.)

A is now shut off from both B and F, the melting ice is removed, and the copper spiral G heated by passing a current of electricity through it, when the oxygen present is converted into copper oxides. A is next surrounded again by melting ice and its temperature once more reduced to 0° C. C is lowered considerably (to prevent mercury being sucked into the horizontal tube on opening the tap) and A and B are then put into connection. C is adjusted till the mercury in B just reaches x, the level of the mercury in C is read and the pressure of the residual gas calculated as before.

Suppose the initial pressure was P and the final pressure P'. Then the reduction of pressure due to removal of oxygen was $P - P'$. Consequently, since the temperature was the same (0° C) in both cases, the percentage of oxygen by volume is

$$\frac{P - P'}{P} \times 100.$$

199. Determination of the Composition of the Atmosphere by Weight.—This may be ascertained by passing the air over red-hot copper, with which the oxygen combines, as in the experiment just described.

The air is previously freed from carbon dioxide and moisture by being passed over potash and concentrated sulphuric acid. The apparatus used is shown in Fig. 64; it consists essentially of a large glass globe, to which is attached a tube containing metallic copper, and heated in a furnace. The globe is first rendered vacuous by means of a good air-pump, the stopcock is closed, and the globe carefully weighed. The tube containing the copper is then rendered vacuous, closed, and weighed. The copper having been heated to redness, the stopcock is opened sufficiently to allow a slow current of purified air to pass through the tube and into the glass globe. On the way, it is deprived of its oxygen, and if the experiment has been carefully conducted, only nitrogen and argon pass into the globe.

After the apparatus has quite cooled, the globe is again weighed, and the increment gives *the weight of the nitrogen*

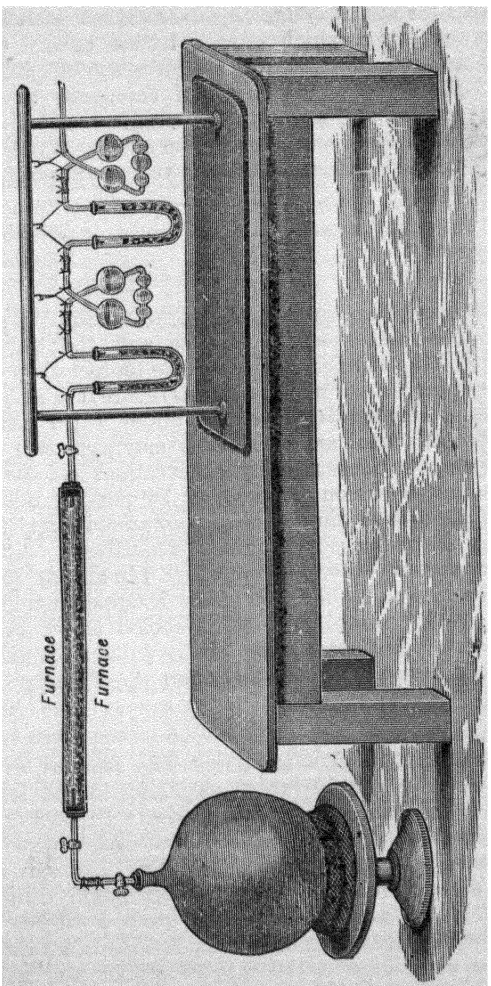


Fig. 64.

and argon. The tube is also weighed again, and the increase there shows *the weight of the oxygen,* together with a little nitrogen and argon which remain in the tube. On exhausting and weighing again, the decrease in weight is added to the increase in weight of the globe to obtain the total nitrogen and argon. The oxygen is given by the difference of the two weighings of the *exhausted* tube.

A series of such determinations gave the composition by weight of air as—

Nitrogen and argon	76·995
Oxygen	23·005

200. Water Vapour in Air.—The amount of water vapour varies with the temperature and the degree of saturation of the air, for the higher the temperature of the air, the more moisture will it take up before it is saturated. The average amount is somewhat under 1 per cent. by volume, but in warm, moist climates may approach 4 per cent. It may be measured by observations on the dew-point (see text-books on physics), or by passing a known volume of air over calcium chloride contained in U-tubes, and noting the increase in weight of the tubes.

The amount of water vapour which the air can contain may be estimated by the fact that 1 cubic mile of air saturated at 35° would deposit, if cooled to 0°, 140,000 tons of rain. But while the air is seldom completely saturated, it never contains less than $\frac{1}{10}$ of the possible amount.

201. Carbon Dioxide in Air.—The amount of this gas in air varies considerably, according to the locality from which the sample of air is taken. In country air there are from three to four volumes of carbon dioxide in 10,000, but in towns the amount is larger, and may reach seven or eight volumes. In badly-ventilated dwellings even ten-fold the normal amount of carbon dioxide may occur. The determination of carbon dioxide is a matter of importance, especially in the case of indoor air, since it serves to show the efficiency of ventilation.

The presence of carbon dioxide in air may be shown by exposing lime-water in a shallow dish; the lime-water is soon covered with a thin pellicle, owing to the formation of calcium carbonate or chalk, which is insoluble in water—

$$\underset{\text{Calcium hydroxide}}{Ca(OH)_2} + CO_2 = \underset{\text{Calcium carbonate}}{CaCO_3} + H_2O.$$

Baryta water may, by Pettenkofer's method, be used as a means of determining the amount of carbon dioxide in air. A known volume of a solution of baryta (which is alkaline) of known strength is shaken up with a measured quantity of air, say 10 litres; part of the baryta is converted into barium carbonate (a neutral body), whilst part remains unaltered. The amount of alkali (the baryta) is now smaller by reason of the conversion of part of it into carbonate by the carbon dioxide. The more carbon dioxide is present, the greater will be the amount of baryta converted into barium carbonate, and the greater will be the difference between the amount of alkali originally taken and that remaining afterwards. By ascertaining the amount of oxalic acid required to neutralise a known volume of the original baryta water, and that required to neutralise the liquid which remains after partial neutralisation as already described, the quantity of carbon dioxide in the 10 litres of air may be ascertained.

202. Other impurities in Air.—The remaining impurities, such as suspended dust and carbon, ammonia, sulphur compounds, hydrochloric acid and chlorides, occur in much smaller and more variable quantities. During thunderstorms oxides of nitrogen are formed, and these give rise to nitrous and nitric acids; ozone is also probably produced under such circumstances. The ammonia, carbon (soot), and sulphur compounds occur in larger quantity in the vicinity of towns, from the combustion of coal, or where decaying refuse is found.

The hydrochloric acid and chlorides come for the most part from manufacturing operations, though it is significant that, especially during high wind, the air in the

neighbourhood of the sea contains much more sodium chloride than is usual.

203. The relation of Animal and Plant Life to Air.—By breathing on a cool glass surface, and by expelling air from the lungs through lime-water, it is easy to demonstrate that expired air contains large quantities of moisture and carbon dioxide. Indeed the expired air from man contains usually over 4 per cent. of carbon dioxide, that is, over one hundred times as much as normal air.

The agencies at work in producing carbon dioxide are—

(1) Respiration of animals and plants; (2) Combustion of fuel; (3) Decay of organic matter; (4) Subterranean causes.

Faraday calculated that nearly five million tons of carbon dioxide were contributed daily to the atmosphere by these processes. Under such a contribution the air would slowly get more and more charged with carbon dioxide, and the percentage of oxygen would diminish.

There are, however, processes constantly in operation which act in the opposite direction.

(1) In the process of assimilation in plants, the green colouring matter (chlorophyll), in presence of direct or diffused sunlight, effects the decomposition of carbon dioxide and liberates oxygen.

(2) Carbon dioxide being moderately soluble in water is carried down by rain, and is also taken up by surface waters and sea water.

The precise extent to which the loss and gain counteract one another is difficult to estimate, but that plant life is an important factor is shown by actual observations on the living plant, and by the variations in the amount of carbon dioxide in air in the neighbourhood of forests in the daytime, when the foliage is exposed to the sun's rays, as compared with night, when assimilation is checked and only respiration goes on.

204. Is Air a compound or a mixture of Nitrogen and Oxygen?—We have seen that a chemical compound shows the following characters:—

(1) It possesses a *definite* composition (see § 67).

(2) The weights of the elements composing it are in proportion to the atomic weights, or in some simple multiple proportion of the atomic weights. This follows from the Atomic Theory—see Chap. VII.

(3) The compound shows distinctive physical and chemical properties, the individual properties of the constitutent elements being more or less completely concealed (see § 66).

(4) When combination takes place, heat is usually evolved.

(5) When gases combine to form a gaseous compound there is generally a contraction in volume, thus—

2 vol. of hydrogen + 1 vol. of oxygen form 2 vol. of water vapour.

3 vol. of hydrogen + 1 vol. of nitrogen form 2 vol. of ammonia.

(6) The simple solution of a gas in water does not affect its chemical composition; for instance, if we dissolve ammonia or carbon dioxide in water, and then, by boiling the solution, expel the gas again, it will be found to be unaltered in character or composition.

Now let us apply these tests to air.

(1) The composition of air varies very little under different circumstances, but even such small variations as are found in its composition do not occur in the case of chemical compounds.

(2) If we divide the relative proportions by weight of nitrogen and oxygen in the air by the atomic weights of nitrogen and oxygen, we shall see whether any simple multiple relation is shown. Of the 76·995 per cent. of nitrogen and argon present in air 0·937 per cent. is argon,

so that the percentage of nitrogen is 76·995—0·937=76·058. We have therefore—

$$\text{Nitrogen } \frac{76{\cdot}058}{14} = 5{\cdot}433;$$

$$\text{Oxygen } \frac{23\,005}{15\,96} = 1{\cdot}441;$$

$$\text{And } 5{\cdot}433 : 1\,441 :: 3{\cdot}77 : 1.$$

That is, to be even approximately in agreement with the result of analysis we should have to assume a compound $N_{15}O_4$ (3·77 : 1 = 15·08 : 4). The same result may be arrived at by considering the volume relations of nitrogen and oxygen in air.

(3), (4), and (5) Nitrogen and oxygen retain their characters with slight modification in air, and a mixture of the two gases in the proper proportions shows precisely the same characters in all respects as air. No heat is evolved when they are brought together, nor does any contraction in volume take place.

Also the density of the atmosphere is found to have the average value calculated for a mixture of the constituent gases. Thus, taking the approximate composition of the air as 4 vol. of nitrogen and 1 vol. of oxygen, we have—

Wt. of 4 vol. of nitrogen (density = 14) = 4 × 14 = 56 units.
„ 1 vol. of oxygen (density = 16) = 1 × 16 = 16 „
„ 5 vol. of air = 72 „

∴ Wt. of 1 vol. of air = $\frac{72}{5}$ = 14·4 units,

i.e. Density of air = 14·4,

which agrees with experimental value.

(6) We have seen (§ 138) that when air is shaken up with water a greater proportion of oxygen dissolves than nitrogen, owing to the greater degree of solubility of oxygen, so that, whilst in the air originally taken one volume of oxygen is associated with approximately four volumes of nitrogen, air dissolved in water consists of one volume of oxygen associated with two volumes of nitrogen.

On all these grounds, therefore, we must admit that air is simply a *mixture* of nitrogen and oxygen.

The following additional reasons may be mentioned.—

(7) When liquid air boils the nitrogen distils off before the oxygen and argon.

(8) The refractive index of air is the mean of those of oxygen and nitrogen; in the case of compounds the value is invariably found to be either above or below the mean of the values for the constituents.

205. Fogs are caused by condensation of water vapour induced by dust. That dust is the cause of fog formation is proved by the fact that in filtered air fogs cannot form. Analysis of the deposit left after a fog showed it to consist of carbon, hydrocarbons, sulphuric acid, iron and its oxides, and silica. During a fog, too, the amount of carbon dioxide increases enormously and reaches from three to five times the normal amount.

Argon and its Companions.

206. In the year 1894 Lord Rayleigh noticed that the density of nitrogen obtained from the air was about 0·4 per cent. greater than that of nitrogen prepared by chemical methods. The only explanation which could be offered was that air contained a small quantity of another inert gas in addition to nitrogen, and that this gas had a greater density than nitrogen. Ramsay took up the question and succeeded in isolating this gas; he passed air freed from carbon dioxide and water vapour over red-hot copper which removed the oxygen, and then over red-hot magnesium [1] which removed the nitrogen. The residue amounted to about 1 per cent. of the air used, and consisted of a very inert gas which Ramsay could not decompose or cause to combine with any known substance. He came to the conclusion that the new gas was an *element*, and on account of its inertness he called it *argon*. Argon

[1] It has recently been found better to mix the magnesium with quicklime.

has a molecular weight of 40 as determined from its density, and its molecule has been shown to contain one atom; the atomic weight is therefore also 40. Argon liquefies at – 187° C. and solidifies at – 189·5° C.

More recently Ramsay has discovered several other new elementary gases in the atmosphere, namely, *helium*, *neon*, *krypton*, and *xenon*. He fractionally distilled large quantities of liquid air, and from the lowest boiling portions isolated two elements, helium and neon. From the portions boiling at a higher temperature than oxygen, nitrogen, and argon, he isolated krypton and xenon. These elements are only present in exceedingly small quantities in the atmosphere; they are all very inert like argon and have not, up to the present, been induced to combine with any known substance.

As in the case of argon, so with these other elements the molecule contains one atom.

Helium has been found in some uranium ores and in certain springs as well as in the atmosphere. Helium is the most difficult of all gases to liquefy, its boiling-point being very near the absolute zero of temperature. Its atomic weight is 4.

The atomic weights of neon, krypton, and xenon are respectively 20, 81·75, and 128.

Ammonia, NH_3.

207. Formation of Ammonia.—

Exp. 205.—Grind up a little sal-ammoniac (ammonium chloride, NH_4Cl) with some dry slaked lime in a mortar. You will notice the characteristic pungent smell of *ammonia*. Hold a piece of moistened red litmus paper above the powder; the colour changes to blue, showing that ammonia in the presence of water has an *alkaline reaction*.

Now introduce the mixture into a *dry* test-tube and warm gently, at the same time holding a second *dry* test-tube just above the first in an inverted position (see

Fig. 65). When the smell of ammonia is very strong where the two tubes meet, close the upper one with your thumb and place it with its mouth underneath water in a dish. Remove your thumb. Water rises very rapidly and fills the tube (or nearly so). Test the liquid in the tube with red litmus paper; it is alkaline.

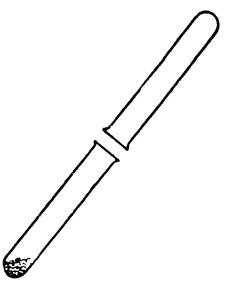


Fig. 65.

We see then that ammonia is a pungent smelling gas which is lighter than air (since it can be collected by upward displacement) and very soluble in water forming an alkaline solution. You will remember that hydrogen chloride is a gas which when dissolved in water behaves as an *acid*; here we meet with a gas which behaves as an *alkali* in solution. Ammonia is a compound of nitrogen and hydrogen (as we shall proceed to prove shortly) and is represented by the formula NH_3 (see § 215).

Its formation from sal-ammoniac and slaked lime is represented by the equation—

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2NH_3 + 2H_2O.$$

Ammonia is evolved whenever animal or vegetable substances containing nitrogen are strongly heated in vessels from which air is excluded, and especially when they are heated with lime or other alkali. Large quantities of ammonia are obtained during the distillation of coal (which contains about $1\frac{1}{2}$ per cent of nitrogen), the coal gas being cooled and then washed with water, by which means any ammonia is separated and obtained in solution.

208. Preparation of Ammonia.—In the laboratory ammonia is usually prepared by the method we have already investigated in Exp. 205, *i.e.* by heating a mixture of sal-ammoniac and slaked lime.

Exp. 206.—Weigh out about 10 gm. of sal-ammoniac and 20 gm. of dry slaked lime, and grind them up in a mortar till they are a fine powder and intimately mixed. Introduce the mixture into a small dry round-bottomed flask, and connect this with a U-tube containing lumps of quicklime or caustic soda,[1] as shown in Fig. 66. Now heat the flask gently, when ammonia will be evolved, which, after being dried by the lime or caustic soda in the U-tube, may be collected in dry cylinders by upward displacement.

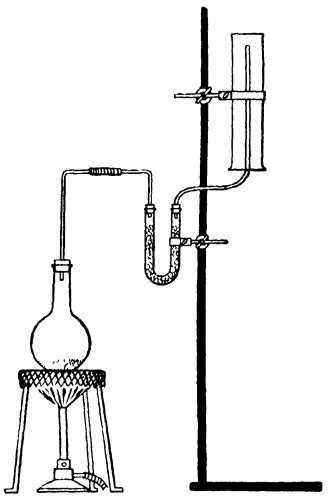


Fig. 66.

Each cylinder is full when a lighted wood-splint will not burn at the mouth. It should be covered with a ground glass plate and replaced by another.

If ammonia is required *pure* it should be collected over mercury.

209. Properties of Ammonia.—Ammonia is a colourless gas, lighter than air, and having a very pungent odour, which, however, is not disagreeable if the gas is largely diluted with air; in the pure condition ammonia is injurious when breathed in quantity. At $-34°$ C. under ordinary pressure, and at 0° C. under a pressure of 7 atmospheres, dry ammonia condenses to the liquid form (see below, Carré's apparatus).

[1] The ordinary drying agents for gases—sulphuric acid, calcium chloride, and phosphorus pentoxide—cannot be used in the case of ammonia, since it combines readily with them.

Ammonia is the most soluble of all inorganic gases; water at 0° C. dissolves over 1000 times its volume of the gas, and at 15° C. more than 700 times its volume. Owing to the great solubility of ammonia it cannot be collected over water, and, further, it is essential that in the preparation of the gas all parts of the apparatus should be *dry*.

The aqueous solution of ammonia is lighter than water, and in its most concentrated form has a specific gravity 0·884; it contains 36 per cent. by weight of the gas. The gas may be entirely expelled by boiling the solution.[1]

Ammonia does not support combustion (we have seen that it puts out a lighted match), nor does it burn under ordinary conditions; but if part of the delivery tube of the apparatus used in Exp. 206 is heated strongly, the issuing gas will burn with a pale yellow flame. This is because ammonia easily decomposes into its constituents, nitrogen and hydrogen, the latter of which is an inflammable gas.

210. Ammonium Salts.—

Exp. 207.—Fill two similar jars by displacement with ammonia and hydrogen chloride respectively, and cover the mouth of each jar with a glass plate. Now bring them mouth to mouth, and withdraw the glass plates. The gases as they come into contact form a fine white crystalline powder which remains for some time diffused throughout the jars.

The white crystalline solid formed is *ammonium chloride*. It has been formed by the chemical union of the ammonia and the hydrogen chloride according to the equation—

$$NH_3 + HCl = NH_4Cl.$$

Ammonium chloride can be obtained by neutralising an aqueous solution of ammonia (which we found to have an alkaline reaction in Exp. 205) with hydrochloric acid.

[1] Or by dropping a strong solution of ammonia on sticks of caustic potash in a flask the gas is steadily evolved without heating. This constitutes a convenient laboratory method of preparing ammonia.

Exp. 208.—Pour a little "liquid ammonia"[1] (a strong aqueous solution of ammonia) into an evaporating dish and add dilute hydrochloric acid gradually till the liquid ceases to turn red litmus paper blue. Evaporate to dryness. A white crystalline solid remains behind; this is ammonium chloride.

This method is precisely similar to that we adopted in Exp. 106 for the preparation of sodium chloride (common salt). Further, ammonium chloride very closely resembles sodium and potassium chlorides in properties. This resemblance is explained as follows:—It is supposed that an aqueous solution of ammonia contains a compound of ammonia and water. This compound is similar in composition to sodium hydroxide, NaOH, and potassium hydroxide, KOH, and is represented by the formula NH_4OH, the metals sodium and potassium being replaced by a group of atoms composed of nitrogen and hydrogen, viz. (NH_4). To this group of atoms the name *ammonium* is given, and the compound of ammonia and water is called *ammonium hydroxide*.

The alkaline properties of aqueous ammonia are due to the presence of this compound, and when it reacts with acids it forms *ammonium salts* by the replacement of the hydrogen of the acid by the group *ammonium*, just as sodium and potassium hydroxides form *sodium and potassium salts* by the replacement of the hydrogen of the acid by *sodium* and *potassium* respectively.

The equations representing the action of a few acids on the hydroxides of sodium, potassium and ammonium will bring out this point clearly.

$$\begin{cases} NaOH + HCl = \underset{\text{Sodium chloride}}{NaCl} + H_2O. \\ NH_4OH + HCl = \underset{\text{Ammonium chloride}}{NH_4Cl} + H_2O. \end{cases}$$

$$\begin{cases} KOH + HNO_3 = \underset{\text{Potassium nitrate}}{KNO_3} + H_2O. \\ NH_4OH + HNO_3 = \underset{\text{Ammonium nitrate}}{NH_4NO_3} + H_2O. \end{cases}$$

[1] Be careful not to inhale much of the vapour rising from the liquid, as it is injurious.

$$\begin{cases} KOH + H_2SO_4 = \underset{\text{Potassium hydrogen sulphate}}{KHSO_4} + H_2O. \\ NH_4OH + H_2SO_4 = \underset{\text{Ammonium hydrogen sulphate}}{NH_4HSO_4} + H_2O. \end{cases}$$

$$\begin{cases} 2KOH + H_2SO_4 = \underset{\text{Potassium sulphate}}{K_2SO_4} + 2H_2O. \\ 2NH_4OH + H_2SO_4 = \underset{\text{Ammonium sulphate}}{(NH_4)_2SO_4} + 2H_2O. \end{cases}$$

All attempts to isolate ammonium hydroxide at ordinary temperatures have failed, owing to the ease with which it decomposes into ammonia and water;[1] thus any attempt to concentrate the liquid by evaporation only results in ammonia being driven off in the gaseous state.

The ammonium salts, as already mentioned, strongly resemble the salts of potassium and sodium; they differ from them, however, in one important respect, namely, their behaviour towards heat. We shall study this property at some length.

211. Dissociation.—

Exp. 209.—Put a few pieces of ammonium chloride in a dry test-tube and heat. Note what takes place.

When ammonium chloride is heated, it *apparently* sublimes unchanged, the vapour condensing again to ammonium chloride. It has been shown, however, that the vapour is not that of ammonium chloride, but is a mixture of ammonia and hydrogen chloride,[2] which recombine on cooling—

$$NH_4Cl = NH_3 + HCl.$$

Such a change as this in which a compound splits up on heating into constituents which recombine on cooling is called *dissociation*. That dissociation has taken place in

[1] Ammonium hydroxide has recently been isolated at low temperature.

[2] If, however, the ammonium chloride is *absolutely dry*, it volatilises without dissociation.

this case is proved by the fact that the density of the vapour is only half what it should be if it consisted of NH_4Cl molecules.

The following argument will make this clear:—Each NH_4Cl molecule gives rise to one NH_3 molecule and one HCl molecule, so that if the pressure remains the same the volume of mixed gases will be double the volume which the undissociated ammonium chloride would occupy (by Avogadro's hypothesis). But since the volume is double the density must be one-half what it would be if the salt remained undissociated (the *mass* remaining *the same*).

The dissociation may be proved directly by partially separating the two gases by diffusion.

* **Exp. 210.**—Take a piece of hard glass tube of about 3 cm. bore and 25 cm. long. Fit it with a one-holed cork at each end, through which passes a long piece of clay pipe stem, which has been made red-hot. In the middle of the glass tube place some fragments of the fibrous sal-ammoniac, and at both ends a piece of moist blue litmus paper. Fix in the corks tightly, clamp the tube horizontally, and attach to one of the ends of the pipe stem a scent squirt bellows (Fig. 67). After warming the tube carefully, place a burner under the sal-ammoniac. When the tube is red-hot, blow the bellows and test the gas which comes through the pipe stem with litmus or turmeric paper.

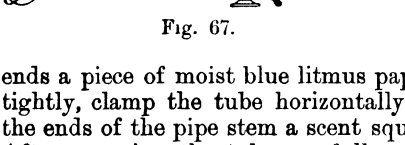


Fig. 67.

We note that the air which passes through the pipe stem is alkaline from the presence of ammonia, while the vapour which is left in the tube is acid. We can explain this when we remember that light gases diffuse much more rapidly through porous substances than heavy ones (§ 80). Ammonia is lighter than hydrochloric acid, and therefore diffuses faster, but it could not do so here unless it were free and not combined.

The ammonium salts of less volatile acids, *e.g.* sulphuric and phosphoric acids, are also dissociated by heat, but in this case the volatile ammonia comes off alone, leaving the acid behind—

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

All ammonium salts give off ammonia when heated with alkalis such as caustic potash, caustic soda, or lime.

212. Liquefaction of Ammonia by Pressure.—If ammonia gas be generated in quantity, and the receiver into which it passes be a closed vessel much smaller than

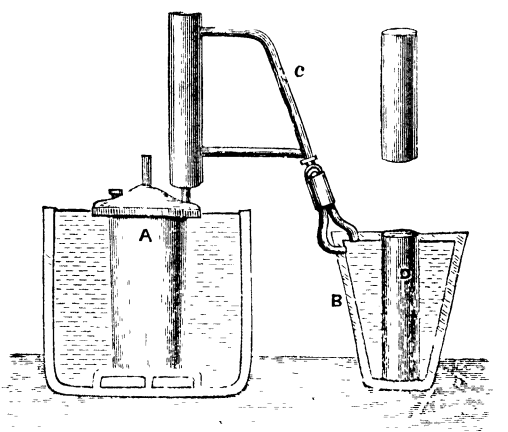


Fig. 68.

the volume of the gas generated, it will be compressed and ultimately condense by its own pressure to the liquid form. This is indeed the method of Faraday (see § 72), and a simple form of apparatus in which this principle is made use of is that of Carré (Fig. 68). It consists essentially of a strong iron cylinder containing concentrated ammonia solution, as shown at A in the figure; this communicates with a receiver B, of relatively small volume, by means of

the tube C. When A is surrounded by hot water, ammonia gas is given off freely and accumulates in the apparatus in such quantity that it condenses in the receiver B, which has been surrounded by cold water.

If we now reverse the arrangement and surround A with cold water, the liquid ammonia will boil very rapidly and pass back as gas into A, and this rapid transformation of liquid into gas will bring about a considerable depression of temperature in B. This vessel is provided with a space D, into which water may be introduced and frozen. By various applications of this principle, liquid ammonia is used on a large scale for obtaining low temperatures.

213. The Constituents of Ammonia.—

***Exp. 211.**—Take a piece of hard glass tube about 50 cm. long and fit it with a one-holed cork at each end. Through one cork pass a short piece of straight glass tube and through the other a delivery tube for collecting over water. Partly fill the tube with dry granulated copper oxide, leaving a space of about 15 cm. empty at the end

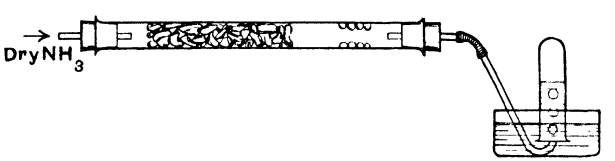


Fig. 69.

to which the delivery tube is attached (Fig. 69). Now attach the straight tube to the U-tube of the apparatus used in preparing dry ammonia in Exp. 206, the U-tube being fitted with a cork and tube bent at right angles. Support the long tube horizontally in a clamp, and place the delivery tube under water. Heat the copper oxide red-hot by a flat-flame burner, then warm the ammonia flask.

After the reaction has been going on long enough for the expulsion of air from the apparatus, collect in a

test-tube any gas which may be given off, and examine it; also note the appearance of the tube. You will find the gas to be *nitrogen*. The colourless drops of liquid which collect in the cool part of the tube may be shown to be *water* by the usual tests.

The *nitrogen* and the *hydrogen* of the water must have come from the ammonia, which therefore contains these two elements since copper oxide contains neither. Part of the oxygen of the water might also be derived from the ammonia, though some of it has evidently come from the copper oxide, a portion of which has been reduced to red metallic copper. That this is not the case however is proved by the fact that if electric sparks are passed through a mixture of nitrogen and hydrogen only, some ammonia is formed.

The reduction of copper oxide by ammonia is represented by the following equation—

$$3CuO + 2NH_3 = N_2 + 3H_2O + 3Cu.$$

Many other metallic oxides are reduced in a similar manner when heated in a current of ammonia.

214. Composition of Ammonia by Volume.—

First Method.—This method depends upon the fact that when electric sparks are passed through gaseous ammonia it is slowly decomposed into its constituents, nitrogen and hydrogen.

† **Exp. 212.**—Dry ammonia is passed into a bent eudiometer over mercury (see Fig. 48, the vapour jacket is omitted), and its volume accurately measured. The sparks are then passed until no further increase in volume occurs; the final volume will be found to be *double* the original volume. If now excess of oxygen (say, double the volume of ammonia taken) be introduced into the eudiometer and the spark passed, the hydrogen will combine with it and form water, which condenses, leaving nitrogen and the *excess* of oxygen added, two-thirds the diminution in volume being the volume of hydrogen. The volume of

nitrogen is found by subtracting the volume of hydrogen calculated from this diminution, from the volume of nitrogen plus hydrogen after the first sparking.

It is found that the volume of hydrogen is three times that of the nitrogen. Further, since the volume of nitrogen plus hydrogen is double the volume of ammonia from which it is formed, the complete composition of ammonia is expressed in the statement:—

Three volumes of hydrogen combine with one volume of nitrogen to form two volumes of ammonia.

This method is not, however, very accurate—for two reasons: (1) the volume of nitrogen plus hydrogen is *not exactly* double that of the ammonia from which it is formed, because the decomposition is never quite complete; (2) when the mixed gases are exploded with oxygen, some of the nitrogen combines with oxygen to form oxides of nitrogen.

Second Method.—This consists in electrolysing a strong aqueous solution of ammonia, when nitrogen and hydrogen are evolved at the positive and negative electrodes respectively.

* **Exp. 213.**—The experiment is carried out in a Hofmann's voltameter (see Fig. 59) fitted with platinum electrodes. The voltameter is filled with strong aqueous ammonia, to which has been added a little ammonium sulphate, to make the liquid a better conductor. When a current from about 4 Grove's or Bunsen's cells is passed through the liquid, gases collect over the positive and negative electrodes in the proportion of 1 : 3 by volume. These gases may be shown to be nitrogen and hydrogen respectively by the usual tests.

Third Method.—One of the most convenient methods of proving the volumetric composition of ammonia depends upon the fact that chlorine is capable of removing the hydrogen from it with liberation of free nitrogen.

* **Exp. 214.**—A long glass tube closed at one end is marked off into three equal parts by indiarubber bands. It is next filled with chlorine at the pneumatic trough by

displacement of chlorine water, and when quite full the mouth is closed by a cork carrying a small dropping funnel; this is done *before* the tube is removed from the trough so as to prevent any chlorine escaping.

The tube is now placed in an upright position and about 10 cubic centimetres of strong ammonia solution are introduced into the funnel. This solution is allowed to flow into the tube drop by drop: the first drop which enters reacts with the chlorine with formation of a yellowish-green flame, and as more ammonia enters dense clouds of ammonium chloride are produced. When all the ammonia has been run in, a little dilute hydrochloric acid is introduced through the funnel to combine with the excess of ammonia.

The gas which now remains in the tube is nitrogen under reduced pressure. In order to bring it to atmospheric pressure the funnel is filled with dilute hydrochloric acid; a tube bent twice at right angles, with one long arm and one short arm, is also filled with dilute acid, and the short arm is attached to the funnel by rubber tubing, whilst the long arm is dipped into some more acid contained in a beaker (see Fig. 70). On now opening the tap hydrochloric acid is sucked into the tube until the pressure is the same as that of the atmosphere. It will then be found that the liquid reaches to the second india-rubber band, *i.e.* the nitrogen occupies one-third of the tube.

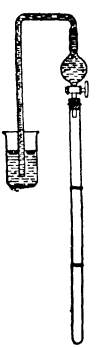


Fig. 70.

Now hydrogen and chlorine unite in equal volumes to form hydrogen chloride, so that the volume of hydrogen extracted from ammonia by the chlorine in the tube would just fill the tube. This hydrogen was originally in combination with the nitrogen left in the tube, so that the relative volumes of hydrogen and nitrogen in ammonia are in the ratio 1 : 3.

215. Formula of Ammonia.—Since, as we have just seen, the volumes of nitrogen and hydrogen which combine to form ammonia are in the ratio 1 : 3, it follows by

Avogadro's hypothesis that the number of molecules of nitrogen and hydrogen which combine are in the same ratio. But the molecules of these two elements each contain two atoms, and therefore—

$$\frac{\text{Number of atoms of nitrogen in ammonia}}{\text{Number of atoms of hydrogen in ammonia}} = \frac{1}{3}$$

The formula of ammonia is, therefore, NH_3 or N_2H_6 or N_3H_9, etc.

Now the relative density of ammonia is 8·5 (H = 1), and consequently its molecular weight is $8{\cdot}5 \times 2 = 17$.

Let us take first the simplest formula, viz. NH_3. Since atomic weight of N = 14 and atomic weight of H = 1, the molecular weight of NH_3 is $14 + 1 \times 3 = 17$. This agrees with the number obtained from the density, so that NH_3 is the correct formula.

Further this formula agrees with the results of Exp. 212, where we found that two volumes of ammonia broke up into one volume of nitrogen and three of hydrogen, the equation for the decomposition being thus represented—

$$\underset{\substack{\text{2 molecules}\\\text{4 vol.}}}{2NH_3} = \underset{\substack{\text{1 molecule}\\\text{2 vol.}}}{N_2} + \underset{\substack{\text{3 molecules}\\\text{6 vol.}}}{3H_2}.$$

If, however, the formula were written, say, N_2H_6 we should have—

$$\underset{\substack{\text{1 molecule}\\\text{2 vol.}}}{N_2H_6} = \underset{\substack{\text{1 molecule}\\\text{2 vol.}}}{N_2} + \underset{\substack{\text{3 molecules}\\\text{6 vol.}}}{3H_2},$$

i.e. *one* volume of ammonia would yield one volume of nitrogen and three of hydrogen, which *does not agree* with the results of experiment.

QUESTIONS.—CHAPTER XVI.

1. Describe a method by which nitrogen may be obtained from air by removal of oxygen.
2. Give two methods for the preparation of nitrogen from ammonia or ammonium salts.

3. State the chief physical and chemical properties of nitrogen.

4. Describe a method of determining accurately the composition of the atmosphere by volume.

5. How may the composition of the air by weight be determined?

6. A mixture of 25 c.c. of air and 50 c.c. of hydrogen is exploded in a eudiometer, and the volume of the residual gas is found to be 60·3 c.c.: find the percentage of oxygen in the air.

7. The percentage composition of air by weight being 76·058 nitrogen, 0·937 argon, and 23·005 oxygen, find the composition by volume.

8. A litre of dry air is passed over heated copper and the increase in the weight of the copper found to be 0·297 gram: find the percentage by weight of oxygen in the air. (1 litre of air weighs 1·293 grams.)

9. How would you show that air contains carbon dioxide, and what means would you adopt for ascertaining the amount of carbon dioxide in air?

10. How do the following impurities originate in air:—carbon dioxide, sodium chloride, ammonia, sulphurous acid?

11. What agencies are at work which tend to remove such impurities as carbon dioxide and ammonia from the air?

12. In what respect does a *mixture* of two gases, such as nitrogen and oxygen, differ in its behaviour from a *compound* of the two gases when shaken up in contact with water?

13. What indications are usually shown that two gases which you have brought together have entered into combination?

14. What reasons are there for supposing that the nitrogen and oxygen in air are mixed, not chemically combined?

15. Write a short account of argon and the other elements recently discovered in the atmosphere.

16. Give a general method by which ammonia may be obtained from nitrogenous animal or vegetable substances.

17. What experiments would you make to show that the composition of ammonia is rightly expressed by the formula NH_3?

18. Describe in detail how you would prepare and collect a few jars of dry ammonia gas. Sketch the apparatus you would employ. What experiments would you perform to illustrate the chief properties of the gas?

19. Compare the properties of an aqueous solution of ammonia with those of an aqueous solution of caustic potash. What happens when an aqueous solution of ammonia is boiled?

20. What would you observe on grinding together some sal-ammoniac and slaked lime? Explain how you would proceed to prepare a crystalline solid from the gaseous product of the reaction. Express by equations the changes which take place.

21. What do you understand by the term *dissociation*? Illustrate your answer by examples.

22. Describe an experiment by which you could show that sal-ammoniac dissociates when heated.

23. What elements does ammonia contain? How would you proceed to prove experimentally the presence of these elements? Sketch the apparatus you would employ.

CHAPTER XVII.

NITRIC ACID. OXIDES OF NITROGEN.

216. Preparation of Nitric Acid.—

Exp. 215.—Introduce 20 grams of nitre (potassium nitrate) into a stoppered retort, and as much concentrated sulphuric acid as will just cover it. Support the retort as indicated in Fig. 71, and slip a small flask over the mouth. Let this flask rest in a trough of cold water and cover the upper side with a wet cloth.

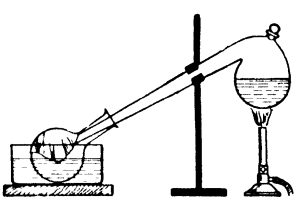


Fig 71.

You will notice that the nitre dissolves in the acid even in the cold. Now apply *gentle* heat. Soon the liquid boils and brown fumes are evolved. These pass over and condense to a large extent in the neck of the retort, forming a yellow liquid which collects in the flask. The condensation is completed in the flask, which is kept cool by the water in the trough and by the wet cloth.

When brown fumes cease to rise, remove the flame and pour the liquid out of the retort into an evaporating dish. It solidifies to a hard white crystalline mass on cooling.

The yellow liquid you have collected in the flask is *concentrated nitric acid* (HNO_3); the crystalline mass consists of potassium hydrogen sulphate ($KHSO_4$). The change which takes place is represented by the equation—

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

Any other nitrate might have been employed in place of potassium nitrate; on the large scale the sodium salt (Chili saltpetre) is used because it is cheaper, and weight for weight yields a larger quantity of nitric acid. This follows from the fact that the formula weight[1] of sodium nitrate ($NaNO_3 = 23 + 14 + 3 \times 16 = 85$) is less than that of potassium nitrate ($KNO_3 = 39 + 14 + 3 \times 16 = 101$), the change which takes place in the case of the sodium salt being precisely similar to that taking place in the case of the potassium salt, viz.

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3.$$

(The student should work out the weights of nitric acid which would be obtained from 100 grams of each salt.)

217. Properties of Nitric Acid.—

Exp. 216.—Dilute some of the nitric acid you have prepared and dip a piece of blue litmus paper into it. The colour changes to bright red, showing that the liquid is strongly acid.

Exp. 217.—Pour a little concentrated nitric acid on to a few *wood shavings* contained in a porcelain dish. You will observe that the wood turns yellow and then brown. Warm gently (in a fume cupboard), and note that the wood rapidly disappears and brown fumes are produced.

Repeat the experiment with *paper*, and note that the results are similar.

Exp. 218.—Put a piece of *cork* or *rubber* into a test-tube, add a little nitric acid, and heat to boiling. Thick brown fumes are evolved and the cork swells up and becomes bright yellow.

These experiments illustrate the destructive action that nitric acid has on organic matter. In many cases the latter is turned yellow; the skin, for example, is at once stained

[1] The *formula weight* of a substance is the weight of it represented by its formula. Thus, since the formula of cupric oxide is CuO, its formula weight is 63 + 16 or 79 units of weight.

yellow by contact with nitric acid. Great care should be taken to avoid allowing the strong acid to come in contact with the skin, and if it should do so wash it off *immediately* or a painful wound will result.

218. Oxidising Action of Nitric Acid.—

Exp. 219. *Action on Charcoal.*—Heat a small piece of charcoal and drop it into a little concentrated nitric acid in a test-tube. There is a violent reaction; red fumes are evolved, the charcoal gradually disappears, and the volume of liquid diminishes. Fit the tube with a cork and delivery tube and pass the evolved gas into some lime-water contained in a second test-tube. The liquid becomes *milky*, showing that *carbon dioxide* was one of the products of the reaction.

The oxygen present in the carbon dioxide must have been supplied by the nitric acid, which therefore *contains oxygen*. We may prove this directly by means of the following experiment.

* **Exp. 220.** *Decomposition of Nitric Acid by Heat.*—Support a clay pipe in the position shown in the diagram (Fig. 72) by means of a retort-stand and clamp (not shown). Attach a short piece of rubber tubing to the stem of the pipe. Partly fill a small trough with water; also completely fill a small cylinder with water and invert it in the trough. Push the loose end of the rubber tubing through the arch of a beehive shelf which is standing in the trough. Now heat the tube strongly at a spot about 9 inches from the bowl by means of a Bunsen

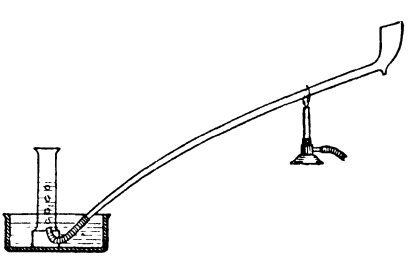


Fig. 72.

burner, and then gradually pour about 5 c.c. of concentrated nitric acid into the bowl. Bubbles of gas escape from the rubber tube. After allowing a few seconds for the air to be displaced from the pipe stem stand the cylinder on the beehive shelf. A gas collects which you can prove to be oxygen by introducing a glowing splinter into it; the splinter bursts into flame.

In the preceding experiment the acid was decomposed when it reached the heated part of the tube, and the gaseous products were pushed forward by the weight of acid above them. One of these products we saw was *oxygen*. It can be shown that the others were *water* and a *brown vapour (nitrogen peroxide)*, which dissolved in the water in the trough.

The change which has taken place is represented by the equation—

$$4HNO_3 = 2H_2O + \underset{\text{Nitrogen peroxide}}{4NO_2} + O_2.$$

Now we saw in Exp. 219 that nitric acid gave up oxygen to carbon and converted it into carbon dioxide. Nitric acid is therefore an *oxidising agent*. It is in fact one of the most powerful oxidising agents known. This is not surprising, since the acid contains over 76 per cent. of its weight of oxygen.

We will investigate other examples of its oxidising action.

Exp. 221.—To a little indigo solution add a few drops of nitric acid and heat. The blue colour disappears and the liquid becomes yellow.

The nitric acid has bleached the indigo by oxidising it to a yellow compound.

Exp. 222. *Action on Sulphur.*—Heat some flowers of sulphur with concentrated nitric acid in an evaporating dish (in the fume cupboard). Brown fumes are evolved and the sulphur gradually disappears. An oily liquid remains which looks like *sulphuric acid*. Pour a few drops

of this liquid into a little water contained in a test-tube. Now pour in some barium chloride solution. A white precipitate is formed. This shows that the oily liquid *is* sulphuric acid (for the formation of a white precipitate with barium chloride is the characteristic test for this acid).

Here the nitric acid has oxidised the sulphur, with the production of sulphuric acid.

Phosphorus and iodine undergo oxidation in a similar way to sulphur with formation of phosphoric acid (H_3PO_4) and iodic acid (HIO_3) respectively. Again, nitric acid oxidises many organic substances such as wood, paper, cork, as you saw in Exps. 217, 218; the evolution of brown fumes in each case was an indication that the nitric acid was being reduced, so that the substance acted upon must have been undergoing oxidation.

219. Properties of real Nitric Acid.—*Pure* nitric acid is a colourless fuming liquid of specific gravity 1·53. It begins to boil at 78° C. with partial decomposition into the same substances as those produced when it is heated more strongly, as in Exp 220. The same decomposition takes place at ordinary temperature on exposure to light, but more slowly. The brown nitrogen peroxide formed dissolves in the excess of acid, forming a yellow solution; this explains the yellow colour acquired by pure nitric acid after standing for some time.

This form of nitric acid is commonly known as *fuming nitric acid.*

220. Action of Heat on Aqueous Solutions of Nitric Acid.—Nitric acid mixes with water in all proportions, and if the dilute solution be concentrated in air at atmospheric pressure it becomes stronger until 68 per cent. of acid is present; it then distils unchanged at 120° C. under normal pressure. Similarly, on distilling an acid stronger than this, it gradually becomes weaker till it contains 68 per cent. of nitric acid, when it passes over unchanged. If the pressure is not normal the composition and boiling-point of the acid which distils unchanged have different values, as in the case of the halogen acids.

The ordinary concentrated nitric acid of the laboratory consists of this 68 per cent. acid and is the acid used for the above experiments. It is a colourless liquid of specific gravity 1·4 and boils (as stated) at 120° C. with little decomposition.

221. Action of Nitric Acid on Metals.—

Exp. 223.—To about 3 c.c. of concentrated nitric acid in a test-tube add a small piece of *copper*. Brown fumes are evolved and the copper disappears, a blue liquid being formed (solution of copper nitrate). Indigo and copper are used as *tests* for nitric acid.

Repeat the experiment, using *zinc* instead of copper. A very violent action takes place, brown fumes are again produced and the zinc disappears. The liquid is colourless this time (it is a solution of zinc nitrate).

Most metals are readily attacked by nitric acid, which is much more active than either hydrochloric or sulphuric acids. Owing to its strongly corrosive action nitric acid is often called *aqua fortis*.

Now we have seen that when metals dissolve in hydrochloric or dilute sulphuric acids one of the products is *hydrogen*. This is very rarely the case, however, when nitric acid is employed. Instead of this brown fumes of nitrogen peroxide are produced, as we have seen in Exp. 223, or else the reduction is carried further (we shall meet with examples of this later). What is the explanation of this difference in behaviour? It depends upon the *oxidising action* of nitric acid. We may suppose that the first action of nitric acid on a metal is to liberate hydrogen and form the nitrate of the metal, but that the hydrogen in the moment of its formation[1] is at once attacked by a further quantity of the acid and *oxidised to water*, the acid being simultaneously reduced to nitrogen peroxide or some other oxide of nitrogen.

[1] *I.e.* before the atoms have united to form molecules. Nitric acid has no action on hydrogen gas which is bubbled through it.

Let us, for example, consider the action of concentrated nitric acid on copper. The products are copper nitrate, nitrogen peroxide, and water, and the change may be represented by the equation—

$$Cu + 4HNO_3 = Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

But we may divide this reaction into two stages—

$$(1)\quad Cu + 2HNO_3 = Cu(NO_3)_2 + \underset{\text{Atomic}}{2H}.$$

[1]

$$(2)\quad 2H + 2HNO_3 = 2H_2O + 2NO_2.$$

If (1) and (2) are added together we have—

$$Cu + 2H + 4HNO_3 = Cu(NO_3)_2 + 2H + 2H_2O + 2NO_2.$$

Omitting the 2H which occurs on each side of the equation we arrive at the original equation which we dissected.

It should be noted that occasionally the metal is converted into the *oxide* and not into the *nitrate*; this happens, for example, in the case of *tin*.

Exp. 224.—Drop a small piece of tin into a test-tube containing a little concentrated nitric acid. A violent action takes place with copious evolution of brown fumes and separation of a white powder.

The white powder is stannic oxide,[2] SnO_2, and the change which takes place may be represented by the equation—

$$Sn + 4HNO_3 = SnO_2 + 4NO_2 + 2H_2O.$$

The action of nitric acid on metals depends very largely on the conditions. The course is determined by the following factors:—

(1) The nature of the metal
(2) The strength of the acid.
(3) The temperature.
(4) The concentration of the products in solution.

[1] When it is desired to represent free atoms of hydrogen (or other element the molecule of which contains more than one atom) in an equation, 2H, etc., should be written in place of H_2, etc., and the word "atomic" should be written underneath the symbol.

[2] Strictly speaking it is a compound of stannic oxide and water.

We have seen, for example, that *concentrated* nitric acid forms *nitrogen peroxide* with the metal copper. Let us now investigate the action of the *dilute* acid on this metal.

222. Action of Dilute Nitric Acid on Copper.—

Exp. 225.[1]—Introduce a few grams of copper turnings into a flask of about ¼ litre capacity provided with a thistle funnel and delivery tube (Fig. 73), and add about 50 c.c. of a mixture of equal volumes of nitric acid and water. Rapid action ensues with evolution of gas, and brown fumes appear in the flask, the liquid at the same time becoming blue. After a time the brown colour disappears. Now collect the gas over water at the pneumatic trough. Remove the cylinder when full in the usual way and replace it by another ; collect in all about four cylinders of the gas. The gas is colourless ; so that so far it resembles hydrogen (the gas produced when such acids as dilute sulphuric and dilute hydrochloric act on metals). But now allow a little air to enter one of the cylinders. Brown fumes are immediately formed, proving that the gas is not hydrogen.

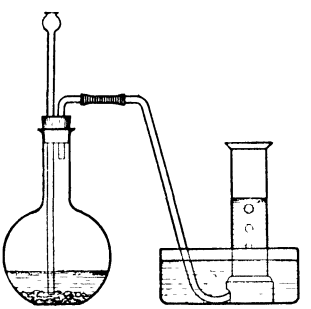


Fig. 73.

The colourless gas you have collected is called *nitric oxide.* It is an *oxide of nitrogen* (see § 223 for a proof of this) and is represented by the formula NO (see §§ 224, 225 for proof of this). The equation expressing the action which has taken place is—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

[1] This experiment should be carried out in a fume cupboard or under a hood, as the gas produced is poisonous.

Nitric oxide represents a further stage in the reduction of nitric acid than nitrogen peroxide (the compound produced when the concentrated acid acts on copper) for it contains less oxygen.

The brown fumes formed when nitric oxide comes in contact with air consist of nitrogen peroxide; they are formed by the combination of the nitric oxide with the oxygen of the air according to the equation—

$$2NO + O_2 = 2NO_2.$$

You will now understand why brown fumes were formed in the flask (in Exp. 225) at first but subsequently disappeared. They were formed by the combination of nitric oxide with the oxygen air in the bottle, and when this was used up their formation ceased. The brown fumes were subsequently driven out of the bottle by the nitric oxide.

223. Properties of Nitric Oxide.—We have seen that nitric oxide is a colourless gas which very readily combines with oxygen, forming nitrogen peroxide

From the fact that we experienced no difficulty in collecting nitric oxide over water, it follows that the gas is either insoluble in water, or only slightly soluble. You may also show this by the following experiment.

Exp. 226.—Invert a cylinder of the gas in a trough of water, and leave it for some time. There is no appreciable rise of the water in the cylinder.

Accurate experiment shows that the gas *is* slightly soluble in water, 100 c.c. of which dissolve about 1·5 c.c. of nitric oxide at the ordinary temperature. The *density* of the gas is found to be *slightly higher* than that of air.

Nitric oxide does not *burn* in air, although as we have seen chemical action takes place at once with formation of brown fumes. Further, it does not support combustion in the ordinary sense, for a taper will not burn in it, nor will burning sulphur and feebly burning phosphorus; brightly burning phosphorus will, however, do so.

Exp. 227.—Introduce a lighted taper into a cylinder of nitric oxide. The taper is extinguished. Now ignite a piece of sulphur in a deflagrating spoon and plunge it into the cylinder: the sulphur is extinguished. Repeat with phosphorus which is *just ignited*: the flame dies out.

Now plunge some *brightly burning* phosphorus into a cylinder of the gas and press the brass plate down tightly (have the rim of the cylinder *well greased* so that the cylinder is air-tight when the brass plate is pressed down). The phosphorus continues to burn brightly and white fumes are formed. Soon the phosphorus goes out, and after a time the white fumes disappear.

Now invert the cylinder in a deep trough of water, keeping the brass plate pressed down tightly till the mouth of the cylinder is under water. Next remove the deflagrating spoon. Water rises in the cylinder at once till it is about half full; no further rise takes place even after leaving for some time, showing that the residual gas is insoluble in water or at any rate nearly so. Test this remaining gas with a lighted taper and with brightly burning phosphorus: both are extinguished and the gas does not burn. It is *nitrogen.*

Test the liquid in the cylinder with blue litmus paper: it is *acid.*

Now we know that when phosphorus burns in air or oxygen a white solid—phosphorus pentoxide—is formed which dissolves in water, forming an acid. The white fumes formed in the previous experiment consisted of this same substance; they disappeared because they dissolved in the water on the sides of the cylinder. But since phosphorus pentoxide is composed of phosphorus and oxygen, and since it is formed by burning phosphorus in nitric oxide, it follows that *nitric oxide* also *contains oxygen.* Further, we have seen that after the combustion nitrogen remains. Hence nitric oxide is a *compound of nitrogen and oxygen.*

You will naturally ask why well-ignited phosphorus would continue to burn in the gas whilst feebly burning phosphorus, burning sulphur, and a lighted taper were

extinguished. The explanation is that before the phosphorus could burn it was necessary that the nitric oxide should be *decomposed into its elements*, the phosphorus then burning in the *free oxygen*. Now phosphorus when feebly burning did not give out sufficient heat to bring about this decomposition, nor did burning sulphur and a burning taper which produce still less heat; brightly burning phosphorus, however, was able to bring about the necessary decomposition, and then the combustion was more vigorous than in air, because the percentage of oxygen in nitric oxide is higher than in air.

Though carbon itself will not burn in nitric oxide, a mixture of nitric oxide and the vapour of carbon bisulphide (a compound of carbon and sulphur, CS_2) burns with a very bright flame. The products are carbon dioxide, sulphur dioxide, and free nitrogen.

$$CS_2 + 6NO = CO_2 + 2SO_2 + 3N_2.$$

Exp. 228.—Pour a small quantity of carbon bisulphide into a jar of nitric oxide, cover with glass plate, and shake up till the liquid has vaporised. Now ignite the mixture.

Nitric oxide unites with ferrous sulphate, and a deep brown compound, $FeSO_4 . NO$, is formed which is soluble in water and is readily decomposed on warming, nitric oxide being evolved. The formation of this compound affords a very delicate test for nitric acid and its salts.

Exp. 229.—Pass nitric oxide into a little ferrous sulphate solution in a test-tube, until the gas is no longer absorbed. Heat the solution obtained.

Note the formation of brown fumes. These are produced by the combination of the nitric oxide driven out of solution with the oxygen of the air.

Exp. 230. *To detect a Nitrate.*—Dissolve a small crystal of potassium nitrate in water, add a crystal of green vitriol to the liquid and shake up till this also dissolves. Now let a little concentrated sulphuric acid trickle down the inside of the test-tube. If this is done carefully the acid will not mix with the solution, but will form a

layer underneath. At the junction of the two liquids a brown ring forms.

The explanation of this is that where the liquids meet the sulphuric acid liberates free nitric acid from the nitrate; the nitric acid in the presence of sulphuric acid then oxidises the ferrous sulphate to ferric sulphate, $Fe_2(SO_4)_3$, and is itself reduced to nitric oxide, according to the equation—

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

The nitric oxide then combines with a further quantity of ferrous sulphate to form the characteristic brown compound.

224. Composition of Nitric Oxide by Volume.—The nitric oxide prepared as in Exp. 225 by the action of nitric acid on copper always contains both nitrogen and nitrous oxide, and is not sufficiently pure for quantitative experiments. Pure nitric oxide may, however, be readily prepared by the action of sulphuric acid on a mixture of ferrous sulphate and potassium nitrate, *i.e.* by utilising the reactions we have investigated in Exps. 229, 230

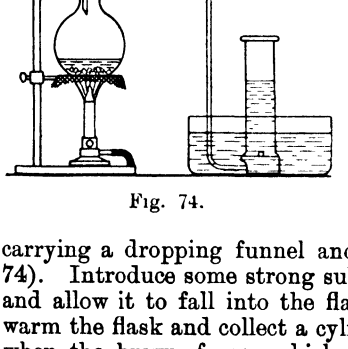


Fig. 74.

***Exp. 231.** *Preparation of pure Nitric Oxide.*—Introduce into a small flask a mixture of 20 grams of ferrous sulphate and 5 grams of nitre, and just cover the mixture with water. Fit the flask with a cork carrying a dropping funnel and a delivery tube (see Fig. 74). Introduce some strong sulphuric acid into the funnel and allow it to fall into the flask drop by drop. *Gently* warm the flask and collect a cylinder of the gas over water when the brown fumes which first form in the jar have

been driven out. Expose the gas in the cylinder to the air. Brown fumes are formed; the gas is *nitric oxide.*

When a spiral of iron wire is heated in nitric oxide the gas is decomposed, the oxygen combining with the iron to form the magnetic oxide of iron, and the nitrogen being set free. This is the basis of one method of determining the composition of the gas.

* **Exp. 232.**—Procure a glass tube about 2 feet long and an inch wide, open at both ends. Fit into one end a rubber cork carrying two thick copper wires, to which a spiral of iron wire about $1\frac{1}{2}$ inches long is attached by means of binding screws. The lower end of the wire should reach about a third of the way down the tube (see Fig. 75). Fill the tube with water, invert it in a trough of water, and displace about three-quarters of the water by pure nitric oxide, prepared by the method described in Exp. 231. Mark the level of the water in the tube by means of a piece of gummed paper.

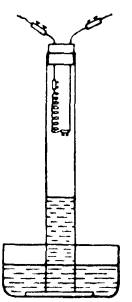


Fig. 75.

Now press the tube down on to a rubber pad placed in the trough of water in which the tube stands, and clamp it to a retort stand (not shown in the diagram). Next pass a current of electricity through the wire. At first this current should not be of sufficient strength to make the wire red-hot (or the water on it would react with the iron and hydrogen would be liberated). When the part of the tube near the wire is warm and quite dry inside you may assume that the wire is dry, and the strength of the current should now be increased till the temperature of the iron wire is raised to bright redness. After about twenty minutes stop the current and allow the tube to cool.

Now raise the tube slightly from the pad. Water rises rapidly up the tube. When the level ceases to rise place a small dish underneath the open end of the tube, and then transfer the latter to a tall cylinder full of water, keeping the end of the tube underneath the water in the dish

during the transference. Lower the tube till the water inside and outside is at the same level, and mark the level with a piece of gummed paper. Now measure the distance from the bottom of the cork to the two pieces of gummed paper. These give you the original and final volumes of gas; you will find that the latter is just half the former.

Now invert the tube and show that the residual gas answers the tests for nitrogen. If any red fumes are produced when the residual gas is exposed to the air the decomposition of the nitric oxide was incomplete.

From this experiment it follows that *nitric oxide* contains *half its volume of nitrogen.*

225. Formula of Nitric Oxide.—From the result which we have just obtained, namely that nitric oxide contains half its volume of nitrogen, it follows by applying Avogadro's Law that one molecule of nitric oxide contains half a molecule of nitrogen, *i.e.* one atom (since the molecule of nitrogen contains two atoms). Its formula may therefore be expressed thus, N_1O_x, where x represents the number of atoms of oxygen in a molecule of the gas.

The value of x may be determined by ascertaining the density of nitric oxide compared with hydrogen. This will be found to be 15, and since the hydrogen molecule, H_2, weighs 2 units, the molecule of nitric oxide must weigh $15 \times 2 = 30$ units, *i.e.* $N_1O_x = 30$. But $N_1 = 14$; therefore $O_x = 30 - 14 = 16$. Now the atomic weight of oxygen is 16, and therefore $x = 1$, *i.e.* the molecule of nitric oxide is represented by NO.

The change which took place in Exp. 232 is represented by the equation—

$$3Fe + 4NO = Fe_3O_4 + 2N_2.$$

226. Quantitative Investigation of the Combination of Nitric Oxide and Oxygen.—We have already seen that nitric oxide and oxygen combine directly to form nitrogen peroxide. This reaction can be studied quantitatively as follows:—

Exp. 233.—Prepare a small jar of oxygen as described in Exp. 29, and place it mouth to mouth with a jar of nitric oxide of equal size (Fig. 76). Now slide out the two covers carefully and at once press the two jars tightly together. (The rims of the jars should be *well greased.*) Brown fumes of nitrogen peroxide form at once. Invert the combination of jars several times to thoroughly mix the gases. Now fill a large jar with caustic soda solution, and support it in an inverted position so that its mouth is slightly below the surface of some caustic soda solution contained in a trough. Next immerse the pair of small jars in the trough in a suitable position, and separate them so that the gases they contain rise into the large cylinder. The brown fumes disappear, being absorbed by the caustic soda, and a little colourless gas (oxygen) remains.

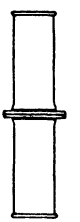


Fig. 76.

Measure the volume of this gas and also the volume of one of the small jars. You will find that the former is half the latter. Now we started with a jar of nitric oxide and a jar of oxygen, and half a jar of oxygen remains. It follows that a jar of nitric oxide has combined with half a jar of oxygen, *i.e.* the gases unite in the proportion of 2 · 1 by volume.

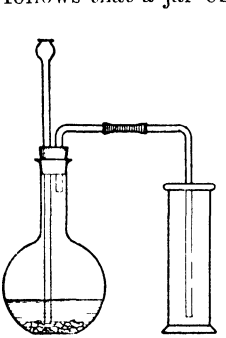


Fig. 77.

227. Preparation and Properties of Nitrogen Peroxide.—

Exp. 234.—[Perform in a fume cupboard.] Introduce a few grams of copper turnings into a flask provided with a thistle funnel and delivery tube and add about 20 c.c. of concentrated nitric acid. Copious brown fumes of nitrogen peroxide are evolved and the flask does not clear after a time as it did when the diluted acid was used, showing that the product of the action is not nitric oxide, but nitrogen peroxide. Collect a few jars of the brown fumes by displacement of air (Fig. 77).

Exp. 235.—Introduce a lighted taper into a jar of the fumes: the taper is extinguished. Try burning sulphur and *feebly burning* phosphorus: the result is the same.

Now introduce some *brightly burning* phosphorus: the phosphorus continues to burn very brightly and a white solid collects on the sides of the jar. This is phosphorus pentoxide, and you can show, as in Exp. 227, that *nitrogen* remains in the cylinder.

Nitrogen peroxide then, like nitric oxide, does not support the combustion of a taper, nor of sulphur and feebly burning phosphorus, but will allow *well ignited* phosphorus to burn in it. The explanation of this is similar to that given in the case of nitric oxide (see § 223).

Exp. 236.—Introduce a little water into a cylinder of nitrogen peroxide. Cover the mouth with a glass plate and shake up. Notice the difficulty of removing the cover. [What is the explanation of this?] Test the solution with blue litmus paper: the colour changes to red, showing that an *acid* is present.

Now add a little potassium iodide and some starch solution. The latter acquires the characteristic blue colour which is produced by *iodine*.

Nitrogen peroxide then dissolves in water, forming an acid and a substance (which may of course be the acid) capable of liberating iodine from potassium iodide. It can be shown that in reality *two acids* are formed—nitric acid and an acid called *nitrous acid*, HNO_2, the change being expressed by the equation—

$$2NO_2 + H_2O = HNO_3 + HNO_2.$$

It is the nitrous acid which liberates the iodine from potassium iodide, and the change may be supposed to take place in two stages. First free hydriodic acid is formed by double decomposition, thus—

$$KI + HNO_2 = KNO_2 + HI$$

The hydriodic acid is then acted upon by a further quantity

of nitrous acid with formation of free iodine and liberation of nitric oxide according to the equation—

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

228. The Nitrates.—These salts may be looked upon as nitric acid in which the hydrogen of the acid is replaced by a metal, thus—

$$HNO_3 \quad KNO_3 \quad NaNO_3 \quad NH_4NO_3 \quad AgNO_3,$$

$$\left.\begin{matrix} HNO_3 \\ HNO_3 \end{matrix}\right\} \; Pb(NO_3)_2 \; Cu(NO_3)_2 \; Ca(NO_3)_2 \; Ba(NO_3)_2.$$

They may be produced by the action of the acid on the metals or on their oxides, hydroxides, or carbonates.

In Exp. 107, for example, you prepared potassium nitrate by the action of nitric acid on caustic potash. This change is represented by the equation—

$$KOH + HNO_3 = KNO_3 + H_2O.$$

All nitrates are readily soluble in water.

229. Action of Heat on Nitrates.—Preparation of Liquid Nitrogen Peroxide.—

Exp. 237. *To prepare Lead Nitrate and investigate the action of heat on it.*—To a few cubic centimetres of *dilute* nitric acid contained in a porcelain basin add fragments of lead, and digest on a water-bath until the acid is saturated and no more of the metal will dissolve. Evaporate the clear liquor to dryness, when a white salt, *lead nitrate*, remains.

Now heat the lead nitrate so prepared in a test-tube. It melts and then evolves brown fumes of nitrogen peroxide. When the evolution of gas ceases a brownish-red solid remains, which becomes yellow on cooling. This substance is *yellow oxide of lead*, PbO. [If the temperature used is sufficiently high the oxide of lead melts, forming a *red liquid.*]

The change which takes place on heating lead nitrate, $Pb(NO_3)_2$, is represented by the equation—

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

Most nitrates decompose similarly on heating, *i.e.* they are converted into an oxide of the metal with evolution of nitrogen peroxide and oxygen. The decomposition of lead nitrate is utilised for the preparation of *liquid* nitrogen peroxide.

* **Exp. 238.** *To prepare Liquid Nitrogen Peroxide.*—Introduce 10 grams of finely-powdered lead nitrate into a retort of "hard" glass (see Fig. 78) connected with a U-tube surrounded by a freezing mixture (pounded ice or

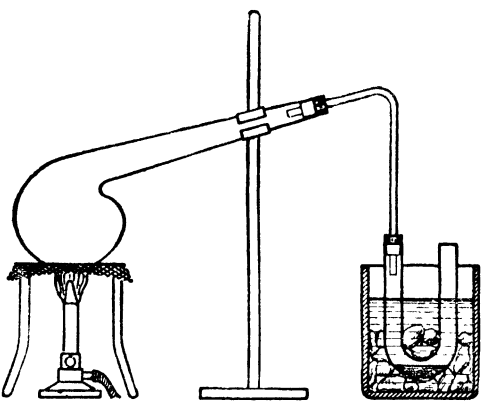


Fig. 78.

snow and salt) and heat strongly. The brown fumes which are given off condense in the U-tube to a colourless liquid. Remove the freezing mixture and note that as the temperature rises the liquid darkens in colour, and at ordinary temperatures is *orange yellow.*

230. Properties of Nitrogen Peroxide.—The liquid obtained as in the experiment just described passes, on strongly cooling, into a colourless solid, melting at $-10°$ C If, on the other hand, its temperature is further raised it continues to get darker, and at 22° C. boils, giving off a brown vapour; the vapour, in its turn, continues to darken

with rise of temperature till it becomes almost black. This change in colour is accompanied by a corresponding change in composition. Thus at low temperatures (−10° C.) nitrogen peroxide has the composition N_2O_4, and at 140° it has completely dissociated into NO_2 molecules, whilst at intermediate temperatures some of the molecules are N_2O_4, others are NO_2. That this is the true explanation is proved by the changes in density which the vapour undergoes with rise of temperature.

In the following table the values of the relative density (H = 1) are given for several different temperatures, and also the corresponding molecular weights.

Temperature	Relative density	Molecular weight
26·7°	38·3	76 6
60·2°	30 1	60·2
100 1°	24 3	48·6
135 0°	23·1	46·2
140·0°	23·0	46·0

Now the molecular weight of N_2O_4 is 92, and that of NO_2 is 46, from which it follows that at 140° C. the dissociation into NO_2 molecules is complete, but at 26·7° C. the greater part of the gas consists of N_2O_4 molecules.

Nitrogen peroxide is decomposed by water, the exact course of the reaction depending on the conditions. Thus with a small quantity of cold water, nitric and nitrous acids are produced according to the equation given towards the end of § 227.

With hot water, however, the reaction proceeds thus—

$$H_2O + 3NO_2 = 2HNO_3 + NO.$$

When liquid nitrogen peroxide is brought in contact with water it dissolves and the solution passes through a series of colour changes—blue, green, and orange. This is supposed to be due to the gradual solution of the nitrogen peroxide in the nitric acid formed. Of course, in the presence of sufficient water all the nitrogen peroxide is decomposed and the solution becomes colourless

Nitrogen peroxide vapour attacks many metals, such as mercury, copper, and iron. It is very poisonous.

231. Direct union of Nitrogen and Oxygen.—When electric sparks are passed through a mixture of nitrogen and oxygen for some time (*e.g.* ordinary air) the gas acquires a brownish tinge. This is due to the combination of a small proportion of the gas with formation of nitrogen peroxide according to the equation—

$$N_2 + 2O_2 = 2NO_2.$$

232. Formation and Properties of Nitrites.—

Exp. 239. *Action of heat on Potassium Nitrate.*—Heat a little nitre in a test-tube. It fuses, and at higher temperature a gas is evolved which you can prove to be oxygen in the usual way. The gas is tinged slightly brown owing to the presence of nitrogen peroxide. When the evolution of gas ceases allow the tube to cool; the residue solidifies to a white mass.

Dissolve this in water, add a little potassium iodide, acidify with dilute sulphuric acid, and then add starch solution. The blue colour which develops shows that iodine has been liberated.

The white solid which remains when potassium nitrate is heated is *potassium nitrite*, KNO_2, its formation from potassium nitrate being represented by the equation—

$$2KNO_3 = 2KNO_2 + O_2.$$

The addition of sulphuric acid to the mixture of potassium nitrite and potassium iodide (in the second part of the experiment) sets free nitrous and hydriodic acids, which then reacted with formation of iodine according to the equation already given.

We see from the result of the preceding experiment that potassium nitrate behaves differently from most nitrates when subjected to the action of heat, for it only gives brown fumes to a very small extent and the residue is the *nitrite* of the metal instead of the oxide

(cf., for example, the action of heat on lead nitrate—Exp. 237). Sodium nitrate when heated behaves like potassium nitrate, *i.e.* oxygen is evolved and a white residue of sodium nitrite, $NaNO_2$, remains; more brown fumes are produced, however, than in the case of potassium nitrate.

If potassium or sodium nitrate is heated with certain metals, such as lead, the decomposition is brought about more readily, the metal taking up the oxygen—

$$\underset{\text{Potassium nitrate}}{KNO_3} + \underset{\text{Lead}}{Pb} = \underset{\text{Potassium nitrite}}{KNO_2} + \underset{\text{Lead oxide}}{PbO}.$$

Exp. 240. *Action of Caustic Potash on Nitrogen Peroxide.*—Invert a jar of nitrogen peroxide in some caustic potash (or caustic soda) solution contained in a dish. Note the very rapid rise of the liquid in the jar accompanied by the disappearance of the brown fumes. Nitrogen peroxide is clearly very soluble in caustic alkalies.

Now pour a *little* caustic potash into a jar of the peroxide, cover with a glass plate, and shake up. Add a little potassium iodide and some starch solution, and then excess of dilute sulphuric acid. What do you observe?

The liberation of iodine in the previous experiment depends upon the fact that potassium nitrite is one of the products of the action of caustic potash on nitrogen peroxide; the change is represented by the equation—

$$2KOH + 2NO_2 = KNO_3 + KNO_2 + H_2O.$$

You will see that it closely resembles the change which takes place when nitrogen peroxide is dissolved in a little cold water (see § 227), the only difference being that the potassium salts of nitric and nitrous acids are formed instead of the acids themselves. The action of caustic soda on nitrogen peroxide is quite similar.

All nitrites are soluble in water, but silver nitrite, $AgNO_2$, is only sparingly soluble, and is formed as a white precipitate when a strong solution of silver nitrate is mixed with a strong solution of sodium nitrite.

233. Formation and Properties of Nitrous Acid.—Free nitrous acid is only known in dilute aqueous solution. It is liberated when an acid such as hydrochloric or sulphuric acid is added to a solution of a nitrite.

The aqueous solution gradually decomposes, however, even at ordinary temperature, and more rapidly on warming, according to the equation—

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

This accounts for the brown fumes produced when a solution of a nitrite is acidified, the nitric oxide produced at once combining with the oxygen of the air.

Exp. 241.—Dissolve a little potassium nitrite in water in a test-tube and add dilute sulphuric acid. Notice the formation of brown fumes, which become more pronounced on warming.

Nitrous acid is capable of acting both as a reducing agent and as an oxidising agent; as the former towards substances which readily give up oxygen, and as the latter towards those which readily take up oxygen. Thus it is rapidly converted into nitric acid by potassium permanganate, the latter being reduced and decolorised. In the presence of dilute sulphuric acid the reaction which takes place may be thus represented—

$$5HNO_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

Exp. 242.—Prepare a little dilute potassium permanganate solution, add excess of dilute sulphuric acid, and then add gradually a solution of potassium nitrite. Shake the vessel containing the permanganate from time to time. The colour of the permanganate becomes fainter and ultimately disappears.

The sulphuric acid liberated nitrous acid from the nitrite, and then the change was as given in the above equation.

On the other hand, as we have already seen, nitrous acid liberates iodine from potassium iodide, and here it exercises

an *oxidising* action, being itself simultaneously reduced to nitric oxide.

Again, nitrous acid, like nitric acid, is able to oxidise ferrous sulphate to ferric sulphate.

Exp. 243.—Dissolve a little ferrous sulphate and a little potassium nitrite in water, mix the solution, and add dilute sulphuric acid. The liquid becomes dark brown.

The colour is due to the formation of the compound of ferrous sulphate and nitric oxide, with which you are already acquainted. The nitrous acid set free by the action of sulphuric acid on the nitrite was reduced to nitric oxide by the ferrous sulphate according to the equation—

$$2HNO_2 + 2FeSO_4 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O + 2NO.$$

The nitric oxide then combined with excess of ferrous sulphate to form the characteristic brown compound.

234. Action of heat on Ammonium Nitrate.—

Exp. 244. *To prepare Ammonium Nitrate and to investigate the action of heat on it.*—Dilute 5 c.c. of nitric acid with an equal bulk of water, and add a little litmus solution, which will become of a bright red colour. Now add ammonia solution little by little until the last drop turns the litmus blue, and concentrate the liquid to a point at which when a drop of it is allowed to cool on the end of a glass rod it crystallises. On standing, crystals of *ammonium nitrate* will be obtained. Filter these off and dry them between blotting-paper.

Now heat the crystals *gently* in a test-tube. They melt and then give off a gas which you will find rekindles a glowing splint just as oxygen does. The gas is not oxygen, however, but *nitrous oxide*. We shall see later how it may be distinguished from oxygen.

Next heat the tube *strongly*. The decomposition is now accompanied by explosions, and when it is complete no solid remains in the tube.

The formation of ammonium nitrate and its decomposition by heat are represented by the equations—

$$\underset{\text{Ammonium hydroxide}}{NH_4OH} + HNO_3 = \underset{\text{Ammonium nitrate}}{NH_4NO_3} + H_2O.$$

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

It will be seen that ammonium nitrate decomposes in quite a different way from any of the other nitrates.

235. Action of Dilute Nitric Acid on Zinc.—

Exp. 245.—Introduce a little water into a test-tube and add about one-seventh of the volume of concentrated nitric acid. Shake up and introduce a few pieces of granulated zinc. There is a brisk effervescence of a colourless gas which you will find rekindles a glowing splint.[1] The tube rapidly gets very hot and the characteristic smell of nitrogen peroxide can soon be detected; at the same time the gas acquires a brownish tinge, rendered more evident by placing a sheet of white paper behind the tube.

The chief product of the action of dilute nitric acid on zinc is nitrous oxide, the change being represented by the equation—

$$4Zn + 10HNO_3 = 4Zn(NO_3)_2 + 5H_2O + N_2O.$$

Other gases are, however, formed, particularly as the temperature rises; one of these is nitric oxide, which accounts for the smell noticed (since nitric oxide combines with atmospheric oxygen to form nitrogen peroxide).

236. Preparation of Nitrous Oxide.—Let us now prepare nitrous oxide on a larger scale and investigate its properties.

[1] It is not at all easy to get this result. If the acid is not just the right strength or if the liquid has become too hot, other gases are present in sufficient quantity to prevent the splint being rekindled, though it may glow rather brighter.

Exp. 246.—Introduce about 30 grams of dry ammonium nitrate into a half-litre flask and heat *gently*—just so as to bring about a steady and *not too rapid* evolution of the gas.[1] The delivery tube should be wider than usual, as the salt is liable to be carried over and to stop up the tube; also stop the experiment when about two-thirds of the salt has been decomposed, or an explosion may ensue. Collect the gas in cylinders over *hot* water, as it is soluble in cold water.

237. Properties of Nitrous Oxide.—

Exp. 247.—Remove the cover from a cylinder of the gas and note that it has an agreeable odour and taste. This shows that it is *not oxygen*. Also note the feeling of exhilaration produced.

Nitrous oxide is familiarly known as "laughing gas," on account of the feeling of exhilaration produced when it is breathed in small quantities. Inhaled in larger quantities it is an anaesthetic, and renders the subject insensible to pain; it is for this reason employed in dentistry.

Exp. 248.—Invert a cylinder of the gas in cold water. The water gradually rises and fills the cylinder, showing that the gas is soluble in water. This again proves that it is *not oxygen*.

Water dissolves rather less than its own volume of nitrous oxide at the ordinary temperature, but the solubility of the gas decreases rapidly with rise in temperature; hence the gas may be readily collected over hot water, but not so satisfactorily over cold water.

Nitrous oxide is much heavier than air, its density being about $1\frac{1}{2}$ times as great; the density is practically identical with that of carbon dioxide.

[1] Be very careful to carry out this injunction in order to avoid explosions. When the gas is coming off steadily remove the flame; replace it when the evolution of gas slackens considerably.

Exp. 249.—Just kindle a piece of sulphur held in a deflagrating spoon and plunge it into the gas. The flame should be extinguished. Repeat after allowing the sulphur to burn for a little while. It should now continue to burn more vigorously than in air.

Note the characteristic odour of "burning sulphur," *i.e.* of sulphur dioxide.

Now burn sulphur in another cylinder of the gas, taking care to press the brass plate of the deflagrating spoon down tightly on to the greased rim of the cylinder. When the combustion ceases invert the cylinder in water and remove the deflagrating spoon. The water does not rise very far up the cylinder, even after leaving for some time. An insoluble gas then has taken the place of the soluble nitrous oxide. Show by the usual tests that this gas is *nitrogen.*

When, therefore, sulphur burns in nitrous oxide, sulphur dioxide is formed and nitrogen remains. Now sulphur dioxide is composed of sulphur and oxygen, for it is formed when sulphur burns in oxygen (see Exp. 33). It follows that *nitrous oxide is composed of nitrogen and oxygen* (as we have already assumed in writing equations). Further, it is a *chemical compound* of these gases, for sulphur if only just ignited will *not* burn in the gas, whereas it *will* burn in *air* which is a *mixture* of nitrogen and oxygen. The explanation of the fact that feebly burning sulphur is extinguished by nitrous oxide, whilst the well-ignited substance is not, is similar to the explanations already given in the case of phosphorus and nitric oxide and nitrogen peroxide, *i.e.* feebly burning sulphur does not give out sufficient heat to decompose the gas, brightly burning sulphur does.

The decomposition of nitrous oxide by heat is, however, much more easily effected than that of the other two oxides, and may be brought about by brightly burning sulphur or a lighted taper, whereas the other oxides require well-ignited phosphorus for this purpose.

The combustion of a taper or sulphur in nitrous oxide is more vigorous than in air, for the same reason that phosphorus burns more brightly in nitric oxide than in air,

namely, that nitrous oxide contains a higher percentage of oxygen than air.

That nitrous oxide is *not* a *mixture* of nitrogen and oxygen may be further shown by the following experiment:—

Exp. 250.—Prepare a cylinder of nitric oxide as in Exp. 225. Bring this cylinder mouth to mouth with a cylinder of nitrous oxide and remove the glass plates. No brown fumes are formed (unless you allow air to get to the mixture), showing that *no free oxygen* is present.

238. Composition of Nitrous Oxide by Volume.—By burning phosphorus in a confined volume of nitrous oxide we may readily show that the gas *contains its own volume of nitrogen.*

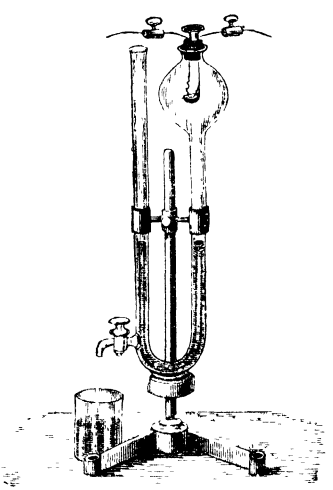


Fig. 79.

† **Exp. 251.**—The experiment is carried out in the apparatus shown in Fig. 79. This consists of a glass U-tube one limb of which terminates in a glass globe. The mouth of the globe is closed by a hollow ground-glass stopper into which are cemented two stout copper wires. One of these carries a small bone-ash dish, and from the other depends a piece of thin platinum wire which rests in the dish and is also in contact with the wire carrying the dish.

Fill the tube with mercury up to a point slightly below the globe. Close the mouth of the globe by a cork carrying a delivery tube reaching nearly to the mercury, and a small

exit tube (see Fig. 80). Pass nitrous oxide (prepared as in Exp. 246 and dried by passing through strong sulphuric acid contained in a wash-bottle) through the delivery tube for about ten minutes, in order to drive out all the air from the globe. The gas issuing from the exit tube should rekindle a glowing splint before you stop the current.

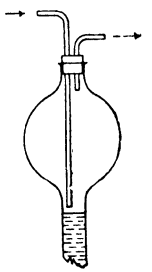


Fig. 80.

Now place a small piece of phosphorus in the bone-ash dish and arrange so that the platinum wire is in contact with the phosphorus as well as with the lead carrying the dish. Rapidly remove the cork from the globe and insert the stopper. Mark the level of the mercury (which will be the same in the two limbs) by means of a piece of gummed paper. Now run out about two-thirds of the mercury from the tube. The gas is thus under reduced pressure, and there is no likelihood that its expansion due to the heat generated during the combustion will force the stopper out. Next pass an electric current from 3 or 4 Grove's cells through the wires. The thin platinum wire soon becomes hot enough to ignite the phosphorus.

When the combustion has ceased and the apparatus has been left sufficiently long to regain the temperature of the air, restore the levels of mercury in the two limbs to equality by pouring mercury into the open limb. You will find that the level of mercury is the same as it was before the combustion, showing that nitrous oxide contains its own volume of nitrogen.

239. Formula of Nitrous Oxide.—Since, as we have just shown, nitrous oxide contains its own volume of nitrogen, it follows from Avogadro's hypothesis that one molecule of nitrous oxide contains one molecule of nitrogen; the formula may therefore be written N_2O_x. But the density of nitrous oxide is 22, corresponding to a molecular weight 44; therefore the weight of oxygen in a molecule of the gas is $44 - 2 \times 14 = 16$ units. It

follows that $x = 1$ (since the atomic weight of oxygen is 16), and the formula is N_2O.

The composition of nitrous oxide may also be determined by exploding the gas with excess of hydrogen in a eudiometer The oxygen is converted into water and the residual gas consists of nitrogen and excess of hydrogen; the amount of the latter is estimated by exploding with excess of oxygen when two-thirds of the diminution in volume represents the hydrogen present.

The change which takes place when the nitrous oxide and hydrogen are exploded is represented by the equation—

$$N_2O + H_2 = H_2O + N_2.$$

240. Action of Nitric Acid on Magnesium.—

Exp. 252.—About one-third fill a test-tube with water, and add one-eighth the amount of concentrated nitric acid. Now drop in a few pieces of magnesium ribbon. There is a violent effervescence of a colourless gas. Cover the mouth of the tube loosely with your thumb so that the gas collects in the tube. In a short time apply a lighted match, immediately after removing your thumb. What do you observe?

You will notice that the tube soon becomes very hot and the gas then becomes slightly brownish and acquires the smell of nitrogen peroxide.

When the magnesium has completely dissolved add some caustic soda solution: a thick white precipitate forms. Now warm.

You will observe the characteristic odour of ammonia at the mouth of the tube. Confirm the presence of ammonia by introducing a piece of moist red litmus into the mouth of the tube: the colour changes to blue.

The gas which ignited with a "pop" in the previous experiment was *hydrogen*, so that magnesium is one of the few metals which *does* give hydrogen when acted upon by dilute nitric acid. *Ammonia* is also formed in large quantity in this reaction; it is not, however, evolved as such, but combines with the excess of nitric acid, forming

ammonium nitrate. You liberated it from this salt in the last experiment by the action of caustic soda—

$$NaOH + NH_4NO_3 = NaNO_3 + H_2O + \underset{\text{Ammonia}}{NH_3}.$$

The white precipitate which formed consisted of magnesium hydroxide, $Mg(OH)_2$; it was produced by the action of caustic soda on the magnesium nitrate, which resulted from the action of nitric acid on the magnesium—

$$Mg(NO_3)_2 + 2NaOH = Mg(OH)_2 + 2NaNO_3.$$

241. Aqua Regia.—The so-called "noble" metals, such as gold and platinum, are not acted upon by nitric acid of any strength, but readily dissolve in a mixture of hydrochloric and nitric acids,[1] which has for this reason been termed *aqua regia*.

The cause of the difference is that hydrochloric and nitric acids mutually interact, setting free chlorine, which, especially in the nascent state, readily attacks gold and platinum—

$$3HCl + HNO_3 = NOCl + Cl_2 + 2H_2O.$$

242. Uses of Nitric Acid.—Nitric acid is largely used in the manufacture of a number of important substances, such as sulphuric acid, nitroglycerine, guncotton, colours, and nitrates. Among the last may be mentioned silver nitrate, which is used in photography, strontium and barium nitrates, which are used in pyrotechny, and lead nitrate, which is employed in calico-printing Nitric acid is also used in Grove's and Bunsen's electric batteries.

243. Nitrogen Pentoxide, or Nitric Anhydride, N_2O_5.—This is a white crystalline solid obtained by the action of a powerful dehydrating agent, such as phosphorus pentoxide, on nitric acid. The acid is introduced into a retort and well cooled by means of a freezing mixture. A quantity of phosphoric oxide equivalent

[1] *Aqua regia* is usually made by mixing nitric acid with three or four times its volume of hydrochloric acid.

to the acid used is gradually added, and on now gently warming the mixture nitrogen pentoxide distils over and is collected in a cooled receiver—

$$4HNO_3 + P_4O_{10} = 2H_2P_2O_6 + 2N_2O_5.$$

Nitrogen pentoxide enters into combination with water with great energy, reproducing nitric acid; it is therefore the *anhydride* of this acid—

$$N_2O_5 + H_2O = 2HNO_3.$$

The pentoxide is an unstable body and undergoes decomposition with explosive violence when heated.

244. Nitrogen Trioxide, or Nitrous Anhydride, N_2O_3, is obtained as a deep-blue liquid by passing nitric oxide into nitrogen peroxide, the temperature not being allowed to rise above — 21° C.,

$$NO + NO_2 = N_2O_3.$$

It is a very unstable compound, and even at — 20° C. commences to decompose into nitrogen peroxide and nitric oxide according to the equation—

$$N_2O_3 = NO_2 + NO.$$

When nitrogen trioxide passes into the gaseous state it undergoes almost complete decomposition in accordance with the above equation. Until recently it was supposed that the decomposition was complete, but it has now been shown that a small proportion of N_2O_3 molecules remain undecomposed in equilibrium with the NO and NO_2 molecules.

QUESTIONS.—CHAPTER XVII.

1. Describe an experiment by which oxygen gas can be obtained from nitric acid.
2. Give striking experiments calculated to illustrate the powerful oxidising action of nitric acid.
3. How would you prepare the nitrates of lead and potassium, and obtain them in the form of crystals?

4. Describe how you would investigate the action of (1) dilute nitric acid, (2) strong nitric acid on copper. What results would you obtain?

5. Describe how you would proceed to prepare a small quantity of nitric acid from nitre. Sketch the apparatus you would employ. What would you observe on dropping the following into strong nitric acid: (1) zinc, (2) red-hot charcoal? Explain the changes which take place as far as you can.

6. Describe fully the action of heat on the nitrates of the following metals: (1) lead, (2) copper, (3) potassium.

7. How would you proceed to prove that nitric oxide contains nitrogen and oxygen? State and explain what you would observe on removing the cover from a jar of nitric oxide.

8. Compare the results obtained on introducing (1) a lighted taper, (2) feebly burning sulphur, (3) well-ignited sulphur, (4) feebly burning phosphorus, (5) well-ignited phosphorus into jars of (*a*) nitric oxide, (*b*) nitrous oxide, (*c*) nitrogen peroxide. How do you account for the differences observed in view of the fact that all these compounds are composed of nitrogen and oxygen only?

9. Describe how you would proceed to prepare crystals of ammonium nitrate. What is the gas evolved on heating this substance? Sketch the apparatus you would use in order to prepare and collect the gas. Also describe the experiments you would perform in order to illustrate its chief properties.

10. How would you test whether or not an aqueous solution contained a nitrate in solution? Explain the test you describe.

11. Describe a method of proving that (1) nitrous oxide contains its own volume of oxygen, (2) nitric oxide contains half its volume of nitrogen. Give diagrams of the apparatus you would employ.

12. How would you proceed to prepare a jar of *pure* nitric oxide? Sketch the apparatus you would use.
13. What is the chemical formula for the molecule of nitric oxide? Explain how this formula is established.
14. Describe experiments which illustrate the chief properties of nitrogen peroxide.
15. Under what conditions do nitrogen and oxygen combine directly? What is the name of the product, how is it usually prepared, and what is the action of water upon it?
16. When potassium iodide, sulphuric acid, and starch solution are added to an aqueous solution of the residue which remains after heating sodium nitrate a blue colour is developed. Explain this.
17. What is *aqua regia*, and on what does its special power as a solvent of metals depend?
18. What are the chief uses of nitric acid?
19. What is the action of heat on a solution of nitrous acid?
20. Give examples (with equations) of (*a*) the oxidising action, (*b*) the reducing action of nitrous acid.
21. By what chemical reactions may nitrites be distinguished from nitrates?
22. How may nitric anhydride be prepared, and what are its chief properties?
23. Describe how you would proceed to investigate the action of nitric acid on magnesium. State the results you would obtain.

CHAPTER XVIII.

SULPHUR AND ITS COMPOUNDS.

SULPHUR.

245. Occurrence.—Sulphur is one of the comparatively few elements which occur in quantity in the uncombined condition. In Europe it is found in the neighbourhood of active or extinct volcanoes in Italy, Sicily, Iceland, etc., being usually associated with mineral matter. In combination with hydrogen it is found as sulphuretted hydrogen in certain mineral springs, and with many metals as mineral sulphides, such as iron pyrites, FeS_2; galena, PbS; zinc blende, ZnS; and cinnabar, HgS. Sulphates of calcium (gypsum) and barium (heavy spar) also occur in some localities in considerable quantity. We see then that sulphur either free or in combination is widely distributed.

246. Examination of Sulphur.—We meet with sulphur commonly in the two forms of brittle rolls, *roll sulphur* or "*brimstone*," and of a fine powder, *flowers of sulphur*. Both of these have a characteristic yellow colour.

Exp. 253.—Examine specimens of sulphur. Shake and boil some sulphur with water, filter and evaporate the filtrate to dryness: note if any residue is left. Heat a small quantity of sulphur on a crucible lid: note any changes.

We observe that sulphur is insoluble in water, and that when heated it melts, turns brown, and then burns with a blue flame, and with the characteristic smell of "burning sulphur." The colour change is worth more careful examination.

Exp. 254.—Take a boiling tube or small round-bottomed flask, and in it place about 50 gm. of sulphur. Warm it gently over a small flame, shaking it all the time. Note any changes and finally allow it to cool again.

We see that sulphur, when heated, first melts to a yellow liquid which rapidly darkens in colour; it then becomes very viscous and brown (at about 250° C.); finally it becomes more liquid again, remaining dark brown until it boils (at about 450° C.). The vapour is reddish-brown and has practically no smell; it condenses as a yellow powder ("flowers of sulphur") in the upper part of the tube or neck of the flask. As the boiling sulphur cools it passes through all the preceding changes in the reverse order.

Now, although sulphur does not dissolve in water, yet it is soluble in some other liquids. One of these is carbon bisulphide, as we saw in Exp. 48.

Exp. 255.—Repeat Exp. 48 and make a sketch of the most symmetrical crystal obtained.

N.B.—The student is reminded that carbon disulphide is a very volatile and extremely inflammable liquid, and that it is therefore **very dangerous** to bring the liquid within a yard of a flame.

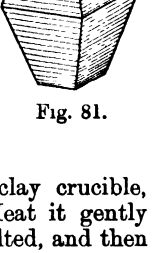


Fig. 81.

Sulphur separates out from solution in carbon bisulphide in pale yellow transparent crystals of the type called *octahedral*, represented in Fig. 81.

Exp. 256.—Take a small beaker or fireclay crucible, and in it put about 30 gm. of sulphur. Heat it gently over a small flame till the sulphur is just melted, and then remove the flame. When a crust has formed pierce two holes through it and pour out the hot liquid from the interior. Crystals are found projecting from the sides of the crucible and hanging from the crust (see Fig. 82). Note their shape. Drop a few of them into a little carbon bisulphide: they dissolve readily.

The crystals obtained in the last experiment differ greatly in appearance from those which separate out from solution in carbon bisulphide. They consist of *long prismatic needles* having an amber colour.

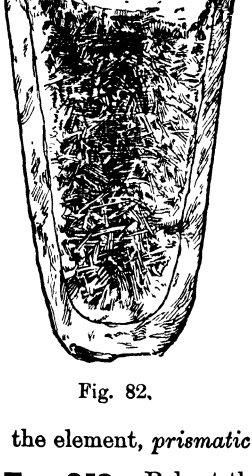


Fig. 82.

Exp. 257.—Leave the octahedral and prismatic crystals of sulphur which you have prepared in Exps. 255, 256 exposed to the air for two or three days. Examine them again.

Octahedral sulphur undergoes no change when exposed to air, whilst prismatic sulphur soon becomes *opaque*. This is because it has changed into a mass of small octahedral crystals. We see then that *octahedral* sulphur is a *stable* form of the element, *prismatic* sulphur an *unstable* form.

Exp. 258.—Reheat the sulphur used in Exp. 254 until it has passed through the viscous stage and has become thin again; then pour the liquid into water. Note the characters of the solid. Shake up a portion of it with carbon bisulphide; it does not dissolve. Leave the remainder to stand for a day and re-examine.

In this experiment we have a third form of sulphur—a soft amber-coloured amorphous variety which can be drawn out like indiarubber and is called *plastic sulphur*. This form is insoluble in carbon bisulphide. It is unstable and soon changes into a hard brittle mass of minute octahedral crystals.

247. Allotropes of Sulphur.—We have now prepared sulphur in three different forms, viz.:—

(1) Octahedral sulphur. (2) Prismatic sulphur.
(3) Plastic sulphur.

Since they are actually made from sulphur and sulphur only they must be allotropes of the element. Of these three forms only one—octahedral sulphur—is stable at the ordinary temperature; the other two forms soon change into it, as we have seen.

Roll sulphur and flowers of sulphur are not allotropes of sulphur distinct from the above. They both consist mainly of minute octahedral crystals, which are so small, however, that they cannot be distinguished without the aid of a lens.

Exp. 259.—Examine some roll sulphur and flowers of sulphur with a pocket lens. Note their crystalline structure.

Now shake up a small quantity of flowers of sulphur with some carbon bisulphide in a test-tube. Note that the greater part dissolves, but a small proportion remains undissolved. Filter. Examine the yellow powder on the filter paper with a lens: it is *amorphous*.

Flowers of sulphur then contains a small percentage of *amorphous* sulphur, which is insoluble in carbon bisulphide. This form gradually changes into octahedral crystals; it has practically the same specific gravity as plastic sulphur, and is essentially the same form of the element. Roll sulphur also contains a small proportion of amorphous sulphur—less, however, than flowers of sulphur.

The different forms of sulphur have slightly different physical constants, as indicated in the following table (in which their behaviour towards carbon bisulphide is also included).

Form.	Melting-point.	Specific Gravity.	Behaviour towards Carbon Bisulphide.
Octahedral	114·5° C.	2·05	Soluble
Prismatic	119·0° C.	1·96	,,
Plastic	114·5° C.	1·95	Insoluble

248. Milk of Sulphur.—This is a variety of sulphur which is much used in medicine. It is produced as a very finely divided white precipitate when a dilute acid is added to solutions of certain sulphur compounds, such as calcium-pentasulphide (formed by boiling flowers of sulphur with milk of lime) and "yellow ammonium sulphide."

Exp. 260.—Add a little hydrochloric acid to a solution of yellow ammonium sulphide. Note the white precipitate which forms. Filter. Note that the filtrate is cloudy, showing that some of the precipitate has passed through. The particles of sulphur must be very small for this to happen.

Milk of sulphur is soluble in carbon bisulphide and consists of octahedral sulphur in a very finely divided state; the smallness of the particles explains why the colour is *white* instead of *yellow*.

249. Extraction of Sulphur.—Sulphur is largely extracted from the crude native sulphur found in the region of volcanoes such as Mount Etna.

The process is carried out as follows:—Impure native sulphur is stacked in a brick kiln on a sloping floor, vertical air spaces being left at intervals. The sulphur is lighted at the bottom; a small quantity burns and the heat produced melts out the rest. The melted sulphur runs down the sloping floor and collects in a trough placed to receive it.

The further purification of the sulphur may be effected by distillation in an iron retort, the vapours being passed into a brick chamber where they condense (Fig. 83). At the outset when the chamber is cool the product obtained is flowers of sulphur, for just as water vapour at temperatures below zero (the melting-point of ice) condenses in the form of snow, so in the case of sulphur there is formed by rapid cooling finely-divided sulphur.

When the temperature of the chamber rises above the melting-point of sulphur, the product of the condensation is *liquid* sulphur, and this is run off into moulds where it is cast into sticks of roll sulphur as "brimstone."

Sulphur is also obtained on the large scale from iron pyrites, FeS_2, by heating the pyrites in a retort to the end of which is attached a long vertical tube. Sulphur is

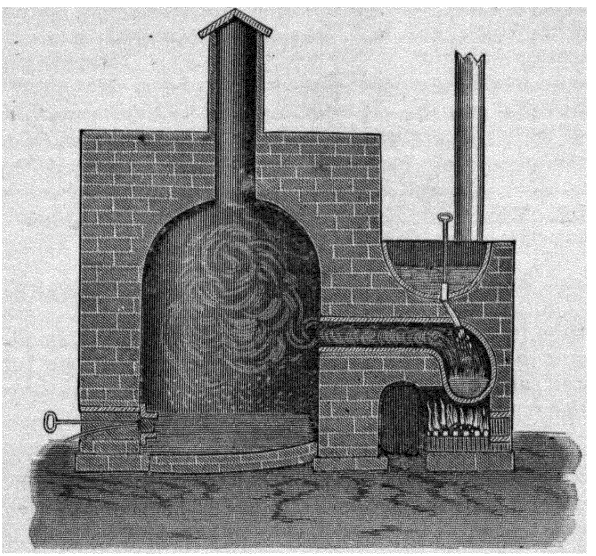


Fig. 83.

driven off in the state of vapour, condenses in the tube, and runs into water contained in a suitable vessel. The decomposition of the pyrites is represented by the following equation—

$$3FeS_2 = Fe_3S_4 + S_2.$$

250. Uses of Sulphur.—Sulphur is largely used in the arts for the production of matches, gunpowder, sulphuric acid, and as a source of sulphurous acid for bleaching wool, straw, and silk.

The use of milk of sulphur in medicine has already been referred to.

Sulphur Dioxide, SO_2.

251. Formation of Sulphur Dioxide.—We have already seen that sulphur burns in air (Exps. 19, 253) or oxygen (Exp. 33), forming a colourless gas, *sulphur dioxide*, which has a characteristic pungent smell (of "burning sulphur"). Since the gas is formed when sulphur burns in *oxygen alone* it must be a compound of *sulphur and oxygen.* It is represented by the formula SO_2.

Let us now investigate other methods of obtaining the gas:—

252. Effect of heating Metallic Sulphides in Air.—

Exp. 261.—Powder a little iron pyrites, and heat it in a 12 cm. length of glass tubing open at each end. Hold the tube in a slanting position. After a time the smell of sulphur dioxide is perceived at the upper end of the tube, as well as a sublimate of sulphur. A reddish-brown powder remains.

Iron pyrites is a compound of iron and sulphur, FeS_2. When heated in air it takes up oxygen with formation of sulphur dioxide and ferric oxide (Fe_2O_3); the latter constitutes the reddish-brown residue. Some of the sulphur, however, escapes combustion and forms the sublimate observed. On the large scale sulphur dioxide is prepared chiefly by burning iron pyrites.

Many other metallic sulphides, *i.e.* compounds of metals and sulphur, behave in a similar manner to iron pyrites when heated strongly in air, *i.e.* the sulphur is converted into sulphur dioxide and an oxide of the metal or the metal remains.

253. Action of Concentrated Sulphuric Acid on Metals.—

Exp. 262. *Action of Concentrated Sulphuric Acid on Copper.*—Introduce a small quantity of copper turnings into a test-tube and cover with concentrated sulphuric acid. No

action takes place. Now heat. You will observe just at first a distinct smell of sulphuretted hydrogen. As the heating is continued effervescence takes place and white fumes are evolved having the characteristic smell of sulphur dioxide. The copper rapidly goes black and after a time a dark greyish powder settles at the bottom of the tube.

When the copper has disappeared, allow to cool, carefully pour off the liquid from the residue, add a little water to the latter, and shake up. Part of the powder dissolves and a blue solution is formed; an insoluble black residue remains at the bottom of the test-tube. Filter the solution, evaporate to small bulk, and allow to cool. Blue crystals separate out. These consist of *copper sulphate.*

The results of the previous experiment are explained as follows:—The copper was converted by the acid partly into anhydrous copper sulphate (white) and partly into cuprous sulphide, Cu_2S (black), the acid being simultaneously reduced to sulphur dioxide. Both of the copper compounds are insoluble in strong sulphuric acid, and they formed the dark grey powder which settled at the bottom of the test-tube. When the contents of the tube were poured into water the anhydrous copper sulphate combined with part of the water to form the hydrated salt, which is blue; this then dissolved, forming a blue solution. The cuprous sulphide, being insoluble, remained as black powder.

Without taking into account the cuprous sulphide the change may be represented by the following equation—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Exp. 263. *Action of Concentrated Sulphuric Acid on Zinc.*—Now add some concentrated sulphuric acid to a little zinc contained in a test-tube. There is hardly any action in the cold; a few bubbles only collect on the surface of the metal. [These are hydrogen.] Now warm. Sulphur dioxide is evolved and a yellow deposit of sulphur forms in the tube.

Here the chief change which takes place may be represented by the equation—

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

When many other metals are heated with concentrated sulphuric acid, sulphur dioxide is evolved and the metal is converted into its sulphate.

254. Action of Sulphuric Acid on Non-Metals.—

Exp. 264.—Heat a little charcoal with some concentrated sulphuric acid in a test-tube. Note the smell of sulphur dioxide. The charcoal gradually disappears.

It can be shown that carbon dioxide is evolved as well as sulphur dioxide in this reaction, the change being represented by the equation—

$$C + 2H_2SO_4 = CO_2 + 2SO_2 + 2H_2O.$$

Sulphur dioxide is also produced when sulphur is heated with concentrated sulphuric acid—

$$S + 2H_2SO_4 = 3SO_2 + 2H_2O.$$

We see then that sulphur dioxide may be obtained by the action of certain non-metals on concentrated sulphuric acid as well as by the action of metals.

255. Action of Acids on Sulphites.—

Exp. 265.—Introduce a little sodium hydrogen sulphite, $NaHSO_3$ ("bisulphite of soda"), into a test-tube and add some dilute hydrochloric acid. Note that sulphur dioxide is evolved with effervescence.

This experiment illustrates a general property of *sulphites*, *i.e.* the salts of sulphurous acid, H_2SO_3, namely, that they are *all* decomposed by acids (even by such a relatively weak acid as acetic acid) with evolution of sulphur dioxide. The change which takes place in the case of sodium hydrogen sulphite is represented by the equation—

$$NaHSO_3 + HCl = NaCl + H_2O + SO_2.$$

256. Laboratory Preparation of Sulphur Dioxide.—For the preparation of sulphur dioxide in the laboratory the reaction investigated in Exp. 262 is utilised. Since the gas is very soluble in water it cannot be collected over water, but it may be collected by downward displacement, as it is more than twice as heavy as air.

Exp. 266. *To prepare and collect Sulphur Dioxide.*—Fit a flask of about $\frac{3}{4}$ litre capacity with a thistle funnel and delivery tube (Fig. 84). Place about 10 gm. of granulated copper in the flask, add 30 to 40 c.c. of concentrated sulphuric acid and heat on a sand bath, moderating the heat as soon as the action commences. Collect the gas in *dry* cylinders by displacement of air. As soon as a burning wood splint is extinguished at the mouth of a cylinder, cover the cylinder with a ground glass plate, and place another in position.

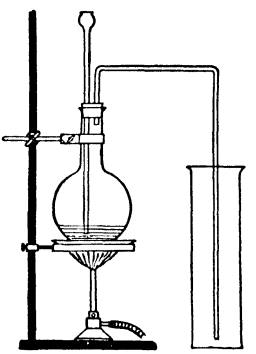


Fig. 84.

If the gas is required dry and pure it should be passed through a sulphuric acid wash-bottle and collected over mercury.

257. Properties of Sulphur Dioxide.—Sulphur dioxide is a heavy, colourless gas having a suffocating odour. It is very soluble in water, which at 0° C. dissolves 80 times its volume of the gas, and at 10° C. 56 times its volume, the solution having an acid reaction.

Exp. 267.—Invert a cylinder of sulphur dioxide in water. The water rises rapidly, showing the great solubility of the gas. Note the acid properties of the solution (which contains *sulphurous acid*), and observe also that it possesses the odour of the gas.

Sulphur dioxide condenses to a liquid under ordinary atmospheric pressure at — 8° C., and under 2 atmospheres pressure at 0° C. It can therefore be obtained *as a liquid* by passing the gas into a vessel surrounded by ice and salt.

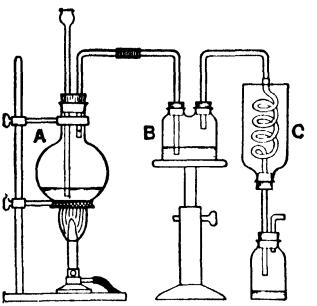


Fig. 85.

The process may conveniently be carried out on the small scale as follows:— Sulphur dioxide is generated in A (Fig. 85) as described in Exp. 262 and is dried in B. It then passes through a spiral glass tube immersed in a freezing mixture of ice and salt contained in the inverted bell-jar C. Here it liquefies and runs down into the glass bottle D, which is also immersed in a mixture of ice and salt. If it is desired to preserve the liquid, it should be collected in a strong glass flask, the neck of which is contracted near the top; when sufficient of the liquid has been run into the flask the neck is sealed off at the contracted part.

Sulphur dioxide does not burn, and does not as a rule support combustion. Metallic potassium, however, when previously ignited, will burn at the expense of oxygen.

Exp. 268.—Put a lighted taper into a jar of the gas: it will be extinguished; nor will the gas itself burn. Show that metallic potassium, when previously ignited, will burn in the gas.

Finely-divided iron will also burn when heated in the gas.

Sulphur dioxide is a strong antiseptic, *i.e.* it kills microbes. On this account it is used for disinfecting rooms and for preserving meat.

258. Reducing and Bleaching action of Sulphur Dioxide.—Sulphur dioxide is a strong reducing agent; its powers as an antiseptic and as a medium for bleaching silk,

straw, and wool are due to its affinity for oxygen. Chlorine bleaches in consequence of its bringing about the oxidation of the colouring matter; sulphur dioxide bleaches, on the contrary, in consequence of its reducing action. The one liberates *oxygen* from water—

$$Cl_2 + H_2O = 2HCl + O,$$

(O: Nascent oxygen)

the other liberates *hydrogen*—

$$H_2SO_3 + H_2O = H_2SO_4 + 2H.$$

(H_2SO_3: Sulphurous acid; H_2SO_4: Sulphuric acid; 2H: Nascent hydrogen)

The nascent hydrogen produced then combines with the colouring matter to produce a colourless compound. In many cases the colour is restored by exposure to air, when the oxygen of the air oxidises the colourless compound back to the original coloured substance. In some cases of bleaching by sulphur dioxide the coloured compound *combines directly with* sulphur dioxide; in such cases the colour may be restored by the addition of an acid, which decomposes the colourless addition product with the evolution of sulphur dioxide. The sulphur dioxide addition product may be also acted upon by the oxygen and moisture of the air, whereby the sulphur dioxide is converted into sulphuric acid and the coloured compound again set free.

Exp. 269.—Throw some rose-leaves into a solution of sulphur dioxide: they are bleached. Now add a few drops of strong sulphuric acid: the colour is restored. Bleach some more of the leaves in the same manner, remove them from the solution, and leave them exposed to the air for some time. The colour will gradually return.

It must be noted that an aqueous solution of sulphur dioxide does not undergo decomposition in the complete absence of air or other oxidising agents; water and sulphur dioxide do not react to give sulphuric acid and hydrogen unless there is some substance present to take up the hydrogen. In the presence of air the solution gradually absorbs oxygen, and the following change takes place—

$$2SO_2 + 2H_2O + O_2 = 2H_2SO_4.$$

(O_2: From the air)

Another good example of the reducing action of sulphur dioxide is its power of converting ferric salts into ferrous salts. Thus ferric sulphate is reduced to ferrous sulphate, and ferric chloride to ferrous chloride—

$$Fe_2(SO_4)_3 + SO_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4.$$
$$2FeCl_3 + SO_2 + 2H_2O = 2FeCl_2 + H_2SO_4 + 2HCl.$$

Potassium permanganate and potassium chromate are also readily reduced, the change being rendered conspicuous by the alterations in colour which result, the purple permanganate being decolorised, and the yellow chromate turned green.

Exp. 270.—Add a solution of sulphur dioxide in water to solutions of potassium permanganate and potassium chromate respectively. Note the colour changes; they may be used as tests for sulphur dioxide, both in the gaseous state and in solution. Potassium chromate is more usually employed for this purpose than potassium permanganate.

259. How to work out an Equation.—It will be useful to discuss the mode of arriving at the equations which express the reactions taking place. Taking the case of potassium permanganate we know that the substances we start with are potassium permanganate, sulphur dioxide, and water, and the products are potassium sulphate and free sulphuric acid. Now potassium permanganate may be considered as made up of two oxides, K_2O and Mn_2O_7 ($K_2O + Mn_2O_7 = K_2Mn_2O_8 = 2KMnO_4$), and manganese sulphate of MnO and SO_3. We may therefore represent the reduction of potassium permanganate to manganese sulphate by reference to the corresponding oxides of manganese, thus—

$$Mn_2O_7 \rightarrow 2MnO + 5O.$$

But Mn_2O_7 corresponds to two molecules of potassium permanganate, and therefore *two molecules of* $KMnO_4$ *yield five atoms of oxygen available for oxidising purposes,*

i.e. of so-called "available oxygen." Now, one molecule of sulphur dioxide requires one atom of oxygen to convert it into sulphur trioxide, the oxide corresponding to sulphuric acid; consequently 5 atoms of oxygen will oxidise 5 molecules of sulphur dioxide. We can now write down the left-hand side of the equation with the exception of an unknown quantity of water, say x molecules—

$$2KMnO_4 + 5SO_2 + xH_2O = \quad .$$

Now since the potassium goes to potassium sulphate and the manganese to manganese sulphate, the right-hand side of the equation may be written—

$$= K_2SO_4 + 2MnSO_4 + yH_2SO_4,$$

where y has to be determined.

It is easy to see that $y = 2$, for only two atoms of sulphur of the $5SO_2$ remain to be accounted for. So far then we may write the equation—

$$2KMnO_4 + 5SO_2 + xH_2 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

But on the right side of the equation we have four atoms of hydrogen, and in order that the left-hand side may have the same number we must make $x = 2$. The correct equation is, therefore—

$$\underset{\text{Violet}}{2KMnO_4} + 5SO_2 + 2H_2O = K_2SO_4 + \underset{\substack{\text{Colourless}\\ \text{(in dilute solution)}}}{2MnSO_4} + 2H_2SO_4.$$

In the case of potassium chromate there is not enough sulphuric acid produced to convert all the potassium and chromium into sulphates, so that some free sulphuric acid must be added. Reasoning in a similar manner to that adopted above the equation representing the reaction is found to be—

$$\underset{\text{Yellow}}{2K_2CrO_4} + 3SO_2 + 2H_2SO_4 = 2K_2SO_4 + \underset{\text{Green}}{Cr_2(SO_4)_3} + 2H_2O.$$

260. Composition of Sulphur Dioxide by Volume.—This may be determined by burning sulphur in oxygen in the apparatus represented in Fig. 86. First the apparatus is *dried thoroughly* by passing hot air through it. (This

is done by attaching a piece of glass tubing to the rubber attachment of a foot-bellows, heating the glass tube in a Bunsen and then driving air through the hot tube the end of which is placed in the U-tube.) Dry mercury (dried by standing in a warm place for some time) is now introduced into the apparatus up to a point just below the globe, and then the air of the globe is displaced by dry oxygen, which is prepared as in Exp. 29 and dried by passing through concentrated sulphuric acid; the method of filling the globe is described in Exp. 251. The level of the mercury is marked by means of gummed paper. The pressure of the oxygen is now reduced by running mercury out, and then a little sulphur burned in it just as in Exp. 251 you burnt phosphorus in nitrous oxide. It is found that, when the apparatus has cooled down and the pressure of the residual gas is made atmospheric again by pouring in mercury through the open limb, the level of the mercury is unchanged.

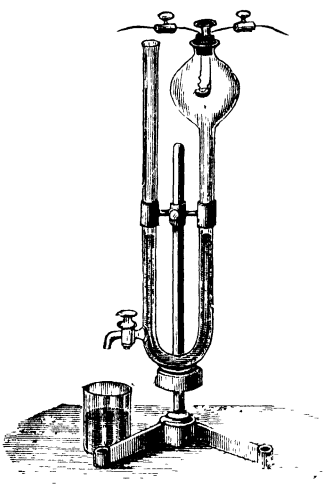


Fig. 86.

This experiment shows that the sulphur dioxide produced by the combustion of sulphur occupies the same volume as the oxygen from which it is formed, i.e. *sulphur dioxide contains its own volume of oxygen.*

261. Formula of Sulphur Dioxide.—Since, as we have just seen, sulphur dioxide contains its own volume of oxygen, it follows from Avogadro's hypothesis that one molecule of sulphur dioxide contains one molecule of

oxygen, *i.e.* the formula of sulphur dioxide may be written S_xO_2 (since O_2 represents the molecule of oxygen).

Now the density of sulphur dioxide relative to hydrogen is 32, so that its molecular weight is 64.

We have therefore—

$$S_xO_2 = 64.$$

But $$O_2 = 2 \times 16 = 32.$$

$$\therefore S_x = 64 - 32 = 32,$$

i.e. $x = 1$, since the atomic weight of sulphur is 32. The formula for sulphur dioxide is therefore

$$SO_2.$$

262. Sulphurous Acid and Sulphites.—We have seen that sulphur dioxide dissolves readily in water, forming an acid. This acid has never been isolated from its dilute aqueous solution, any attempt to concentrate the solution resulting in decomposition with loss of sulphur dioxide. A large number of salts of the acid are known, however, and from their composition that of the acid is deduced. The formulae of some of these salts are—

$$Na_2SO_3,\ K_2SO_3,\ CaSO_3;$$
$$NaHSO_3,\ KHSO_3.$$

These salts are clearly derived from an acid—

$$H_2SO_3\ (= H_2O + SO_2),$$

those in the first row being *normal* salts and those in the second row *acid* salts.

The sulphites of the alkali metals may be prepared by passing sulphur dioxide into solutions of the corresponding hydroxides or carbonates.

Exp. 271.—Take 50 c.c. of a solution of caustic soda, and pass sulphur dioxide into it till it is saturated with the gas. The result is an apple green solution containing sodium hydrogen sulphate, $NaHSO_3$, but which does not easily give crystals of that composition.

$$NaOH + SO_2 = NaHSO_3.$$

Now saturate another 50 c.c. of the caustic soda solution with sulphur dioxide and then add the same quantity of caustic soda. Crystals separate out on standing. Filter them off and dry.

These crystals consist of the normal sulphite, Na_2SO_3, the acid sulphite first formed reacting with a second molecule of caustic soda thus—

$$NaOH + NaHSO_3 = Na_2SO_3 + H_2O.$$

In a similar way, substituting caustic potash for caustic soda, the sulphites of potash may be prepared. The normal sulphites of all metals excepting the alkali metals are insoluble in water, and may be obtained as precipitates by the addition of a soluble salt of the metal to a solution of an alkaline sulphite. Thus if barium chloride is used a white precipitate of barium sulphite is formed—

$$BaCl_2 + Na_2SO_3 = BaSO_3 + 2NaCl.$$

Sulphites slowly take up oxygen from the air, passing into sulphates. Sodium sulphite, for example, is converted into sodium sulphate—

$$2Na_2SO_3 + O_2 = 2Na_2SO_4.$$

As already mentioned, all sulphites are decomposed by acids with evolution of sulphur dioxide.

Sulphur Trioxide, SO_3.

263. Formation of Sulphur Trioxide.—Not only does sulphur dioxide take up oxygen in the presence of water as we saw in § 258; the two gases are also capable of combining directly in the presence of certain heated substances, such as *spongy platinum*[1] or *ferric oxide*, which act as catalytic agents. The oxide formed by the combination of sulphur dioxide with oxygen is called *sulphur trioxide*; obviously it contains a higher percentage of

[1] Prepared by heating asbestos saturated with a solution of ammonium platinum chloride. The metal is deposited on the asbestos in a finely divided state.

oxygen than the dioxide. It is represented by the formula SO_3, and the equation expressing its formation from sulphur dioxide is—

$$2SO_2 + O_2 = 2SO_3.$$

The apparatus shown in Fig. 87 may be employed to illustrate the formation of sulphur trioxide. The left-hand half of the figure represents a sulphur dioxide appar-

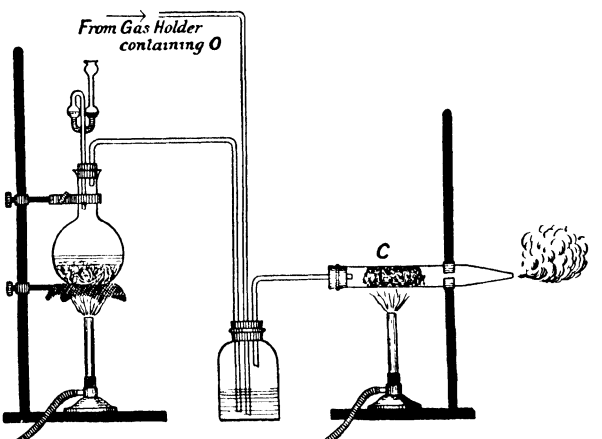


Fig. 87.

atus. This gas is passed through concentrated sulphuric acid in the bottle to remove moisture, and together with it oxygen from a gas-holder. Both gases then pass over the heated spongy platinum in the horizontal tube, and dense white fumes appear at the exit.

These are fumes of sulphur trioxide. If the fumes are led into a test-tube immersed in ice, white silky needles are obtained.

Sulphur trioxide may also be obtained by distilling sulphuric acid with a powerful dehydrating agent, such as phosphoric oxide when water is removed—

$$P_4O_{10} + 2H_2SO_4 = 2H_2P_2O_6 + 2SO_3.$$

264. Properties of Sulphur Trioxide.—At ordinary temperatures sulphur trioxide forms white transparent needles, which melt at 15° C. and boil at 46° C.; at a red heat it breaks up into sulphur dioxide and oxygen. It combines very eagerly with water, evolving much heat, and in contact with water gives a hissing sound like that of the quenching of hot iron; sulphuric acid is thereby formed according to the equation—

$$H_2O + SO_3 = H_2SO_4.$$

It is of interest to add that sulphur trioxide enters into direct combination with certain metallic oxides, with the production of the corresponding sulphates: for instance, when baryta (barium oxide) and sulphur trioxide are mixed they combine to form barium sulphate, and so much heat is evolved that the mass becomes red-hot—

$$BaO + SO_3 = BaSO_4.$$

Sulphuric Acid, H_2SO_4.

265. Formation of Sulphuric Acid from Green Vitriol.—Sulphuric acid was first obtained from green vitriol (crystallised ferrous sulphate); hence its common name *oil of vitriol.*

Exp. 272.—Heat carefully some crystals of green vitriol (ferrous sulphate) in a test-tube, holding the tube with the open end directed downwards, so that any liquid formed does not run back into the hot part of the tube. After a time a yellowish liquid collects, and, if it tends to run out of the tube, a second test-tube may be placed in a convenient position to catch it. The liquid is found to be strongly acid to litmus, and to give a white precipitate with barium chloride; hence it is *sulphuric acid.*

The residue in the tube consists of reddish-brown ferric oxide.

266. Manufacture of Sulphuric Acid.—We have seen that an aqueous solution of sulphur dioxide gradually takes up oxygen from the air and becomes sulphuric acid, but the change is slow, and sulphuric acid cannot be obtained in quantity by this method.

If, however, a substance is present which readily gives up oxygen the change proceeds much more rapidly. On the large scale the following method is adopted:—Sulphur dioxide, air, steam, and a little nitric acid vapour are allowed to interact in large chambers. The first change which takes place is the reduction of the nitric acid to nitric oxide by the sulphur dioxide, thus—

$$(1)\ 3SO_2 + 2HNO_3 + 2H_2O = 3H_2SO_4 + 2NO.$$

The nitric acid then takes up oxygen from the air, forming nitrogen peroxide—

$$(2)\ 2NO + O_2 = 2NO_2.$$

This nitrogen peroxide oxidises a further quantity of sulphur dioxide with formation of sulphuric acid (in the presence of water), and nitric oxide is re-formed—

$$(3)\ SO_2 + NO_2 + H_2O = H_2SO_4 + NO.$$

Reaction (2) is then repeated, followed again by (3). The change thus becomes *continuous*, nitric oxide acting as a "carrier" of oxygen from the air to the sulphur dioxide; so that only a small quantity of nitric acid is theoretically required to bring about the conversion of an indefinitely large amount of sulphur dioxide, oxygen, and water into sulphuric acid.

It is, however, observed that if the chambers are insufficiently supplied with steam, white crystals ("lead chamber crystals") are formed, consisting of a substance the chemical name of which is nitro-sulphonic acid. According to the above theory the formation of nitro-sulphonic acid is not essential to the process, and does not occur in chambers working normally. Other more complex explanations have therefore been proposed, but their consideration is outside the limits of this work.

In brief outline the process is carried out as follows on the large scale:—

The *sulphur dioxide* in works where a very pure acid is made is obtained by burning brimstone, but in the very large majority of cases iron pyrites is used as the source of the gas. This is burnt in a series of "kilns," and the heat arising from the combustion is sufficient to render the operation continuous, fresh charges being added from time to time—

$$4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2.$$

The *nitric acid* from which the oxides of nitrogen are derived is prepared by the action of concentrated sulphuric acid on Chili saltpetre, $NaNO_3$—

$$NaNO_3 + H_2SO_4 = NaHSO_4 + HNO_3;$$

the acid fumes are carried into the flues along which the sulphur dioxide and air pass, and there intermingle with these gases.

The *air* is drawn in through the pyrites burners or kilns, the draught being maintained by means of a chimney, and by adjustment of the doors of the kilns so as to admit the quantity of air which experience has shown to be necessary.

The *steam* is supplied from low pressure boilers, and introduced into the "chambers" in such a way as to become intimately associated with the other products.

The reaction ending in the production of sulphuric acid does not take place under the circumstances very rapidly, and it is necessary to provide for a lengthened period of contact between the various bodies which take part in it. The gases are led into a series of large chambers where they meet with the steam. These are usually three in number, and have a total capacity of 100,000 to 150,000 cubic feet, the relation of the sulphur burnt to the capacity of the chamber being such that the average time occupied by the gas in traversing the chambers is something like three hours. The walls and floor of the chambers are constructed of sheet-lead supported on a wooden framework, lead being a metal which is scarcely attacked at all by sulphuric acid of the strength produced in the chambers.

The chambers are kept cool enough to serve as condensers, so that the acid collects on the floor, and is drawn off periodically.

267. Laboratory representation of the Sulphuric Acid Manufacture.—The formation of sulphuric acid may be represented in the laboratory by taking a large flask (5 litres) and fitting it with a cork provided with five holes through which pass tubes delivering—

(1) Sulphur dioxide (for preparation see Exp. 266),
(2) Nitric oxide („ „ „ Exp. 225),
(3) Steam,
(4) Oxygen from a gasholder;

while the fifth hole is provided with a tube opening into the air. The arrangement is shown in Fig. 88.

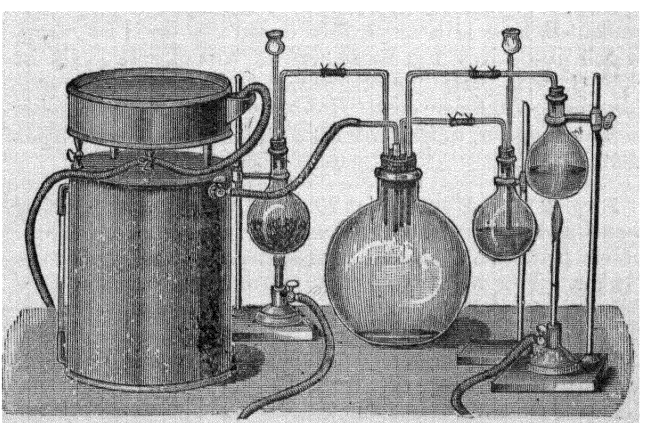


Fig. 88.

Pass some sulphur dioxide, nitric oxide, steam, and oxygen into the flask, then shut off the steam supply; crystals of nitrosulphonic acid (lead chamber crystals) may be seen to form. On clearing the flask of red fumes by a current

of oxygen, and then passing in more steam, these crystals will dissolve with the evolution of red fumes. After allowing the reaction to go on for some minutes, the liquid condensed in the flask may be tested for sulphuric acid.

268. "Contact Process" for the Manufacture of Sulphuric Acid.—A large quantity of sulphuric acid is now manufactured by the "contact process," which consists of passing carefully purified sulphur dioxide and air over heated spongy platinum, and conducting the fumes of sulphur trioxide formed into 98 per cent. sulphuric acid (which is found to be a better absorbent than water). In order to keep the strength of the absorbing acid at 98 per cent. water or dilute acid is continuously added, the excess of concentrated acid being drawn off.

269. Properties of Sulphuric Acid.—The pure concentrated acid is a thick oily liquid (sp. gr. 1·84), from which it derives the name, *oil* of vitriol. It boils at 338° C., with partial decomposition, so that when the acid containing 100 per cent. H_2SO_4 is distilled the residue becomes weaker, until it reaches a strength of about 98·5 per cent. H_2SO_4, at which it remains constant.

Exp. 273.—Measure out 20 c.c. of water in a measuring vessel and pour it into a beaker. Then measure out 80 c.c. of concentrated sulphuric acid and pour it slowly into a beaker. You will notice that the mixture becomes very hot. (Read its temperature with a thermometer. It will be somewhere about 100° C.) Allow the liquid to stand till it is cold and then pour it into the measuring vessel. You will find that the liquid occupies considerably less than 100 c.c. (probably about 92 c.c.).

We see then that when sulphuric acid is mixed with water much heat is evolved and that the mixing is accompanied by a considerable contraction in volume.

The formation of so much heat shows the great affinity which sulphuric acid has for water, and we should expect that a definite chemical compound of the acid and water

is formed. The large contraction in volume when the acid and water are mixed confirms this supposition; the contraction reaches a maximum, viz. 8 per cent., of the sum of the volumes of acid and water when the ratio of acid to water corresponds to a hydrate of the formula $H_2SO_4.2H_2O$, and this has probably a definite existence.

The highly corrosive properties of sulphuric acid depend largely on its great affinity for water; thus it rapidly chars sugar, wood, and many other organic substances.

Exp. 274.—Pour some concentrated sulphuric acid on a lump of sugar contained in a porcelain dish. Note that the sugar rapidly turns black. Repeat the experiment, using wood splints. Note that these also are charred.

Now sugar is a compound of carbon, hydrogen, and oxygen, the last two being present in the proportions in which they are contained in water; the acid therefore extracts water, leaving a mass of carbon. Wood, again, consists mainly of cellulose, which is also a compound of carbon, hydrogen, and oxygen, in which the last two are present in the same proportions as in water; so that here, also, the acid extracts water, leaving carbon.

On account of the great attraction which sulphuric acid has for water it is frequently used for drying the ordinary gases.

When sulphuric acid vapour is heated to a temperature of about 450° C. it is almost completely dissociated into water and sulphur trioxide; this is shown by the fact that the vapour density [1] is only half what it should be if the molecules consisted of H_2SO_4.

The following considerations will show that the low value of the vapour density proves that dissociation has taken place. Since each molecule of sulphuric acid gives two molecules on dissociation, one of H_2O and one of SO_3, it follows from Avogadro's hypothesis that the volume of the dissociation products will be double the volume of the sulphuric acid from which they are derived (on reduction

[1] The *vapour density* of a substance is its density in *the state of vapour* compared with hydrogen.

to standard conditions). Consequently the vapour density will be half the theoretical value, which agrees with the experimental result as stated above.

When the mixture of water and sulphur trioxide obtained by heating sulphuric acid vapour has its temperature still further raised the sulphur trioxide breaks up into sulphur dioxide and oxygen. Thus, when sulphuric acid is dropped on red-hot bricks it decomposes, as represented in the following equation—

$$2H_2SO_4 = 2H_2O + 2SO_2 + O_2.$$

This fact has been utilised as a means of manufacturing oxygen from sulphuric acid on the large scale.

Sulphuric acid is an oxidising agent, though a much weaker one than nitric acid, as we should expect from the smaller percentage of oxygen it contains and the very much higher temperature required to break it up with separation of free oxygen. Thus it is only when *hot and concentrated* that sulphuric acid exhibits oxidising properties. We have already (§§ 253, 254) met with examples of the oxidation of both metals (copper and zinc) and non-metals (carbon and sulphur) by sulphuric acid; most of the remaining metals and some other non-metals are also oxidised by the hot concentrated acid.

270. Action of Sulphuric Acid on Metals.—*Dilute* sulphuric acid dissolves some metals, such as zinc, iron, and magnesium, with formation of a sulphate of the metal and hydrogen.

Concentrated sulphuric acid has practically no action on common metals in the cold, a few bubbles only of hydrogen being produced. When warmed, however, it reacts with most metals, producing sulphates of the metals and sulphur dioxide mixed with hydrogen; in the case of copper and nickel some sulphide is produced at the same time. As a type of the reaction which takes place between a metal and strong sulphuric acid, we may write the equation which expresses the main result of the interaction of copper and sulphuric acid, viz.—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

As regards the actual *modus operandi* of the reaction two explanations have been advanced. The first suggests that the primary reaction is the formation of a sulphate of the metal and hydrogen. The hydrogen, being in the nascent state, oxidises itself at the expense of the oxygen of the sulphuric acid, forming water and sulphur dioxide thus—

$$\begin{cases} Cu + H_2SO_4 = CuSO_4 + 2H, \\ \qquad\qquad\qquad\qquad\quad \text{Nascent} \\ 2H + H_2SO_4 = SO_2 \quad + 2H_2O. \\ \text{Nascent} \end{cases}$$

The second explanation suggests that the primary action is the oxidation of the metal by the acid, and that this is followed by solution of the oxide in an excess of acid. Thus—

$$\begin{cases} Cu + H_2SO_4 = CuO + H_2O + SO_2. \\ CuO + H_2SO_4 = CuSO_4 + H_2O. \end{cases}$$

In the following table a *résumé* of the action of sulphuric acid on the common metals is given; the gaseous products are not mentioned because, in all cases, with *cold dilute* acid hydrogen is evolved, and with *hot concentrated* acid sulphur dioxide (with some hydrogen).

Metal.	Products with cold dil. H_2SO_4.	Products with hot conc. H_2SO_4.
Magnesium	$MgSO_4$	$MgSO_4$
Zinc	$ZnSO_4$	$ZnSO_4$
Iron	$FeSO_4$	$Fe_2(SO_4)_3$ and $FeSO_4$
Cadmium	$CdSO_4$	$CdSO_4$
Mercury	No action	Hg_2SO_4 (Hg in excess) $HgSO_4$ (H_2SO_4 in excess)
Lead	No action	$PbSO_4$ (action slow)
Copper	No action in absence of air	$CuSO_4$ and Cu_2S
Tin	No action	$SnSO_4$
Silver	No action	Ag_2SO_4
Aluminium	$Al_2(SO_4)_3$ (action slow)	$Al_2(SO_4)_3$
Bismuth	No action	$Bi_2(SO_4)_3$
Nickel	$NiSO_4$ (action slow)	$NiSO_4$ and NiS
Antimony	No action	$Sb_2(SO_4)_3$
Gold	No action	No action
Platinum	No action	No action

271. The Sulphates.—These are the salts produced by the replacement of the hydrogen in sulphuric acid by metals. They are produced by the action of sulphuric acid on the metals (in some cases), or on metallic oxides, hydroxides, or carbonates. They may also be prepared by evaporating the salts of the more volatile acids, such as hydrochloric and nitric acids, to dryness with sulphuric acid; the more volatile acid is driven off and a sulphate of the metal is formed. Thus in Exp. 163 we obtained sodium hydrogen sulphate, $NaHSO_4$, by the action of sulphuric acid on sodium chloride.

Three crystalline sulphates which have long been known, *i.e.* ferrous sulphate, $FeSO_4, 7H_2O$, copper sulphate, $CuSO_4, 5H_2O$, and zinc sulphate, $ZnSO_4, 7H_2O$, were called respectively green, blue, and white *vitriol*, from their colours and the glassy transparency of their crystals (L. *vitrum*, glass).

The sulphates are remarkable for their tendency to form well-defined crystalline double sulphates, *e.g.* alum, $K_2SO_4, Al_2(SO_4)_3, 24H_2O$.

Insoluble sulphates may be obtained by mixing a solution of a soluble salt of the metal whose sulphate is required with a solution of a soluble sulphate, when double decomposition takes place with precipitation of the insoluble salt. The sulphates of lead, calcium, barium, and strontium are insoluble or only slightly soluble in water, the rest being readily soluble.

Sulphuric acid, like sulphurous acid, is a dibasic acid and forms two classes of sulphates, the *normal* sulphates such as Na_2SO_4, $CaSO_4$, and the *acid* sulphates such as $NaHSO_4$, either one or the other being formed according to whether the base or the acid is in excess.

272. Test for Sulphuric Acid and Sulphates.—

Exp. 275.—Add barium chloride to a solution which contains either sulphuric acid, or a sulphate acidified with hydrochloric acid: a white precipitate is formed consisting of barium sulphate. This is the only common barium salt which is insoluble in water and acids, and the forma-

tion of the precipitate is therefore characteristic, and may be taken as a sure indication of the presence of sulphuric acid either in the free state or in the form of a salt.

273. Uses of Sulphuric Acid.—Sulphuric acid is the most important of all the acids. It is very largely used in the manufacture of other acids, such as nitric and hydrochloric acids, in the manufacture of salt-cake—the first stage in the older process for the manufacture of washing-soda—and in the conversion of normal calcium phosphate, $Ca_3(PO_4)_2$, into the acid calcium phosphate, $CaH_4(PO_4)_2$; the latter is much used for agricultural purposes as a fertiliser, because it is soluble in water, whereas the normal salt is insoluble and so is much less easily assimilated by plants. Sulphuric acid is used in the laboratory for drying gases, as already mentioned, and for the preparation of such gases as carbon monoxide and ethylene (see *post*). It is also largely employed in making *storage cells* or *accumulators* for the generation of the electric currents.

Sulphuretted Hydrogen, H_2S

274. Combination of Sulphur with Metals.—Many metals combine with sulphur when heated with it, forming *sulphides*. We have already met with an example of this in Exp. 117, in which iron and sulphur combined to form ferrous sulphide according to the equation—

$$Fe + S = FeS.$$

Sulphur combines very readily with copper, as may be seen in the following experiment:—

Exp. 276.—Heat sulphur to the boiling-point in a boiling tube until the upper part of the tube is filled with its vapour, and then plunge into it thin sheet copper or a helix of copper wire; the metal glows, and enters into combination with the sulphur to form cuprous sulphide, Cu_2S—

$$2Cu + S = Cu_2S.$$

275. Action of Acids on Sulphides.—

Exp. 277.—Introduce a small lump of ferrous sulphide into a test-tube and add some dilute sulphuric or hydrochloric acid. Note the effervescence of a colourless gas having the characteristic "odour of rotten eggs." Moisten a piece of filter paper with a solution of lead acetate and hold it in the mouth of the tube. The paper is blackened.

The gas produced in this reaction is called *sulphuretted hydrogen* or *hydrogen sulphide*. It is a compound of hydrogen and sulphur (see below for proof) and is represented by the formula H_2S. The equations expressing the action of dilute sulphuric and hydrochloric acids on ferrous sulphide are—

$$FeS + H_2SO_4 = FeSO_4 + H_2S,$$
$$FeS + 2HCl = FeCl_2 + H_2S.$$

Many other metallic sulphides give off sulphuretted hydrogen when treated with sulphuric or hydrochloric acid; in some cases the cold dilute acid brings about the change, but in others hot concentrated hydrochloric acid is required.[1]

276. Preparation of Sulphuretted Hydrogen.—The gas is most conveniently prepared by utilising the reaction investigated in Exp. 277.

Exp. 278.—Introduce a few pieces of ferrous sulphide into a Woulfe's bottle fitted with a thistle funnel and delivery tube leading to a wash-bottle containing a *little* water. Pour some dilute sulphuric acid down the funnel and collect several jars of the sulphuretted hydrogen evolved over *hot* water after allowing sufficient time for the air to be driven out of the apparatus.

Sulphuretted hydrogen cannot be collected over cold water as it is too soluble; and owing to its offensive

[1] Hot concentrated sulphuric acid cannot be used because it reacts with sulphuretted hydrogen (see *post*).

nature, and to the fact that it is only slightly heavier than air, it should not be collected by displacement of air; also mercury is inadmissible because it attacks the gas. Since, however, the solubility in water rapidly decreases with rise in temperature, *hot* water may be used.

The gas obtained in this way always contains free hydrogen on account of the iron present in the ferrous sulphide (which is prepared by heating iron and sulphur together) To obtain sulphuretted hydrogen free from hydrogen, sulphide of antimony, Sb_2S_3, is heated in a flask with *concentrated* hydrochloric acid—

$$Sb_2S_3 + 6HCl = \underset{\text{Antimony chloride}}{2SbCl_3} + 3H_2S.$$

The gas is passed through a wash-bottle containing water to remove hydrogen chloride, and may then be collected as before. If *dry* sulphuretted hydrogen is required, the gas, after washing, should be passed through a U-tube containing calcium chloride to absorb the water vapour (sulphuric acid cannot be used because it reacts with the gas, as already stated). It may then be collected in a glass globe from which the air has been exhausted.

277. Properties of Sulphuretted Hydrogen.—We have already seen that sulphuretted hydrogen is a colourless, evil-smelling gas (it is *poisonous* if inhaled in quantity) which possesses the property of blackening lead acetate paper. The latter property (which affords a very delicate test for the gas) depends on the formation of *lead sulphide*, PbS, which is black—

$$\underset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + H_2S = PbS + \underset{\text{Acetic acid}}{2C_2H_4O_2}.$$

Let us continue the study of the properties of sulphuretted hydrogen.

Exp. 279.—Invert a jar of the gas in cold water. The water gradually rises and fills the jar.

Now pour out a little of the liquid contained in the wash-bottle used in Exp. 278; this liquid is an aqueous

solution of sulphuretted hydrogen. Notice that the solution has the smell of the gas. Drop into it a piece of blue litmus: it is slightly reddened.

Sulphuretted hydrogen is moderately soluble in water which at ordinary temperature dissolves about three times its volume of the gas; the solution possesses *slightly acid* properties.

Exp. 280.—Apply a lighted taper to the mouth of a jar of the gas; then push the taper down into the jar. Note the results.

Sulphuretted hydrogen burns with a blue flame, forming sulphur dioxide in a free supply of air (or oxygen). In a limited supply of air free sulphur is formed; this, together with the cooling effect of the sides of the jar on the burning gas, accounts for the slight yellow deposit formed in the above experiment.

* **Exp. 281.**—Repeat Exp. 68, substituting ferrous sulphide for zinc. Test the liquid formed by the burning gas for water.

Water then is also formed when sulphuretted hydrogen burns in air.[1] Since water and sulphur dioxide (also free sulphur) are produced when sulphuretted hydrogen burns, it follows that the gas contains *hydrogen* and *sulphur*. It may, however, also contain oxygen. Let us test this point.

* **Exp. 282.**—Fit a piece of combustion tube about 20 cm. long with two corks, through which pass single tubes. Place some sulphur in the long tube, and clamp it horizontally. Fit up an apparatus for preparing dry hydrogen, and attach it to one of the tubes. Pass hydrogen through the apparatus until the tube *is free from air*, heat the sulphur, and test the gas which comes out of the other end of the horizontal tube by smell and by lead acetate paper: it is sulphuretted hydrogen.

[1] Since sulphuretted hydrogen prepared from ferrous sulphide contains some free hydrogen this proof is not complete. However, if the pure gas prepared from antimony sulphide as described in § 276 is used, the result is the same.

Since the only elements present were hydrogen and sulphur it follows that sulphuretted hydrogen is a compound of these two elements and contains no oxygen.

The equations representing the combustion of the gas in a free supply and in a limited supply of air respectively are—

$$2H_2S + 3O_2 = 2H_2O + 2SO_2,$$

and

$$2H_2S + O_2 = 2H_2O + 2S.$$

278. Decomposition of Sulphuretted Hydrogen by Heat and by Metals.—

* **Exp. 283.**—Fit up a Woulfe's bottle with a thistle funnel and horizontal delivery tube about a foot long. Generate sulphuretted hydrogen in the bottle and when the air has been driven out (shown by the gas smelling strongly at the end of the delivery tube) heat the horizontal tube at about the middle by means of a Bunsen burner. A yellow deposit of sulphur forms near the open end of the tube.

We see then that sulphuretted hydrogen is easily broken up into its elements by heat. It is also very readily broken up by the action of metals, many of which act upon it even at ordinary temperature; the metal combines with the sulphur, and free hydrogen is liberated. The tarnishing of silver when exposed to the air of towns is an example of this; the air contains a small percentage of sulphuretted hydrogen produced during the combustion of coal, which usually contains a small quantity of iron pyrites (FeS_2); this sulphuretted hydrogen in the air attacks the silver, producing a layer of silver sulphide, which is black. On heating many metals in the gas the same change is brought about much more rapidly; tin and cadmium, for instance, very readily bring about the complete decomposition of a confined volume of the gas on the application of gentle heat.

$$Sn + H_2S = SnS + H_2.$$

279. Reducing Action of Sulphuretted Hydrogen.—From the ease with which the gas is decomposed with liberation of hydrogen, we should expect sulphuretted hydrogen to behave as a reducing agent. Let us investigate this by experiment.

Exp. 284.—Pass sulphuretted hydrogen through (1) potassium permanganate solution acidulated with dilute sulphuric acid, (2) potassium dichromate solution acidulated with dilute sulphuric acid, (3) nitric acid. Note the results.

You will observe that in each case sulphur is deposited, and further that in (1) the potassium permanganate is decolorised, in (2) the colour changes from orange to green, and in (3) brown fumes of nitrogen peroxide are formed.

In each of these cases, then, the sulphuretted hydrogen has acted as a reducing agent. The hydrogen is oxidised to water and the sulphur set free. The changes which have taken place may be represented by equations thus—

(1) $2KMnO_4 + 5H_2S + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5S.$
(2) $K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S.$
(3) $H_2S + 2HNO_3 = 2NO_2 + 2H_2O + S.$

Other examples of the reducing properties of sulphuretted hydrogen are its action on concentrated sulphuric acid, which is converted into sulphur dioxide, and on ferric chloride, which is reduced to ferrous chloride—

$$H_2S + H_2SO_4 = SO_2 + 2H_2O + S.$$
$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S.$$

The action of sulphur dioxide on sulphuretted hydrogen is interesting.

* **Exp. 285.**—Bring together jars of sulphuretted hydrogen and sulphur dioxide. Sulphur is set free and deposited on the walls of the jars.

The change is represented by the equation—

$$2H_2S + SO_2 = 2H_2O + 3S.$$

Here, then, we have the hydride and oxide of an element reacting with formation of water and liberation of the element. Sulphur dioxide in this case assumes the unusual rôle of *oxidising* agent. Sulphur is also precipitated when solutions of the two gases are mixed.

The action of the halogens on sulphuretted hydrogen has been referred to in Chapter XV.

280. Formation of Metallic Sulphides by Precipitation.—

Exp. 286.—Make solutions of copper sulphate, stannous chloride, zinc sulphate, and sodium chloride. Add to each a little of the solution of sulphuretted hydrogen contained in the wash-bottle used in Exp. 278, or pass some of the gas through the solutions.

The following results will be obtained:—

With copper sulphate, a black precipitate of cupric sulphide—

$$CuSO_4 + H_2S = \underset{\text{Cupric sulphide}}{CuS} + H_2SO_4.$$

With stannous chloride, a chocolate precipitate of stannous sulphide—

$$SnCl_2 + H_2S = \underset{\text{Stannous sulphide}}{SnS} + 2HCl.$$

With zinc sulphate, a white precipitate of zinc sulphide—

$$ZnSO_4 + H_2S = \underset{\text{Zinc sulphide}}{ZnS} + H_2SO_4.$$

This precipitate in incomplete, *i.e.* not all the zinc is precipitated.

In the case of sodium chloride there is no precipitate (sodium sulphide is soluble in water), and in any case would be decomposed by the co-formed hydrochloric acid.

Now add some hydrochloric acid to the tubes containing the precipitates: the sulphide of zinc will dissolve with evolution of sulphuretted hydrogen; the sulphides of copper and tin remain undissolved.

Metallic sulphides may be divided into three classes :—

(1) Sulphides insoluble in water and dilute mineral acids.

(2) Sulphides which are insoluble in water, but soluble in dilute mineral acids.

(3) Sulphides which are soluble even in water.

This different behaviour of sulphides towards water and acids is much utilised in *analytical chemistry* for the separation of the metals.

281. Composition of Sulphuretted Hydrogen by Volume.—

* **Exp. 287.**—Take a long test-tube (or small round-bottomed flask) fitted with a tight cork, and in it place some pieces of tinfoil or finely divided tin. Fill the tube or flask with pure dry sulphuretted hydrogen by downward displacement, and *when all the air has been displaced*, remove the delivery tube slowly, and cork up the tube. Carefully heat the tube and tin; and when all action appears to have stopped, allow the tube to cool and remove the cork under water. Note any change of volume, and apply a light to the gas left.

Since there is no change in volume it follows that sulphuretted hydrogen *contains its own volume of hydrogen.*

282. Formula of Sulphuretted Hydrogen.—Since sulphuretted hydrogen contains its own volume of hydrogen, it follows from Avogadro's hypothesis that one molecule of the gas contains one molecule, *i.e.* two atoms, of hydrogen. Its formula may therefore be written—

$$H_2S_x.$$

Now the density of sulphuretted hydrogen has been found to be 17; its molecular weight is therefore—

$$2 \times 17 = 34.$$

Then $$H_2S_x = 34.$$

$$\therefore S_x = 34 - 2 = 32.$$

But 32 is the atomic weight of sulphur.

$$\therefore x = 1,$$

and the formula of sulphuretted hydrogen is

$$H_2S.$$

QUESTIONS.—CHAPTER XVIII.

1. Describe all that happens when sulphur is heated to its boiling-point and then allowed to cool without catching fire.

2. Chalk is insoluble in carbon bisulphide. Describe exactly how you would obtain crystals of sulphur from a mixture of chalk and flowers of sulphur.

3. What happens to sulphur when it is burnt (*a*) in oxygen, (*b*) in air? Why is the flame brighter in the first case than in the second?

4. Describe the chief forms of sulphur, and say how each variety is obtained.

5. How would you make and collect sulphuretted hydrogen? State the chief properties of this gas.

6. What experiments would you perform in order to show that sulphuretted hydrogen contains hydrogen and sulphur, and no other element?

7. Describe the preparation and properties of sulphur dioxide. What experiments would you make to show that this gas is a reducing agent?

8. Describe exactly what you would do in order to obtain (*a*) sulphur dioxide, (*b*) hydrogen, from concentrated sulphuric acid.

9. Describe a method by which sulphur dioxide may be converted into the trioxide, and give a diagram of the necessary apparatus. What are the chief properties of the trioxide?

10. Describe experiments illustrating the great attraction which sulphuric acid has for water.

11. State all you would observe on heating metallic copper with concentrated sulphuric acid for some time, allowing the mixture to cool, and then pouring it into a little water. Explain the results as far as you can.

12. Sketch the apparatus you would employ in order to collect the gaseous product of the action of hot strong sulphuric acid on copper. Describe the experiments you would perform to demonstrate the chief properties of the gas.

13. State exactly what you would observe on heating a little iron pyrites in a hard glass tube in a current of air. Explain the changes which have taken place as far as you can.

14. How would you proceed to prepare a little sulphuric acid from flowers of sulphur?

15. Describe two experiments which illustrate the oxidising action of sulphuric acid.

16. Describe how you would proceed to prepare some *liquid* sulphur dioxide.

17. What happens when chlorine is passed into a solution of sulphur dioxide? How would you prove experimentally that your answer is correct? Express the change which takes place by an equation.

18. Describe how you would proceed to investigate the action of heat on ferrous sulphate crystals (green vitriol), and state the results you would obtain.

19. "Sulphur dioxide contains its own volume of oxygen." Explain the meaning of this statement, and show how you would prove the truth of it by experiment.

20. Describe the preparation of the normal and acid sulphites of soda; what is the action of sulphuric acid on them?

21. Describe how sulphur dioxide becomes transformed into sulphuric acid on the large scale; give equations.

22. Compare the reactions between the metals zinc, mercury, and iron respectively, and (1) dilute sulphuric acid, (2) hot concentrated sulphuric acid.

23. What explanations of the action of hot strong sulphuric acid on copper have been suggested?

24. Write down the formulae of the normal sulphates of copper, potassium, lead, iron, and aluminium.

25. What are the chief uses of sulphuric acid?

26. Describe experiments which illustrate the reducing properties of sulphuretted hydrogen.

27. What is the formula for sulphuretted hydrogen and how may it be established experimentally?

CHAPTER XIX.

CARBON AND THE OXIDES OF CARBON.

Carbon.

283. Occurrence.—Carbon is found in nature in a state of comparative purity as diamond and graphite, the latter known as mineral plumbago, from which black-lead pencils are made. These forms do not, however, occur in any very considerable quantity, and the sources from which the large supplies of carbon are obtained are coal and vegetable matter.

The tissue of plants is very constant in composition, and disregarding the moisture, and the mineral ash left after combustion amounting usually to about 1 per cent., *dried wood* is found to consist of

Carbon	50 per cent.
Hydrogen	6 „
Oxygen and nitrogen	44 „

Where plants undergo decay and form thick accumulations of *peat*, the relative proportion of the carbon increases, and the following may be taken as the average composition of peat, leaving out of account moisture and mineral matter—

Carbon	58 per cent.
Hydrogen	5 „
Oxygen and nitrogen	37 „

In deposits of peat and the remains of vegetation which have lain for long periods of time this process of parting with the more volatile constituents and consequent increase in the proportion of carbon goes on, and instead of peat we have a much denser product known as *brown coal* or

lignite, in which the structure of the vegetation composing it can, however, still be observed. Lignite varies greatly in composition, especially in regard to the amount of moisture and ash. Excluding these, it contains on the average—

Carbon	66 per cent.
Hydrogen	5 ,,
Oxygen and nitrogen	29 ,,

In the older formations of the earth's crust there are large deposits of *coal*, which have resulted from long-continued action similar to the foregoing. The seams of coal occur in the older geological formations, and are overlaid by other strata. The vegetable tissue from which coal is derived has thus been subjected to immense pressure and to increased temperature, and under these agencies, acting over long periods of time, the changes already noticed in the passage from woody tissue to lignite have been still further accentuated. Coal is darker in colour, denser, and more brittle; as to composition, the following numbers may be compared with those given for wood, peat, and lignite—

	Bituminous coal.	Anthracite.
Carbon...	84 per cent.	94 per cent.
Hydrogen	5 ,,	3 ,,
Oxygen and nitrogen	11 ,,	3 ,,

Over 200 million tons of coal are brought to the surface in the United Kingdom annually.

In many localities, especially in South Russia and the United States, there are large deposits of *petroleum*—a mixture of various oils, but all composed of carbon and hydrogen, and hence termed hydrocarbons. Petroleum occurs in small quantities at Heathfield in Sussex. There also occurs in Scotland a kind of shale from which large quantities of hydrocarbons and other substances can be obtained by distillation.

And when we add the very extensive series of carbon compounds which have been prepared in the laboratory from coal and petroleum, and the products, such as starch,

sugar, turpentine, albumen, stearin, etc., elaborated by plants and animals, we are in a position to appreciate the immense importance of the element carbon. The study of such bodies is indeed set apart as a special branch of the science, and known as *Organic Chemistry*, or the *Chemistry of the Carbon Compounds*.

Finally, carbon occurs in combination with oxygen as carbon dioxide in the air, and in vast deposits of limestone and dolomite. The carbon dioxide in air, being less than 4 volumes in 10,000, might be regarded as insignificant, but the mass of the atmosphere is such that at this computation there must be very nearly a billion tons of carbon in it.

284. Allotropes of Carbon.—(1) *Diamond* is a crystalline form of carbon; it is found in South Africa and Brazil, usually as octahedra or cubes, or as some modifications of these. Its value is due to its great hardness and brilliancy of lustre, and to the fact that it does not oxidise or undergo change even in the presence of corrosive substances. It is the densest form of carbon, having a specific gravity of about 3·5, and is difficult to ignite in even oxygen.

It is therefore not to be wondered at that the composition of diamond remained unknown until the time of Lavoisier, although it had been previously observed that diamond could be burnt and left no appreciable residue. Lavoisier about a century ago, by means of a burning glass, ignited diamond in air enclosed over mercury, and found that when it burnt, the gas which was formed turned lime-water milky and was carbon dioxide. Dumas, later, showed that carbon dioxide was the *only product* obtained when diamond is burnt in oxygen, and that every 12 parts by weight of diamond yielded 44 parts of carbon dioxide, according to the equation—

$$\underset{12}{C} + \underset{32}{O_2} = \underset{44}{CO_2}.$$

Diamond consists, therefore (with the exception of a minute quantity of ash), of pure carbon.

Moissan has recently succeeded in preparing small diamonds artificially from charcoal by means of the electric furnace. Iron and carbon are placed in a crucible which is then introduced into an electric furnace and raised to a high temperature. The iron melts and dissolves the carbon; on now placing the crucible in a bath of molten lead the outer layer of iron solidifies, and as it contracts it exerts great pressure on the still liquid metal inside. Under these conditions some of the carbon crystallises out in the form of diamond. The iron is dissolved out in hydrochloric acid, and the residue is found to contain small diamonds, some of which are colourless, others are black (called carbonado). A portion of the residue is also in the form of graphite.

(2) *Graphite.*—This also occurs naturally, being found usually in the older crystalline rocks. Cast-iron contains plates of this form of carbon, which can be seen at a freshly-fractured surface, *i.e.* the carbon crystallises from solution in melted iron at ordinary pressures in the form of graphite: it is found accumulated at the base of blast furnaces. It is a soft, dark-grey substance, with an almost metallic lustre, and possesses a much lower specific gravity (2·2) than diamond.

It is usually found massive, but occasionally in six-sided crystals. When rubbed on paper it leaves a black mark, and is therefore used in making lead pencils. It is (unlike diamond) a good conductor of heat and electricity, and on the latter account is used in electrotyping. Graphite is very infusible, and for this reason is largely used in the manufacture of "plumbago" crucibles. It is also used as a lubricant for machinery and for polishing gunpowder. When strongly heated in oxygen graphite burns with formation of carbon dioxide; the ash which is left consists of silica, ferric oxide, and alumina. Graphite is oxidised when gently heated with a mixture of potassium chlorate and nitric acid, whilst diamond is unattacked.

Artificial graphite is now manufactured by heating charcoal or coke with large excess of iron in the electric furnace.

(3) *Amorphous carbon* is familiar to us as charcoal, lamp-black, or animal charcoal, which, however, are usually more or less impure forms of carbon.

285. Preparation of Charcoal.—This may be obtained by strongly heating wood or many other organic bodies in vessels from which air is excluded; or by the action of dehydrating substances, such as concentrated sulphuric acid, on these bodies.

Exp. 288.—Heat a few pieces of wood in a hard glass tube over the flame of a Bunsen burner. First moisture collects on the sides of the tube and the wood begins to char. As the heating is continued dirty white pungent vapours are at first given off and burn at the mouth of the tube if a light is applied; when these are no longer to be seen, throw out the contents of the tube into water. The black charred product is wood charcoal.

Exp. 289.—Make about 100 grams of sugar into a thick syrup by dissolving it in a small quantity of hot water, place it in a deep glass beaker and allow to cool; then pour in about 100 c.c. of concentrated sulphuric acid. Presently the liquid will blacken and froth considerably, and a mass of black charcoal much more bulky than the sugar originally taken will be formed. Wash this thoroughly with water till free from acid, and there remains carbon in a granular condition.

Where wood is scarce, charcoal is prepared from it by distillation, as already mentioned; but where it is plentiful and waste is not important, the logs are arranged in heaps, covered with sods or earth to allow only a small supply of air, and then slowly burned.

286. Properties of Charcoal.—The chemical composition and properties of charcoal vary considerably with the kind of wood used and the temperature at which it is charred. When charred at a low temperature the charcoal is soft and light in colour, and it burns easily; it also

contains a lower percentage of carbon than when charred at a high temperature. Thus a specimen of charcoal made at a temperature of about 300° C. contained 70 per cent. of carbon and 4·5 per cent. of hydrogen, while when made at a full white heat it contained 96 per cent. of carbon and 0·5 per cent. of hydrogen.

Wood charcoal has a specific gravity of about 1·5; yet when dry it floats on water. This is explained when a piece of charcoal is placed on water under the receiver of an air pump: as the pump is worked, air escapes from the charcoal and it gradually sinks. The charcoal is porous, and the air contained in its pores reduces its apparent specific gravity to about 0·2, the specific gravity of air being only about 0 0013 (water = 1).

Charcoal also absorbs other gases to a varying extent.

Cocoa-nut charcoal, under favourable conditions, was found to absorb of—

Ammonia	172	times its volume.
Hydrogen chloride ..	165	,, ,, ,,
Nitrous oxide ...	99	,, ,, ,,
Carbon dioxide ...	97	,, ,, ,,

On the other hand, charcoal only absorbs slightly more than its own volume of hydrogen.

* **Exp. 290.**—Fill a test-tube with dry ammonia gas by displacement, and stand it over mercury in a trough. Heat a small piece of charcoal red hot in the crucible tongs, and plunge it, while still glowing, under the mercury; then allow it to rise into the test-tube. The mercury rises in the tube as the ammonia is rapidly absorbed by the charcoal.

This property of charcoal is used in deodorising and disinfecting sewers and hospital wards. The charcoal not only absorbs gases and the effluvia evolved by putrefying matter, but also rapidly oxidises them by means of the oxygen already present in its pores: this oxygen is more active than ordinary gaseous oxygen, and is even capable of killing bacteria.

Exp. 291.—Mix a little finely-powdered wood charcoal with water, and pour the whole on to a filter paper in a funnel. Pour some sulphuretted hydrogen water through the charcoal and test the filtrate by lead acetate solution. No black precipitate of lead sulphide is formed, showing that the sulphuretted hydrogen has been oxidised by the oxygen absorbed in the charcoal.

Charcoal also possesses the power of decolorising liquids; for this purpose animal charcoal is more generally used (see § 288).

Charcoal burns in air without flame or smoke, unless it has been prepared at a low temperature and is therefore very impure; in excess of air carbon dioxide (CO_2) is produced, but in a limited supply of air much carbon monoxide (CO) is formed.

Charcoal is more easily oxidised than graphite, for whilst the latter requires a mixture of hot concentrated nitric acid and potassium chlorate, the former is oxidised by hot concentrated nitric acid alone (and also by hot concentrated sulphuric acid).

287. Reducing action of Charcoal.—On account of the ease with which it combines with oxygen, charcoal (and other forms of amorphous carbon) acts as a strong reducing agent at high temperatures.

We have already had an example of a *gaseous* reducing agent in hydrogen, which, owing to its affinity for oxygen, reduces many oxides to the metallic condition. Also in sulphurous acid we have an instance of a *liquid* reducing agent, its activity being due to the ease with which it undergoes oxidation to sulphuric acid. In carbon we have a *solid* reducing agent which finds very frequent employment in operations conducted at high temperatures, the carbon under such conditions being oxidised to carbon monoxide or dioxide at the expense of the oxygen contained in the bodies with which it is mixed. Thus, some important metallurgical operations involving a reduction of oxides to the metal are carried out with the use of

carbon in the form of coke or coal, which it oxidises to carbon monoxide or carbon dioxide in the process.

An example of the reduction of a metallic oxide by charcoal was met with in Exp. 12 in which litharge was converted into metallic lead. The change is represented by the equation—

$$2PbO + C = 2Pb + CO_2.$$

Similarly, oxide of copper or bismuth may be reduced, and metallic copper or bismuth obtained from them. The reduction of oxide of zinc and oxide of tin are examples of similar processes carried out on the large scale.

288. Animal Charcoal, or Bone Black.—Another kind of charcoal is made by heating bones in closed iron retorts. It is a very porous mixture of charcoal with the mineral constituents of the bones, chiefly calcium phosphate. It is used for decolorising raw sugar, as it has the property already referred to of removing many colouring matters from solution.

Exp. 292.—Shake up with animal charcoal a hot solution of indigo or litmus for a few moments and then pour it on a filter; the filtrate will be colourless. That the colouring matter is removed by the animal charcoal and not by the filter may be shown by pouring a similar solution, which has not been treated by animal charcoal, through a filter paper.

289. Lamp-black may be made by burning resin or turpentine, and bringing a cool surface, *e.g.* the under-side of a porcelain basin filled with cold water, into the flame. In this form, after treatment with chlorine, a particularly pure and finely-divided form of carbon is prepared.

Lamp-black is used in making paint and printers' ink.

290. Gas-carbon and Coke.—Two forms of amorphous carbon are obtained by the destructive distillation[1] of coal

[1] The process of *destructive distillation* consists in distilling a complex substance, such as wood or coal, out of contact with air.

(see §§ 321, 322), namely, *gas-carbon* and *coke*. The former is nearly pure carbon, but the latter contains all the non-volatile products present in the coal. Gas-carbon is very hard and has a specific gravity of 2·35. It is a good conductor of electricity, and is on this account used for making the carbon electrodes of arc lights.

291. Other Properties of Carbon.—In whatever form it occurs, carbon is infusible, but it volatilises without fusion at the temperature of the electric furnace. It cannot be considered an element of great chemical activity, since at ordinary or moderate temperatures it does not combine directly with any of the elements except fluorine. At high temperatures, however, carbon does unite directly with a considerable number of elements, *e.g.* oxygen, sulphur, hydrogen, nitrogen, iron, and aluminium.

292. Proof that the Allotropic Modifications of Carbon all consist of the same Element.—The best proof consists in showing that, whichever allotropic modification is used, the ratio of the weight of carbon dioxide formed to that of the substance taken is the same, viz. 44 : 12. The experiment may be carried out in the following manner :—A small quantity of any form of carbon (say

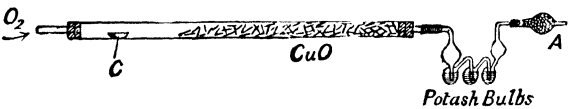


Fig. 89.

graphite) is accurately weighed out in a porcelain "boat" [1] *C* (Fig. 89); this is then introduced into one end of a hard-glass tube, the greater part of which is filled with granulated copper oxide. The tube is closed at each end with a one-holed rubber cork through which passes a short glass tube.

The end of the tube at which the boat is placed is connected with a supply of dry oxygen, the other end with a

[1] See Fig. 34 (*a*) for a larger diagram of the "boat."

series of bulbs containing strong caustic potash solution These bulbs, together with a calcium chloride tube *A* (the object of which is to absorb any water vapour driven out of the potash solution by the current of hot gas, and which if allowed to escape would introduce an error into the final weighing of the bulbs), are weighed, before being placed in position. The tube is now heated in a furnace; at first only the burners under the copper oxide are lighted, but when this becomes red-hot the heating is extended to the boat, and a slow current of oxygen is passed through the tube. The carbon burns to carbon dioxide, which passes on and is absorbed by the caustic potash with formation of potassium carbonate according to the equation—

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

Any carbon monoxide which is at first formed owing to incomplete combustion is converted into carbon dioxide during its passage over the heated copper oxide. When nothing remains in the boat but a trace of ash, and when bubbles of gas cease to be absorbed in the potash bulbs, the latter are disconnected, and, after cooling, are reweighed (together with the calcium chloride tube). The increase in weight gives the weight of carbon dioxide formed. The boat is also allowed to cool, and is reweighed. The difference between the final weight of the boat (which includes the weight of the ash) and the weight of the boat + graphite (previously determined) gives the actual weight of graphite burnt (*i.e.* the ash is allowed for).

Let W_1 = weight of boat + graphite,

W_2 = weight of boat + ash.

Then $W_1 - W_2$ = weight of graphite burnt.

Also let W_3 = weight of potash bulbs + calcium chloride tube before absorption,

and W_4 = weight of potash bulbs + calcium chloride tube after absorption.

Then $W_4 - W_3$ = weight of carbon dioxide formed.

It will then be found that whatever form of carbon is used the ratio $W_4 - W_3 / W_1 - W_2$ is equal to 44/12 or 11/3.

Carbon Dioxide (Carbonic Acid Gas), CO_2.

293. Occurrence.—The presence of this gas in air and water has already been mentioned, and also the part it plays in the animal and vegetable kingdoms. It is given off in large quantities from lime-kilns, in which the limestone is decomposed by heat into quicklime and carbon dioxide. Processes of fermentation and putrefaction also give rise to the gas. Whenever an explosion of fire-damp occurs in coal mines carbon dioxide is formed in large quantities, and constitutes what the miners call the *after-damp* or *choke-damp*.

294. Preparation of Carbon Dioxide.—The usual method of preparing carbon dioxide, namely, by the action of dilute hydrochloric acid on limestone or marble, has already been described in Exp. 81. The reaction which takes place is represented by the equation—

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

Although somewhat soluble in water, the gas may be collected over water, but as it is much heavier than air, it is usually collected by downward displacement.

All carbonates, when treated with dilute hydrochloric acid, liberate carbon dioxide; many, such as limestone, liberate it when heated.

295. Properties of Carbon Dioxide.—These have already been studied by experiment in § 48. Carbon dioxide is a colourless gas with a faintly acid taste and smell. It is a heavy gas, its density being about $1\frac{1}{2}$ times as great as that of air.

Carbon dioxide is soluble in water, which at ordinary temperature dissolves about its own volume of the gas. As with other gases, the amount dissolved increases directly as the pressure under which solution takes place, and soda-water being water charged with the gas under about four atmospheres pressure contains about four times its volume of the gas. The aqueous solution of carbon dioxide possesses feebly acid properties, for it is able to change the

colour of litmus from blue to *claret* (not to the *bright red* produced by strong acids such as hydrochloric and sulphuric); carbon dioxide can also, like other acids, decolourise phenol-phthalein which has been rendered pink by the addition of a small quantity of alkali.

Exp. 293.—Pass a stream of carbon dioxide through a few cubic centimetres of water to which some drops of litmus solution have been added, and note that the litmus assumes a claret tinge; contrast this with the effect of adding litmus to water containing a little hydrochloric or sulphuric acid. Notice also that, by boiling, the carbon dioxide is expelled, and the litmus assumes its original colour. A solution of carbon dioxide in water is therefore very unstable, and possessed of a feebly acid character.

Exp. 294.—Pass the expired air from the lungs, or carbon dioxide prepared from marble and washed free from hydrochloric acid by passing through water, through a slightly alkaline solution of phenol-phthalein; the pink liquid becomes colourless.

Carbon dioxide is in general a non-supporter of combustion and of animal life. Certain metals, however, such as magnesium and potassium, will burn in it with liberation of carbon.

$$2Mg + CO_2 = 2MgO + C.$$
$$4K + 3CO_2 = 2K_2CO_3 + C.$$

It is decomposed by the green colouring-matter of plants called chlorophyll in presence of sunlight, carbon being assimilated and oxygen set free in the process.

Though the harmful effects of carbon dioxide are mainly due to suffocation (*i.e.* absence of oxygen), yet at the same time the gas seems to exercise a directly poisonous action on the system; for air containing more than one volume of it per thousand (*i.e.* about three times the normal quantity) has a distinctly depressing effect, and often gives rise to headache. This effect may, however, be due to other impurities in the expired air from which the extra carbon dioxide is derived.

296. Liquid and Solid Carbon Dioxide.—Under a pressure of 36 atmospheres at 0° C. the gas condenses to the liquid form, and in this form it is prepared on a tolerably large scale and stored in steel cylinders. If the nozzle of one of these cylinders be opened, the pressure being released, the liquid is rapidly transformed into gas. The amount of heat absorbed by the passage from the liquid to the gaseous condition is considerable, and the issuing gas becomes so far cooled that a part of it condenses again even to the solid form. Solid carbon dioxide is a white, snow-like substance which passes only comparatively slowly into the gaseous condition again. The depression of temperature caused by its passage from the solid to the gaseous condition is such that mercury can be readily cooled down to — 40° C. and obtained as a solid body.

297. Composition of Carbon Dioxide by Volume.—This may be shown by a method similar to that employed in the case of sulphur dioxide, *i.e.* by burning carbon (say charcoal) in a confined volume of oxygen (see § 260). It will be found that when the experiment is completed, the level of mercury is the same as it was before the combustion of the charcoal, showing that carbon dioxide *contains its own volume of oxygen.*

298. Formula of Carbon Dioxide.—Since as we have just seen carbon dioxide contains its own volume of oxygen, it follows from Avogadro's hypothesis that one molecule of the gas contains one molecule of oxygen, and the formula may be written C_xO_2.

Now the density of carbon dioxide relative to hydrogen is 22 (see § 77); hence its molecular weight is $2 \times 22 = 44$. This agrees with the value $x = 1$ in the formula just given, for C = 12, O = 16, and $C_1O_2 = 12 + 2 \times 16$ or 44. The formula for carbon dioxide is therefore CO_2.

The composition by weight of the gas agrees with this formula, for, as already stated in § 284, 12 parts by weight of carbon unite with 32 parts of oxygen to produce 44 parts of carbon dioxide.

299. The Carbonates.—We have seen in a previous paragraph that a solution of carbon dioxide in water shows a feebly acid reaction. For this reason, and from a consideration of the salts known as the carbonates, carbon dioxide is to be regarded as the anhydride of carbonic acid, and the composition of the acid, although never isolated, may be taken as H_2CO_3.

Carbonic acid has two atoms of hydrogen replaceable by metals, and is therefore a *dibasic* acid. In the acid carbonates or *bicarbonates* only half the hydrogen is so replaced; thus $KHCO_3$ is potassium bicarbonate ("bicarbonate of potash"), and $NaHCO_3$ is sodium bicarbonate ("bicarbonate of soda"). In the normal carbonates the whole of the hydrogen is replaced, as with K_2CO_3, potassium carbonate, and Na_2CO_3, sodium carbonate.

Exp. 295.—Prepare a *strong* solution of caustic soda by dissolving 5 grams of stick soda in 10 c.c. of distilled water. When the liquid is cold (cool it under the tap) pass carbon dioxide through it. After a time a white powder separates out. When no more precipitate appears to form, filter and wash with a very little cold water. Now dry the powder between filter paper and examine it with a lens: it is crystalline.

This crystalline powder is sodium hydrogen carbonate, $NaHCO_3$. Its formation is represented by the equation—

$$NaOH + CO_2 = NaHCO_3.$$

Exp. 296.—Pass carbon dioxide through a boiling[1] dilute solution of caustic soda till the gas ceases to be absorbed. Now allow the liquid to cool: large transparent crystals separate out.

These crystals consist of normal sodium carbonate combined with water of crystallisation and are represented by the formula $Na_2CO_3, 10H_2O$; they are popularly known as *washing soda*.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$
$$Na_2CO_3 + 10H_2O = Na_2CO_3, 10H_2O.$$

[1] This prevents the formation of the bicarbonate (see § 302).

By using caustic potash in place of caustic soda in Exps. 295, 296 the corresponding potassium salts are obtained.

300. Effect of Heat on Carbonates.—

Exp. 297.—Heat in a test-tube some of the washing soda crystals you prepared in Exp. 296. Note that they melt and finally leave a white powdery residue, while water collects in the cool part of the tube.

Test whether any carbon dioxide is evolved by means of a drop of lime-water on the end of a glass rod. There is no result. Add a little hydrochloric acid to the residue when cold. It effervesces and carbon dioxide is evolved (test with lime-water), showing that it is still a carbonate.

All that has happened then on heating washing soda is that it has lost water (its water of crystallisation). The change is represented thus—

$$Na_2CO_3, 10H_2O = Na_2CO_3 + 10H_2O.$$

Exp. 298.—Now repeat the experiment with some of the bicarbonate of soda you prepared in Exp. 295. You will find that both water and carbon dioxide are evolved and that a white residue remains closely resembling that obtained in Exp. 297. Test it with hydrochloric acid; it effervesces and carbon dioxide is produced.

The residue obtained on heating sodium bicarbonate is in fact the same substance as that remaining when washing soda is heated—namely anhydrous sodium carbonate, and the decomposition of the bicarbonate is represented by the equation—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

All other bicarbonates decompose on heating in a similar way to the sodium salt (cf. § 143).

Normal potassium carbonate like the corresponding sodium compound withstands a high temperature without decomposition, but other normal carbonates undergo decomposition on heating, giving off carbon dioxide and

forming an oxide of the metal. Magnesium carbonate, for example, leaves a residue of magnesium oxide on heating.

$$MgCO_3 = MgO + CO_2.$$

Ammonium carbonate decomposes in an exceptional manner, ammonia, carbon dioxide, and water being the products.

$$(NH_4)\,CO_3 = 2NH_3 + CO_2 + H_2O.$$

Both the normal and acid carbonates of sodium, potassium, and ammonium are soluble in water; the carbonates of other common metals are insoluble, but the bicarbonates are soluble. The student will remember, for example, that normal calcium carbonate, $CaCO_3$, is insoluble in water, whereas the bicarbonate, $CaH_2(CO_3)_2$, is soluble.

The insoluble carbonates may be obtained (1) by the addition of alkaline carbonates to a soluble salt of the metal—

$$Na_2CO_3 + BaCl_2 = \underset{\text{Barium carbonate}}{BaCO_3} + 2NaCl;$$

(2) by passing carbon dioxide into a solution of the hydroxide—

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

301. Test for Carbonates.—

Exp. 299.—Add dilute hydrochloric acid to some washing soda and to some bicarbonate of soda contained in separate test-tubes. In both cases an effervescence will be observed, and on decanting the gas downwards into a second tube containing lime-water, and shaking up, a turbidity will be produced in the lime-water owing to the formation of calcium carbonate.

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2.$$
$$NaHCO_3 + HCl = NaCl + H_2O + CO_2.$$

§ It will be remembered that excess of CO_2 transforms this into the soluble bicarbonate—

$$CaCO_3 + H_2O + CO_2 = CaH_2(CO_3)_2.$$

This test is a perfectly general one for both normal carbonates and bicarbonates.

302. Distinction between Normal Carbonates and Bicarbonates.—If a carbonate is insoluble in water it must be a normal salt. If it is soluble further experiment is necessary before we can decide to which class it belongs

Exp. 300.—Dissolve some washing soda and some bicarbonate of soda in water in separate test-tubes. Heat each tube. Note that in the latter case a gas is evolved with effervescence. Show by the lime-water test that the gas is carbon dioxide.

The normal carbonate undergoes no change when its solution is boiled. The bicarbonate has decomposed just as it does when the solid is heated, the normal carbonate remaining in solution.

Exp. 301.—Add a solution of magnesium sulphate (Epsom salts) to solutions of (1) washing-soda, (2) sodium bicarbonate contained in separate test-tubes. There is a white precipitate in the former case, but not in the latter. Now boil the solution containing the bicarbonate. A precipitate forms.

These results depend, of course, upon the facts that (1) normal magnesium carbonate is insoluble in water whilst the bicarbonate is soluble, (2) bicarbonates are converted into normal carbonates on boiling their aqueous solutions.

Both the tests investigated in Exps. 300, 301 may be used in general to decide whether a soluble carbonate is a normal salt or a bicarbonate.

Carbon Monoxide, CO.

303. Formation of Carbon Monoxide.—

† **Exp. 302.**—Fill a hard glass tube about two feet long with small lumps of charcoal (Fig. 90), and support it in a gas furnace (not shown). Do not light the burners of the furnace yet.

Generate a *slow* current of carbon dioxide in the flask, A, mixing the ordinary dilute hydrochloric acid with an equal volume of water before use. The wash-bottle, B, is half-filled with a *strong* solution of caustic soda. When all the air has been expelled from the horizontal tube, as shown

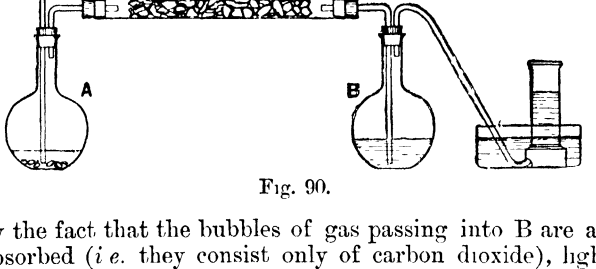


Fig. 90.

by the fact that the bubbles of gas passing into B are all absorbed (*i e.* they consist only of carbon dioxide), light the burners of the furnace and place a jar of water on the shelf of the pneumatic trough. After a time bubbles of a colourless gas escape from B and collect in the jar.

Do not let any of the gas escape into the air, as it is **very poisonous.** Having filled three jars with the gas discontinue heating, collect any more gas which comes off in a fourth jar, then detach B to prevent "sucking back."

Now remove the cover from the second jar of the gas and apply a lighted taper: the gas burns with a beautiful blue lambent flame. Push the taper down into the jar: it is extinguished. When the combustion is finished introduce a little lime-water into the jar and shake up: the milkiness produced shows that carbon dioxide is formed by the combustion of the gas. Invert the third jar in water and leave for a time. There is no appreciable rise of the liquid, showing that if the gas is soluble at all it is only very slightly so. [*Burn* the gas in this and in the fourth jar. That in the first jar contains air from B and the mixture may be explosive; allow it to escape *in a fume chamber.*]

The gas which you have prepared is called *carbon monoxide.* Since (1) it has been produced by the action

of carbon on carbon dioxide, and (2) it burns in air, with re-formation of carbon dioxide, we may infer that it is a compound of carbon and oxygen containing a smaller percentage of oxygen than the dioxide. It may be shown to have the formula CO (see § 307), and the changes which take place when it is formed from carbon dioxide and carbon and when it burns in air are respectively represented by the equations—

$$CO_2 + C = 2CO.$$
$$2CO + O_2 = 2CO_2.$$

The method of formation of carbon monoxide, investigated in Exp. 302, may be observed in a coke or red-hot cinder fire, on the surface of which the blue flames of the burning gas may be seen. The air passing in at the base of the fire at the lower part of the grate unites with carbon, forming carbon dioxide, and this as it passes over the mass of red-hot carbon in the upper part of the grate is transformed into carbon monoxide.

Carbon monoxide is invariably produced when carbon or compounds of carbon are burnt in a *limited supply of air*. Thus it occurs in small quantity in chimney gases, especially where the air-supply during combustion is not in sufficiently large excess. The gases from blast or other furnaces in which an excess of carbon is present, and in which a reducing operation is being performed, consist largely of carbon monoxide.

The gas is also formed during the dry distillation of wood, coal, and such organic bodies.

304. Methods of Preparation of Carbon Monoxide.—One of the best methods of preparing carbon monoxide in the laboratory consists in gently warming a mixture of sodium formate ($NaCHO_2$) and concentrated sulphuric acid in a flask.

$$NaCHO_2 + H_2SO_4 = NaHSO_4 + H_2O + CO.$$

The gas may be collected over water unless it is required dry, when it should be passed through a sulphuric acid wash-bottle and collected over mercury.

Another convenient method of preparation consists in heating roughly-powdered potassium ferrocyanide, $K_4FeC_6N_6$, $3H_2O$, with concentrated[1] sulphuric acid. The change which takes place is represented by the equation—

$$K_4FeC_6N_6 + 11H_2SO_4 + 6H_2O = 4KHSO_4 + FeSO_4 + 6NH_4HSO_4 + 6CO.$$

The water required for this reaction is derived partly from the water of crystallisation of the ferrocyanide and partly from the 1·5 per cent. of water present in the sulphuric acid.

Carbon monoxide may also be prepared by warming oxalic acid, $C_2H_2O_4$, with concentrated sulphuric acid, but in this case carbon dioxide is simultaneously produced and must be removed by passing the mixed gases through a strong solution of caustic potash; the carbon monoxide may then be collected over water as before. In this reaction the elements of water are removed from the oxalic acid by the sulphuric acid, and the change may be represented by the equation—

$$C_2H_2O_4 + H_2SO_4 = CO + CO_2 + \underbrace{H_2O + H_2SO_4}.$$

On the large scale carbon monoxide is prepared by the method we investigated in Exp. 302. Thus "producer gas" or "generator gas," used in some manufacturing operations, consists largely of carbon monoxide, and is obtained by passing air over a high column of red-hot coke or anthracite.

When steam is passed over red-hot coke a mixture of carbon monoxide and hydrogen is formed, which is known as *water-gas*—

$$H_2O + C = CO + H_2.$$

Water-gas is used on the large scale as a source of heat.

[1] *Dilute* sulphuric acid gives rise to the formation of hydrocyanic acid (HCN).

305. Properties of Carbon Monoxide. — Carbon monoxide is a colourless, tasteless gas, having a faint odour; it is only slightly soluble in water, 100 volumes of water at ordinary temperatures dissolving less than three volumes of the gas. It is also very difficult to condense, the liquid boiling under atmospheric pressure at $-190°$ C. The density of the gas is very slightly less than that of air.

Carbon monoxide burns in air or oxygen with a bright blue flame, carbon dioxide being produced. If an electric spark is passed through a mixture of carbon monoxide and oxygen, within certain limits combination takes place with explosion; the reaction is most violent when the volume of carbon monoxide is twice that of the oxygen.

Owing to the readiness with which carbon monoxide combines with oxygen, it is a powerful reducing agent at high temperatures. Thus many metallic oxides, *e g.* those of copper and iron, are reduced to the metal when heated in a current of the gas.

$$CuO + CO = Cu + CO_2$$
$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

We have seen in Exp. 302 that carbon monoxide does not support the combustion of a taper; the same applies to other common combustibles—wood, etc.

Carbon monoxide combines directly with the vapour of sulphur, forming carbonyl sulphide (COS), and in sunlight with chlorine, forming carbonyl chloride ($COCl_2$), also known as phosgene gas. Finely-divided nickel and iron unite with the gas on heating, forming compounds called *carbonyls*; nickel carbonyl is represented by the formula $Ni(CO)_4$ and iron carbonyl by $Fe(CO)_5$; both these compounds are liquids.

Carbon monoxide dissolves in a solution of cuprous chloride in strong hydrochloric acid or ammonia, with formation of a compound $Cu_2Cl_2.CO$. A solution of cuprous chloride is used as an absorbent for the gas in gas analysis.

Carbon monoxide is a very poisonous gas, this property depending on its power of combining with the colouring

matter of the blood called hæmoglobin, to form a bright red compound, carboxyhæmoglobin.

306. Composition of Carbon Monoxide by Volume.—The composition of carbon monoxide is determined as described in the following experiment.

† **Exp. 303.**—Some carbon monoxide (prepared by warming sodium formate with strong sulphuric acid) is introduced into a eudiometer (see Fig. 46), and the levels of mercury in the eudiometer and in the trough are read. Excess of oxygen is next introduced and the levels of mercury again read. Also the temperature and pressure of the air are noted. The eudiometer is now pressed down on to an indiarubber pad and an electric spark is passed through the mixture of gases, when the whole of the carbon monoxide unites with oxygen to form carbon dioxide.

When the tube has cooled down again to the temperature of the air the levels of mercury are read a third time. Finally a piece of solid caustic potash is allowed to rise to the top of the mercury. This absorbs the carbon dioxide, and when the mercury ceases to rise final readings of the levels of mercury in the eudiometer and in the trough are taken.

All the volumes measured must now be reduced to standard conditions. When this has been done suppose that the following results are obtained:—

Vol. of carbon monoxide taken	= 20 c.c.
Vol. of carbon monoxide + oxygen taken	= 70 c.c.
Vol. of carbon dioxide + uncombined oxygen	= 60 c.c.
Vol. of uncombined oxygen	= 40 c.c.

Then—

Vol. of oxygen taken = 70 − 20 or 50 c.c.

∴ Vol. of oxygen which combined with 20 c.c. of carbon monoxide = 50 − 40 or 10 c.c.

Also Vol. of carbon dioxide formed = 60 − 40 or 20 c.c.

Therefore 20 c.c. of carbon monoxide combined with 10 c.c. of oxygen to form 20 c.c. of carbon dioxide.

From the results of the previous experiment we see that *carbon monoxide combines with half its volume of oxygen to form its own volume of carbon dioxide.* But we have seen that carbon dioxide contains its own volume of oxygen; therefore *carbon monoxide contains half its volume of oxyyen.*

307. Formula of Carbon Monoxide.—Since, as we have just seen, one volume of carbon monoxide combines with half a volume of oxygen to form one molecule of carbon dioxide, it follows by applying Avogadro's hypothesis that one molecule of carbon monoxide combines with half a molecule, *i.e.* one atom, of oxygen to form one molecule of carbon dioxide. But the molecule of carbon dioxide contains one atom of carbon and two of oxygen; therefore the molecule of carbon monoxide must contain one atom of carbon and one of oxygen.

The formula for carbon monoxide is therefore

$$CO.$$

The density of carbon monoxide affords a confirmation of this formula. The gas is fourteen times as heavy as hydrogen, and therefore its molecular weight is 2×14 or 28, that of hydrogen being 2.

Now $C = 12$, $O = 16$, and therefore the molecular weight of carbon monoxide is given by

$$CO = 12 + 16 \text{ or } 28,$$

which is the same value as that deduced from the density.

Carbon Bisulphide, CS_2.

308. This compound occurs in traces in coal gas, and is formed in quantity when sulphur vapour is passed over red-hot charcoal. It is a colourless liquid, which refracts light strongly; it is very volatile, boiling at 46° C. and giving off a very inflammable vapour. When pure it has

a sweetish, ethereal smell, but usually the impurities which it contains render it very disagreeable. One of its most remarkable properties is its solvent action: indiarubber, fats, and some of the non-metallic elements such as phosphorus, sulphur, and iodine, which are otherwise difficult to obtain in solution, are readily dissolved by bisulphide of carbon.

In consequence of its high refractive power for light, it is frequently employed as a means of producing a spectrum, the liquid being introduced into a hollow glass prism.

Carbon bisulphide (CS_2) is the analogue in composition of carbon dioxide (CO_2), and thiocarbonic acid (H_2CS_3), the analogue of carbonic acid (H_2CO_3), is known; carbon monosulphide (CS) corresponding to carbon monoxide (CO) has also been obtained. Thus a number of bodies are known containing sulphur in place of oxygen, the sulphur compound resembling the corresponding oxygen compound in chemical properties.

QUESTIONS.—CHAPTER XIX.

1. Compare the properties of the allotropic modifications of carbon.
2. Describe how you would prove by experiment that charcoal is able to (1) absorb large quantities of certain gases, (2) decolorise certain liquids, (3) act as a reducing agent.
3. How would you prove experimentally that the allotropic modifications of carbon are all composed of the same elementary substance?
4. How would you prepare carbon monoxide from the dioxide? Sketch the apparatus you would use. How would you reconvert the monoxide into the dioxide?
5. Describe the method by which carbon monoxide is usually prepared in the laboratory. What are the chief properties of the gas?

6. Describe how you would prepare specimens of the normal and acid carbonates of sodium from caustic soda. How would you distinguish these salts in solution?

7. Taking the atmospheric pressure as 15 lb. on the square inch, calculate the weight of carbon in a column of the air whose base is a square mile, the carbon dioxide present being 0 06 per cent. by weight.

8. Describe how Moissan has succeeded in preparing artificial diamonds.

9. How would you prove that sugar contains carbon?

10. How is wood charcoal manufactured? Describe experiments illustrating its chief properties.

11. What is animal charcoal, how is it prepared, and for what purpose is it used?

12. You desire to collect a specimen of carbon monoxide as free as possible from air or carbon dioxide, using oxalic acid as the source of the gas: how would you proceed?

13. How would you proceed to determine the volume ratio in which carbon monoxide and oxygen unite to form carbon dioxide? What result would you obtain?

14. Describe how it may be proved experimentally that carbon dioxide contains its own volume of oxygen.

15. How is the formula CO_2 for carbon dioxide established?

16. 0·1931 gram of diamond gave on complete combustion 0·704 gram of carbon dioxide. Calculate the percentage of ash in the diamond (C = 12, O = 16).

17. What volume of ammonia will be absorbed by 10 grams of charcoal if the density of the charcoal is 1·5 and if it absorbs 172 times its volume of the gas?

18. By what tests can *normal* carbonates be distinguished from *acid* carbonates?

19. What are the *characteristic* properties of bisulphide of carbon? What are the products formed, and their relative volumes, when this body is burnt in oxygen?

20. 15 c.c. of carbon monoxide were exploded with 20 c.c. of oxygen. After treating the product with excess of caustic potash 12·5 c.c. of gas remained. Deduce from this the formula for carbon monoxide, assuming carbon dioxide to be represented by CO_2.

CHAPTER XX.

HYDROCARBONS.

Marsh Gas, or Methane, CH_4

309. Preparation of Marsh Gas.—

***Exp. 304.**—Weigh out roughly 10 grams of fused sodium acetate and about four times the quantity of soda lime.[1] Powder them up together in a mortar so that they become intimately mixed.

Gently heat the mixture in a dish to drive off moisture and then introduce it while still warm into a small round-bottomed flask of hard glass (or into a hard glass tube). Support the flask in a nearly horizontal position, but sloping slightly downwards towards the neck as in Fig. 91. (The object of this arrangement is to prevent water which condenses in the neck of the flask from running back on to the hot glass and cracking it.) Close the flask with a cork fitted with a delivery tube and heat the flask gently at first, then strongly. After a time collect, over water, a test-tube full of the gas which is evolved and test it with a

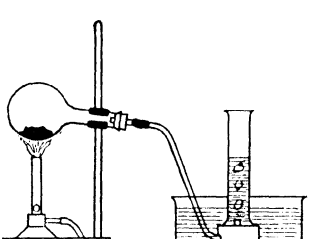


Fig. 91.

[1] *Soda lime* is a mixture of caustic soda and lime produced by slaking lime with a solution of caustic soda. It is used instead of pure caustic soda in this experiment because the latter would melt readily on strongly heating and attack the glass of the containing vessel.

wooden splint, *taking the same precautions as you would if the gas were hydrogen.* If the gas burns quietly all the air has been expelled from the apparatus, but if there is a "pop" you must wait a short time and test again. When the test is satisfactory collect several jars over water.

The gas which you have collected is called *marsh gas* because it is frequently generated in marshes or pools where vegetable matter is in course of decay. Another name for the gas is *methane.* The "blowers" in coal-mines discharge large quantities of this gas, which from its inflammable nature is termed "fire-damp," and it is also formed in the destructive distillation of wood or coal, coal gas containing usually about 35 per cent. of marsh gas

310. Properties of Marsh Gas.—

***Exp. 305.**—Examine a jar of marsh gas for colour, taste, and smell. Also invert a jar in water for some time and note the result.

Marsh gas is a colourless, odourless, tasteless gas; it is only slightly soluble in water, 100 volumes of which absorb about 4 volumes of the gas at ordinary temperature. Marsh gas is one of the difficultly liquefiable gases, requiring a pressure of 140 atmospheres at 0° C.

***Exp. 306.**—Apply a lighted taper to the mouth of a jar of the gas; push the taper down into the jar. What do you observe? When the gas has ceased to burn pour some lime-water into the jar and shake up. What happens?

We see from this experiment that marsh gas burns with a pale blue[1] nearly non-luminous flame, but does not support the combustion of a taper. Further, when the gas burns *carbon dioxide* is formed, showing that marsh gas contains *carbon.*

[1] The flame of marsh gas as prepared in Exp. 304 will probably be rather luminous owing to the presence of ethylene as impurity.

* **Exp. 307.**—Invert an empty jar over a jar of marsh gas, remove the cover, and leave for about 20 seconds. Apply a light to the mouth of each jar. The gas in the upper jar burns with a slight explosion, but that in the lower jar does not burn.

The marsh gas has therefore passed from the lower to the upper jar, showing that it is considerably *lighter than air*. It is in fact one of the lightest gases known, its density being not much greater than half that of air.

* **Exp. 308.**—Repeat Exp. 68, replacing the hydrogen generator by a marsh gas generator such as you have employed in Exp. 304. Test the colourless liquid which you obtain by burning the gas: it is water.

Water then is a product of the combustion of marsh gas, which must therefore contain *hydrogen*. We have already shown that it contains *carbon*. That these are the *only* elements present in the gas is proved by the fact that when hydrogen is passed over charcoal heated to a high temperature some marsh gas is formed. As we shall prove below the formula for marsh gas is CH_4. Its formation from sodium acetate and soda lime is represented by the equation (the lime taking no part in the reaction)—

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

The change which takes place when marsh gas burns in air is expressed thus—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

With oxygen or air within certain limits marsh gas forms an explosive mixture,[1] and the explosions occurring in coal-mines are usually due to the firing of such a mixture.

* **Exp. 309.**—Prepare a jar of chlorine and place it mouth to mouth with a jar of marsh gas (the jars should be of the same size). Place the jars in a *shady place* (*not*

[1] It is hardly necessary to point out that the mixture only explodes when heated by a flame or spark.

in *bright sunlight*), remove the glass covers and leave. Examine after a time. You will find that the colour of the chlorine has disappeared and that the jar is filled with white fumes. On removing the cover you will recognise the smell of hydrogen chloride. Confirm its presence by pouring a little silver nitrate into the jar and shaking up, when a white precipitate will form

The change which takes place when equal volumes of chlorine and marsh gas are brought together consists in the replacement of one of the hydrogen atoms of marsh gas by one atom of chlorine forming *methyl chloride*, CH_3Cl (a gas); the displaced hydrogen atom combines with an atom of chlorine forming hydrogen chloride.

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

If the gases are mixed in equal volumes in direct sunlight the same change takes place *with explosive violence.*

If excess of chlorine is present and the action takes place in diffused daylight the remaining atoms of hydrogen of marsh gas are gradually replaced with formation successively of compounds represented by the formulae, CH_2Cl_2, $CHCl_3$, and CCl_4.

The equations expressing the reactions which take place are as follows—

$$CH_3Cl + Cl_2 = \underset{\text{Methylene chloride}}{CH_2Cl_2} + HCl.$$

$$CH_2Cl_2 + Cl_2 = \underset{\text{Chloroform}}{CHCl_3} + HCl.$$

$$CHCl_3 + Cl_2 = \underset{\text{Carbon tetrachloride}}{CCl_4} + HCl.$$

Finally, if marsh gas is mixed with excess of chlorine *in direct sunlight* an explosion occurs with separation of carbon—

$$CH_4 + 2Cl_2 = C + 4HCl.$$

The process of the gradual replacement of the hydrogen atoms of marsh gas by chlorine is called *substitution* and the compounds produced, methyl chloride, etc., are called

substitution products. Bromine forms similar substitution products with marsh gas, but its action is slower; iodine by itself, however, has no action on the gas.

311. Preparation of Pure Marsh Gas.—Marsh gas as prepared by the method of Exp. 304 is by no means pure; it is contaminated with ethylene, C_2H_4, and hydrogen. The former may be removed to a large extent by passing the gas through a wash-bottle containing concentrated sulphuric acid, which absorbs the gas.

Pure marsh gas may be obtained by the action of nascent hydrogen on methyl iodide, CH_3I.

$$CH_3I + \underset{\text{Nascent}}{2H} = CH_4 + HI.$$

The methyl iodide is dissolved in a mixture of alcohol and water and zinc-copper couple added. The two last react with formation of hydrogen, which then reduces the methyl iodide. The presence of alcohol is necessary because methyl iodide is insoluble in pure water.

312. The Formula of Marsh Gas.—This may be determined by exploding a known volume (say 30 c.c.) of the pure gas with an excess of oxygen (120 c.c.) in a eudiometer; the carbon and hydrogen unite with oxygen to form carbon dioxide and water vapour respectively. No diminution in volume will occur if the experiment be performed at 100° C., that is, so long as the water remains in the form of vapour; but when the water condenses, a diminution of 60 c.c. will be recorded. Carbon dioxide and the excess of oxygen remain, and the amount of the former may be found by absorbing it with caustic potash; this will give a reduction of 30 c.c., the oxygen excess being 60 c.c. Expressing this shortly we have—

2 vol. marsh gas + 8 vol. oxygen = 4 vol. water vapour + 2 vol. carbon dioxide + 4 vol. oxygen.

Now water vapour contains its own volume of hydrogen, and two volumes of marsh gas therefore consist of four volumes of hydrogen and that amount of carbon which

is contained in two volumes of carbon dioxide, *i.e.* one atom. This would give us the formula CH_4.

We find, by weighing, that the density of marsh gas as compared with hydrogen is 8, so that its molecular weight must be 16: this agrees with the formula CH_4, for $C = 12$, $H_4 = 4 \times 1$, and $12 + 4 = 16$.

Ethylene or Olefiant Gas, C_2H_4.

313. Preparation of Ethylene.—

† **Exp. 310.**—Cautiously with stirring add 120 c.c. of concentrated sulphuric acid to 20 c.c. of rectified spirit. Pour the mixture into a wide-mouthed flask of about a

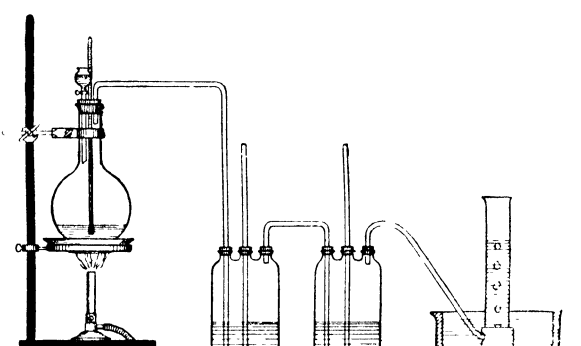


Fig. 92.

litre capacity, fitted with a cork through which pass (1) a rather wide delivery tube, (2) a thermometer, (3) a tap funnel (see Fig. 92). Heat on a sand bath until the temperature rises to 165° C. and keep as near this as possible. If the alcohol is impure a good deal of frothing occurs, which is, however, less troublesome if sand has been introduced into the flask. The gas which is evolved should be passed through a couple of wash-bottles containing a solution of caustic soda to absorb carbon dioxide and sulphur dioxide,

and collected over water, first testing whether the air has been driven out of the apparatus as you did in the case of marsh gas.

Syrupy phosphoric acid of such a concentration that it boils at 200° C. may with advantage be substituted for sulphuric acid. When this is used the frothing and charring are avoided, and, carbon dioxide and sulphur being absent, the washing of the gas may be dispensed with.

The gas which you have collected is called *ethylene* or *olefiant gas*. It occurs as one of the products of the destructive distillation of coal.

314. Properties of Ethylene.—

* **Exp. 311.**—Examine the gas for colour and odour. Invert a jar in water. The water rises very slowly.

Ethylene is a colourless gas with a feeble pleasant odour. It is slightly soluble in water, 100 c.c. of which absorb about 15 c.c. of the gas at ordinary temperatures. Ethylene is more easily condensed to the liquid form than marsh gas, as it only requires a pressure of 43 atmospheres at 0° C. Its density is very slightly greater than that of air.

* **Exp. 312.**—Apply a lighted taper to a jar of the gas. It burns with a luminous smoky flame, black particles of carbon collecting on the sides of the jar. Pour a little lime-water into the jar: it becomes milky, showing that carbon dioxide has been formed during the combustion.

The separation of carbon and the formation of carbon dioxide prove that ethylene contains *carbon*.

By burning the gas at a jet as in Exp. 68 it may be shown that *water* is a product of the combustion of ethylene, which must therefore contain *hydrogen*. It can further be proved that carbon and hydrogen are the only elements present in the gas, which is represented by the formula C_2H_4.

Ethylene forms much more explosive mixtures with oxygen or air than marsh gas; if oxygen is mixed with the gas in the proportion of 3 : 1 the mixture explodes with extreme violence when a flame is brought in contact with it.

* **Exp. 313.**—Bring together jars of chlorine and ethylene of equal size. Remove the covers. Note the disappearance of the colour of chlorine and the formation of an oily liquid.

The change which taxes place consists in the direct combination of the two gases to form a compound, ethylene chloride, $C_2H_4Cl_2$.

$$C_2H_4 + Cl_2 = C_2H_4Cl_2.$$

The name *olefiant gas* was given to ethylene on account of the formation of this oily liquid.

Bromine and iodine form similar oily liquids by direct combination with ethylene. On account of this property of forming *addition* compounds ethylene is said to be *unsaturated*; marsh gas, which only forms *substitution* compounds, is said to be *saturated*.

In marsh gas carbon is exerting its full valency of 4, and so it cannot take up any more atoms; in ethylene carbon is not exerting its full valency, and can therefore form addition compounds.

If ethylene is brought together with *excess* of chlorine in direct sunlight an explosion takes place, carbon particles separate out, and hydrogen chloride is produced.

$$C_2H_4 + 2Cl_2 = 2C + 4HCl$$

315. Changes which take place during the formation of Ethylene from Alcohol and Sulphuric Acid.—Alcohol behaves towards sulphuric or phosphoric acid like a base such as caustic potash, forming a compound of similar formula and in some respects similar properties.

$$KOH + H_2SO_4 = KHSO_4 + H_2O,$$

$$C_2H_5OH + H_2SO_4 = \underset{\substack{\text{Ethyl hydrogen sulphate}\\ \text{or}\\ \text{Ethyl sulphuric acid}}}{C_2H_5HSO_4} + H_2O.$$

The group of elements C_2H_5 is called *ethyl*.

When ethylsulphuric acid is heated, however, it decomposes with formation of ethylene and sulphuric acid.

$$C_2H_5HSO_4 = C_2H_4 + H_2SO_4.$$

The last two equations represent, therefore, the two stages of the reaction which takes place in the preparation of ethylene.

When ethylene is passed into *cold* sulphuric acid it is slowly absorbed with formation of ethylsulphuric acid, *i.e.* the last reaction is reversed.

$$C_2H_4 + H_2SO_4 = C_2H_5HSO_4.$$

316. The Formula of Ethylene.—This is determined by a method similar to that employed in the case of marsh gas. It is found that on explosion with excess of oxygen ethylene reacts with three times its volume of oxygen, yielding twice its volume of carbon dioxide and twice its volume of steam. This is in agreement with the formula C_2H_4, for the gas

$$\underset{2\text{ vol.}}{C_2H_4} + \underset{6\text{ vol.}}{3O_2} = \underset{4\text{ vol.}}{2CO_2} + \underset{4\text{ vol.}}{2H_2O}.$$

This formula is confirmed by determining the density of the gas, which is found to be 14, corresponding to a molecular weight of $2 \times 14 = 28$.

Now $\quad C = 12$ and $H = 1$,

$$\therefore\ C_2H_4 = 2 \times 12 + 4 \times 1 = 28,$$

i.e. the molecular weight deduced from the formula C_2H_4 is the same as that deduced from the density of the gas.

Acetylene, C_2H_2.

317. Formation of Acetylene.—

† **Exp. 314.**—Place a small lump of calcium carbide under a jar of water inverted in a trough of water. Bubbles of gas rise from the lump and collect in the jar.

When the jar is full of gas[1] (or when the action has ceased) cover the mouth with a glass plate and stand the jar upright. Remove the cover and *at once*[2] apply a light. The gas burns with a very luminous smoky flame. Show by the lime-water test that carbon dioxide has been formed during the combustion.

The gas you have prepared is called *acetylene.* The separation of carbon particles and formation of carbon dioxide, when it burns, proves that it contains *carbon.*

It can further be shown that *water* is formed when acetylene burns, so that the gas also contains *hydrogen.* Since also acetylene is formed when carbon and hydrogen are strongly heated together (*e.g.* by passing a powerful electric discharge between carbon poles in an atmosphere of hydrogen) it follows that carbon and hydrogen are the only two elements present in the gas. It is represented by the formula C_2H_2 (see below, § 320).

Acetylene occurs in small quantity in coal gas and is formed when coal gas is burnt in an insufficient supply of air (*e.g.* when a Bunsen burner "strikes back") or when the flame is cooled by impinging on a cold surface.

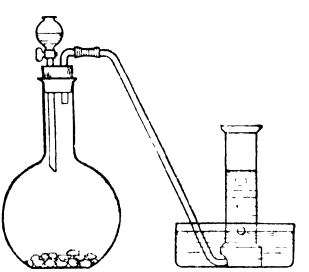


Fig. 93.

318. Preparation of Acetylene.—Acetylene may be conveniently prepared by allowing water to drip slowly from a dropping funnel on to some calcium carbide contained in a small flask (Fig. 93) and collecting the gas over water after testing whether the air has been driven

[1] If gas is still being evolved collect it in a second jar and burn it. Do not let it escape into the air, as it is *very poisonous.*

[2] To prevent an explosion. The gas forms a very explosive mixture with air.

out of the apparatus as in the case of marsh gas. The change which takes place is represented by the equation—

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

319. Properties of Acetylene.—Pure acetylene is a colourless gas which possesses a pleasant smell. The unpleasant odour of the gas produced by the action of water on calcium carbide (which you will have observed in Exp. 316) is due to the presence of impurities; so also the unpleasant smell observed when a Bunsen burner "strikes back" is not due to acetylene.

Acetylene is fairly soluble in water, which dissolves about its own volume of the gas at ordinary temperatures; it is fairly easily condensed to a liquid requiring a pressure of about 50 atmospheres at 0° C. The gas is slightly lighter than air, its density being 13 times that of hydrogen.

Acetylene burns in air with a very luminous smoky flame, and forms very explosive mixtures with air or oxygen (within certain limits). By using a burner with a very fine hole, the flame of acetylene becomes non-smoky and exceedingly luminous. As might be expected, the gas is employed to a considerable extent for illuminating purposes, *e.g.* in bicycle lamps, and, more recently, for house illumination where coal gas is not available; it is generated as required by the action of water on calcium carbide, for it cannot safely be stored under pressure on account of its tendency to explode when compressed. Acetylene is also used to increase the luminosity of other gases, such as oil gas, or coal gas below illuminating power.

Acetylene resembles ethylene in that it combines *directly* with chlorine or bromine, *i.e.* it is unsaturated; also whereas one molecule of ethylene only combines with *one* molecule of a halogen, one molecule of acetylene will combine with *either one or two molecules, i.e.* acetylene is *more unsaturated* than ethylene.

$$C_2H_2 + Br_2 = \underset{\text{Acetylene dibromide}}{C_2H_2Br_2}.$$

$$C_2H_2Br_2 + Br_2 = \underset{\text{Acetylene tetrabromide}}{C_2H_2Br_4}.$$

Acetylene is absorbed by a solution of cuprous chloride in ammonia with formation of a brown precipitate, cuprous acetylide, Cu_2C_2, in which the hydrogen atoms of the acetylene are replaced by copper.

320. Formula of Acetylene.—When acetylene is exploded with excess of oxygen in a eudiometer it is found that two volumes of acetylene combine with five volumes of oxygen to form four volumes of carbon dioxide and two volumes of water vapour. This is explained if we assume the formula C_2H_2 for the gas—

$$\underset{4\text{ vol.}}{2C_2H_2} + \underset{10\text{ vol.}}{5O_2} = \underset{8\text{ vol.}}{4CO_2} + \underset{4\text{ vol.}}{2H_2O}$$

The formula is confirmed by the density of the gas, which, as already stated, is 13 times that of hydrogen. This gives 2×13 or 26 as the molecular weight of the gas.

Now since C = 12 and H = 1, we have

$$C_2H_2 = 2 \times 12 + 2 \times 1 = 26.$$

321. Hydrocarbons.—We have now studied three compounds each of which is composed of the elements carbon and hydrogen only. Such compounds are called *hydrocarbons*, and their number is very great.

The composition of the three we have considered is simple, but some hydrocarbons are very complex; one, for example, contains 60 atoms of carbon and 122 atoms of hydrogen. Hydrocarbons containing a small number of atoms of carbon and hydrogen are usually gaseous, such as marsh gas and ethylene; those whose composition is more complex are at ordinary temperatures liquid, such as benzene, C_6H_6, and oil of turpentine, $C_{10}H_{16}$, or solid, such as naphthalene, $C_{10}H_8$, and anthracene, $C_{14}H_{10}$.

Coal Gas and Wood Gas.

322. Action of Heat on Coal.—

Exp. 315.—Examine a coal fire, or heat a small piece of coal in a gas flame. You will notice the softening of the coal where it is heated, the giving off of an inflam-

mable gas, and the final burning of the coal. The coal also lights easily.

Exp. 316.—Take a jar[1] of oxygen and lower into it a small piece of coal on a deflagrating spoon after lighting a corner. When the coal has stopped burning, test the contents of the jar for water by means of anhydrous copper sulphate and for carbon dioxide by lime-water.

The products of combustion are thus seen to be carbon dioxide and steam.

Exp. 317.—Fit up the apparatus shown in Fig. 94. A is a dry hard glass tube half filled with *dry* coal dust. Before heating this tube it must be shaken to make an air-space over the coal dust. The wide test-tube B should be almost completely immersed in a beaker of cold water. The corks must fit tight. Heat the tube carefully. Note the formation of brown fumes; these mostly condense in B, and a liquid collects which separates into two layers. Test the gas issuing at C with paper moistened with lead acetate solution; note the blackening, showing the presence of *sulphuretted hydrogen*. Hold a drop of lime-water on the end of a glass rod in the gas: it becomes milky, proving that *carbon dioxide* is present.

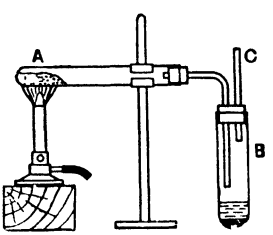


Fig. 94.

After some time apply a light[2] to the gas at C; it burns with a luminous flame: it is *coal gas*. When the flame goes out, disconnect the apparatus. Test the light coloured upper layer of liquid in B with red litmus paper: the litmus is turned blue, owing to the presence of *ammonia*. This upper layer is an aqueous solution of ammonia and

[1] The jar must have been dried.

[2] It will be safest first to test whether the air has been completely displaced from the apparatus as you would in the case of hydrogen. (Nearly half the gas is hydrogen.)

other substances and is called *gas liquor*; the thick dark brown lower layer is *coal tar*. Now break the tube A and note the hard *coke*.

This process of distilling coal out of contact with air[1] is repeated on the large scale in the manufacture of coal gas, the coal being heated in fireclay retorts and the volatile products condensed by passing through a series of vertical pipes. The condensed products are collected in a suitable receiver where they separate into two layers, gas liquor and coal tar, as in Exp. 317.

The gas which passes on is carefully purified from *ammonia* (by passing through water), sulphuretted hydrogen (by ferric hydroxide), and carbon dioxide (by slaked lime), and is then stored in gas-holders over water.

A ton of coal yields about 10,000 cubic feet of coal gas, which varies in composition, but contains approximately—

Hydrogen	50 per cent.
Marsh gas	35 ,,
Carbon monoxide	8 ,,
Ethylene, etc....	5 ,,
Nitrogen and oxygen	3 ,,

Thus about 96 per cent. of the product has little or no illuminating power, this property being mostly due to the 5 per cent. of ethylene, etc.

Gas liquor is an aqueous solution of ammonia and ammonium salts—chiefly the sulphide and carbonate; the amount of free ammonia is very small. Gas liquor is the source of practically all the ammonia and ammonium salts of commerce.

Coal tar is a complex mixture of substances which are separated by suitable processes. Among the most important are benzene (liquid), naphthalene (solid), anthracene (solid), and carbolic acid or phenol (solid), which constitute the raw material of the dye manufacturer.

[1] The small amount of air present in the tube at the commencement is very rapidly burnt up.

323. Coke.—The residue in the retorts after the distillation of all the volatile products from coal is composed of two substances, *coke* and *gas-carbon*. The former is found in the centre of the retorts and consists principally of carbon, but contains all the non-volatile mineral matter present in the coal (*i.e.* the ash), and also small quantities of hydrogen, nitrogen, and oxygen; the latter occurs as a deposit on the roof and sides of the retorts and is nearly pure carbon. Gas-carbon has been sufficiently fully treated in § 290. We shall, however, study coke at somewhat greater length.

The amount of ash in coke varies with the coal used, but the average composition is—

Carbon	91·5 per cent.
Hydrogen	0·4 ,,
Nitrogen and oxygen	2·1 ,,
Ash	6·0 ,,

Exp. 318.—Try to light a piece of coke in a flame: it does not burn so readily as coal, and requires a higher temperature to set it on fire.

The temperature obtained by burning coke is very high, and, as there are no volatile products, there is generally neither luminous flame nor smoke from dry coke.

Blue flames are often noticed playing above a brightly burning coke fire: these are flames of carbon monoxide, formed by the reaction between carbon dioxide and red-hot carbon as already explained in § 303.

Coke is not only obtained as a by-product in the manufacture of coal gas, but it is also specially manufactured by heating coal to redness in coke ovens. The coke so prepared is very dense and is used in iron-smelting.

324. Action of Heat on Wood.—When wood is heated in the air it chars, gives off inflammable gases, and burns, leaving a black mass of charcoal, which slowly burns away.

Exp. 319.—Repeat Exp. 317, using wood splints instead of coal dust. Note the formation of a water distillate (which is *acid* to litmus), tar, inflammable gas, and charcoal.

Thus the distillation of wood and of coal in absence of air gives similar products; for we obtain wood gas, a water distillate, wood tar, and charcoal. *Wood gas* is used for illuminating purposes in Germany and Switzerland The temperature of distillation must be very high, however, or the gas does not contain sufficient illuminating gases (heavy hydrocarbons) to be of any use for lighting purposes. The high temperature decomposes a large quantity of liquid oils which would simply distil over if a lower temperature were used.

This decomposition is helped by the use of cast-iron retorts instead of clay retorts.

The composition of wood gas as used for illuminating purposes varies between the following wide limits:—

Hydrogen	18 to 42 per cent.
Marsh gas	9 to 35 ,,
Carbon monoxide	22 to 62 ,,
Ethylene, etc.	9 to 35 ,,

Practically no sulphur compounds are produced, but a considerable amount of carbon dioxide is given off, which is removed by slaked lime as in the case of coal gas.

The watery distillate contains only a small quantity of ammonia (there is much less nitrogen in wood than in coal), but a number of organic substances are prepared from it, of which the chief are wood vinegar (acetic acid), wood spirit (methyl alcohol), and acetone. The presence of acetic acid explains the acid reaction of the aqueous distillate.

Wood tar contains many organic substances, of which creosote is the most important; the latter is used for the preservation of timber.

The residue left in the retort after the distillation is *wood charcoal*, which has already been fully described in §§ 285-287.

QUESTIONS.—CHAPTER XX.

1. Describe how you would proceed to prepare and collect a few cylinders of marsh gas. What experiments would you perform in order to demonstrate the chief properties of the gas?

2. How would you prove experimentally that marsh gas contains the elements carbon and hydrogen?

3. State what you know about the action of chlorine on marsh gas. Give equations.

4. Explain how the formula for marsh gas may be established experimentally.

5. 20 c.c. of marsh gas are exploded with 50 c.c. of oxygen. What will be the volume of the resulting gas? Also what diminution in volume will take place on treating the resulting gas with excess of caustic potash?

   All volumes are supposed to be measured under standard conditions of temperature and pressure.

6. Describe in detail the preparation of ethylene from alcohol.

7. Explain the terms—*substitution compound, addition compound, unsaturated compound, saturated compound.*

8. How may marsh gas be distinguished from ethylene?

9. Describe with equations the chemical changes which take place when ethylene is burnt in air and in chlorine.

10. Under what circumstances is acetylene formed during combustion of hydrocarbons? Can you suggest any means of determining the amount of acetylene in a mixture of hydrogen and acetylene?

11. Describe how you would investigate experimentally the action of heat on coal in the absence of air.

12 Write a short account of the chief products of the destructive distillation of coal.

13. Describe how you would proceed to prepare and collect a few jars of acetylene, using calcium carbide. What experiments would you perform in order to demonstrate the chief properties of the gas? For what purposes is the gas employed?

14. How is the formula of acetylene established?

15. 30 c.c. of ethylene are exploded with 150 c.c. of oxygen and the resulting gas treated with excess of caustic soda. What volume of gas will remain and of what will it consist?

All volumes are supposed to be measured at atmospheric temperature and pressure.

16. 10 c.c. of acetylene measured at 120° C. and 750 mm. pressure are exploded with 80 c.c. of oxygen measured at the same temperature and pressure. What will be the volume of the resulting gas if the temperature and pressure suffer no change, and of what will it consist?

CHAPTER XXI.

COMBUSTION.

325. Development of Heat in Chemical Reaction.—During the course of his experiments the student has frequently had occasion to notice that heat is developed when chemical reaction takes place.

For example, when water is added to quicklime sufficient heat is developed to convert some of the water into steam (Exp. 156), and when nitric acid is added to magnesium or zinc the mixture very soon becomes very hot.

The great majority of chemical reactions are in fact accompanied by the liberation of heat, though the amount set free varies very much with the nature of the reaction.

326. Incandescence.—When the temperature of a body is raised to such a degree that it gives out light, it is said to be incandescent, or in a state of *incandescence*.

Exp. 320.—Take pieces of platinum wire, iron wire, magnesium ribbon, black lead, charcoal, and some iron filings. Heat the first five and drop the filings through a flame, holding the burner aslant. In each case light is given out. While the platinum and iron wires and black lead return to the same state on cooling, the magnesium, charcoal, and iron filings are changed by oxidation.

Exp. 321.—Heat carefully about two grams of a finely powdered mixture of potassium ferrocyanide and potassium dichromate in a porcelain basin, removing the flame as soon as a change takes place. Note that the change from yellow to red is attended by incandescence.

Incandescence may thus be produced either by external heating or by the heat arising from chemical change.

Liquids and gases may also become so hot as to be incandescent, as in the flash seen during the explosion of a mixture of hydrogen and oxygen. The most common example of the incandescence of gases is afforded by flames.

327. Flame.—Whenever a gas or vapour is brought into an atmosphere with which it can react chemically, and the heat generated is sufficient to bring about incandescence of the particles, flame is produced. The heat is generated and the incandescence effected in the region where the reaction is carried on, that is, at the surface where contact occurs between the two gases, as is seen when a jar of hydrogen burns mouth downwards. When we speak of hydrogen and coal gas as being combustible gases, and of air as being a supporter of combustion, we imply that hydrogen and coal gas, when once ignited, burn in air. In ordinary flames this is the case; it is, however, possible to cause a jet of air to burn in coal gas.

† **Exp. 322.**—Fit the bottom of an ordinary paraffin-lamp chimney with a cork through which pass two tubes —one being of metal, short and wide enough to take a lighted taper and projecting half an inch or more into the chimney; the other of glass, about as thick as a penholder and projecting outwards for attachment to the tube conveying coal gas. Set the chimney upright in a clamp and cover the top with a piece of fine wire gauze. Close the metal tube with the finger or a small cork, turn on the gas, and after the air has been swept out of the chimney light the gas escaping from the top. The flame here obtained is an ordinary one.

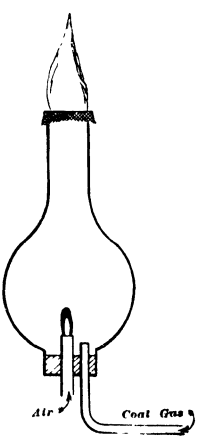


Fig. 95.

Remove the finger and at once thrust a lighted taper up the metal tube, when a small flame will appear at its top.

Evidently the ingoing air is burning, while the coal gas is acting as supporter of combustion (Fig. 95).

Note.—If there is a good supply of gas there need be no fear of explosion.

Whether, however, coal gas burns in air or air in coal gas the flame marks the surface of contact between the air and the coal gas, and is the region where the chemical changes take place which transform the hydrogen and carbon of the coal gas into water and carbon dioxide as ultimate products.

Where the gases are intimately mixed and then ignited the burning takes place with great rapidity, and an explosion of a more or less violent nature ensues; but where a regular supply of the combustible product impinges upon the atmosphere in which it burns, a more or less steady flame is the result, the particular form of which is determined by the nature of the jet and the shaping influence of air-currents.

328. Point of Ignition.—

Exp. 323.—Place in small basins or little tin saucers two or three drops of benzoline, a few drops of paraffin, and a small piece of paraffin wax, and apply a light to each. The benzoline burns at once, the paraffin oil must be slightly warmed, while the paraffin wax must be heated over a burner before it will light.

This experiment illustrates the fact that, before flame can be produced at all, the temperature of the combustible body must first reach a certain limit known as the *point of ignition.* Conversely, a flame is extinguished if its temperature is by any means reduced below the point of ignition of the vapours consumed in it. The ignition point varies with different bodies: the vapour of carbon bisulphide may be ignited by a glass rod heated only to 150° C., whilst for hydrogen or coal gas a dull red heat (600° C.) is insufficient.

The temperature at which paraffin oil ignites is called its "flashing point," and it is illegal to sell paraffin for

burning purposes whose flashing point as determined by special apparatus is below a certain standard for this means that the more volatile constituents have not been properly removed, so that at temperatures very little above the ordinary they are vaporised and form an explosive mixture with the air.

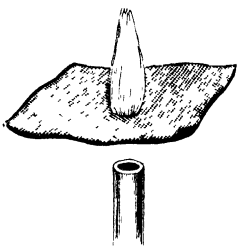


Fig. 96.

Exp. 324.—Hold a piece of wire gauze (about thirty meshes to the inch) horizontally over a Bunsen burner and about an inch above the orifice (Fig. 96). Turn on the gas and light it on the upper side of the gauze. The flame will not be communicated to the stream of gas on the under side of the gauze.

This is explained by the fact that the metal of the wire gauze is a good conductor of heat. The heat received from the flame is rapidly conducted away by the gauze and dissipated, chiefly by radiation. This continuous loss of heat prevents the temperature of the gauze from reaching the ignition point of the gas, and, as the gas below the gauze can only become heated by contact with the gauze, it does not become ignited.

Exp. 325.—Now turn out the burner (Exp. 324), and light the gas *below* the gauze. Note that the gas does not ignite above the gauze until the latter becomes red hot.

Exp. 326.—Make a piece of the wire gauze into a cylindrical roll, and place a candle within it. Now direct the flame of a Bunsen burner against the outer surface of the gauze; the wax may be melted, but the candle cannot be lighted unless the gauze is heated to redness.

The reason for these results will be gathered from the explanation given above.

The *Davy Lamp* (Fig. 97) is a similar arrangement to that used in Exp. 326, in which an oil lamp is shut in by a layer of gauze; and, even if such a lamp be entirely surrounded with inflammable gas, this will not become ignited, although the inflammable gas which passes through the gauze may burn inside it and fill the space above the oil lamp with flame. If, however, the gauze becomes strongly heated, or if the flame should be mechanically driven through the meshes, communication with the inflammable atmosphere outside may be established, and ignition will then take place.

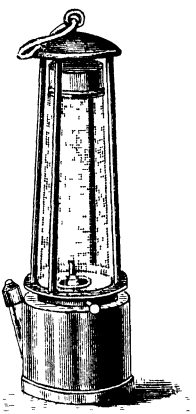


Fig. 97.

329. The Candle Flame.—The inflammable matter in a candle is the wax or tallow, consisting of compounds containing carbon and hydrogen. The wax is melted and passes up into the wick, which serves as a still supplying the vapours of carbon compounds to the space immediately surrounding it. That such a space exists containing combustible vapours may easily be shown by the following experiment:—

Exp. 327.—Depress a sheet of stout paper quickly into a candle flame to the level of the top of the wick, and hold it steadily there for about a second. On withdrawing it, a ring of sooty deposit will be seen, and within it a clear space. Secondly, take a glass siphon-tube, as shown in Fig. 98, and bring the shorter limb into the centre of the flame; presently yellowish-brown vapours will be seen to pass down the tube and issue at the other end. These vapours will be found to be inflammable, and may be burnt at the end of the tube.

Exp. 328.—Now examine the candle flame carefully and you will distinguish—

(1) A central non-luminous zone surrounding the wick, and containing vapours of carbon compounds—the zone of no combustion (A in Fig. 98);

(2) A blue non-luminous zone, B, at the base;

(3) A luminous zone, C, surrounding the dark central zone; and

(4) A faintly luminous mantle, D. Under ordinary circumstances this zone is not easily seen, but if a little finely-powdered common salt is sprinkled over the flame, it will flash out as a golden-yellow fringe, the colour of which is due to the salt.

The mantle can also be seen as a golden band above the wick by looking just above the glowing tip of the wick which bends over to the side of the flame.

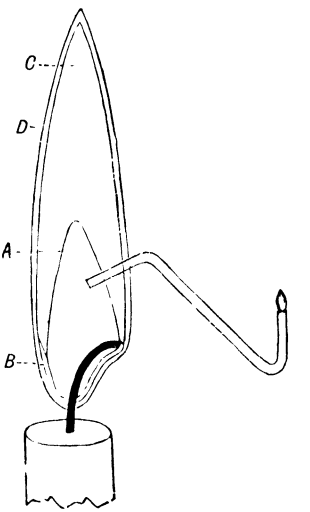


Fig. 98.

The changes which take place in the different zones are somewhat as follows:—(A) Vaporisation of the carbon compounds. As these pass up this zone decomposition takes place, with gradual formation of acetylene and from it of dense hydrocarbons, and finally of free carbon particles.

(B) The hydrocarbons present undergo partial combustion, with formation of carbon monoxide, hydrogen, and water—

$$CH_4 + O_2 = CO + H_2 + H_2O,$$
$$C_2H_4 + O_2 = 2CO + 2H_2.$$

(C) The changes which take place in this zone are very complex. The formation of dense hydrocarbons and separation of carbon particles is continued. Also incomplete

combustion takes place with formation of carbon monoxide, carbon dioxide, hydrogen, and steam. The luminosity of this zone is due to the presence of the solid carbon particles and dense hydrocarbons, which become incandescent owing to the heat evolved by the chemical reactions which are taking place.

(D) Here the products of zones (B) and (C) are mixed with excess of air and burnt completely to carbon dioxide and water.

330. The Gas Flame.—A coal-gas flame has the same four zones as a candle flame unless the jet is very small. As its size is reduced the luminous zone gradually diminishes relatively to the non-luminous zones, and when the jet is very small it entirely disappears. The flame now consists of three zones only, and presents the appearance shown in Fig. 99.

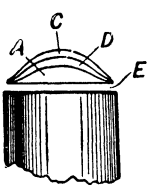


Fig. 99.

A is the zone of no combustion. B is the zone of incomplete combustion; it is blue, like zone B in Fig. 98, to which it corresponds. In the mantle C the combustion is complete. Between the flame and the burner there is a space E containing unburnt gas; it is part of the zone of no combustion.

Exp. 329.—Examine a gas-jet when turned on full, and note the zones as in the candle flame (§ 329). The mantle can be shown to be hot by means of a thin piece of wire held across the flame. Note the changes in the character of the flame as the gas is gradually lowered, and the gradual disappearance of the luminous zone.

331. Luminosity of Flame.—There are three factors, some or all of which are concerned in the luminosity of flame—(1) the presence of solid particles; (2) the density of the flame gases; (3) the temperature. At one time it was believed that (1) and (3) were the sole causes; this was Davy's theory, and it was supported by the following facts:—

(*a*) Most flames in which no solid particles can be present are practically non-luminous: *e.g.* hydrogen burning in oxygen.

(*b*) Non-luminous flames become luminous when solid particles are introduced into them: *e.g.* finely divided charcoal or lime blown into a hydrogen flame makes it luminous.

(*c*) A glass rod held in a candle flame becomes covered with soot only on the under side. If the interior of the flame consisted of vapours which deposited soot because they were cooled down by the rod, the deposit should be all round.

(*d*) Luminous flames, like that of a candle, when placed between a brighter light and a screen, cast a shadow; non-luminous flames cast no shadow.

That the luminosity of some flames is not due to the presence of incandescent solid particles is shown by the existence of luminous flames in which no solid matter can possibly be formed: *e.g.* the flame produced when phosphorus or phosphoretted hydrogen burns in oxygen, or carbon bisulphide in nitric oxide. At the temperature of the flame in these cases all the possible products of combustion are gases. According to Frankland's theory, luminosity is due to the presence of heated gases, the luminosity increasing with the density of the gases. This is supported by the following facts:—

(*a*) A candle burns at high altitudes or in an artificially rarefied atmosphere with greatly reduced luminosity.

(*b*) The flame of hydrogen burning in oxygen becomes luminous when the gases are under a pressure of two atmospheres.

The effect of the temperature of a flame upon its luminosity may be studied by experiment.

Exp. 330.—Make a short coil of stout copper wire by giving it half a dozen turns round a piece of glass rod about 5 mm. in diameter, leaving only a small space between one coil and the next. Bring the coil into the upper part of the luminous zone of a candle flame: the

flame will become smoky; if it be quickly depressed to the level of the wick, the flame loses its luminosity, and, indeed, may be extinguished altogether.

Now fill a gas jar with oxygen and lower a lighted candle into it: the flame becomes much shorter and brighter.

In the first case, copper, which is a good conductor of heat, conveys away heat from the flame, and lowers its temperature to such an extent that the solid particles of carbon can no longer keep up their luminosity; they escape combustion and pass off as smoke. Indeed, the vapours may also be cooled below their ignition point, in which case the flame is extinguished altogether.

In the second case, the heat given out is not utilised in raising the temperature of the nitrogen of the air, but is all available for heating the particles of carbon.

Thus, raising the temperature of a flame increases its luminosity, and lowering its temperature decreases its luminosity.

The effect of cooling is often noticed in very cold weather, when the gas, if carried by exposed pipes, does not possess its usual illuminating power: this is partly due to the condensation of volatile liquid and solid hydrocarbons contained in the gas, and also to the extra amount of heat required to raise both gas and air to the temperature of incandescence.

In ordinary flames used for various purposes all three causes operate and may be utilised.

332. The Batswing and Fishtail Flames.—In these flames the gas is made to issue from a narrow slit (fishtail) or from two jets which impinge on each other (batswing).

By these devices the flame is flattened. This enlarges the surface of gas exposed to the air, and thus increases the rate of combustion and the luminosity.

333. The Bunsen Flame.—This flame is produced by mixing air with the gas which is to be burned, in such quantity as to render the flame practically non-luminous.

The gas is supplied through a small jet placed inside a wide tube, so that the rush of gas sucks in air through holes at the bottom of the tube; the mixture of gas and air passes up the tube, and is ignited at its mouth.

The Bunsen flame consists of three zones (Fig. 100). The innermost zone A is the zone of *no combustion.* In B (which is pale blue) *incomplete combustion* takes place since coal gas is in excess of air, whilst in C (which is very pale blue) the combustion is complete, air being in excess.

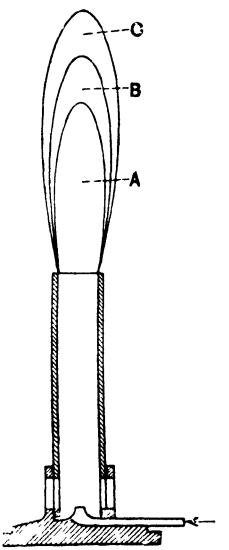


Fig. 100.

The non-luminosity of a Bunsen flame is caused by (1) increased oxidation by which the separation of solid particles of carbon is prevented, or at any rate reduced; (2) dilution by the nitrogen of the air—this raises the temperature required for the decomposition of the hydrocarbons of coal gas; (3) cooling by the large volume of air introduced. The result of (2) and (3) is that the gases reach the outer zone where air is in excess and are completely burnt up before they attain the temperature at which dense hydrocarbons are formed and carbon particles separate.

It should be noted that a Bunsen flame is *considerably hotter* than an ordinary coal gas flame, the cooling effect of the air introduced being more than counterbalanced by the extra heat resulting from increased oxidation.

334. Oxidising and Reducing Flames.—The foregoing paragraphs show that heated hydrocarbon vapours have the power of combining with oxygen in the gaseous condition to form carbon monoxide or dioxide, hydrogen, and water vapour. They have thus the power of abstract-

ing oxygen from many solid oxides or other bodies containing oxygen. This property may readily be shown either by means of the flame of a Bunsen burner or of the mouth blowpipe.[1]

* **Exp. 331.**—Partially close the holes at the base of the Bunsen burner until there appears a well-defined luminous tip (A in Fig. 101) within the flame owing to the reduction of the air supply. Now introduce within the luminous area a small amount of barium sulphate on a loop of thin platinum wire, and hold it there steadily for two or three minutes.

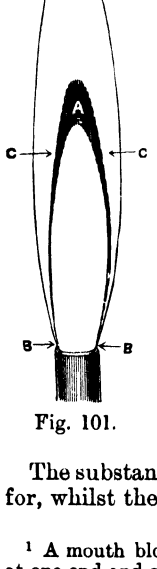


Fig. 101.

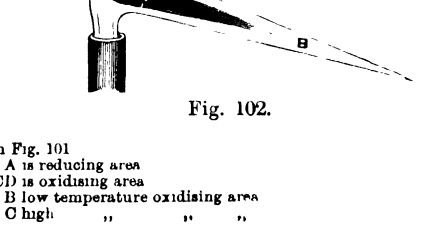


Fig. 102.

In Fig. 101
A is reducing area
BCD is oxidising area
B low temperature oxidising area
C high " " "

In Fig 102
A is reducing area
B is oxidising area

The substance will be found to have changed in character, for, whilst the barium sulphate originally taken is unacted

[1] A mouth blowpipe is a hollow metal tube with a mouth-piece at one end and a nozzle at the other at right angles to the length of the tube. The nozzle is arranged in the position shown in Fig. 102 and air is blown through the tube.

upon by hydrochloric acid, the resulting body when moistened with dilute hydrochloric acid evolves an odour of sulphuretted hydrogen.

The sulphate of barium ($BaSO_4$) has been deprived of its oxygen, and has become barium sulphide (BaS); this on treatment with dilute hydrochloric acid is transformed into the soluble chloride of barium with the evolution of sulphuretted hydrogen (H_2S)—

$$BaS + 2HCl = BaCl_2 + H_2S$$

Similarly, oxide of lead or copper may be reduced to metallic lead or copper when brought into the inner flame, A, of the blowpipe (Fig. 102). Wherever in a flame the hydrocarbons predominate and the supply of oxygen is limited such a *reducing* action prevails; and wherever in a flame the supply of oxygen is in excess of that required to consume the hydrocarbons, as in the outer zone of the candle or the Bunsen burner or the blowpipe flame, an *oxidising* action is experienced. This may be shown by bringing metallic tin or other metals into the outer margin of the Bunsen flame.

335. Definition of "Combustion."—The term *combustion* has hitherto been used in the popular sense to indicate the burning of a substance in air. Chemists, however, usually assign a broader meaning to the term, as follows:—*Combustion is chemical reaction between two substances accompanied by the production of heat and light.* There is no restriction as to the nature of the reacting substances. Some writers include under the term combustion such processes of oxidation as the rusting of iron in moist air, in which heat only, not light, is produced; but this is, perhaps, carrying the use of the term too far.

Usually the substance which is *outside* during the combustion is spoken of as a *supporter of combustion*, and that which is *inside* as the *combustible body*; but, as has been shown above in the case of coal gas and air, the supporter of combustion and the combustible body can change places. This holds also in other cases, the terms being only relative.

Since the external substance is usually air, a substance is commonly said to be combustible or not according to whether it will or will not burn in air. Thus, hydrogen, phosphorus, and carbon monoxide are combustible; chlorine and nitrous oxide are not combustible.

Again, a substance is said to be a *supporter of combustion* if it will allow the same substances to burn in it as burn in air (*e.g.* coal gas, hydrogen, a taper). Chlorine and nitrous oxide are supporters of combustion; sulphuretted hydrogen, carbon monoxide, and hydrogen are not.

Strictly speaking, however, any two substances which can exist in the gaseous state and which can combine chemically with sufficient evolution of heat may occupy towards each other the positions of supporter of combustion and combustible body interchangeably. For example, a jet of hydrogen will burn in chlorine, and a jet of chlorine will burn in hydrogen. In the former case hydrogen is the combustible body and chlorine the supporter of combustion; in the latter the reverse. Again, phosphorus burns in oxygen; but it would be possible to burn oxygen in phosphorus vapour, in which case the latter would be the supporter of combustion.

336. Heat of Combustion.—Whenever carbon, hydrogen, or bodies containing carbon and hydrogen burn, by combining with the oxygen of the air (the carbon to form carbon monoxide or dioxide, and the hydrogen to form water), the amount of heat accompanying the change is perfectly definite and constant for a given weight of the substance burnt.

If a gram of pure carbon be burnt to carbon dioxide, the heat given out will be sufficient to raise the temperature of 8,080 grams of water from 0° C. to 1° C.; this is expressed shortly by the statement that the *heat of combustion* of one gram of carbon is 8,080 thermal units or calories.[1] So, in like manner, the combustion of one gram of hydrogen is

[1] The *unit quantity of heat* called the *calorie* is the amount of heat required to raise the temperature of one gram of water from 0° C. to 1° C.

found to give rise to the evolution of 34,200 thermal units. Hydrogen, therefore, on combustion gives out more than four times the amount of heat evolved by the same weight of carbon.

Bituminous coal consists chiefly of carbon, but, as it contains some hydrogen, it should give out more heat on combustion than the same weight of carbon, and it would do so but for the fact that it contains usually 15 to 20 per cent. of oxygen, sulphur, nitrogen, and mineral ash, which are practically unproductive of heat. In anthracite, however, these constituents amount to little more than 5 per cent., and the heat of combustion of this kind of coal is greater than that of bituminous coal.

Petroleum, consisting entirely of carbon and hydrogen, and containing much more hydrogen than coal, actually does give out more heat than the same weight of carbon.

Fuel being employed for heating purposes, the amount of heat generated in its combustion is of primary importance, and the following table shows at a glance the comparative value of different substances which are applicable as fuels:—

Hydrogen ...	34,200	thermal units per gram consumed.
Petroleum ...	12,000	,, ,,
Coal ...	7,500 to 8,500	,, ,,
Carbon ...	8,080	,, ,,
Wood ...	about 3,000	,, ,,

QUESTIONS.—CHAPTER XXI.

1. Explain the term *incandescence*, and describe experiments which show how it may be produced.
2. What conditions are necessary for the production and continuance of combustion? How would you show them experimentally?
3. Describe an experiment by which air may be made to burn in coal gas.
4. Explain what is meant by *point of ignition* and *flash point*.

5. Explain the principle of the *Davy lamp*, and describe an experiment which illustrates it.

6. Describe the structure of a candle flame, and explain the nature of the chemical changes which take place in the different zones.

7. Describe the appearance of a coal-gas flame which is burning very low.

8. Discuss the explanations which have been put forward to account for the luminosity of flame.

9. Give a diagram of the Bunsen flame, and indicate on it
   (*a*) the reducing area;
   (*b*) the oxidising area;
   (*c*) the high temperature oxidising area;
   (*d*) the low temperature oxidising area.

10. What are the causes of the non-luminosity of a Bunsen flame?

11. How may calcium sulphate be reduced to calcium sulphide
   (*a*) in the blowpipe flame,
   (*b*) in the Bunsen flame?

12. Explain carefully what you understand by *combustion*, and *supporter of combustion*.

13. What volume of water may be raised from 10° C. to 50° C. by the heat derived from the combustion of 10 grams of hydrogen and 10 grams of carbon respectively?

14. Explain the term *heat of combustion*, and compare the heats of combustion of the common kinds of fuel.

15. When a chemical change takes place heat is generally developed. Describe three experiments which illustrate this in a marked manner.

CHAPTER XXII.

PHOSPHORUS AND ITS COMPOUNDS. SILICA.

337. Properties of Ordinary Phosphorus.—

* **Exp. 332.**—Take a stick of phosphorus from the bottle, place it in a dish of water and cut off a small piece (*not larger than a pea*); then return the stick to the bottle. Take up the piece you have cut off on the point of a knife and examine it. Now place it in a dish of water and warm on a water-bath. Note when the phosphorus melts and take the temperature with a thermometer. Allow the dish to cool again and when the water has become quite cold remove the phosphorus (which has solidified) by means of a knife, dry it by filtering it with blotting-paper, and drop it into a little carbon bisulphide contained in a test-tube. Shake up gently: the phosphorus dissolves. Pour the solution into a dish and leave it in the fume cupboard. When the carbon bisulphide has evaporated examine the residue of phosphorus. You will find that it is crystalline

[In order to get rid of the phosphorus, which should never be left about owing to its *highly inflammable nature*, ignite it with a lighted taper and allow it to burn away *in the fume cupboard.*]

Ordinary phosphorus is a yellowish, translucent, crystalline solid which can be readily cut with a knife. It has a specific gravity of 1·84, it melts at 44° C., and boils at 290° C. It is insoluble in water (in which liquid it is kept), but readily dissolves in bisulphide of carbon.

Exp. 333.—Cut off another small piece of phosphorus, put it in a dish, dry it by touching it with filter paper, and convey it into a dark room. Note that the phosphorus becomes faintly luminous and emits white fumes which have a smell resembling that of garlic.

The white fumes are due to the slow oxidation of the phosphorus by the oxygen of the air and consist of a number of oxides and oxyacids of phosphorus. The cause of the luminosity has not been established with certainty, but it is probably connected in some way with the presence of ozone.

When ordinary phosphorus is heated very slightly above its melting point (to 45° C.) it ignites in air and burns with great brilliancy, forming phosphoric oxide, P_4O_{10} (mixed with some phosphorous oxide, P_4O_6). On account of the ease with which phosphorus undergoes oxidation it must be kept under water.

If ordinary phosphorus is brought in contact with chlorine, bromine, or iodine, even at ordinary temperature combination takes place with such violence that flame is produced.

Ordinary phosphorus acts as a powerful poison.

338. Properties of Red Phosphorus.—

Exp. 334.—Examine a lump of red phosphorus; break it and note the fracture. Try to dissolve it in water and carbon bisulphide. Take a piece into a dark room and note that it does not become luminous or give off any fumes.

Red phosphorus is a reddish-brown solid having a lustre somewhat resembling that of iron; it breaks with a conchoidal fracture. Red phosphorus was at one time thought to be an amorphous substance, but it has been shown to possess a distinctly crystalline structure. The specific gravity of red phosphorus is 2·1. It is insoluble in both water and carbon bisulphide and is non-poisonous.

Red phosphorus only undergoes oxidation very slowly at ordinary temperatures, if indeed it changes at all; it may therefore be freely handled without danger. Compare these properties with those of yellow phosphorus.

Exp. 335.—Introduce a little red phosphorus into a deflagrating spoon and heat in a Bunsen burner. When the phosphorus ignites introduce it into a gas-jar and press the brass plate down tightly. Combustion proceeds brilliantly with formation of white clouds, which settle down in the form of a powder. When the flame has gone out examine the white powder and then pour some water into the jar; the powder dissolves and the solution is found to be acid to litmus.

The powder formed when red phosphorus burns is seen to resemble that formed when ordinary phosphorus burns both in appearance and properties (see Exp. 20); it is in fact the same substance—phosphoric oxide, P_4O_{10} (mixed with some phosphorous oxide). The temperature at which red phosphorus ignites in air is 260° C.

Red phosphorus only combines with the halogens on heating, not at ordinary temperatures as ordinary phosphorus does.

339. Allotropes of Phosphorus.—We have now investigated two substances which differ very considerably in properties, but to both of which we have given the name phosphorus. The fact that both these substances are converted into the same compound (phosphoric oxide) when they burn supports the view that they are allotropes of the element phosphorus. If this is the case it should be possible to transform the one into the other. Let us see if this can be done.

Transformation of Red into Ordinary Phosphorus.—

† **Exp. 336.**—Introduce a little red phosphorus (A, Fig. 103) into a short piece of fairly wide glass tubing fitted up as shown in the diagram. Displace the air from the tube by coal gas by attaching the rubber tube of a gas supply

to the straight glass delivery tube. When the displacement of air is complete (test by collecting a test-tube of the gas issuing at B and applying a light) close the end of the delivery tube B with a short piece of rubber tubing

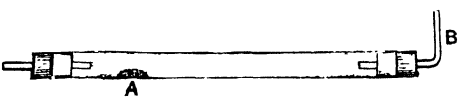


Fig. 103.

which is fixed over a short piece of glass rod. Now stop the current of gas, detach the rubber supply tube and *at once* (to prevent ingress of air) close the end of the short glass delivery tube with a similar glass rod and rubber stopper. Now weigh the tube carefully.

Next attach the rubber supply tube, again turn on the gas quite gently, replace the stopper at B by a glass gas jet[1] attached by means of rubber tubing, and ignite the issuing gas. Now heat the tube at A; the phosphorus volatilises and condenses as nearly colourless liquid drops in the cool part of the tube. Allow the tube to cool, still passing coal gas; the liquid drops solidify to a slightly yellow solid resembling ordinary phosphorus.

When the tube is *quite cold* blow out the flame, remove the gas jet and close B by its glass stopper; then turn off the gas and close the inlet tube with its stopper. Reweigh; the weight is the same as before.

Now pass air through the tube (in a fume cupboard) till the smell of coal gas can no longer be detected at B. Next remove the tube to a dark room. The phosphorus will be observed to glow and fume just as ordinary phosphorus does. [Get rid of this phosphorus by warming the tube in a fume cupboard till it burns.]

We have therefore succeeded in transforming red phosphorus into yellow phosphorus by heating it in coal gas (the object of which is to exclude air). Moreover,

[1] If the gas were burnt at the end of B, coal gas would have to be allowed to escape while B cooled down preparatory to the final weighing.

since the two weighings of the tube were the same, it follows that the red phosphorus did not lose or gain anything during its conversion into ordinary phosphorus, *i.e.* both forms consist of *phosphorus only* and are true allotropes.

Transformation of Ordinary Phosphorus into Red Phosphorus.—This change may be carried out as follows:—

† **Exp. 337.**—Fill a small, strong, round-bottomed flask with carbon dioxide by displacement. Drop in a small piece of yellow phosphorus and cork up tightly (tie the cork down). Place the flask in an air oven and maintain it at a temperature of 240-250° for some time. The colour of the phosphorus gradually changes to red. When the change appears to be complete allow the flask to cool. Then try to dissolve the phosphorus in carbon bisulphide.

The formation of red phosphorus from the ordinary variety is most simply shown by burning some of the latter in a dish floating on water under a bell-jar. The residue in the dish consists partly of red phosphorus.

The temperature at which ordinary phosphorus changes to red phosphorus is about 240-250° C.; the converse change takes place at 350° C. (out of contact with air of course; in air, as already mentioned, red phosphorus inflames at 260° C.).

340. Occurrence of Phosphorus in Nature.—Phosphorus is not found free in nature in either form. The chief source of the element is calcium phosphate, $Ca_3(PO_4)_2$, which is found widely distributed; it forms the essential constituent of the minerals apatite and sombrerite and also of bone ash (which is obtained by the dry distillation of bones).

In small quantities phosphates are very widely distributed; all fertile soils contain a small percentage, and they are always found in plants, being essential to plant-life

341. Manufacture of Ordinary Phosphorus.—The first step in the manufacture of phosphorus from bone-ash consists in treating it with sulphuric acid, whereby a double decomposition takes place—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

When the decomposition is complete, the product is filtered through cinders; the calcium sulphate remains on the filter, and the phosphoric acid passes through

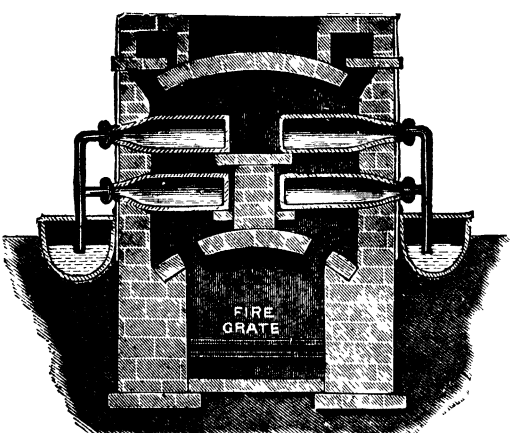


Fig. 104.

The liquid is then concentrated, mixed with charcoal, and further heated almost to dryness, the phosphoric acid losing water and being converted into metaphosphoric acid ($H_2P_2O_6$)—

$$2H_3PO_4 = H_2P_2O_6 + 2H_2O.$$

Finally, the granular product is heated to full redness in clay retorts placed horizontally in series over a fire (Fig. 104), when the following reaction takes place—

$$H_2P_2O_6 + 6C = H_2 + 6CO + 2P.$$

Luted into the mouth of each retort is an iron pipe, bent at right angles and dipping into water; the vapour of phosphorus is thus led into the water, and there condensed out of contact with air. The temperature of the water is high enough to keep the phosphorus in the liquid state, and it can be run off or ladled out from time to time It is further refined by re-melting in water, and filtering through chamois leather or canvas to remove suspended matter, and then finally cast into sticks.

Phosphorus is also extracted from bone-ash by an electric process recently invented and known as the *Readman-Parker-Robinson process.* An intimate mixture of bone-ash and charcoal, together with certain other substances added as fluxes, is heated to a high temperature and then introduced into an electric furnace. This consists of an iron box lined with bricks, through the sides of which pass two large carbon electrodes connected with the poles of a powerful dynamo. On passing the current the mixture is raised to a still higher temperature, and the bone-ash and charcoal react with liberation of phosphorus. This distils off through a pipe and is condensed as described in the previous process.

342. Manufacture of Red Phosphorus.—Red phosphorus is prepared on the large scale by heating ordinary phosphorus at 250° C. in cast-iron pots from which air is excluded, and removing the unconverted phosphorus which remains by boiling the finely-divided product with caustic soda solution (which dissolves ordinary phosphorus but has no effect on the red modification).

343. Matches.—Lucifer matches are tipped with a mixture of ordinary phosphorus and certain substances, *e.g* lead peroxide and potassium nitrate, which readily part with oxygen. "Safety" matches contain no phosphorus, being tipped with a mixture of potassium chlorate and antimony sulphide (Sb_2S_3), the sulphur being the inflammable body; in this case the match is ignited by rubbing it on a prepared surface of red phosphorus and powdered glass. In either case the heat requisite to

promote chemical action and to ignite the phosphorus is generated by friction on a rough surface.

Phosphorus Trihydride, or Phosphine, PH_3.

344. Preparation of Phosphine.—This gas, which is the analogue of ammonia, is obtained by heating ordinary phosphorus in a flask with caustic soda solution. As obtained in this way it is spontaneously inflammable in air on account of the presence of a small quantity of a liquid hydride, P_2H_4; so, to prevent the gas taking fire in the flask, the air is, previous to heating, displaced from the apparatus by coal gas. The end of the delivery tube dips under water as shown in Fig. 105, and as each bubble of gas reaches the surface it inflames and produces a ring of white smoke (phosphoric oxide).

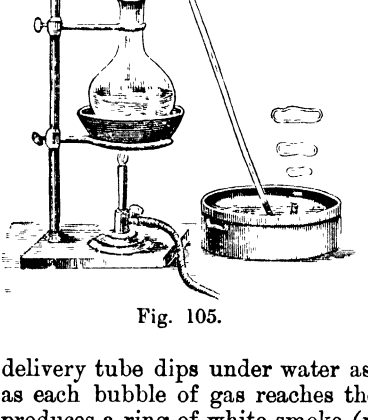


Fig. 105.

The reaction which takes place is—

$$4P + 3NaOH + 3H_2O = 3NaH_2PO_2 + PH_3.$$

Sodium hypophosphite

Phosphine is also formed, along with a considerable quantity of the liquid hydride, when phosphide of calcium (obtained by heating together lime and phosphorus in a closed crucible) is brought into contact with water.

Pure phosphorus trihydride is prepared by warming phosphonium iodide, PH_4I (see below), with caustic potash or soda, the reaction being analogous to that employed in the preparation of ammonia—

$$PH_4I + NaOH = PH_3 + NaI + H_2O.$$
$$NH_4Cl + NaOH = NH_3 + NaCl + H_2O.$$

The gas may be collected over water; it is not spontaneously inflammable.

345. Properties of Phosphine.—It is a colourless gas which condenses only when cooled to — 90° C. It is very slightly soluble in water, and possesses a penetrating garlic-like odour which is evident even with very small quantities of the gas; it is very poisonous. If free from other hydrides, it is not inflammable in air at ordinary temperatures; heat decomposes the gas into its elements more readily than the corresponding nitrogen compound, ammonia.

Just as ammonia combines directly with the haloid acids hydrochloric acid, hydrobromic, etc., to form ammonium chloride, ammonium bromide, etc., so phosphorus trihydride forms similar compounds. The combination with hydriodic acid to form phosphonium iodide—

$$PH_3 + HI = PH_4I,$$

takes place very readily.

PHOSPHORIC OXIDE (OR PHOSPHORUS PENTOXIDE), P_4O_{10}.

346. Preparation of Phosphoric Oxide.—This is the chief product of the combustion of phosphorus in excess of air or oxygen, and we have already obtained it in this way. The oxide may be prepared in quantity by performing the combustion in a glass bolt-head with two side tubes, through one of which passes air dried over fused calcium chloride, and through the other the fumes are aspirated, a bottle being placed between the aspirator and the side tube to intercept the phosphoric oxide (Fig. 106).

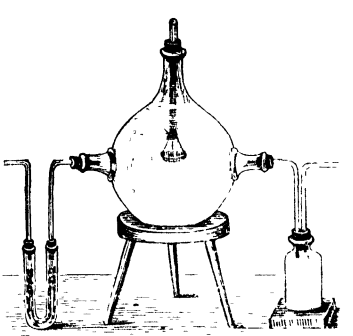


Fig. 106.

A small piece of phosphorus carefully dried between filter paper is introduced through the neck of the bolt-head into a small basin attached as shown, and then successively other pieces, until sufficient of the oxide has been prepared. After the first piece has been ignited by touching it with a hot wire, the basin will be hot enough to start the combustion of the subsequent portions as they are dropped into it.

The pentoxide so obtained always contains a small quantity of phosphorous oxide, from which it may be freed by passing it in the gaseous form along with oxygen over gently-heated finely-divided platinum. (Compare preparation of sulphur trioxide.)

347. Properties of Phosphoric Oxide.—

Exp. 338.—Examine some phosphoric oxide. Leave a little exposed to the air and note the result. Throw a little into some water contained in a dish; note the effect. Test the liquid with litmus. Evaporate down till the residue ceases to diminish in volume: a thick liquid remains.

Phosphoric oxide is an amorphous white powder, which when left in contact with moist air gradually absorbs moisture and deliquesces. When thrown into water combination takes place with a hissing noise, and metaphosphoric acid is formed.

$$P_4O_{10} + 2H_2O = 2H_2P_2O_6.$$

When the liquid is evaporated the metaphosphoric acid takes up more water and forms orthophosphoric acid or ordinary phosphoric acid, H_3PO_4.

$$H_2P_2O_6 + 2H_2O = 2H_3PO_4.$$

The syrupy residue obtained in Exp. 338 consists of this acid.

The great affinity of phosphoric acid for water renders it a valuable agent for completely drying gases, whilst in contact with acids it frequently deprives them of water, forming anhydrides.

$$2H_2SO_4 + P_4O_{10} = 2H_2P_2O_6 + 2SO_3.$$
$$4HNO_3 + P_4O_{10} = 2H_2P_2O_6 + 2N_2O_5.$$

Similarly it chars wood, paper, and many organic substances by its dehydrating action.

Orthophosphoric Acid (*Ordinary Phosphoric Acid*), H_3PO_4.

348. Preparation of Orthophosphoric Acid.—Orthophosphoric acid is obtained by dissolving phosphoric oxide in water and boiling the solution as we have just seen. It is prepared by oxidising red phosphorus with nitric acid.

* **Exp. 339.**—Introduce about 10 grams of red phosphorus into a large retort and cover it with concentrated nitric acid. Warm gently in a fume cupboard. The phosphorus gradually dissolves, and red fumes of nitrogen peroxide are evolved. The change which takes place may be represented by the equation—

$$2P + 10HNO_3 = 2H_3PO_4 + 10NO_2 + 2H_2O.$$

When all the phosphorus has disappeared transfer the liquid to a porcelain dish and evaporate to small bulk. Add a little more nitric acid and again evaporate. Repeat this operation till no brown fumes are produced on evaporation, showing that all the phosphorous acid, H_3PO_3, which is formed at first to some extent has been oxidised to phosphoric acid. Continue the last evaporation till acid fumes (nitric acid) cease to be evolved. Allow the thick residue to stand in a cool place: colourless crystals will separate after a time.

349. Properties.—Phosphoric acid is a colourless deliquescent crystalline solid, melting at 41·7° C.; the crystals consist of hard rhombic prisms. It is a tribasic acid, each of the atoms of hydrogen being replaceable by a metal.

When phosphoric acid is heated it loses water and is converted into *pyrophosphoric acid*, $H_4P_2O_7$.

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

At red heat pyrophosphoric acid loses a molecule of water and is converted into metaphosphoric acid, $H_2P_2O_6$.

$$H_4P_2O_7 = H_2P_2O_6 + H_2O.$$

350. The Phosphates.—The phosphates of the alkali metals sodium, potassium, and of ammonium are soluble in water, and are obtained by the addition of the alkaline hydroxides to phosphoric acid. The amount of the alkali added may be sufficient to bring about the replacement of one, two, or three atoms of the hydrogen by the metal, thus—

$$NaOH + H_3PO_4 = \underset{\text{Sodium dihydrogen phosphate}}{NaH_2PO_4} + H_2O.$$

$$2NaOH + H_3PO_4 = \underset{\text{Disodium hydrogen phosphate}}{Na_2HPO_4} + 2H_2O.$$

$$3NaOH + H_3PO_4 = \underset{\text{Normal sodium phosphate}}{Na_3PO_4} + 3H_2O.$$

The normal salt, Na_3PO_4, has a very pronounced *alkaline* reaction; of the acid salts one—the disodium salt—is slightly alkaline, the other is acid to litmus.

The salt ordinarily known as "sodium phosphate" is the disodium salt, Na_2HPO_4. It is prepared as follows:—

Exp. 340.—Add caustic soda solution to a solution of phosphoric acid till the liquid is distinctly alkaline to litmus. Evaporate to small bulk and allow to crystallise.

The crystals which separate have the composition represented by the formula—

$$Na_2HPO_4, 12H_2O.$$

The normal phosphates of almost all other metals are insoluble in water, but soluble in dilute mineral acids. They may be prepared by adding a soluble salt of the metal in question to an aqueous solution of a phosphate of an alkali metal.

$$2Na_3PO_4 + 3CaCl_2 = \underset{\substack{\text{Calcium phosphate.}\\ \text{White ppt.}}}{Ca_3(PO_4)_2} + 6NaCl.$$

$$Na_3PO_4 + 3AgNO_3 = \underset{\substack{\text{Silver phosphate.}\\ \text{Yellow ppt.}}}{Ag_3PO_4} + 3NaNO_3.$$

Phosphorus Trichloride, PCl_3.

351. Preparation.—This compound is prepared by passing dry chlorine over red phosphorus heated in a glass retort; the trichloride distils over and is collected in a flask cooled by water.

$$2P + 3Cl_2 = 2PCl_3.$$

Properties. — Phosphorus trichloride is a colourless mobile liquid boiling at 76° C. It is decomposed by water with formation of phosphorous and hydrochloric acids.

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

It combines directly with chlorine to form phosphorus pentachloride, and on heating unites with oxygen, forming phosphorus oxychloride, $POCl_3$.

$$PCl_3 + Cl_2 = PCl_5.$$
$$2PCl_3 + O_2 = 2POCl_3.$$

Phosphorus Pentachloride, PCl_5.

352. Preparation.—Phosphorus pentachloride is prepared by passing chlorine into phosphorus trichloride contained in a flask, using a wide delivery tube so that the end will not be stopped up by the solid pentachloride.

$$PCl_3 + Cl_2 = PCl_5.$$

Properties.—The pentachloride is a light yellow solid, which passes directly into vapour at 168° C., without melting, undergoing partial decomposition into the trichloride and chlorine. With a small quantity of water phosphorus pentachloride yields phosphorus oxychloride, $POCl_3$—

$$PCl_5 + H_2O = POCl_3 + 2HCl;$$

but with excess of water phosphoric acid is formed—

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl;$$

or, writing both stages in one equation—

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

Silica, SiO_2.

353. Occurrence of Silica.—

Exp. 341.—Examine specimens of rock crystal and flint. Note the shape of the crystals of the former; the flint does not appear to be crystalline. Try to scratch each with a knife; also to scratch a piece of glass with each.

Rock crystal and flint are both forms of *silica*, which is the oxide of a non-metal silicon and is represented by the formula SiO_2. Silica is found very widely distributed in nature and occurs in a variety of forms. Two of these forms are crystalline—*quartz* and *tridymite*. The crystals of quartz consist of hexagonal prisms terminating in hexagonal pyramids (see Fig. 107),[1] whilst those of tridymite consist of hexagonal plates.

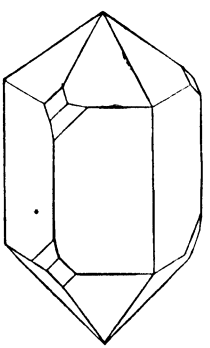


Fig. 107.

When quartz is colourless it is called *rock crystal*; the crystals are, however, frequently coloured, giving us such varieties as *amethyst*, *smoky quartz*, and *rose quartz*.

Silica occurs in the amorphous form as *opal*, whilst flint, agate, and chalcedony consist of intimate mixtures of amorphous silica with one or other of the crystalline forms. Sandstone consists of quartz grains derived from the disintegration of crystalline rocks—granites, etc., cemented together by ferric oxide, calcium carbonate or amorphous silica. Sand is composed mainly of grains of quartz and results from the disintegration of sandstone; more rarely it is derived directly from the parent rocks, granites, etc., from which sandstone itself originates.

Silica is also found in combination with various metallic oxides as *silicates*, which constitute such a large portion of

[1] As a general rule only one end of the crystal is developed, the other end being embedded in the matrix

the earth's crust. *Clay* and *slate*, for example, consist of aluminium silicate in a more or less pure state, and the minerals *serpentine* and *orthoclase felspar* are composed of magnesium silicate and a double silicate of potassium and aluminium respectively. The element silicon is not found in the free state, and is not easy to isolate from its compounds, so that although it constitutes nearly one-fourth of the mass of the earth's crust it is yet a substance rarely met with even in the laboratory.

354. Properties of Silica.—In the pure crystallised form as rock crystal silica is a lustrous transparent substance so hard that it readily scratches glass and is not scratched by a knife.

Exp. 342.—Boil some white sand with a little water for some time, filter and evaporate the filtrate to dryness. Repeat the experiment, using successively dilute and strong hydrochloric acid and caustic soda solution. Note whether in any case there is a residue.

We see from this experiment that sand is insoluble in water, hydrochloric acid,[1] and caustic soda. Similarly it is found to be insoluble in other acids (except hydrofluoric acid, see below, § 359) and alkalis. The same is true of all anhydrous forms of silica except that *amorphous* silica is attacked by *alkalis*.

355. Formation of Sodium and Calcium Silicates.

* **Exp. 343.**—Powder up a little white sand *very finely*. Grind it up well in a mortar with rather less than twice its weight of anhydrous sodium carbonate, introduce the mixture into a platinum crucible, and heat strongly in a blowpipe flame. Note that the mass fuses and a gas (carbon dioxide) escapes with effervescence. When effervescence ceases a transparent liquid remains. Pour this

[1] There may be a slight residue in the case of hydrochloric acid owing to the presence of impurities (cementing materials as above) in the sand.

out on to an iron slab. Note that it loses most of its transparency. Break it with a hammer: it is *crystalline* and *brittle*. Powder up a little of the product and boil up with water. It should dissolve completely (with the exception perhaps of a few particles of sand which remain unattacked)

The change which has taken place consists in the conversion of sodium carbonate into sodium silicate (Na_2SiO_3) with liberation of carbon dioxide—

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

Sodium silicate then is a crystalline solid (salt) soluble in water. It is known as "water glass" and is used for preserving eggs and the stone of buildings. If caustic soda were used in place of sodium carbonate in Exp. 343, the same substance would be formed according to the equation—

$$2NaOH + SiO_2 = Na_2SiO_3 + H_2O.$$

Exp. 344.—Add some strong hydrochloric acid to the sodium silicate solution you obtained in the previous experiment. A gelatinous precipitate separates out unless the solution was too weak.

This precipitate consists of silicic acid, H_2SiO_3, formed according to the equation—

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl.$$

If the solution of sodium silicate is weak the silicic acid remains in solution.

* **Exp. 345.**—Repeat Exp. 343, using equal weights of quicklime and sand. After a time the mixture fuses to a transparent liquid. When this is poured out on to an iron slab it loses most of its transparency. Show as before that it is *crystalline* and *brittle*. Powder a portion and boil with water. It does not dissolve. Add some dilute hydrochloric acid: solution takes place (with, however, separation of a gelatinous precipitate of silicic acid. H_2SiO_3, if the solution is strong).

When the lime and sand are heated together they combine to form calcium silicate ($CaSiO_3$)—

$$CaO + SiO_2 = CaSiO_3.$$

Calcium silicate is insoluble in water, but dissolves in mineral acids with formation of silicic acid. If the solution is dilute, the silicic acid remains in solution; but, if strong, it separates out as a gelatinous mass—

$$CaSiO_3 + 2HCl = CaCl_2 + H_2SiO_3.$$

356. Formation and Properties of Glass.—

* **Exp. 346.**—Repeat Exp. 343, using a mixture of sand, anhydrous sodium carbonate, and lime in the proportions of 4 : 2 : 1, and replacing the platinum crucible by a porcelain one. When the mass is thoroughly melted and effervescence has ceased allow the crucible and its contents to cool very slowly,[1] replacing the blowpipe flame by an ordinary Bunsen flame and *gradually* lowering this. When the flame is quite small (it should now be some distance below the crucible) turn it out, place the lid on the crucible, and leave till quite cold. Now break the crucible with a hammer. Notice that the contents have a *glassy* appearance and break with a *conchoidal* fracture, *i.e.* the substance is *non-crystalline*. It is *glass*. Compare its appearance and fracture with that of a piece of glass such as a broken bottle.

Exp. 347.—Weigh a clean dry flask. Boil some distilled water in it for an hour, renewing the water as required. Then pour off the water into a dish, wash out the flask with distilled water, and dry by blowing a current of hot air through it. Cool. Re-weigh. There will be no change in weight. Further, on evaporating the water which was boiled in the flask to dryness there will be no residue. Glass, then, is *insoluble in water*.

Next repeat the experiment, using strong hydrochloric acid instead of water. [Perform the experiment in a

[1] Otherwise the glass tends to fly to pieces when fractured.

fume chamber.] You will find that glass is *insoluble in acids.*[1]

Now in Exp. 346 we used the necessary ingredients for the formation of sodium and calcium silicates and we see that the combination of these two silicates has produced a substance—glass—differing essentially from either. If we had used potassium carbonate in place of sodium carbonate in Exp. 346, potassium silicate would have been formed instead of sodium carbonate, but the final product would have resembled that actually obtained in the experiment. Also a similar product would have been obtained if lead oxide had been used instead of lime; then lead silicate would have been formed instead of calcium silicate. We may therefore define *glass* as a *transparent, non-crystalline solid, consisting essentially of a silicate of an alkali metal combined with either calcium or lead silicate.*

357. Manufacture of Glass.—The materials used to supply *silica* in glass-making are chiefly quartz, flint, and white sand; the *lime* is supplied by calc spar, marble, chalk, or limestone; the *soda* by soda ash or sodium sulphate and charcoal; the *potash* by potashes; the *lead oxide* by red lead or litharge (in each case these substances are in order of desirability). The required quantities, mixed with broken glass to help the fusion, are charged into fire-clay pots heated in a furnace to bright redness. The silicates gradually form and are kept melted until all bubbles of air or carbon dioxide have risen and impurities have settled down. The molten glass is then allowed to cool till viscous, and is blown or rolled into sheets. The final cooling must be done slowly, *i.e.* the glass must be *annealed*; otherwise it is hard and brittle when cold.

358. Varieties of Glass.—The properties of glass vary to a large extent with the bases of the silicates of which it is composed: thus, excess of soda gives a glass which is easily melted and easily worked, *e.g. window glass*

[1] Glass is, however, slowly attacked by caustic alkalis.

and *fusible glass*, used for chemical apparatus, etc.; excess of lime gives a tough glass, used for bottle making; excess of potash gives a very infusible glass, used for combustion tubing—it is, however, hard to work; excess of lead oxide and potash gives a heavy *flint glass*, used in the making of lenses for telescopes, etc.—it is also very bright and sparkling, and is used in making the best table glass and artificial gems, but it does not resist acids and alkalis, and is not used for chemical apparatus.

The colours of glass are due to the presence of certain metallic oxides. Ferrous oxide gives it a green colour, as in bottle glass; oxide of manganese gives it a pink or black colour, and is sometimes added to correct the green tint given by ferrous oxide; oxide of cobalt gives a blue colour; oxide of chromium, or cupric oxide, green; cuprous oxide, or gold, ruby red. The addition of oxides of tin or antimony or of bone ash gives rise to an opaque enamel appearance in glass.

359. Etching of Glass.—We have seen that glass is not attacked by water or by ordinary acids. There is one acid, however—namely, hydrofluoric acid (HF)—which readily acts on it. This acid is used for etching glass, *e.g.* for marking the scale divisions on thermometers. This process may be illustrated by the following experiment:—

* **Exp. 348.**—Coat a sheet of glass with wax and write on it with a sharp point. Place some powdered fluor spar in a small leaden trough; add strong sulphuric acid, and mix to a thin paste. Hydrofluoric acid will be freely evolved. Place the glass with the wax downwards on the trough, and leave it for a few minutes. Now remove the wax and you will find the writing etched into the glass.

The hydrofluoric acid has attacked the silica in the glass, forming silicon tetrafluoride (SiF_4), a volatile compound, and water—

$$4HF + SiO_2 = SiF_4 + 2H_2O.$$

QUESTIONS.—CHAPTER XXII.

1. Describe experiments which illustrate the chief properties of ordinary phosphorus.
2. Write down in parallel columns the physical properties of ordinary and red phosphorus. What differences are there in chemical behaviour between the two allotropes?
3. How is phosphorus extracted from bone-ash?
4. How is red phosphorus prepared (*a*) on the large scale, (*b*) in the laboratory? Under what conditions is it converted into the yellow variety?
5. How is phosphoric oxide prepared?
   What would you observe (1) on dropping phosphoric oxide into water, (2) on introducing blue litmus into the resulting liquid? Explain the results.
6. What is the action of phosphoric oxide on (1) sulphuric acid, (2) nitric acid, (3) wood? Give equations in the case of (1) and (2).
7. Describe how you would proceed to prove that ordinary and red phosphorus are allotropes.
8. How is phosphine prepared in a pure state? Compare its properties with those of ammonia.
9. What is the action of water on the trichloride and on the pentachloride of phosphorus? Give equations.
10. Describe in detail the preparation of phosphoric acid from phosphorus.
11. Describe how you would prepare some crystals of the substance represented by the formula Na_2HPO_4, $12H_2O$. What is the name of this substance?
12. What is meant by saying that orthophosphoric acid is a *tribasic* acid? Write down the names and formulae of a few phosphates that are soluble in water.

13. Describe the preparation of the chlorides of phosphorus.

14. 50 grams of caustic soda are mixed with 61·25 grams of orthophosphoric acid. What salt will be produced and how much of it will be obtained?
(Na = 23, O = 16, H = 1, P = 31.)

15. What is the chemical nature of *silica*? What do you know of its occurrence in Nature? Make a sketch of a quartz crystal.

16. Describe the experiments you would perform to illustrate the chief properties of silica.

17. What would you observe on heating some powdered sand with potassium carbonate in a crucible? How would you explain the change which takes place?

18. Compare the appearance and properties of the substances produced when sand is heated with (1) sodium carbonate, (2) lime, and (3) a mixture of sodium carbonate and lime. What is the chemical nature of each of the products?

19. What is *glass*? Describe how you would investigate its chief properties.

20. How is glass manufactured? Enumerate the chief varieties of glass, and indicate how they differ in composition.

21. Describe how you would proceed to etch a design on a piece of glass.

SECTION III.

STUDY OF SOME METALS AND THEIR COMPOUNDS. ELECTROLYSIS.

CHAPTER XXIII.

METALS AND NON-METALS.

360. Physical Properties of Metals.—

Exp. 349.—Examine specimens of metals of different kinds, *e.g.* iron, steel, lead, copper, silver, aluminium, magnesium, zinc, mercury, and tin, scraping them with a knife in order to expose the fresh surface of the metal; also specimens of gold leaf, Dutch metal, etc. Examine also specimens of sodium, potassium, and calcium, *being very careful not to let them touch anything moist.* (Since the last three metals oxidise very readily it is particularly necessary to scrape them with a knife in order to expose the metallic surface.) Test them for opacity by looking at a candle or gas flame through them (the leaf may be held between two sheets of glass).

Examine their behaviour towards heat by holding one end of the piece in a flame by means of the tongs and touching the other end of the metal. (Of course sodium, potassium, and calcium could not be examined this way.) Examine their behaviour towards the electric current by seeing if they will ring an electric bell when used instead of one wire.

We note that metals are solids (except mercury, which is a liquid), having a shiny surface, which reflects light in a peculiar way, *i.e.* they are *lustrous*; they also do not allow light to pass through them, *i.e.* they are *opaque*; they become hot at some distance from the part heated in the flame, *i.e.* they *conduct heat*; and they carry the electric current which rings the electric bell, *i.e.* they *conduct electricity*.

Even gold leaf, which is less than $\frac{1}{250000}$ in. in thickness, preserves its lustre, though it begins to let light pass through.

We also associate other physical properties with the name metal, but these are much more variable than the four preceding properties.

One important property is *hardness*. Steel is one of the hardest substances in common use, though many gems, *e.g.* diamond, are harder. The property of relative heaviness or high *density* is also associated with the idea of a metal. Lead is very dense, as it is eleven times as heavy as an equal bulk of water, whilst platinum, the densest of the common metals, has a specific gravity of 21·4 (relative to water); on the other hand aluminium and magnesium are not very dense, their specific gravities being 2·6 and 1·75 respectively, and sodium and potassium will float on water.

Other very useful properties of metals are those of *malleability*, *tenacity*, and *ductility*. A body is said to be *malleable* when it can be hammered or bent into different shapes without cracking, and *tenacity* denotes the property which enables it to resist breaking by stretching forces. *Ductility* denotes the property in virtue of which a substance can be drawn into a fine wire without breaking. Gold is the most malleable and ductile metal: a sovereign can be hammered out to cover 50 square feet or drawn into 10 miles of fine wire.

On the whole, then, we can identify a *metal* as an opaque, lustrous substance, which conducts heat and electricity and possesses to some extent the properties of hardness, comparatively high density, malleability, tenacity, and ductility. Metals are also as a general rule only volatilised at very high temperature.

361. Physical Properties of Non-Metals.—Whereas metals are all solid at ordinary temperature with the exception of mercury which is a liquid, non-metals (*i.e* elements which are *not* metals) are found in all three states. Thus oxygen and chlorine are gases, bromine is a liquid, and sulphur and carbon are solids.

Non-metals generally have a low specific gravity and are bad conductors of heat and electricity. If solid they are brittle, and if they possess any lustre at all it is quite different from that of metals, which can only be described as "metallic."

Exp. 350.—Examine specimens of charcoal and roll sulphur. Note their lightness and brittleness; also that they are dull, not lustrous. Examine their behaviour towards heat and electricity as in Exp. 349.

The bad conducting power of sulphur may be shown by holding a piece in the hand, grasping it rather tightly. The crackling sound emitted is due to the crackling of the sulphur owing to its unequal expansion.

Also examine specimens of iodine and graphite, comparing their lustre with that of some metals, tin, copper, etc.

The non-metals which are not gases at ordinary temperature are as a rule transformed into vapour at comparatively low temperature.

362. Chemical Properties of Metals and Non-Metals.—It cannot be said that the physical properties considered in the two preceding paragraphs furnish a means of drawing a sharp line of demarcation between the two classes of elements—*metals* and *non-metals*. For example, carbon in the form of diamond has a specific gravity three and a half times that of sodium, and in the form of graphite it is a good conductor of both heat and electricity, and has a lustre rather metallic. Again the three non-metals, carbon, silicon, and boron, are notable for the fact that they are more difficult to volatilise than any of the metals.

The chemical properties of elements on the whole provide a more definite means of classification than their physical

properties. We have seen in §§ 107, 106, 110 that the metals form *basic oxides* (*i.e.* oxides which are acted upon by acids with formation of salts and water), whilst non-metals form either *acidic oxides* (*i.e.* oxides which combine with water to form acids) or *neutral oxides*. Even this distinction is, however, by no means exact for the higher oxides of some metals, *e.g.* chromium trioxide, CrO_3, and manganese heptoxide, Mn_2O_7, are strongly acidic, forming well-defined stable salts with bases (*e.g.* potassium chromate, K_2CrO_4, and potassium permanganate, $KMnO_4$). Again, oxides, like alumina, Al_2O_3, and tin (stannic) oxide, SnO_2, act as bases in the presence of acids; but towards strong bases, like caustic potash, these weak bases behave as acidic oxides, forming potassium aluminate and potassium stannate. (See § 108.)

Another chemical property which distinguishes metals from non-metals is their *behaviour towards acids*. In general when a metal is acted upon by an acid a *salt* of the metal is formed and hydrogen or some other gas (or gases) is evolved (as we have seen in Chap. VI., etc.). Non-metals, on the other hand, are not as a rule attacked by acids at all; if they are acted upon, either an *oxide* of the *non-metal* or an *acid* containing it is formed, not a salt (see §§ 218, 254). Here, again, the distinction is not absolute, for the metal *tin* is converted into its *oxide* by nitric acid, as we saw in Exp. 224.

There are a few elements which cannot satisfactorily be placed in either class. Thus arsenic and antimony, in their physical properties, resemble the metals, since they have a metallic lustre and are good conductors of heat and electricity; in their chemical properties, however, they resemble the non-metals; for they form acidic oxides and are insoluble in dilute mineral acids. Such elements are called *metalloids*.

Hydrogen, again, is another element which is difficult to classify. Its physical properties (except the fact that it conducts heat) and some of its chemical properties place it amongst the non-metals, but, since metals will displace hydrogen from acids and will also displace other metals from their salts, hydrogen might be considered

to be a metal. It is most convenient to put it with the metalloids.

It will be seen that the distinction between metals and non-metals is really only one of convenience; the two classes merge into each other without any clear line of division, and the same element may be a metal from some points of view and a non-metal from others.

QUESTIONS.—CHAPTER XXIII.

1. Into what two classes may elements be divided? What are the characteristic properties of each class?
2. What are *metalloids*? Illustrate your answer by discussing examples.
3. State fully how you would proceed to investigate whether a given solid substance was a metal or a non-metal.
4. Charcoal is called a non-metal, zinc a metal, and arsenic a metalloid; show by discussing the physical and chemical properties of these elements that the classification is justifiable.

CHAPTER XXIV.

SODIUM AND ITS COMPOUNDS.

363. Properties of Sodium.—

Exp. 351.—Take a lump of sodium and cut off a small piece with a knife. Examine the freshly cut surface. Try to bend the piece you have cut off; then hammer it and note the result.

Sodium is a soft, malleable metal possessing a silvery lustre when freshly cut, but rapidly tarnishing through oxidation even at ordinary temperatures.

The specific gravity and melting-point of the metal are both very low; it is slightly lighter than water (we saw in Exp. 57 that it floats on water) and melts at 95·6° C., *i.e.* at a temperature a little below the boiling-point of water.

Sodium decomposes water at ordinary temperature with liberation of hydrogen and formation of caustic soda (see Exp. 57). When heated in air it burns with a bright yellow flame, forming a mixture of two oxides, sodium monoxide, Na_2O, and sodium peroxide, Na_2O_2. (See Exp. 111.)

364. Preparation of Sodium.—Sodium is prepared by the electrolysis of fused caustic soda, sodium and hydrogen being set free at the kathode and oxygen at the anode. The sodium collects in the fused state on the surface of the electrolyte (*i.e.* the liquid undergoing electrolysis); it is kept out of contact with the air by a suitable arrangement. The change may be represented by the equation—

$$2NaOH = 2Na + H_2 + O_2.$$

365. Sodium Monoxide, Na_2O.—As just stated, this oxide is one of the products of the combustion of sodium in air (or oxygen). In the pure state it is described as a greyish mass which melts at a dull red heat. It combines very readily with water, forming sodium hydroxide—

$$Na_2O + H_2O = 2NaOH.$$

366. Sodium Peroxide.—Sodium dioxide, Na_2O_2, is made on the large scale by heating sodium in air which has been freed from carbon dioxide and moisture. It is a white solid when pure, though slightly yellow as usually prepared, and is a strong oxidising agent; on this account it is used in the chemical analysis of minerals resisting chemical attack, such as chrome iron-stone.

It reacts with hydrochloric acid, forming hydrogen peroxide, and the liquid so produced is called *soda-bleach*; this liquid is prepared on the large scale and is used for bleaching straw.

* **Exp. 352.**—Procure some sodium peroxide and examine it. Add a little of it to some dilute hydrochloric acid. Show that the liquid contains hydrogen peroxide as in Exp. 157.

367. Preparation of Caustic Soda, Sodium Hydroxide, NaOH.—We have already prepared caustic soda in one way (Exp. 57), namely, by dissolving the metal in water and evaporating the solution. Let us now investigate another method.

Exp. 353.—Take 30 gm. of washing soda (sodium carbonate) and place them in a small iron saucepan with 300 c.c. of water and 10 gm. of slaked lime. Boil for some time, keeping the water made up to about 300 c.c., until a few drops of the liquid when filtered do not effervesce on the addition of hydrochloric acid. When this is the case, filter, evaporate half the filtrate to dryness, and keep the other half.

Examine the solid which remains on evaporation, and with it and the solution you have reserved repeat Exp. 105. Test the residue obtained by filtration for carbonates.

You will find that the white solid obtained by evaporation has all the properties of caustic soda and that the white precipitate which you filtered off is a carbonate. It must of course be calcium carbonate, since it was formed by the action of slaked lime on sodium carbonate. The change which has taken place is represented by the equation—

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

The reaction just investigated is utilised for the preparation of caustic soda on the large scale. Caustic soda is also obtained in large quantities by the electrolysis of an aqueous solution of common salt; the sodium which is liberated at one pole is allowed to react with water when caustic soda is produced.

368. Properties of Caustic Soda.—Caustic soda is a white deliquescent solid very soluble in water, forming a strongly alkaline solution. Either in the solid state or in solution it rapidly absorbs carbon dioxide from the air, forming sodium carbonate.

$$2NaOH + CO_2 = Na_2CO_3 + H_2O.$$

Exp. 354. *Preparation of Soap.*—Boil some suet with a dilute solution of caustic soda until it is mostly dissolved, pour off the clear liquid, add some salt. Flocks will separate out and rise to the surface. Filter some of them off and boil them with water: they dissolve. Feel the solution: it is *soapy*. Now make a solution of ordinary yellow soap in water and show that when salt is added similar flocks separate; also show that they are soluble in water.

We see, then, that when suet is boiled with caustic soda it dissolves with formation of *soap*. In place of suet we might have used other fats, *e.g.* mutton fat and lard, or oils such as olive oil and linseed oil; in each case the fat or oil dissolves and soap is formed.

Caustic soda is a very important article of commerce; it is chiefly employed on the large scale for soap-making, but is also used in the manufacture of paper and in the refining of oils.

369. Occurrence, Extraction, and Uses of Sodium Chloride (Common Salt), NaCl.—This is by far the commonest sodium compound. It is found as rock salt in various parts of the world, notably in this country in Cheshire; it is also the chief solid constituent of sea-water, and occurs in salt springs in various places.

In some cases salt is obtained in the solid state direct from the mines. More usually, however, it is first dissolved and brought to the surface in the form of brine and the salt then recovered from this by evaporation in pans.

A certain amount of salt is also obtained from sea water, especially in the more sunny parts of the Continent, such as Spain and the South of France. The sea water is run into pans called *salterns* and allowed to evaporate by exposure to the air and sun. The salt obtained is termed *bay-salt*; it contains some of the other salts in the sea water.

Common salt is used for culinary purposes and for glazing earthenware. It is also the primary source of most other sodium compounds, *e.g.* washing soda, "salt cake" (sodium sulphate), caustic soda, and of the metal itself. Some idea may be formed of the extensive use which is made of common salt from the fact that about two million tons of it are produced annually in this country, three-fourths of this in Cheshire and the rest chiefly in Worcestershire and Durham.

370. Preparation of Pure Sodium Chloride.—Pure sodium chloride may be obtained by neutralising pure caustic soda or sodium carbonate with pure hydrochloric acid. The following is a convenient method of obtaining the pure salt from ordinary common salt.

* **Exp. 355.**—Prepare a cold saturated solution of common salt and pass into it a stream of hydrogen chloride prepared as in Exp. 165. Crystals of sodium chloride soon begin to fall out of solution. When a sufficient quantity has collected it should be filtered off, washed with a little pure strong hydrochloric acid, and allowed to dry in the air (or by gently warming in a dish).

The method just used depends upon the fact that sodium chloride is insoluble in strong hydrochloric acid; it is therefore precipitated when the solution becomes sufficiently acid, the impurities remaining in solution.

371. Properties of Sodium Chloride.—As ordinarily seen sodium chloride is a white finely crystalline substance. When, however, the crystals are large enough they are seen to consist of colourless cubes having a glassy lustre.

* **Exp. 356.**—Leave some ordinary common salt exposed to the air and also some of the *pure* salt prepared as in Exp. 355. Notice that on a wet day the former becomes damp, while the latter does not.

Pure sodium chloride, then, is not deliquescent, whereas ordinary common salt is; this is because the latter contains a small amount of magnesium chloride, which is a very deliquescent salt.

Exp. 357.—Heat a little dry common salt in a test-tube. Note that the crystals break up with a crackling sound but do not melt. Next heat a little of the salt on a platinum wire in the Bunsen flame, and note the very bright yellow colour imparted to the flame.

Sodium chloride melts only at a high temperature; at a still higher temperature it can be vaporised unchanged. The bright yellow colour which it imparts to a Bunsen flame is characteristic of *sodium* salts.

Exp. 358.—Determine the solubility of common salt in water at ordinary temperature and at 100° C. (see Exp. 47). You will find that the salt is only slightly more soluble at the higher temperature, thus furnishing an exception to the general rule that the solubility of a salt increases rapidly with rise in temperature.

372. Preparation of Sodium Sulphate, Na_2SO_4.—We have prepared sodium sulphate in Exp. 108 by neutralising caustic soda with sulphuric acid. Let us now investigate another method of obtaining the salt.

Exp. 359.—Weigh an evaporating basin and cover glass, and into it put 6 gm. of common salt. Pour in carefully 5 gm. of concentrated sulphuric acid, which you have weighed out into a small beaker, and replace the cover. Allow the hydrochloric acid to come off, warm gently, and then weigh again. Now heat the basin cautiously at first, then more strongly, and observe what happens. When all the fumes have stopped, allow the basin to cool, and weigh again. Compare losses and note that they are about the same. Also examine the solid left.

The reaction between common salt and sulphuric acid appears, then, to take place in two stages, resulting in about equal losses of hydrogen chloride; the first stage takes place at ordinary temperature, the second on heating. The first stage has been shown to correspond to the formation of sodium hydrogen sulphate, $NaHSO_4$, according to the equation—

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

At high temperature the acid sulphate reacts with another molecule of common salt with formation of the normal sulphate, Na_2SO_4 (the white residue), and evolution of a second molecule of hydrogen chloride—

$$NaCl + NaHSO_4 = Na_2SO_4 + HCl.$$

Sodium sulphate is manufactured in enormous quantities from common salt by a method which is the same in principle as that of Exp. 359; it is termed *salt-cake* commercially.

Exp. 360.—Dissolve the residue of sodium sulphate obtained in Exp. 359 in water, evaporate until it begins to crystallise, and allow to stand. Collect the crystals and dry them on filter paper. Examine them and note that they are transparent and have a glassy lustre. Heat some of the salt in a dry test-tube; it fuses, then loses water, which condenses on the sides of the tube, and a white residue remains. Leave some of the crystals exposed to the air for a time; note that they become powdery on the surface.

The crystals you have prepared consist of hydrated sodium sulphate, Na_2SO_4, $10H_2O$, and are known as *Glauber's salt.* When they are heated they lose their water of crystallisation and anhydrous sodium sulphate remains. Water of crystallisation is also lost when the crystals are exposed to the air, *i.e.* they *effloresce*; the white powder which forms consists of the anhydrous salt.

Glauber's salt is employed in medicine as an aperient, whilst salt-cake is used in enormous quantities in the manufacture of sodium carbonate (see § 374) and is also employed in glass-making.

373. Properties of Sodium Carbonate, Na_2CO_3.— We have already prepared this salt in Exp. 296 by the action of carbon dioxide on a boiling solution of caustic soda. The crystals obtained have the composition represented by the formula Na_2CO_3, $10H_2O$, and are known as *soda crystals, washing soda,* or simply *soda.*

Exp. 361.—Dissolve some crystals of washing soda in water and note that they are very soluble; test the solution with red litmus paper; it is alkaline. Now concentrate the solution and allow to crystallise below 30° C. Examine the crystals: they are large and transparent, and possess a glassy lustre. Leave them exposed to the air for some time: they gradually lose water, and become covered with an opaque white powder, the composition of which is Na_2CO_3, H_2O.

374. Preparation of Sodium Carbonate from Sodium Sulphate.—

Exp. 362.—Prepare some anhydrous sodium sulphate by heating Glauber's salt in a dish till all the water is driven off. Mix the salt with powdered charcoal and heat in a crucible. When cold dissolve in water and filter. Add a little hydrochloric acid to the filtrate. Note the effervescence of gas: what does it smell like? Hold a piece of paper, moistened with lead acetate solution, in the gas: what happens?

We see that by the action of heated charcoal on sodium sulphate a substance is formed which is soluble in water and gives off sulphuretted hydrogen when acted upon by hydrochloric acid. This substance must therefore be *sodium sulphide*, Na_2S. It is produced according to the equation—

$$Na_2SO_4 + 4C = Na_2S + 4CO.$$

(The carbon monoxide formed burns in the air to carbon dioxide.)

* **Exp. 363.**—Make a mixture of sodium sulphate, powdered charcoal, and chalk in the proportion of 14 gm. of the dry sulphate, 5 gm. of charcoal, and 10 gm. of chalk. Place the mixture in a crucible, put on the cover, and heat it over a blowpipe or blast burner for 10 minutes or until no more gas is given off. Pour the molten mass on to an iron tray, and then put it into water. When the lumps have disappeared, filter the liquid, evaporate the solution somewhat and allow to stand. Crystals separate out. Examine their properties as in Exps. 297, 361. Test also the residue on the filter with hydrochloric acid.

The crystals which separate out consist of sodium carbonate (impure). The changes which have taken place are first the reduction of sodium sulphate to sodium sulphide by the heated charcoal, and secondly the interaction of sodium sulphide and calcium carbonate with formation of sodium carbonate and calcium sulphide.

$$Na_2S + CaCO_3 = Na_2CO_3 + CaS.$$

The calcium sulphide is contained in the insoluble residue, which therefore gives off sulphuretted hydrogen when treated with an acid.

The process we have just investigated is a very important one; it is used on the large scale for the manufacture of sodium carbonate and is called the *black ash process* from the colour of the mass resulting from the reaction (which is due to the presence of unchanged carbon) or the *Le Blanc process* after the discoverer.

The student will probably be inclined to ask why it was necessary to use charcoal in this process; why not act on sodium sulphate with chalk alone? The answer is that though some sodium carbonate would be formed according to the equation—

$$Na_2SO_4 + CaCO_3 = Na_2CO_3 + CaSO_4,$$

the change would be *very much less* complete than when the sulphate is first reduced to sulphide, unless a large excess of chalk were used; and further, when the mass was lixiviated (*i.e.* extracted with water) the reaction would be to a large extent reversed owing to the fact that calcium carbonate is much less soluble than the sulphate.

375. Uses of Sodium Carbonate.—Sodium carbonate is used in large quantities in the manufacture of glass, soap, and other compounds of sodium. The action of sodium carbonate on greasy materials is very characteristic.

Exp. 364.—Take two bottles, and into each put some water and a few drops of olive oil. Into one bottle put some sodium carbonate, and shake them both. The water containing the sodium carbonate becomes creamy and takes very much longer to clear than the other.

Washing soda thus helps to separate oils and fats into small particles, forming *emulsions*, and so enables them to be washed away by water; hence it is much used for washing greasy vessels. The removal of hardness of water by means of washing soda has been fully explained in § 144.

376. Sodium Hydrogen Carbonate or Sodium Bicarbonate, $NaHCO_3$.—The preparation of sodium bicarbonate from caustic soda has been described in Exp. 295. It may also be readily obtained from the normal carbonate

Exp. 365.—Make a saturated solution of sodium carbonate, and pass carbon dioxide into the solution. Collect the powder which separates and dry it by means of filter paper. Examine it with a lens. Also try the effect of acids on it.

The formation of sodium bicarbonate from the normal carbonate is represented by the equation—

$$Na_2CO_3 + H_2O + CO_2 = 2NaHCO_3.$$

Sodium bicarbonate is a white crystalline powder only moderately soluble in water; the solution is slightly alkaline.

* **Exp. 366.**—Determine the solubilities of the normal and acid carbonates of sodium at the ordinary temperature as in Exp. 47. You will find that the former is much the more soluble salt.

Compare the effect of solutions of the two salts on red litmus paper; the blue colour produced by the normal carbonate is much deeper than that produced by the bicarbonate.

On heating sodium bicarbonate it is decomposed with evolution of carbon dioxide and water vapour, leaving a residue of the normal salt as we saw in Exp. 298.

$$\underset{\substack{2\times(23+1+12+3\times16)\\ \text{or } 168}}{2NaHCO_3} = Na_2CO_3 + \underset{\substack{2+16\\ \text{or } 18}}{H_2O} + \underset{\substack{12+2\times16\\ \text{or } 44}}{CO_2}.$$

The decomposition can be investigated quantitatively and shown to agree with the equation just given in the following manner:—

* **Exp. 367.**—Weigh about 2 gm. of sodium bicarbonate in a weighed crucible, and heat it to redness. Find the loss of weight per cent.

* **Exp. 368.**—Fit a test-tube with a cork and calcium chloride tube either straight (Fig. 108) or U-shaped and weigh it. Put in about 2 gm. of sodium bicarbonate and

weigh again. Now heat the salt until the weight is constant, and find the percentage loss, which consists of carbon dioxide only.[1]

Now the loss of weight in Exp. 367 is due to the loss of both water and carbon dioxide, and should therefore be $\frac{18+44}{168} \times 100$, or 37 per cent. as calculated from the equation. The loss of weight in Exp. 368 is due to the loss of carbon dioxide only, for the water is retained in the calcium chloride tube. The loss should therefore be $\frac{44}{168} \times 100$, or 26 per cent. according to the equation. See how closely your results agree with the percentages just given.



Fig. 108.

The use of bicarbonate of soda (or *baking soda* as it is called) in cookery depends upon the decomposition it undergoes on heating, the evolution of carbon dioxide causing the dough to rise.

Bicarbonate of soda is also used in the preparation of effervescing drinks. For this purpose it is mixed in the dry state with an acid, usually tartaric acid; on adding water the two substances react with the evolution of carbon dioxide, which causes the effervescence.

377. Preparation and Properties of Sodium Nitrate, $NaNO_3$.—Sodium nitrate, or Chili saltpetre as it is also called, is found in the almost rainless districts of Chili, Peru, and Bolivia.

Exp. 369.—Proceed as in Exp. 107 to prepare some sodium nitrate, using caustic soda in place of caustic potash. Examine the crystals which separate out, comparing them with ordinary saltpetre crystals. Test their solubility in water.

Weigh some of the dry crystals in a watch glass and

[1] A slight error is introduced here owing to the fact that when the tube is weighed at the end of the experiment it is full of carbon dioxide in place of air.

leave exposed to the air for some time. Note any change in appearance and re-weigh.

Sodium nitrate is very soluble in water, from which it separates as the anhydrous salt in the form of colourless transparent crystals with a glassy lustre. These crystals are very nearly cubes (hence sodium nitrate is also called *cubic nitre*), thus differing in shape from the long prismatic crystals of ordinary saltpetre. Sodium nitrate also differs from ordinary saltpetre in that it is *deliquescent*.

The action of heat on sodium nitrate has been discussed in § 232. The salt—like nitrates in general—is a strong oxidising agent, as may be illustrated by the following experiments:—

* **Exp. 370.**—Heat a few grams of sodium nitrate in a test-tube until it fuses, and then drop into it one or two fragments of dry charcoal. The charcoal will ignite and burn with violence, being oxidised by the nitrate to carbon dioxide.

* **Exp. 371.**—Repeat the experiment, introducing a few small shavings of lead: the lead will be oxidised at the expense of the nitrate and transformed into yellow oxide of lead according to the equation—

$$Pb + NaNO_3 = PbO + NaNO_2.$$

Sodium nitrate cannot, however, be used in place of potassium nitrate in the manufacture of gunpowder, because it is deliquescent as stated above.

Sodium nitrate is largely used as a manure, and also in the manufacture of sulphuric acid, nitric acid, and potassium nitrate. The last salt is obtained by boiling together strong solutions of Chili saltpetre and potassium chloride, when a double decomposition takes place and sodium chloride, which at the boiling temperature is the least soluble salt, separates out and is removed by canvas filters; potassium nitrate is crystallised out from the mother liquor.

$$NaNO_3 + KCl = NaCl + KNO_3.$$

QUESTIONS.—CHAPTER XXIV.

1. Describe the experiments you would perform to illustrate the chief properties of metallic sodium.

2. How is sodium peroxide prepared, what is it like, and what is the action of hydrochloric acid on it?

3. You are provided with some washing soda. How would you proceed to prepare from it a sample of pure caustic soda? Describe the appearance and characteristic properties of this substance.

4. Describe how you would prepare a specimen of *pure* sodium chloride from sea-salt. What experiments would you perform in order to illustrate the chief properties of common salt?

5. You are provided with the following substances:—common salt, charcoal, chalk, and sulphuric acid. Describe how you would prepare a specimen of pure soda crystals. Express by equations the changes which take place in your preparation.

6. Explain how you would prove that common salt is a compound of sodium and chlorine.

7. How would you prepare some bicarbonate of soda from the normal carbonate? Compare the properties of the two carbonates. For what purposes are they used respectively?

8. How would you proceed to prepare a specimen of sodium nitrate from Glauber's salt? Describe experiments which illustrate its powerful oxidising properties.

9. How may potassium nitrate be prepared from sodium nitrate? Compare the properties of the two salts.

CHAPTER XXV.

CALCIUM AND ITS COMPOUNDS.

378. Properties of Calcium.—

* **Exp. 372.**—Procure a piece of calcium, cut off some shavings with a knife, and examine the freshly cut surface; leave the piece exposed to the air for a night and examine again. Heat some of the shavings on the lid of a crucible for some time, noting any change that takes place.

Calcium is a lustrous white metal which is malleable and rather harder than lead, being difficult to cut. It retains its lustre in dry air, but in moist air it soon takes up oxygen and becomes coated with a white deposit of quicklime, CaO. When the metal is heated in air the conversion into the oxide is more rapid, and if the heating is sufficiently strong the metal burns with a bright flame.

* **Exp. 373.**—Drop some calcium shavings one by one into some water contained in a small test-tube. Note that the metal dissolves rapidly with effervescence and that a heavy milky stream falls from the metal (which floats, though it is heavier than water, being buoyed up by the gas bubbles adhering to it) through the liquid. At first the milkiness disappears on shaking the tube after the metal has dissolved. As more calcium is added, however, the milkiness becomes permanent and a white solid collects at the bottom of the test-tube.

In order to identify the gas produced drop some shavings of calcium into water, cover them with a small inverted funnel, arranging that the stem of the funnel is completely immersed in water, and invert over the stem a test-tube full of water. When gas ceases to collect in the test-tube remove it, closing the mouth with the thumb

before it leaves the water, turn it right side up and apply a light. What happens? what is the gas? Test the liquid in the tube with red litmus paper: it is alkaline.

We see from our experiment that calcium decomposes water rapidly at the ordinary temperature with liberation of hydrogen and formation of a white solid, which at first dissolves in the water, but after a time collects as a white precipitate. The white solid is calcium hydroxide, $Ca(OH)_2$, which is slightly soluble in water, forming an alkaline solution. The change which takes place is represented by the equation—

$$Ca + 2H_2O = Ca(OH)_2 + H_2.$$

When calcium is heated in *nitrogen* to dull redness rapid combination takes place, the metal becoming incandescent. The product is calcium nitride, Ca_3N_2, a dark yellow crystalline substance—

$$3Ca + N_2 = Ca_3N_2.$$

379. Calcium Oxide, Quicklime, or Lime, CaO.—We have seen above that calcium readily combines with the oxygen of the air at ordinary temperature and more rapidly still on heating with formation of the oxide, quicklime—

$$2Ca + O_2 = 2CaO$$

We also know that when chalk or limestone or any other form of calcium carbonate is heated in the air carbon dioxide is given off, and quicklime is left. The change which takes place is represented by the equation—

$$CaCO_3 = CaO + CO_2.$$

Manufacture of Quicklime.—On the large scale quicklime is manufactured from chalk or limestone by the process called *lime-burning*, in which the chalk or limestone is heated to bright redness in a kiln which is so constructed that sufficient air can be passed through it to carry away the carbon dioxide as soon as it is set free. The fuel used to heat the chalk may be wood, coke, or coal, all of which leave little ash. The materials used should not be too dry, as the steam formed assists in the removal of the carbon dioxide.

Two kinds of kilns are still in use. The older form of kiln is egg-shaped and has a fire-grate at the bottom. A layer of large pieces of limestone is arranged over this in the form of an arch, and above this smaller pieces are placed until the kiln is filled. A fire is lighted under the arch of limestone, and kept burning for three days and three nights, by which time the whole of the limestone is converted into quicklime and can be raked out at the bottom. This process is intermittent, but is modified in the more modern one so as to be continuous.

In the latter process the kilns are bucket-shaped. The fuel and limestone are charged in alternate layers in the proportion of about four parts of limestone to one part of fuel, and at the base of the kiln are gratings and dampers for admitting and regulating the air supply. The lime is raked out at the bottom of the kiln from time to time and more limestone and fuel introduced at the top.

Lime prepared in this way contains any impurities present in the original chalk or limestone together with the ash of the fuel used. If required pure, it is made by heating pure marble or calcite or Iceland spar in a platinum dish in a draught of air in a suitable furnace.

380. Properties and Uses of Quicklime and Slaked Lime.—Pure quicklime is a very white and very infusible amorphous substance. When heated to a high temperature it becomes incandescent and gives out a bright white light, the *lime light*. This is used in the optical lantern by heating a cylinder of compressed lime in an oxyhydrogen flame;[1] and in the Welsbach incandescent light by heating a lime gauze in a Bunsen burner. At the temperature of the electric furnace, however, lime can be fused.

Quicklime combines very readily with water with formation of calcium hydroxide, $Ca(OH)_2$, according to the equation—

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

Much heat is developed during the process which is known

[1] An oxyhydrogen flame is one in which hydrogen is burnt in oxygen; it is very hot.

as *slaking* quicklime, and the hydroxide is commonly called *slaked lime*. Slaked lime is a white powder slightly soluble in water forming an alkaline solution known as *lime-water*; *milk of lime* is lime-water containing undissolved lime in suspension.

Exp. 374.—Mix some lime with water in a mortar and pound into a thick paste. Allow it to stand in the air: it gradually dries, shrinks, and hardens. Test with acid: it effervesces, giving off carbon dioxide.

The properties we have investigated in the previous experiment are utilised in the preparation of *mortars* and *cements*. *Mortar* is made by mixing a paste of slaked lime and water with three times its weight of sharp sand. The sand prevents the mass from shrinking and falling to pieces on drying. The causes of the hardening of mortar are (1) loss of water, (2) the conversion of lime into calcium carbonate by the action of atmospheric carbon dioxide, and (3) the chemical combination of the slaked lime and sand to form hydrated calcium silicate; the last cause is, however, the least important.

Limestone may contain considerable amounts of impurities. Thus, if the impurity is magnesium carbonate, the lime formed from it will contain magnesia, and will only slake slowly with a small rise of temperature; such lime is called *poor*. If the impurity is clay (from 15 to 30 per cent.), the lime formed will set and harden under water, and is known as hydraulic mortar or *Portland cement*. Portland cement is manufactured on the large scale by burning an intimate artificial mixture of limestone and clay in kilns.

Lime is also used on a large scale in many operations, such as the manufacture of caustic soda, of bleaching powder, and of ammonia, and in the purification of coal-gas, etc. Further, it is employed in agriculture, where its actions on the soil are very varied.

Quicklime absorbs water so readily that it is used for the dehydration of alcohol and for the drying of ammonia, which would combine with the drying agents calcium chloride and sulphuric acid.

381. Calcium Carbonate, $CaCO_3$.—This compound is found in enormous masses in Nature in more or less pure forms as *chalk*, *limestone*, and *marble*.

Chalk is a white soft substance which when examined under the microscope is seen to be made up of the hard parts of the skeletons of tiny marine animals; their remains must have accumulated in former oceans, and were consolidated by subsequent deposits of a different kind—*e.g.* clay—until some geological change elevated them above their original position.

When acted upon by dilute acids chalk gives off carbon dioxide and forms a calcium salt of the acid; it often leaves a residue of hard silica or silicates, so that it is for the most part calcium carbonate, which, however, is frequently mixed with silica or silicates.

When chalk is well shaken with water the larger particles settle first, and the small particles may be poured off in suspension in the water: they settle later, and are sold under the names of *whiting* and *precipitated chalk*.

Chalk is largely used for polishing, as a colour, as a source of carbon dioxide, and as a source of lime. It is also employed in the manufacture of calcium carbide.

We have already seen that calcium carbonate is insoluble in pure water but dissolves in water containing carbon dioxide, *i.e.* in carbonic acid, forming the bicarbonate. Now soil water is usually saturated with carbon dioxide, so that in chalk or limestone districts this water becomes saturated with calcium bicarbonate. These solutions may deposit the calcium carbonate on evaporation either as crystalline *calcite* or as *stalactites* and *stalagmites*. Examples of the two latter are to be seen in many of the limestone caverns in Derbyshire.

When chalk is heated in the air it loses carbon dioxide and is converted into quicklime, as we have already seen (§ 46), but if it is heated strongly in a confined space so that the carbon dioxide cannot escape, it is converted into more compact forms of calcium carbonate, namely, *limestone* or *marble*. It is doubtless by the action of heat on chalk that these forms of calcium carbonate have been produced in Nature.

382. Preparation and Properties of Calcium Chloride.—

Exp. 375.—Take about 20 c.c. of hydrochloric acid in an evaporating basin; add chalk or marble until some remains undissolved. Filter, and evaporate till crystals begin to form. Allow to cool. Dry the crystals which separate with blotting-paper as quickly as possible. Heat some of them in a test-tube and observe what happens. Leave some exposed to the air and note the result. Dissolve some of the crystals in water and test with (1) red and blue litmus paper, (2) silver nitrate solution. Also dissolve in water the residue obtained by heating the crystals and apply the two tests just mentioned.

The colourless crystals you have prepared consist of calcium chloride combined with water of crystallisation and are represented by the formula $CaCl_2, 6H_2O$; the white residue obtained on heating the crystals is the anhydrous salt, $CaCl_2$ (called *fused calcium chloride*). Both the crystalline and the anhydrous salts are very deliquescent, and the latter is used for drying gases, as we have seen. Also they both dissolve very readily in water forming solutions which are neutral to litmus, and which give a white precipitate with silver nitrate, proving the presence of a chloride.

Exp. 376.—Heat a little calcium chloride on platinum wire in a Bunsen flame and note the *red* colouration produced.

This red colouration is characteristic of *calcium* salts, but more especially of the *chloride* (and other halogen salts).

Exp. 377.—To a solution of calcium chloride add caustic potash. Filter off the precipitate and wash well with water. Test it for calcium, for chlorides, and by litmus.

We see from this experiment that caustic potash gives a white precipitate with calcium chloride, which contains calcium and is alkaline, but is free from chlorides. This

precipitate must be the hydroxide of calcium, slaked lime. The equation which represents the reaction is—

$$CaCl_2 + 2KOH = Ca(OH)_2 + 2KCl.$$

383. Preparation of Calcium Sulphate.—

Exp. 378.—Dissolve some calcium chloride in water and add dilute sulphuric acid. Filter off the white precipitate which forms and wash it well. Introduce a little of the precipitate into a test-tube and shake up with a considerable quantity of distilled water. If sufficient water is added the precipitate dissolves completely. Add some barium chloride solution: a white precipitate forms, proving the presence of a *sulphate*. Take up a little of the first precipitate on a platinum wire, moisten it with hydrochloric acid,[1] and hold it in a Bunsen flame. Note the red colouration, showing the presence of calcium.

We see that the white precipitate is a sulphate and contains calcium, *i.e.* it is *calcium sulphate*. Its formation from calcium chloride and sulphuric acid is represented by the equation—

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl.$$

Calcium sulphate occurs native in a number of different forms. The anhydrous salt is found as *Anhydrite*. *Selenite*, *gypsum*, and *alabaster* each contain two molecules of water of crystallisation.

When gypsum is heated to a temperature of about 140° C., most of its water of crystallisation is driven off and a white mass is left, which when powdered constitutes *Plaster of Paris*. If this powder is made into a paste with water rapid combination takes place with rise of temperature, and in a short time the whole sets to a hard mass. On this property depends the employment of Plaster of Paris as a cement and for making plaster casts. If gypsum is heated to a temperature of 200° C. it loses the

[1] The hydrochloric acid acts on the calcium sulphate converting some of it into the chloride, which gives the red colouration much more vividly than the sulphate does.

property of setting when made into a paste with water; hence care must be taken to regulate the temperature when converting it into Plaster of Paris.

Calcium sulphate is slightly soluble in water (one part in 400), and is one cause of the permanent hardness of water (see § 144).

384. Calcium carbide, CaC_2, as ordinarily seen is a greyish black solid and is prepared on the large scale by heating limestone with coke or coal in the electric furnace.

$$CaCO_3 + 4C = CaC_2 + 3CO.$$

The pure substance has, however, been obtained in the form of colourless or yellow crystals.

The most important property of calcium carbide is the fact that when treated with water it yields acetylene, as we have seen in Exp. 314. This property explains its production on the large scale, the acetylene obtained from it being used for lighting purposes (for motor car and cycle lamps, for enriching coal gas, etc.).

QUESTIONS.—CHAPTER XXV.

1. What are the chief physical and chemical properties of metallic calcium?

2. What is quicklime? How is it made on the large scale? What is its behaviour towards (*a*) air, (*b*) water?

3. What does mortar usually consist of? Why does mortar harden? How could you prove that your explanation was correct?

4. Describe and explain what you observe when you pass carbon dioxide through lime-water.

5. Give an account of the preparation and properties of calcium chloride; compare it with common salt.

6. Describe how you would prepare a specimen of pure calcium sulphate from chalk.

7. In what natural forms does calcium sulphate occur? How is *Plaster of Paris* made, and on what special property does its value depend?

8. How is calcium carbide prepared and what is its appearance? For what important purpose is this compound used?

CHAPTER XXVI.

IRON AND ITS COMPOUNDS.

385. Occurrence and Extraction of Iron.—Iron is the most important of all the metals. It has been found in the *metallic* state in Greenland and other parts of the world, and especially in meteorites, some of which consist almost wholly of iron and nickel. It occurs chiefly, however, in the form of oxides, carbonate, and sulphide. The most important British ore is *clay ironstone*, an earthy form of ferrous carbonate.

In extracting the metal the ores are first calcined to drive off carbon dioxide, moisture, and sulphur. The residue, which consists of ferric oxide and earthy matter, is introduced into a *blast furnace* together with coke and limestone At the high temperature of the furnace the carbon monoxide produced from the coke by the action of the air blast introduced reduces the oxide of iron to the metallic state, and the molten metal is periodically run off into moulds consisting of a network of channels formed in sand. The bars of iron so obtained are called *pigs*. The limestone undergoes decomposition, at the temperature of the furnace, and the lime formed combines with the earthy matter present to form a fusible *slag*.

Iron, as produced in the blast furnace, is known as *cast-iron*, and contains a number of impurities, the chief of which is carbon. To obtain pure iron from cast-iron, the latter is melted in a current of air and stirred about (*puddled*), whereby the impurities are oxidised, carbon passing away as carbon dioxide. The product is called *wrought-iron*.

Cast-iron is converted into *steel* by introducing the molten metal into a large pear-shaped steel vessel (called a *converter*) lined with suitable material to withstand the high temperature, and blowing air through till the impurities are oxidised. A quantity of carbon (in the form of *ferro-manganese* or *spiegel-eisen*, an alloy of iron and manganese containing about 6 per cent. of carbon) is now added, which is considerably less than that originally present in the cast-iron.

386. Properties of Iron and Steel.—The properties of *wrought-iron*, *cast-iron*, and *steel* differ considerably. This difference depends chiefly upon the quantity of carbon present. *Wrought-iron*, which is nearly pure iron, is a soft, grey, malleable metal possessing considerable tensile strength (*i.e.* a heavy weight can be hung on to a tolerably thin iron wire without breaking it). As the percentage of carbon increases, the iron becomes harder and less malleable; up to a certain point the tensile strength increases, but beyond this it diminishes. *Cast-iron*, which contains the highest percentage of carbon, is very brittle, and its tensile strength is much smaller than that of wrought-iron.

Steel is very tough, possessing even greater tenacity than wrought-iron, and it possesses the remarkable property of becoming very hard on being heated up and then suddenly cooled. If it is now heated again to a moderate temperature it becomes softer, and by varying the temperature the hardness can be regulated. This process is called "tempering," and the steel is said to "take a temper"; wrought-iron and cast-iron cannot be tempered.

387. Uses of Iron and Steel.—*Wrought-iron* was formerly used for a great variety of purposes, but steel has now taken its place to a very large extent. The greater part of the wrought-iron manufactured at the present time is employed for making the cores of electromagnets used in dynamos and electric motors. A considerable amount is also employed by the blacksmith, who requires a metal which can be easily worked at a red heat; horse-shoes, for instance, are made of wrought-iron.

Cast-iron is, as its name implies, used for *castings*—*e.g.* fire-grates, fly-wheels, and pistons; its value for this purpose depends upon (1) its low melting-point compared with wrought-iron and steel; (2) the fact that on cooling from a temperature somewhat above the melting-point a considerable expansion takes place which enables the molten metal to fill every part of a mould into which it is poured.

The purposes for which *steel* is employed are innumerable: it is used for making tools, guns, armour-plating for ships, boiler-plates, rails, girders for bridges, etc., etc. Pure iron melts at about 2000° C., cast-iron at about 1600° C. The melting-point of pure iron is therefore about 1000° C. higher than that of copper. We should regard iron, then, as a metal with an extremely high melting-point.

All the forms of iron (wrought-iron, cast-iron, and steel) if exposed to moist air become coated with the hydrated oxide of the metal (iron rust). Pure dry air has no effect at ordinary temperatures upon iron.

388. Action of Acids on Iron.—We have already studied the action of dilute sulphuric and hydrochloric acids on iron. The investigation should now be made more complete.

Exp. 379.—Examine the action of concentrated hydrochloric and sulphuric acids both hot and cold on iron; also the action of dilute and concentrated nitric acid. Test any gases given off, evaporate the solutions, and examine the residues.

The action of the three acids used is as follows:—

Hydrochloric acid, whether dilute or concentrated, gives hydrogen and ferrous chloride, $FeCl_2$.

Sulphuric acid when dilute gives hydrogen and ferrous sulphate, $FeSO_4$. The concentrated acid has no action in the cold, but on heating the metal dissolves with liberation of sulphur dioxide and formation of ferric sulphate, $Fe_2(SO_4)_3$, and ferrous sulphate.

Nitric acid, whether dilute or concentrated,[1] readily dissolves iron with formation of brown fumes, which are very copious in the latter case. With the dilute acid nitrogen peroxide, nitric oxide, nitrous oxide, and free nitrogen are all evolved in varying quantities, and the solution contains ammonium nitrate, ferrous nitrate ($Fe(NO_3)_2$), and ferric nitrate ($Fe(NO_3)_3$). The chief products when the concentrated acid is used are nitrogen peroxide, nitric oxide, and ferric nitrate.

389. The Sulphates of Iron.—We have prepared one of the sulphates of iron—ferrous sulphate—in Exp. 101 by dissolving the metal in dilute sulphuric acid. The green crystals obtained are known as *green vitriol* and have the composition represented by the formula $FeSO_4$, $7H_2O$. The effect of heat on these crystals has been investigated in Exps. 104 and 272. The first change consists in the loss of water of crystallisation, and formation of a white salt having the composition $FeSO_4$, H_2O. Then a complex decomposition takes place, resulting in the formation of sulphuric acid fumes, and a residue of ferric oxide remains.

Exp. 380.—Add some ferrous sulphate solution to a solution of potassium permanganate, acidulated with dilute sulphuric acid : the colour disappears.

This illustrates the *reducing action* of ferrous sulphate, which is also exemplified by its action on nitric acid investigated in Exp. 230.

Exp. 381.—Leave some crystals of green vitriol exposed to the air for several days and then examine them again. Note that they have become covered with a yellow coating.

This change is due to absorption of oxygen from the air, and again illustrates the readiness with which ferrous sulphate takes up oxygen.

[1] The *pure concentrated* acid has, however, no action.

390. Ferric Sulphate.—

Exp. 382.—Heat some ferric oxide (rouge) with a little concentrated sulphuric acid, evaporating to dryness. Allow to cool and then add water.

The residue dissolves, forming a brown solution from which colourless crystals of hydrated ferric sulphate may be obtained with difficulty. If these crystals are heated they lose water and are converted into a white powder—anhydrous ferric sulphate. The action of sulphuric acid on ferric oxide is represented by the equation—

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O.$$

Ferric sulphate is most conveniently prepared by heating ferrous sulphate solution with nitric acid in the presence of sulphuric acid. The equation for the reaction which takes place is given after Exp. 230.

Exp. 383.—Add some ferric sulphate solution to a solution of potassium permanganate acidulated with sulphuric acid. The colour of the permanganate is not affected.

Ferric sulphate is not then a reducing agent like the ferrous salt

391. The Oxides of Iron.—

Exp. 384.—Take some ferrous sulphate crystals, wash them with water, and then dissolve them in cold water acidulated with sulphuric acid. Add caustic potash, filter and wash as rapidly as you can, and dry part of the gelatinous mass on blotting-paper. When dry, heat some of the solid in a dry test-tube and observe what happens. After a time examine the part of the mass you left moist and note the result.

We note that the green gelatinous precipitate becomes much darker on drying; when heated it gives off water and turns first black and finally brown. The mass which was left moist soon becomes brown.

Exp. 385.—Repeat the previous experiment, using ferric sulphate instead of ferrous, and washing the precipitate before drying it on blotting-paper. Dry some of the brown gelatinous precipitate on the water-bath and heat in a dry test-tube, as before.

We note that the dried precipitate gives off water when heated and leaves a grey solid.

The green and brown precipitates formed in Exps. 384 and 385 consist respectively of ferrous hydroxide, $Fe(OH)_2$,§ and ferric hydroxide, $Fe(OH)_3$—

$$FeSO_4 + 2KOH = Fe(OH)_2 + K_2SO_4.$$

$$Fe_2(SO_4)_3 + 6KOH = 2Fe(OH)_3 + 3K_2SO_4.$$

When ferrous hydroxide is heated it loses water and is converted into ferrous oxide, FeO, which is black—

$$Fe(OH)_2 = FeO + H_2O.$$

Ferrous oxide, however, is very unstable and takes up oxygen from the air with great readiness, forming ferric oxide (the brown solid finally obtained in Exp. 384)—

$$4FeO + O_2 = 2Fe_2O_3.$$

Unless therefore the heating is conducted *in absence of air* the formation of the black ferrous oxide is by no means complete. Ferrous hydroxide is also very unstable, and in the moist state takes up oxygen and water and is converted into brown ferric hydroxide—

$$2Fe(OH)_2 + 2H_2O + O_2 = 2Fe(OH)_3.$$

When ferric hydroxide is heated it loses water and is converted into ferric oxide (the grey solid obtained in Exp. 385)—

$$2Fe(OH)_3 = Fe_2O_3 + 3H_2O$$

It will be noticed that ferric oxide varies in colour according to the precise way in which it is prepared. When the different forms are finely powdered, however, the colour is in all cases some shade of red. The ferric oxide

§ *Pure* ferrous hydroxide is *white*; the green colour is due to partial oxidation.

obtained by the action of heat on green vitriol is used for polishing (jeweller's *rouge*) and for making oil paint.

Ferric oxide only dissolves in acids with difficulty, the best solvent being fairly concentrated boiling sulphuric acid.

Iron rust consists chiefly of ferric oxide combined with water, but it also contains some ferrous carbonate.

392. Magnetic Oxide of Iron, Fe_3O_4.—

* **Exp. 386.**—Weigh out 2 grams of ferrous sulphate crystals, dissolve in water, acidify with sulphuric acid, add some nitric acid, and boil till brown fumes cease to be evolved even on the addition of a few more drops of nitric acid. Now add caustic potash to the solution till a precipitate begins to form[1] and *just* redissolve this with dilute sulphuric acid.

Next weigh out 1 gram of ferrous sulphate crystals, dissolve in water, and add the solution to that just prepared. Shake up in order to mix thoroughly and then add caustic potash. Filter off the black precipitate which forms, wash it, and dry on the water-bath.

Powder the brownish-black solid which is obtained and test it with a magnet: it is attracted.

The magnetic solid which you have prepared is *magnetic oxide of iron*, Fe_3O_4 (combined with a little water). The changes which have taken place are as follows:—The ferrous sulphate which you boiled with nitric acid was oxidised to ferric sulphate. The ferric sulphate formed was equivalent to *two* grams of ferrous sulphate, and you subsequently added *one* gram of ferrous sulphate, so that the solution to which you added caustic potash contained equal numbers of molecules of ferrous and ferric sulphates (since each molecule of ferric sulphate is formed from two molecules of ferrous sulphate—see equation after Exp. 230).

The effect of adding caustic potash to this solution is to produce a black precipitate, which may be considered as a compound of equal numbers of molecules of ferrous and

[1] The object of this is to neutralise the excess of nitric acid so that it does not oxidise the ferrous sulphate subsequently added.

ferric hydroxides, and this compound when dried on the water-bath loses water, and is converted into magnetic oxide of iron, which we may consider as a compound of one molecule of ferrous oxide and one molecule of ferric oxide.

One molecule of ferrous oxide = FeO
,, ,, ,, ferric oxide = Fe_2O_3
,, ,, ,, magnetic oxide of iron = Fe_3O_4

Magnetic oxide of iron is the oxide produced when iron burns in air or oxygen (Exp. 35)—

$$3Fe + 2O_2 = Fe_3O_4.$$

It is also formed when steam or carbon dioxide is passed over heated iron, hydrogen and carbon monoxide being the other products of the respective reactions—

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$
$$3Fe + 4CO_2 = Fe_3O_4 + 4CO.$$

On the other hand, when hydrogen and carbon monoxide are passed over heated magnetic oxide of iron (or any other oxide of iron) the oxide is reduced to the metal, and steam and carbon dioxide are respectively re-formed.

$$Fe_3O_4 + 4H_2 = 3Fe + 4H_2O.$$
$$Fe_3O_4 + 4CO = 3Fe + 4CO_2.$$

These are examples of the *reversibility of chemical reaction*, which has already been discussed in § 41 (*q.v.*). In order to express the fact that these changes proceed one way or the other, according as steam or hydrogen is in excess in the first case, and carbon dioxide or carbon monoxide is in excess in the second case, the equations may be written thus—

$$3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2,$$
$$3Fe + 4CO_2 \rightleftharpoons Fe_3O_4 + 4CO,$$

the sign $\rightleftharpoons$ being intended to imply the reversibility of the reaction.

* **Exp. 387.**—Add some dilute sulphuric acid to the magnetic oxide of iron you prepared in Exp. 386: it dissolves, forming a brownish solution. Add a little potassium permanganate solution: it is decolorised.

The brown colour of the solution shows that *ferric* sulphate is present, and the decolorisation of the potassium permanganate proves the presence of *ferrous* sulphate. The change which has taken place is represented by the equation—

$$Fe_3O_4 + 4H_2SO_4 = FeSO_4 + Fe_2(SO_4)_3 + 4H_2O.$$

We see then that when magnetic oxide of iron dissolves in sulphuric acid it behaves like a compound of ferrous and ferric oxides, the salts corresponding to both these oxides being formed. This is what we should expect when we consider the method of preparing the oxide investigated in Exp. 386. The behaviour of the oxide towards other acids is similar.

393. The Chlorides of Iron.—In Exp. 102 we prepared ferrous chloride by dissolving iron in hydrochloric acid. The green crystals which were obtained have the composition represented by the formula $FeCl_2$, $4H_2O$. Also by passing dry hydrogen chloride over heated iron wire we obtained the anhydrous salt as white feathery crystals (Exp. 168). Both the anhydrous salt and the green crystals are deliquescent and dissolve very readily in water.

* **Exp. 388.**—Prepare a solution of ferrous chloride by dissolving iron in hydrochloric acid. Pass chlorine through part of the solution till the liquid smells strongly of the gas; notice that the almost colourless solution has become brown. Now heat till the smell of chlorine has disappeared[1] and then divide the solution into two portions. To one portion add caustic potash and to the other hydrochloric acid and a little potassium permanganate solution.

[1] If any precipitate forms it should be redissolved by adding hydrochloric acid.

Also divide the remainder of the ferrous chloride solution, through which chlorine was not passed, into two parts and the same reagents. Compare the results.

We see that ferrous chloride gives a *greenish* precipitate with caustic potash and *decolorises* potassium permanganate, but after passing chlorine through the solution to saturation, caustic potash gives a *brown* precipitate and the solution *does not decolorise* potassium permanganate. The explanation is that the chlorine has combined with the ferrous chloride to form ferric chloride (which gives a brown solution).

$$2FeCl_2 + Cl_2 = 2FeCl_3.$$

Ferrous chloride, like ferrous sulphate, gives a precipitate of ferrous hydroxide with caustic potash, whereas ferric chloride, like ferric sulphate, gives a brown precipitate of ferric hydroxide

$$FeCl_2 + 2KOH = Fe(OH)_2 + 2KCl.$$
$$FeCl_3 + 3KOH = Fe(OH)_3 + 3KCl.$$

Also ferrous chloride resembles ferrous sulphate in that it is a reducing agent and decolorises potassium permanganate, whilst ferric chloride, like ferric sulphate, does not possess reducing properties.

Passing chlorine over heated iron wire in an apparatus similar to that used in Exp. 168, nearly black crystals of anhydrous ferric chloride may be obtained.

$$2Fe + 3Cl_2 = 2FeCl_3.$$

These crystals are very deliquescent and dissolve readily in water, forming a brown solution which becomes yellow on dilution. The same solution may be obtained by dissolving ferric oxide in hot concentrated hydrochloric acid, or ferric hydroxide in the dilute (or concentrated) acid.

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$
$$Fe(OH)_3 + 3HCl = FeCl_3 + 3H_2O.$$

From the solution of ferric chloride several brown crystalline hydrated salts have been obtained by varying the conditions under which the crystals separate; the

compound containing the greatest amount of water of crystallisation is represented by the formula $FeCl_3, 6H_2O$.

QUESTIONS.—CHAPTER XXVI.

1. Write an account of the properties and uses of wrought-iron, cast-iron, and steel.
2. Give an account of the action of acids on iron.
3. Describe how you would prepare the two sulphates of iron and convert each into the other. How would you distinguish between ferric and ferrous salts?
4. Illustrate by means of iron compounds the meaning of oxidation and reduction.
5. Give an account of the preparation and compare the properties of the oxides of iron.
6. Describe the preparation of the chlorides of iron. What is the appearance of these salts? State and explain what you would observe on adding a solution of caustic potash to a solution of each salt.

CHAPTER XXVII.

MAGNESIUM, ZINC, LEAD, AND COPPER, AND THEIR OXIDES.

394. Properties of Magnesium.—We have already made a considerable study of the properties of magnesium. It is a bright white metal of low specific gravity (1·75) and melts at 633° C., that is to say, below dull red heat. Magnesium undergoes no change in dry air, but in moist air it becomes covered with a superficial layer of oxide. We have already seen that when magnesium is heated in air it burns readily; let us examine this change a little more carefully.

Exp. 389.—Heat a piece of magnesium ribbon on a crucible lid in a Bunsen flame. The metal soon catches fire and burns with a very bright white flame and formation of white fumes. At this stage remove the flame. A light white powdery residue remains, which will, however, be found to be yellowish green inside on breaking up with a knife. Now heat the residue up again; you will find that the yellowish green portions of the residue change to white with incandescence.

The white fumes and white residue produced consist of magnesium oxide and are formed by the combination of the magnesium with the oxygen of the air.

$$2Mg + O_2 = 2MgO.$$

The yellowish green portion of the residue consists of magnesium nitride, Mg_3N_2, and is formed by the combination of the magnesium with the nitrogen of the air.

$$3Mg + N_2 = Mg_3N_2.$$

When magnesium nitride is heated fairly strongly in air it is converted into the oxide, sufficient heat being produced to render the powder incandescent.

$$2Mg_3N_2 + 3O_2 = 6MgO + 2N_2.$$

The property exhibited by magnesium of readily uniting directly with nitrogen is shared by only a few other elements, one of which is calcium (see § 378). The light emitted by burning magnesium is made use of in pyrotechny, in signalling, and (on account of its richness in chemically active or "actinic" rays) in photography. Magnesium in the form of powder acts as a powerful reducing agent at high temperature. For example, silicon is a difficult element to isolate, but it can be obtained from silica by heating with magnesium powder.

$$2Mg + 3SiO_2 = 2MgSiO_3 + Si.$$

Also most metallic oxides are reduced to the metal by heating with powdered magnesium.

The action of magnesium on water and acids has already been fully discussed in §§ 35, 53, 240.

395. Magnesium Oxide, Magnesia, MgO.—This is a white powder produced, as we have seen, by burning magnesium in air. Magnesia only combines slowly with water, differing in this respect from quicklime, which, as we have seen, has a great attraction for water; moreover, magnesium hydroxide, $Mg(OH)_2$, the compound produced, is only very slightly soluble in water, whereas slaked lime is moderately soluble.[1] The aqueous solution of magnesium hydroxide is slightly alkaline to litmus.

Magnesia is a very infusible substance, and is therefore used for making crucibles and fire-bricks. When strongly heated it emits a very bright light, and on this account pencils of magnesia are employed in the Drummond light. It is also used in medicine.

[1] One part by weight of magnesium hydroxide dissolves in 55,000 parts of water, whereas one part of slaked lime requires only 400 parts of water.

Exp. 390.—Add magnesia to dilute sulphuric, hydrochloric, and nitric acids respectively a little at a time, shaking after each addition. In each case the oxide will dissolve for a time and then a point will be reached when it remains undissolved even on warming. Now filter, evaporate each filtrate to small bulk and allow to stand. Colourless crystals separate out in each case. Filter these off and dry them between blotting-paper. Dissolve some of each in water, and test the solutions with litmus papers; now add some caustic potash to each and note the result; finally test each for sulphate, chloride, and nitrate by the usual tests.

In each case the oxide dissolves in the acid forming the corresponding salt which separates out from solution in crystals containing water of crystallisation—

$$MgO + H_2SO_4 = \underset{\text{Magnesium sulphate}}{MgSO_4} + H_2O,$$

$$MgO + 2HCl = \underset{\text{Magnesium chloride}}{MgCl_2} + H_2O,$$

$$MgO + 2HNO_3 = \underset{\text{Magnesium nitrate}}{Mg(NO_3)_2} + H_2O.$$

These salts all dissolve readily in water, forming solutions which are neutral to litmus. The solution of each salt gives a white precipitate of magnesium hydroxide with caustic potash. The reaction in the case of the nitrate, for example, is represented by the equation—

$$Mg(NO_3)_2 + 2KOH = Mg(OH)_2 + 2KNO_3.$$

The sulphate is the most important of the three salts. The crystals which are represented by the formula $MgSO_4, 7H_2O$ are known as "Epsom salts," having been discovered in a mineral spring at Epsom Epsom salts is prepared on the large scale from the salt deposits at Stassfurt in Germany, which contain considerable quantities of magnesium sulphate associated with other salts. It is used medicinally and also in dyeing.

396. Properties of Zinc.—Zinc is a white metal with a bluish tinge, and melts at 419° C., *i.e.* at a considerably lower temperature than magnesium. It is rather brittle at ordinary temperatures, but at about 100°-150° C. it becomes ductile and may be drawn into wire and rolled into sheet; above 200° C. it loses its cohesion and may be readily powdered. Zinc is only very slightly acted upon by air at ordinary temperatures. On this account it is used for *galvanising* iron; this consists in coating iron with a thin layer of zinc by dipping it in the melted metal.

* **Exp. 391.**—Introduce some thin zinc turnings into a porcelain crucible and heat first with a Bunsen flame and then as strongly as possible with a blowpipe flame. When the crucible becomes white-hot the metal burns with a bright greenish-white flame and formation of clouds of white fumes; a white powdery residue remains in the crucible.

The white residue and white fumes consist of zinc oxide, and the change which takes place is represented by the equation—

$$2Zn + O_2 = 2ZnO.$$

The action of acids on zinc has been studied in §§ 53, 221, 235, 253. It should be mentioned that though dilute sulphuric and hydrochloric acids readily dissolve ordinary zinc which contains impurities such as iron, they are practically without action on the *pure* metal. For a discussion of the cause of this behaviour a larger work should be consulted.

397. Zinc Oxide, ZnO.—

Exp. 392.—Shake up some zinc oxide with water, filter and evaporate the filtrate to dryness. Also add the oxide to dilute sulphuric acid till it ceases to dissolve, concentrate and allow to crystallise.

Zinc oxide is a white amorphous powder insoluble in water but readily soluble in acids with formation of the

corresponding salts. The sulphate (called *white vitriol*) is obtained in the previous experiment as colourless crystals having the composition represented by the formula, $ZnSO_4$, $7H_2O$.

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

The chloride and nitrate are similarly produced by using hydrochloric and nitric acids in place of sulphuric acid; on evaporation syrupy liquids are formed, from which colourless crystals may be obtained, but only with difficulty as the salts are exceedingly deliquescent, especially the chloride.

Zinc oxide is used as a pigment under the name *zinc white* and has the advantage over white lead (which it to some extent replaces) that it is not blackened by the sulphuretted hydrogen of the air (since sulphide of zinc is white).

398. Properties of Lead.—Lead is a soft, bluish-grey metal with a bright lustre at a freshly cut surface; it tarnishes in air and is superficially acted upon by water containing dissolved air, especially in presence of carbon dioxide or in water containing certain salts in solution. This behaviour of lead towards water is of extreme importance, since drinking water is always conveyed, for some distance at any rate, through leaden pipes, so that there is always the possibility of contamination of the water unless proper precautions are taken. The lead hydroxide which may be formed is itself slightly soluble in water, whilst the carbonate which is also a possible product is soluble in water containing carbon dioxide. Thus we may get drinking water containing poisonous lead compounds. If, however, the water is "permanently" hard (see § 144) a protective layer of lead sulphate will form, and the further solvent action of the water be thus prevented.

Lead is very malleable but possesses little tenacity; its specific gravity is about 11·5, and it melts at 327° C. The softness and malleability of lead and its low melting-point render it of great value in the arts. It is, for instance, used in making piping and rifle-bullets, the metal being heated and forced through perforations of the required shape.

399. Action of Acids on Lead.—

Exp. 393.—Examine the reactions of lead with strong and dilute hydrochloric, nitric, and sulphuric acids, both in the cold and on heating.

We note that lead is slightly soluble in hot concentrated hydrochloric acid, forming a small quantity of white crystals (lead chloride) on cooling. Lead is also slowly acted upon by hot concentrated sulphuric acid, being converted into a white substance (lead sulphate) with liberation of sulphur dioxide.

Lead dissolves readily in nitric acid, both concentrated and dilute, on warming, but only slowly in the cold, brown fumes being formed. When the concentrated acid is used the chief product, other than lead nitrate, is nitrogen peroxide, and the brown fumes are very copious; in the case of the dilute acid, however, a much larger proportion of the lower reduction products of nitric acid—nitrous oxide, free nitrogen, etc.—are produced, and the brown fumes are less pronounced. The lead nitrate separates out from the solutions in white crystals on evaporation and cooling.

400. The Oxides of Lead.—In Exp. 8 we investigated the effect of heating lead in air and we found that a yellow solid was formed; this substance was lead monoxide, PbO.

$$2Pb + O_2 = 2PbO.$$

At red heat lead monoxide melts, forming a red liquid which solidifies on cooling to a yellow flaky solid (in which form the oxide is known as *litharge*). Lead monoxide is only very slightly soluble in water, forming a slightly alkaline solution. When the monoxide is heated to dull redness in a current of air for 24 hours, it takes up oxygen and is converted into another oxide, *red lead* or *minium*, Pb_3O_4.

$$6PbO + O_2 = 2Pb_3O_4.$$

Red lead is a red crystalline powder which on heating darkens in colour and then decomposes into the yellow oxide and oxygen.

$$2Pb_3O_4 = 6PbO + O_2.$$

Red lead is insoluble in water.

401. Action of Nitric Acid on the Oxides of Lead.—We have already seen in Exp. 114 that litharge dissolves in dilute nitric acid with formation of white crystals of lead nitrate. The reaction is expressed by the equation—

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O.$$

Let us now examine the action of nitric acid on red lead.

Exp. 394.—Warm some dilute nitric acid in a dish and then add a few grams of red lead and stir. Note that the *red* colour of the powder changes to *brown*. When this change is complete filter, evaporate the filtrate and allow to cool. White crystals separate out. Wash the brown residue on the filter and dry it in an air oven. Investigate the action of heat on this brown powder.

The brown powder which is obtained is a third oxide of lead, namely *lead peroxide*,[1] PbO_2, and the crystals consist of lead nitrate. The change which has taken place is represented by the equation—

$$Pb_3O_4 + 4HNO_3 = 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Red lead then acts as a compound of lead monoxide (two molecules) and lead peroxide (one molecule).

When lead peroxide is heated oxygen is evolved and a residue of the monoxide remains.

$$2PbO_2 = 2PbO + O_2.$$

Lead peroxide is insoluble in water.

402. Action of Hydrochloric Acid on the Oxides of Lead.—

Exp. 395.—Boil some litharge with concentrated hydrochloric acid. The litharge dissolves, and when the solution cools white crystals separate out. Pour off the supernatant liquid and add some cold water: the crystals do not dissolve. Now boil the water: the crystals dissolve but separate out again on cooling.

[1] Also called *puce oxide of lead.*

The crystals consist of lead chloride, which is only slightly soluble in cold water, but readily soluble in hot.

$$PbO + 2HCl = PbCl_2 + H_2O.$$

The action of hot concentrated hydrochloric acid on red lead has already been investigated in Exp. 175; the oxide dissolves with evolution of chlorine and formation of lead chloride. The behaviour of lead peroxide is similar, the change being represented by the equation—

$$PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O.$$

403. Action of Sulphuric Acid on the Oxides of Lead.—

* **Exp. 396.**—Examine the action of hot concentrated sulphuric acid on the three oxides of lead.

Each of the oxides is converted into a white insoluble powder, lead sulphate, and in the cases of red lead and lead peroxide, oxygen is evolved. The changes are represented by the equations—

$$PbO + H_2SO_4 = PbSO_4 + H_2O.$$
$$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + 6H_2O + O_2.$$
$$2PbO_2 + 2H_2SO_4 = 2PbSO_4 + 2H_2O + O_2.$$

The action of dilute hydrochloric and sulphuric acids on the oxides of lead is similar to the action of dilute nitric acid; the monoxide is converted into the corresponding salt, the peroxide is unacted upon, and red lead gives the peroxide together with the salt corresponding to the monoxide. The changes do not, however, take place as readily as in the case of nitric acid owing to the insolubility of the salts formed; these form a coating on the oxide and so retard the action.

404. Properties of Copper.—Copper is a metal which appears red by reflected light, but extremely thin plates of it transmit green light. Its specific gravity is about 9; it possesses the properties of toughness and malleability to a high degree, and is the second best conductor of heat and electricity known. On this last property depends its use

in the manufacture of electric cables. Copper melts at 1080° C.; it is therefore not easy to melt the metal, but thin wire, or foil, may be fused in the hottest parts of the Bunsen flame. Dry air is without action on the metal at ordinary temperatures, but in presence of moisture and carbon dioxide it becomes corroded and coated with a deposit of green basic carbonate (verdigris). Copper is largely employed in making domestic utensils and electric batteries, as well as in electro-plating and electro-typing.

405. Action of Acids on Copper.—We have already carried out investigations on the action of the common acids on copper. We have seen that nitric acid whether dilute or concentrated readily attacks the metal with formation of oxides of nitrogen and a blue solution of copper nitrate, and that hot concentrated sulphuric acts on it with formation of sulphur dioxide, copper sulphate, and cuprous sulphide. Let us now complete the investigation.

* **Exp. 397.**—Examine the action of dilute sulphuric acid and dilute and concentrated hydrochloric acid on copper turnings.

You will find that there is very little action in any of these cases. Concentrated hydrochloric acid does, however, dissolve the metal very slowly with liberation of hydrogen and formation of cuprous chloride.

$$2Cu + 2HCl = Cu_2Cl_2 + H_2.$$

406. Preparation and Properties of Cupric Oxide.—When metallic copper is heated in air it becomes coated with a greyish-black scale which readily peels off and is easily converted into a black powder (see Exp. 4). This substance is cupric oxide, CuO, and its formation as just described is represented by the equation—

$$2Cu + O_2 = 2CuO.$$

It is also produced on heating copper nitrate (see Exp. 138), and this is the best method of preparation (the copper nitrate being obtained by dissolving copper in nitric acid).

Cupric oxide is a powerful oxidising agent at high temperatures, as it is readily reduced to the metal, *e.g.* by heating in a current of hydrogen, coal gas, or carbon monoxide. It is very largely used in the analysis of organic substances, the carbon of which is burnt to carbon dioxide and the hydrogen to water when they are heated in contact with the oxide; the latter is again reduced to the metal.

When cupric oxide is strongly ignited it loses a part of its oxygen and is converted into cuprous oxide (Cu_2O), which is red.

$$4CuO = 2Cu_2O + O_2.$$

407. Action of Acids on Cupric Oxide.—Cupric oxide is insoluble in water, but we have seen in Exp. 113 that it readily dissolves in dilute sulphuric acid with formation of cupric sulphate (or copper sulphate as it is more frequently but less correctly termed), according to the equation—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

Exp. 398.—Investigate the action of dilute hydrochloric and nitric acid on cupric oxide.

Cupric oxide dissolves readily in both hydrochloric and nitric acids on gently warming, and from the solutions greenish blue crystals of cupric chloride ($CuCl_2$, $2H_2O$) and blue crystals of cupric nitrate ($Cu(NO_3)_2$, $2H_2O$) respectively separate on evaporation.

$$CuO + 2HCl = CuCl_2 + H_2O.$$
$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

Both these salts, like copper sulphate, dissolve readily in water.

Exp. 399.—Add ammonia gradually to a solution of copper sulphate. Note that a pale blue precipitate first forms, but redissolves again as more ammonia is added, forming a deep blue solution. Repeat the experiment with cupric nitrate and cupric chloride: the results are similar.

The formation of this deep blue solution is very characteristic of cupric salts; the changes which take place are, however, complex, and are not yet fully understood.

QUESTIONS.—CHAPTER XXVII.

1. Compare and contrast the metals lead and copper as regards physical properties. Describe briefly the behaviour of water towards lead.

2. In what respects do the metals zinc and magnesium resemble each other, and in what do they differ?

3. Describe the experiments you would perform in order to demonstrate the chief properties of the substance formed when magnesium burns in oxygen. Give the name and chemical formula of this substance. For what purposes is it employed?

4. What would you observe on heating magnesium strongly in nitrogen? Describe the chief properties of the product.

5. Describe how you would proceed to prepare some Epsom salts from magnesia. What happens when a solution of caustic soda is added to one of Epsom salts? Give the equation for the reaction.

6. Describe how you would prepare some zinc oxide. What experiments would you perform to illustrate its properties? For what purpose is it employed in the arts?

7. Write an account of the action of the common mineral acids on lead.

8. How would you proceed to prepare specimens of litharge and red lead? Compare the action of hydrochloric and nitric acids on them.

9. Describe how you would prepare some lead peroxide given litharge. Compare the action of sulphuric and hydrochloric acids on lead peroxide and red lead.

10. Describe how you would proceed to prepare a specimen of pure cupric oxide from metallic copper. What experiments would you perform in order to demonstrate the chief properties of the oxide?

CHAPTER XXVIII.

MODES OF FORMATION OF SALTS.

408. Many examples of the various ways in which salts are formed have been given in the foregoing pages. We shall now collect these methods together and classify them.

409. Method 1. Direct Union of a Metal and a Non-Metal.—This method is largely employed for the production of the anhydrous salts of the halogen acids, since most metals unite directly with the halogens. When the metal forms two salts, one containing a higher percentage of halogen than the other, it depends upon the relative masses of the metal and the halogen which react, whether the higher or the lower salt is formed. Iron, for instance, yields ferr*ic* chloride ($FeCl_3$) with excess of chlorine; but if the iron is in excess, ferr*ous* chloride ($FeCl_2$) is formed—

$$2Fe + 3Cl_2 = 2FeCl_3.$$
$$Fe + Cl_2 = FeCl_2.$$

Similarly, tin yields stannic chloride ($SnCl_4$) or stannous chloride ($SnCl_2$), according as chlorine or the metal is in excess—

$$Sn + 2Cl_2 = SnCl_4.$$
$$Sn + Cl_2 = SnCl_2.$$

The combination of mercury and iodine affords another example, HgI_2 or Hg_2I_2 being formed according as iodine or mercury is in excess (see § 188).

Many sulphides can also be readily obtained by the direct union of metals with sulphur (see Exps. 117, 276).

410. Method 2. Interaction of Metals and Acids.—When acids act on metals, a salt of the metal is almost invariably obtained as one of the products. In some cases, *e.g.* when dilute hydrochloric, dilute sulphuric, or acetic acid acts on magnesium, zinc, or iron, hydrogen is the only other product, and these reactions are used in the preparation of hydrogen, as we have seen. In other cases the reactions are more complex, and these have been fully discussed in the foregoing chapters.

The action of a haloid acid on a metal always results in the formation of its *lower* salt when it forms more than one. Thus, with hydrochloric acid, iron forms ferrous chloride, $FeCl_2$, and with tin it forms stannous chloride, $SnCl_2$. We should expect this because the nascent hydrogen which is liberated in the reaction is a strong reducing agent, and would immediately reduce the higher salt if any were formed.

When the acid is a strong oxidising agent, *e.g.* nitric acid, the nascent hydrogen which may be supposed to be liberated at first is immediately oxidised to water, and it depends upon the relative masses of the metal and the acid whether the lower or the higher salt is formed. This may be illustrated by the following experiments.

* **Exp. 400.**—Warm a small quantity of mercury with excess of nitric acid till the metal has dissolved. Now add hydrochloric acid to the solution; no precipitate will be formed, proving the absence of any mercur*ous* nitrate (which with hydrochloric acid would form a white precipitate of mercurous chloride). The mercury has been entirely converted into mercur*ic* nitrate.

* **Exp. 401.**—Next allow some mercury to remain in contact with about half its volume of dilute nitric acid for some time. Pour off the supernatant liquid from the mercury and add hydrochloric acid; a white precipitate is at once formed, showing that when the mercury is in excess of the acid, it is converted into mercur*ous* nitrate.

Salts of the haloid acids may be obtained by acting on a metal with either the gaseous acid or its aqueous solution; if the anhydrous salt is required, only the former method can be employed in many cases, because, on evaporating the aqueous solution of the salt to dryness and igniting to drive off water, the salt and the water react on each other with formation of the halogen acid and the oxide of the metal. Ferric chloride, for instance, is decomposed by water on evaporation to dryness and igniting, with formation of ferric oxide and hydrogen chloride—

$$2FeCl_3 + 3H_2O = Fe_2O_3 + 6HCl.$$

* **Exp. 402.**—Prepare some ferric chloride as in Exp. 388. Evaporate the solution to dryness and ignite. Notice the evolution of acid fumes (hydrogen chloride). When these cease to come off allow the residue to cool, and then try to dissolve it in water: it is insoluble (whereas ferric chloride is soluble).

411. Method 3. Interaction of a Metal with a Salt of another Metal.—In general one metal will displace another from its salts when the oxide of the former is more strongly basic than that of the latter, *i.e.* the oxide reacts more readily with acids. Thus iron displaces copper from a solution of copper sulphate (as we saw in Exp. 1), and zinc displaces silver from a solution of silver nitrate—

$$Fe + CuSO_4 = Cu + FeSO_4.$$
$$Zn + 2AgNO_3 = 2Ag + Zn(NO_3)_2.$$

412. Method 4. Direct Union of a Basic Oxide and an Acidic Oxide.—Many basic oxides combine directly with acidic oxides to form salts. For example, when barium oxide, BaO, and sulphur trioxide, SO_3, are mixed together they combine to form barium sulphate with such energy that the mass becomes red-hot—

$$BaO + SO_3 = BaSO_4.$$

Again, quicklime and carbon dioxide readily unite to form calcium carbonate—

$$CaO + CO_2 = CaCO_3.$$

413. Method 5. Interaction of Bases and Acids.—This is the most general method. It has been fully discussed and illustrated in the foregoing chapters.

414. Method 6. Interaction of an Acid with a Salt of a Weak Acid.—The chief examples of this method consist of the preparation of salts by the action of acids on *carbonates.*

Exp. 403.—Add chalk, a little at a time, to some dilute nitric acid contained in a beaker till the further addition ceases to cause effervescence. Filter and evaporate the filtrate to dryness in a porcelain dish. The white residue is *calcium nitrate.*

$$CaCO_3 + 2HNO_3 = Ca(NO_3)_2 + H_2O + CO_2.$$

415. Method 7. Interaction of an Acid with a Salt of a more Volatile Acid.—An example of this method is the conversion of a nitrate into a sulphate by heating with strong sulphuric acid. The volatile nitric acid is driven off, leaving the salt of the much less volatile sulphuric acid behind.

Thus when potassium nitrate is gently heated with sulphuric acid, potassium hydrogen sulphate is formed—

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

Another example is the conversion of sodium chloride into the sulphates of sodium, which was investigated in Exps. 163, 359.

416. Method 8. Interaction of a Base with a Salt of a more Volatile Base.—When caustic potash or soda is heated with an ammonium salt, the volatile base, ammonia, is driven off and the corresponding potassium salt remains—

$$2KOH + (NH_4)_2SO_4 = K_2SO_4 + 2NH_3 + 2H_2O.$$

417. Method 9. Interaction of a Base with a Salt of an Insoluble Base.—The majority of the hydroxides of the metals are insoluble in water. If, then, a solution of a soluble base such as caustic potash or soda is added to a salt of a metal which forms an insoluble hydroxide, double decomposition takes place with precipitation of the insoluble hydroxide and formation of a salt of potassium or sodium; for it is observed that, *when an insoluble substance can be formed by double decomposition, that substance is usually formed.* For example, on adding caustic potash to a solution of copper sulphate, $CuSO_4$, cupric hydroxide, $Cu(OH)_2$, is precipitated, and potassium sulphate, K_2SO_4, goes into solution—

$$2KOH + CuSO_4 = Cu(OH)_2 + K_2SO_4.$$

The cupric hydroxide can be separated from the potassium sulphate by filtration.

418. Method 10. Interaction of Two Salts.—Representing the double decomposition between two salts by the equation—

$$A + B = C + D,$$

this method of preparation can be used for a salt, C, when that salt is less soluble or more volatile than A, B, or D For example, silver chloride, AgCl, is insoluble in water, whereas silver nitrate, $AgNO_3$, potassium chloride, KCl, and potassium nitrate, KNO_3, are all soluble. We can therefore prepare silver chloride by mixing solutions of silver nitrate and potassium chloride; silver chloride is precipitated and may be separated from the soluble salts by filtration—

$$AgNO_3 + KCl = AgCl + KNO_3.$$

Again, mercuric chloride, $HgCl_2$, is volatile, whilst sodium chloride, sodium sulphate, Na_2SO_4, and mercuric sulphate, $HgSO_4$, are non-volatile. If, therefore, a mixture of mercuric sulphate and sodium chloride is heated together, double decomposition takes place and mercuric chloride passes away as vapour, condensing again on a cool surface.

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

419. Method 11. Interaction of Two Bases.—A few bases, notably the oxides and hydroxides of zinc, tin, and aluminium, are soluble in caustic potash or caustic soda solution with formation of salts. The explanation is that, in the presence of a strong base such as caustic potash, a substance which generally acts as a weak base may act as a weak acid. The following equations represent the formation of salts in this manner :—

$$2KOH + Zn(OH)_2 = \underset{\text{Potassium zincate (in solution only)}}{K_2ZnO_2} + 2H_2O.$$

$$2NaOH + Al_2O_3 = \underset{\text{Sodium aluminate}}{2NaAlO_2} + H_2O.$$

$$2KOH + SnO_2 = \underset{\text{Potassium stannate}}{K_2SnO_3} + H_2O.$$

420. Method 12. Interaction of Metals with Bases.—A few metals are soluble in potash solution with evolution of hydrogen, more especially zinc and aluminium. The salts obtained are the same as those produced when the oxides or hydroxides of the metals are used instead of the metals themselves, as in the preceding method: thus when aluminium is dissolved potassium aluminate is formed—

$$2Al + 2KOH + 2H_2O = \underset{\text{Potassium aluminate}}{2KAlO_2} + 3H_2.$$

Most metals are attacked slowly by fused potash, silver being the most resistant.

Of the twelve methods enumerated, the 1st, 2nd, 5th, 6th, and 9th are far the most important.

QUESTIONS—CHAPTER XXVIII.

1. Discuss the effect of mass on the nature of the products obtained by the action on metals of (1) the halogens, (2) nitric acid

2. Why would you expect to get only the *lower* salt when a haloid acid acts on a metal which can give rise to two series of salts ?

3. Why cannot anhydrous ferric chloride be obtained by evaporating the aqueous solution of the salt to dryness ? How is the anhydrous salt obtained ?

4. Express by equations the action of (1) barium monoxide on sulphur trioxide, (2) zinc on silver nitrate, (3) caustic potash on ammonium sulphate, (4) caustic soda on zinc hydroxide.

5. Under what conditions can a salt be conveniently prepared by the interaction of two other salts ?

6. Give examples of the formation of salts from (1) two bases, (2) a metal and a base.

CHAPTER XXIX.

PHENOMENA OF ELECTROLYSIS.

421. Some examples of Electrolysis have already been met with incidentally in the preceding chapters, but the more obvious phenomena of electrolysis should be studied more systematically. In the following explanations some knowledge of the elements of electricity is assumed.

Electrolysis of Copper Sulphate.—

Exp. 404.—Fit up an apparatus similar to that used in Exp. 72. Pour some copper sulphate solution into the bottle and pass a current from two or three Grove's cells through the liquid. You will observe that gas bubbles arise only from the *positive* electrode (*i.e.* piece of platinum foil connected with the *positive* or *platinum* pole of the battery); the *negative* electrode (*i.e.* the piece of platinum foil connected with the *negative* or *zinc* pole of the battery) becomes covered with a red coating of *metallic copper*. Collect some of the gas evolved at the positive electrode in a test-tube by displacement of water and test it with a glowing splint: it is *oxygen*.

We see then that when an electric current is passed through a solution of copper sulphate, using platinum electrodes, oxygen is evolved at the positive electrode and copper set free at the negative electrode. It is found further that sulphuric acid gradually accumulates in the liquid.

Such an action—the decomposition of a liquid by an electric current—is called *electrolysis*, and the liquid is called the *electrolyte*. The vessel in which the decomposition takes place is called the *electrolytic cell*.

The course which the current takes during its circuit is as follows:—Starting from the positive (platinum) pole it flows along the connecting wire to the positive electrode (which is called the *anode*), thence through the liquid to the negative electrode (called the *kathode*), and finally back to the battery along the other connecting wire.

The following explanation of the phenomenon investigated in Exp. 404 is at present generally accepted.

It is supposed that when copper sulphate ($CuSO_4$) is dissolved in water, some (in dilute solution the greater part) of the molecules are dissociated into two "ions."

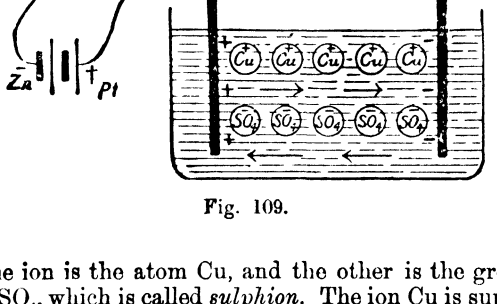


Fig. 109.

The one ion is the atom Cu, and the other is the group of atoms SO_4, which is called *sulphion*. The ion Cu is supposed to carry a *positive* charge of electricity and the ion SO_4 a *negative* charge. When the electrodes are introduced into the liquids they attract the charged ions; the negative electrode attracts the positively charged ions, *i.e.* the copper ions, and the positive electrode attracts the negatively charged ions, *i.e.* the sulphions. This is in accordance with the ordinary law of electric attraction. There is consequently a stream of Cu ions proceeding towards the negative electrode, and a stream of SO_4 ions proceeding towards the positive electrode. This is represented diagrammatically in Fig. 109, in which $\overset{+}{Cu}$ stands for a positively charged copper ion, and $\overset{-}{SO_4}$ stands for a negatively charged sulphion.

When a Cu ion reaches the negative electrode it gives up its electric charge, and is deposited on the electrode as a thin film. At the same time an SO_4 ion reaches the positive electrode and gives up its charge. An uncharged sulphion is, however, incapable of a separate existence, and immediately reacts with the water in contact with the positive electrode, with formation of sulphuric acid and liberation of oxygen.

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

The ion Cu, which is attracted to the kathode, is called the *kathion*; and the ion SO_4, which is attracted to the anode, is called the *anion*.

422. Electrolysis in General.—The process of electrolysis is very general in its application. All acids, alkalies, and salts in solution are electrolytes to a greater or less extent; that is to say, they can be decomposed by an electric current. In the case of salts, the kathion (or kathions) consists of the atom (or atoms) of metal [1] in the molecule, the remainder of the molecule forming the anion. In the case of acids, the kathion (or kathions) consists of the atom (or atoms) of hydrogen in the molecule.

The properties of these ions are different from those of the substances as we ordinarily know them; *e.g.* ionic sodium does not decompose water. But when the ions reach the electrodes their charge is neutralised, and they resume their normal chemical properties. Hence it frequently happens that further chemical action takes place at one or both electrodes between the discharged ions and the liquid or the metal of which the electrodes are composed.

423. Electrolysis of Water.—Pure water does not conduct electricity, but when an acid, base, or salt is dissolved in it, it becomes an electrolyte.

An experiment in which water acidulated with dilute sulphuric acid is decomposed by the electric current has

[1] In the case of double salts such as potassium ferrocyanide, $K_4FeC_6N_6$, the *anion* contains one of the *metals* (see § 427).

already been described (Exp. 73). The part played by the sulphuric acid is explained as follows:—The acid on solution dissociates into three ions, two of hydrogen (H) and one of sulphion (SO_4). The hydrogen ions carry positive charges of electricity and the sulphion a negative charge.[1] On passing the current, the H ions are attracted to the negative electrode, where they give up their charge and acquire the properties which we ordinarily associate with hydrogen. One of these is that free atoms of hydrogen cannot exist separately; they therefore combine to form molecules, in which form the gas passes off and may be collected. The sulphions are attracted to the positive electrode, and after giving up their charges undergo a secondary reaction with water with liberation of oxygen, as already described in the previous paragraph.

Let us start with, say, two[2] molecules of sulphuric acid, and trace the changes which they undergo. We may represent the primary change which takes place on passing the current by the equation—

$$2H_2SO_4 = 2H_2 + 2SO_4.$$

The $2H_2$ is evolved at the kathode and the $2SO_4$ liberated at the anode reacts with water thus—

$$2SO_4 + 2H_2O = 2H_2SO_4 + O_2.$$

The O_2 is evolved at the anode.

We therefore finish with the same amount of sulphuric acid with which we started, *i.e.* 2 molecules, and the net result of passing the current has been to break up two molecules of water into two molecules of hydrogen and one molecule of oxygen. The same result would have been arrived at if we had taken any other number of sulphuric acid molecules, from which it follows that the amount of sulphuric acid in the cell remains unchanged, and the gases ultimately liberated are the constituents of pure water.

[1] The negative charge carried by the sulphion is *twice* as large as the positive charge carried by each of the hydrogen ions, so that the total charge on the three ions into which the molecule of sulphuric acid dissociates is equal to zero.

[2] *Two* molecules are used instead of one to avoid writing an *atom* of oxygen in the second equation.

424. Electrolysis of Hydrochloric Acid.—If strong hydrochloric acid be substituted for dilute sulphuric acid the ions are hydrogen and chlorine. On passing the current, hydrogen at once appears at the kathode, but no chlorine makes its appearance, for two reasons: firstly, because chlorine is soluble in the acid solution; and, secondly, because the chlorine, while still in the condition of free atoms (*nascent* chlorine), attacks the platinum anode, converting it into the soluble platinum chloride ($PtCl_4$). If the anode be a plate of gas carbon, on which chlorine, even when nascent, has no action, and if the solution be saturated with chlorine beforehand, hydrogen and chlorine appear in equal volumes, as we saw in Exp. 188.

425. Electrolysis of Solutions of Alkalies.—When caustic soda (NaOH) dissolves in water it separates into the two ions, sodium and hydroxyl (OH). On passing a current through the solution the former is liberated at the kathode and the latter at the anode. Neither of these, however, appears, because of secondary actions, the sodium immediately decomposing water with evolution of hydrogen and re-formation of caustic soda, and two of the hydroxyl groups breaking up into oxygen, which escapes, and water, which remains. Considering the changes which four[1] molecules of caustic soda undergo we have as the primary change on passing the current—

$$4NaOH = 4Na + 4OH.$$

The following secondary changes then take place. At the kathode—

$$4Na + 4H_2O = 4NaOH + 2H_2.$$

At the anode—

$$4OH = 2H_2O + O_2.$$

The net result is that the amount of caustic soda remains unchanged and water is decomposed into hydrogen and oxygen. It will therefore be seen that the electrolysis of

[1] Four molecules are used for a similar reason to that referred to in the foot-note on p. 500.

dilute sulphuric acid and of caustic soda solution both bring about the same result, namely, the decomposition of water.

426. Electrolysis of Solutions of Salts.—Here the immediate products of the decomposition (ions) are the metal and the acid radicle—SO_4, Cl, NO_3, etc.—the former, like the metal of an alkali and the hydrogen of an acid, always going to the kathode, and the latter always going to the anode when the current is passed. But whether these ions actually appear or not after giving up their charges to the electrodes depends upon the nature of the ions and the presence or absence of secondary actions between them and the liquid or the electrodes.

Except in the case of those metals which decompose water at the ordinary temperature (sodium, potassium, and a few others), the metal is always deposited on the kathode; but, except in the case of some of the hydracids (hydrochloric acid, hydriodic acid, etc.), the acid radicle rarely appears as such, even if no action takes place between it and the anode. In the case of sulphates, as we have seen, the acid radicle SO_4 reacts with water forming sulphuric acid, with liberation of oxygen. In the case of nitrates the radicle NO_3 behaves in a similar manner, yielding nitric acid and liberating oxygen—

$$4NO_3 + 2H_2O = 4HNO_3 + O_2.$$

If a solution of zinc sulphate ($ZnSO_4$) be electrolysed between platinum electrodes, zinc is deposited on the kathode, and for every atom of zinc deposited an atom of oxygen is liberated at the anode and a molecule of sulphuric acid goes into solution. But if a plate of zinc replace the platinum anode, the SO_4 group, instead of reacting with water, simply combines with the zinc to form zinc sulphate. Then for every molecule of zinc sulphate decomposed, and for every atom of zinc deposited at the kathode, an atom of zinc is dissolved and a molecule of zinc sulphate re-formed at the anode; so that the kathode gains exactly as much zinc as the anode loses, and the average composition of the solution remains unaltered.

With copper sulphate ($CuSO_4$) electrolysed between copper electrodes the action is less simple. Copper is deposited on the kathode, but at the anode some of the SO_4 directly unites with the copper to re-form copper sulphate, and some reacts with water forming sulphuric acid, with liberation of oxygen. And of this oxygen some escapes, while some unites with the copper to form copper oxide (CuO), which in part incrusts the plate, and in part dissolves in the acid with re-formation of copper sulphate—

$$CuO + H_2SO_4 = CuSO_4 + H_2O.$$

427. Double Salts.—This is a convenient place at which to briefly discuss the nature of *double salts*. These are complex salts formed by the union of two simple salts, *e.g.* a molecule of potassium sulphate, K_2SO_4, and one of aluminium sulphate, $Al_2(SO_4)_3$, together with 24 molecules of water, unite together to form a molecule of potassium aluminium sulphate or alum—

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

Double salts may be divided into two classes, according to their behaviour in solution. Some break up into the simple salts of which they are composed, and these then decompose further into ions in the usual way; thus alum breaks up into K_2SO_4 and $Al_2(SO_4)_3$, and these salts then yield the ions K, Al, and SO_4. Others do not decompose in this way, but ionise immediately, yielding a complex anion containing one of the metals; for example, potassium chloride, KCl, unites with platinum chloride, $PtCl_4$, to form the double salt $2KCl + PtCl_4$ or K_2PtCl_6; on dissolving this salt in water the kathions consist of K and the anions of the complex group $PtCl_6$. This salt may therefore be considered to be derived from the acid H_2PtCl_6, chloroplatinic acid, and is called potassium chloroplatinate.

Other examples of the first class of double salts are carnallite, $KCl, MgCl_2, 6H_2O$, and ferrous ammonium sulphate, $(NH_4)_2SO_4, FeSO_4, 6H_2O$, and of the second class, potassium ferrocyanide, $K_4FeC_6N_6$, which yields the complex anion FeC_6N_6.

428. Faraday's Laws of Electrolysis.—Faraday discovered two very important laws connected with the quantities of elements set free at the electrodes during electrolysis. They may be stated as follows:—

1st Law.—The quantity of an element set free during a given time is proportional to the strength of the current.

2nd Law.—The quantities of the elements deposited in the same circuit are in the ratio of their chemical equivalents.

The second law affords a very useful method of determining chemical equivalents of metals. For suppose the same current is passed successively through three electrolytic cells containing respectively (*a*) acidulated water, (*b*) a solution of silver nitrate, (*c*) a solution of copper

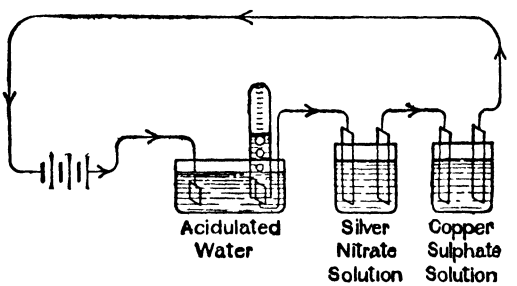


Fig. 110.

sulphate, by connecting the cells in series with a battery as shown diagrammatically in Fig. 110 (the arrows indicate the direction of flow of the current). These cells form part of the same circuit, and according to Faraday's second law the weights of hydrogen collected and of silver and copper deposited on the kathodes are in the ratio of their chemical equivalents. In order, then, to find the equivalents of silver and copper, all that is necessary is to divide the weights of these elements deposited after passing the current for a suitable time by the weight of hydrogen evolved.

Suppose for example the weights were as follows: —

Hydrogen	0·0104 gram.
Silver	1·123 grams.
Copper	0·328 gram.

Then we have—

$$\frac{\text{Chemical Equivalent of Silver}}{\text{Chemical Equivalent of Hydrogen}} = \frac{1{\cdot}123}{0{\cdot}0104}.$$

$$\therefore \frac{\text{Chemical Equivalent of Silver}}{1} = \frac{1{\cdot}123}{0{\cdot}0104}.$$

$$\text{Chemical Equivalent of Silver} = 108.$$

Similarly—

$$\frac{\text{Chemical Equivalent of Copper}}{\text{Chemical Equivalent of Hydrogen}} = \frac{0{\cdot}328}{0{\cdot}0104}.$$

$$\therefore \text{Chemical Equivalent of Copper} = 31{\cdot}5.$$

If the equivalent of one metal is known, all that is necessary in order to find the equivalent of a second is to include cells containing salts of each in the same circuit and find the increase in weight of the kathodes after a suitable time.

Suppose, for example, the equivalent of silver is known to be 108 and the weights of silver and copper deposited when the same current is passed through solutions of silver nitrate and copper sulphate are 2·16 grams and 0·63 gram. Then we have—

$$\frac{\text{Chemical Equivalent of Copper}}{\text{Chemical Equivalent of Silver}} = \frac{0{\cdot}63}{2{\cdot}16}.$$

$$\therefore \frac{\text{Chemical Equivalent of Copper}}{108} = \frac{0{\cdot}63}{2{\cdot}16}.$$

$$\text{Chemical Equivalent of Copper} = \frac{0{\cdot}63}{2{\cdot}16} \times 108$$

$$= 31{\cdot}5.$$

It should be noted that the equivalent of copper found above is its equivalent *in copper sulphate*, i.e. in the *-ic* state. If a solution of a *cuprous* salt (say cuprous chloride

dissolved in hydrochloric acid) were used, the equivalent would be found to be twice as great, *i.e.* 63. A similar remark applies to other elements which form -ous and -ic salts.

429. Useful Applications.—Electro-depositions.—The principle of electrolysis has many useful applications in the arts. One of the oldest of these is the process of *electro-plating*. Here the object to be plated is thoroughly cleaned and slightly roughened, and made the kathode of an electrolytic cell, the anode being a plate of the metal to be deposited, and the electrolyte a solution of a salt of that metal, the current being supplied by a battery or dynamo. A thin and firmly adherent film of the metal —gold, silver, nickel, or what not—is deposited on the article to be plated, and the strength of the solution is kept up by the action of the electrolyte on the anode. Compare with this the above description of the electrolysis of zinc sulphate, when a zinc anode is used.

The most important electro-plating industry is electro-*silvering*. In this case the salt is a double cyanide[1] of silver and potassium, the "bath" being prepared by dissolving one part (by weight) of silver cyanide and two of potassium cyanide in 40 of distilled water. The current is maintained until the deposit amounts to about one ounce per square foot, which corresponds to a thickness of about $\frac{1}{800}$ inch.

Electro-*gilding* is the art of coating objects with gold. The bath is a solution of the double cyanide of gold and potassium. The details are similar to those for electro-silvering, except that the current employed is weaker and the deposit thinner.

Electro-*nickeling* is the art of coating objects (usually of steel, such as the handle-bars of bicycles) with nickel. The bath is a slightly acid solution of the double sulphate of nickel and ammonium. A good coat consists of about $\frac{2}{3}$ ounce per square foot, which represents about $\frac{1}{1000}$ inch in thickness.

[1] Cyanides are derived from hydrocyanic acid, HCN.

Electro-*coppering* is the easiest of all the plating processes. The bath is simply a strong and very slightly acid solution of copper sulphate. When *iron* is the metal to be coppered the simple copper sulphate bath is unsuitable, because the sulphate would be rapidly decomposed by the iron; in this case the bath consists of an alkaline solution of the double tartrate of copper and sodium obtained by adding excess of sodium hydroxide to a solution of copper sulphate and tartaric acid.

In *electrotyping*, the object is to produce not a thin adherent coat, but a thick one, which may be readily detached from the mould which serves as the kathode, and which reproduces, with the utmost fidelity, all the form and relief of the original article. Engraved wood blocks, for instance, are thus reproduced in copper. A mould is first prepared in gutta-percha, plaster of Paris, or some other substance. The face of this mould is then black-leaded to form a conducting film, and the mould is hung in a solution of sulphate of copper, in which it becomes the kathode, the anode being a sheet of copper suspended in the solution. When the deposited copper forms a layer of sufficient thickness it is removed from the mould, backed with type metal, and mounted type-high[1] on a wood block.

430. Electrometallurgy.—Many metals are now economically extracted from their compounds by electrolysis—sodium, for instance, the electrolyte being caustic soda melted by heat. Sodium and hydrogen separate at the kathode (the latter being allowed to escape), and oxygen at the anode. Aluminium is similarly obtained by the electrolysis of alumina dissolved in a bath of molten fluorides of aluminium, sodium, and calcium. Crude copper is also economically refined by using it for an anode, and re-depositing it in a state of purity upon rods or sheets of copper which serve as kathodes. In these cases the current is derived from a dynamo driven by steam- or water-power.

[1] *I.e.* the face is brought level with the face of the type.

QUESTIONS.—CHAPTER XXIX.

1. Describe what you would observe on passing a current of electricity through aqueous solutions of the following substances, using platinum electrodes:—(1) copper sulphate; (2) sulphuric acid; (3) caustic potash.

2. Explain the meaning of the terms—*electrolysis*, *ion*, *anode*, *kathode*.

3. What do you understand by an *electrolyte*? Describe and explain as far as you can what takes place when an electric current is passed through (i) a solution of caustic soda, (ii) fused caustic soda.

4. Describe and explain what takes place when a current of electricity is passed through a solution of zinc sulphate between platinum electrodes.

5. The same electric current is passed through solutions of copper sulphate and stannic chloride. What will be the relationship between the weights of metals deposited, and what law do they illustrate?

6. Give Faraday's Laws of Electrolysis, and explain how you would prove them.

7. Describe a method of determining the *chemical equivalent* of copper by means of electrolysis.

8. Write a short account of the applications of the principle of electrolysis which have been made in the arts.

9. What are double salts? Into what two classes can they be divided? Illustrate your answer by examples.

SECTION IV.—CHEMICAL CALCULATIONS.

CHAPTER XXX.

CHEMICAL CALCULATIONS.

431. The Relations between Weight and Volume of Gases.—From Avogadro's hypothesis it follows at once that the densities of gases are proportional to their molecular weights. In order to express the weight of any gas it is convenient to remember as the basis of calculation that 1 *litre of hydrogen at the standard temperature* (0° *C.*) *and pressure* (760 *mm. of mercury*) *weighs* 0·09 *gram*, or that 11·11 litre of hydrogen weigh one gram.

If, then, we desire to ascertain the weight of any other gas under like conditions, we commence by expressing in chemical symbols the molecule of the gas thus—

The molecule of	hydrogen	is expressed by		H_2 (2)
,, ,,	nitrogen	,,		N_2 (28)
,, ,,	oxygen	,,		O_2 (32)
,, ,,	chlorine	,,		Cl_2 (71)
,, ,,	ozone	,,		O_3 (48)
,, ,,	phosphorus	,,		P_4 (124)
,, ,,	water vapour	,,		H_2O(18)
,, ,,	hydrochloric acid	,,		HCl (36·5)
,, ,,	carbon dioxide	,,		CO_2 (44)
,, ,,	nitric oxide	,,		NO (30)
,, ,,	sulphur dioxide	,,		SO_2 (64)
,, ,,	sulphuretted hydrogen	,,		H_2S (34)
,, ,,	ammonia	,,		NH_3(17)

and so on.

The relative weights are, then, those stated in parenthesis after the symbol in the above list, as derived from the respective atomic weights.

Thus the weight of a litre of nitrogen is 14 times that of a litre of hydrogen or (0·09 × 14) grams; a litre of carbon dioxide weighs (0·09 × 22) grams; a litre of sulphuretted hydrogen weighs (0·09 × 17) grams.

The alternative method of expressing the same facts is perhaps more readily applied in chemical calculations, viz. that 11·11 litres of hydrogen weigh 1 gram, or 22·22 litres of hydrogen weigh 2 grams, the same number of grams as that used for expressing the molecular weight. In this form the statement is quite general, that the molecular weight being *m*, 22·22 litres of any gas whatever weigh *m* grams.

22·22 litres	of	nitrogen	weigh	28 grams.
22·22 „	„	oxygen	„	32 „
22·22 „	„	chlorine	„	71 „
22 22 „	„	sulphur dioxide	„	64 „
22·22 „	„	ammonia	„	17 „

It is convenient to remember both forms of the expression, as one or the other is more readily adapted for the purpose of calculation according to the terms which are given. For instance, if it be desired to calculate the weight of a certain volume of a gas, the former expression lends itself more readily for the purpose—as in the following example:—

(1) Required the weight of 100 c.c. of carbon dioxide at 0° C. and 760 mm. pressure—

1,000 c.c. (1 litre)	of	hydrogen	weigh	0·09 gram.
„	„	carbon dioxide	„	1·98 „
100 cub. centimetres	of	„	„	0·198 „

Should the weight of the gas be given, and its volume is to be determined, the second form of expression is more easily applied.

(2) Required the volume occupied by 0·5 gram of ammonia at 0° C. and 760 mm. pressure—

17	grams of	ammonia	occupy 22·22 litres.
1	gram „		occupies 1·307 „
0·5	„ „		„ 0·653 „

It is useful also to bear in mind that air is 14·435 times as heavy as hydrogen, since frequently the densities of vapours as actually determined by experiment are stated in terms of air as unit.

Thus the density of carbon dioxide is found by experiment to be 1·53, air being the unit.

The density compared with hydrogen is therefore 1·53 × 14·435, or 22·1, a value agreeing well with that deduced from the accepted composition of this gas.

432. Correction for Temperature and Pressure.—We shall first consider the influence of variations of *temperature* on the volume of a gas, and consequently on the weight of a given volume.

We have seen (Chap. VIII.) that a gas at 0° C. expands $\frac{1}{273}$ of its volume for each increment of one degree Centigrade in temperature. The more general form of expression, viz. that the volume of the gas is proportional to the absolute temperature (see § 70), will be found the most useful, as a few examples will show. In order to make the calculation it is, in the first place, necessary to convert the temperatures as ordinarily stated into absolute temperatures.

(3) A litre of gas is measured at 0° C.; what volume will it occupy at − 20° C., and what at 50° C.?

0° C. = 273° absolute.
− 20° C. = 253° „
+ 50° C. = 323° „

Volume required is at −20° C. $1 \text{ litre} \times \frac{253}{273} = 926{\cdot}8 \text{ c.c.}$

„ „ „ + 50° C. $1 \text{ litre} \times \frac{323}{273} = 1183{\cdot}2 \text{ c.c.}$

(4) The volume of a gas measured at 10° C. is found to be 150 c.c.; what volume would it occupy at the standard temperature (0° C.)?

10° C. = 283° absolute.

Volume required is at 0° C. $150 \times \frac{273}{283} = 144{\cdot}7 \text{ c.c.}$

(5) The volume of a gas measured at 15° C. is found to be 250 c.c.; what volume would it occupy at − 15° C. and at 57° C. respectively?

$$15° \text{ C.} = 288° \text{ absolute.}$$
$$-15° \text{ C.} = 258° \quad \text{„}$$
$$+57° \text{ C.} = 330° \quad \text{„}$$

Volume required at $-15°$ C. $= 250 \times \frac{258}{288} = 224{\cdot}0$ c.c.

„ „ „ $+57°$ C. $= 250 \times \frac{330}{288} = 286{\cdot}5$ c.c.

And now let us consider the effect of variation in *pressure*. According to Boyle's Law (see § 71), the volume of a gas is inversely proportional to the pressure to which it is subjected when the temperature is constant.

(6) A gas measured at standard atmospheric pressure (760 mm.) is found to occupy 1·5 litres; what volume will it occupy at 1,000 mm. and at 100 mm. pressure?

Required volume at 1,000 mm. is $1{,}500 \times \frac{760}{1{,}000} = 1{,}140$ c.c.

„ „ „ 100 mm. is $1{,}500 \times \frac{760}{100} = 11{,}400$ c.c.

(7) The volume of a gas at 500 mm. pressure is found to be 250 c.c.; what would it measure under 5 atmospheres pressure?

$$5 \text{ atmospheres} = (760 \times 5) \text{ mm.} = 3{,}800 \text{ mm.}$$

Required volume at 5 atmos. $= 250 \times \frac{500}{3{,}800} = 32{\cdot}9$ c.c.

Finally, an example is given of the allowance for both temperature and pressure in the same expression.

(8) A gas occupies 190 c.c. at 13° C. and 740 mm. pressure; what volume would it occupy at standard temperature and pressure (0° C. and 760 mm.), and what at −130° C. and 780 mm. pressure?

$$13° \text{ C.} = 286° \text{ absolute.}$$
$$0° \text{ C.} = 273° \quad \text{„}$$

$$\text{Volume at } 0^\circ \text{C. and } 760\,\text{mm.} = 190 \times \frac{273 \times 740}{286 \times 760} = 176\ 6\ \text{c.c.}$$

$$-130^\circ \text{ C.} = 143^\circ \text{ absolute.}$$

$$\text{Volume at } -130^\circ \text{ C. and } 780 \text{ mm.} = 190 \times \frac{143 \times 740}{286 \times 780} \text{ c.c.}$$

$$= 90{\cdot}1 \text{ c.c.}$$

433. The Relation between Weight and Volume of Liquids.—The specific gravity of liquids is expressed in terms of pure water at 15° C. as unit. The following table shows that the specific gravity of water varies at different temperatures, water at 4° being taken as 1 :—

Specific gravity of	water	at	0° = 0·99987
,,	,,	,,	2° = 0·99997
,,	,,	,,	4° = 1·00000
,,	,,	,,	10° = 0·99975
,,	,,	,,	15° = 0·99916
,,	,,	,,	20° = 0·99826
,,	,,	,,	25° = 0·99712

In ascertaining the density of a liquid by comparison with water it is more convenient to make the determination at ordinary temperatures, and hence it is usual to adopt the specific gravity of water at 15° C. as the basis of comparison.

When we say that the specific gravity of a liquid is 1·8 we mean that it is heavier than water in the proportion 1·8 : 1 ; since 1 c.c. of water weighs 1 gram, 1 c.c. of such a liquid will weigh 1·8 grams.[1] The following examples will show how the specific gravity of liquids enters into chemical problems.

[1] This is not strictly accurate, since the gram is the weight of 1 c.c. of water *at* 4° *C.* The correction, however, is only made in case a very exact expression is desired, and for ordinary purposes it is omitted. In any case the actual weight may be obtained by multiplying the result by 0·99916.

(9) What is the weight of 100 c.c. of sulphuric acid of sp. gr. 1·84?

100 c.c. of water weighs 100 grams.
" " sulphuric acid of the density given } " 184 "

(10) Hydrochloric acid of sp. gr. 1·112 contains 21 per cent. by weight of hydrogen chloride; find the volume of hydrogen chloride in 10 c.c. of such acid.

By the method used in the previous problem 10 c.c of hydrochloric acid will weigh 11·12 grams.

$\therefore \frac{11{\cdot}12 \times 21}{100} = 2{\cdot}3352$ grams is the weight of hydrogen chloride contained in it.

36·5 grams of HCl. occupy 22·22 litres;

2·3352 grams occupy $\frac{22{\cdot}22 \times 2{\cdot}3352}{36{\cdot}5}$ litres

$= 1{\cdot}421$ litres.

434. The Relation between Weight and Volume of Solids, like that of liquids, is expressed in terms of water as unit. Thus, diamond is 3·5 times as heavy as water, and its sp. gr. is 3·5; the sp. gr. of graphite is 2·2, of mercury 13·6.

The weights of these bodies that occupy the same volume as 1 gram of water (that is, 1 c.c.) are 3·5, 2·2, and 13·6 grams respectively.

This relation is seldom necessary in chemical calculations

435. Calculation of the Percentage Composition of a Body.—When the chemical composition of a body is expressed by symbols, the proportions of the respective elements contained in it are the weights of the elements as determined from the table of atomic weights.

HCl indicates a compound formed by the union of 1 part by weight of hydrogen with 35·5 parts by weight of chlorine.

H_2O indicates a compound formed by the union of 2 parts by weight of hydrogen with 16 parts by weight of oxygen.

CO_2 indicates a compound formed by the union of 12 parts by weight of carbon with 32 (*i.e.* 2 × 16) parts by weight of oxygen.

P_4O_{10} indicates a compound formed by the union of 124 (*i.e.* 4 × 31) parts by weight of phosphorus with 160 (*i.e.* 10 × 16) parts by weight of oxygen.

H_3PO_4 indicates a compound formed by the union of 3 parts by weight of hydrogen, 31 parts by weight of phosphorus, and 64 (*i.e.* 4 × 16) parts by weight of oxygen.

36·5	parts	by	weight	of	HCl	contain	1	pt. of H and 35·5	pt. of Cl.
18	,,	,,			H_2O	,,	2	,, H and 16	,, O.
44	,,	,,			CO_2	,,	12	,, C and 32	,, O.
142	,,	,,			P_2O_5	,,	62	,, P and 80	,, O.
98	,,	,,			H_3PO_4	,,	3	,, H, 31 of P and 64	of O.

The *percentage* composition is merely the statement of the relative weights of each of the constituents in 100 *parts* of the compound.

Thus, if 18 parts by weight of water contain 2 parts of hydrogen and 16 parts of oxygen, then 100 parts of water will contain—

$$\frac{2 \times 100}{18} \text{ parts of H, } i.e \text{ 11·11 pt.;}$$

and

$$\frac{16 \times 100}{18} \text{ ,, O, } i.e. \text{ 88·88 pt.;}$$

and this represents the percentage composition of water.

(11) Find the percentage composition of potassium chlorate, $KClO_3$—

$$\begin{aligned} K &= 39·1 \\ Cl &= 35·5 \\ O_3 &= 48·0 \\ &\overline{122·6} \end{aligned}$$

$$\text{Percentage amount of K} = \frac{39{\cdot}1 \times 100}{122\,6} = 31{\cdot}89$$

$$\text{,, ,, Cl} = \frac{35{\cdot}5 \times 100}{122{\cdot}6} = 28{\cdot}95$$

$$\text{,, ,, O} = \frac{48 \times 100}{122{\cdot}6} = \underline{39{\cdot}16}$$

$$\underline{\underline{100{\cdot}00}}$$

(12) Find the percentage amount of water of crystallisation in $FeSO_4, 7H_2O$.

$$\begin{aligned} Fe &= 56 \\ S &= 32 \\ O_4 &= 64 \\ 7H_2O &= \underline{126} \\ &\quad 278 \end{aligned}$$

278 parts of $FeSO_4, 7H_2O$ contain 126 parts of water.

$$\text{Percentage of water} = \frac{126 \times 100}{278} = 45{\cdot}32.$$

436. Determination of the Formula of a Substance.—The question which even more frequently arises in practice is the converse one, the determination of the formula of a substance from the results of analysis of the substance.

Suppose a compound of three elements, A, B, and C, contains p per cent. of the element A by weight, q per cent. of B, and r per cent. of C. Let $A_x B_y C_z$ represent the formula of the compound, x, y, and z being the relative numbers of atoms of A, B, and C respectively. Then if a, b, and c denote the atomic weights of the elements A, B, and C, we shall have ax parts by weight of A, by parts of B, and cz parts of C. But the given percentage composition shows that these parts by weight are in the ratio $p : q : r$; therefore—

$$ax : by : cz :: p : q : r;$$

$$\therefore x : y : z :: \frac{p}{a} : \frac{q}{b} : \frac{r}{c}.$$

Hence, if we divide the percentage amount of each element by the atomic weight of the element, and reduce the ratio of the numbers so obtained to its simplest form, we obtain the ratio $x : y : z$ in its simplest form.

(13) For example, suppose the percentage composition of a body as deduced from analysis is—

Sulphur	=	23·7	per cent.
Oxygen	=	23·7	„ „
Chlorine	=	52·6	„ „
		100·0	

Dividing the percentage of each element by its atomic weight we have—

$$S = 32. \quad \frac{23{\cdot}7}{32} = 0{\cdot}74.$$

$$O = 16. \quad \frac{23{\cdot}7}{16} = 1{\cdot}48.$$

$$Cl = 35{\cdot}5. \quad \frac{52{\cdot}6}{35\,5} = 1{\cdot}48.$$

Dividing the numbers so obtained by their highest common factor[1]—which is obviously 0·74—we obtain the relative number of atoms of each element in whole numbers.

$$S. \quad \frac{0{\cdot}74}{0{\cdot}74} = 1.$$

$$O. \quad \frac{1{\cdot}48}{0{\cdot}74} = 2.$$

$$Cl. \quad \frac{1{\cdot}48}{0{\cdot}74} = 2.$$

The simplest formula for the compound is therefore—

$$S_1O_2Cl_2 \quad \text{or} \quad SO_2Cl_2.$$

This, then, is the *empirical formula* as deduced solely from the consideration of the results of the analysis. It is quite consistent with such a calculation that the formula

[1] The highest common factor can generally be seen by inspection.

should be $S_2O_2Cl_4$, or $S_3O_6Cl_6$, or any such multiple. Which of these is to be finally accepted can only be decided after a determination of the vapour density of the body, or of its chemical constitution and character, and this would be the *molecular formula* of the body.

In the case under consideration the vapour density of the compound is 67·5, corresponding to a molecular weight of 67·5 × 2 or 135.

Now—

$$SO_2Cl_2 = 32 + 2 \times 16 + 2 \times 35{\cdot}5$$
$$= 135.$$

The molecular formula for the compound is therefore the same as its empirical formula, *i.e.* SO_2Cl_2.

(14) Find the formula of a substance having the composition—

Mg =	9·76
S =	13·01
O =	26·01
Water of crystallisation =	51·22
	100·00

Here we proceed as before, except that the relative number of *molecules* of water of crystallisation is found by dividing by the *molecular weight* of water—

Mg. $\frac{9\ 76}{24} = 0\ 406.$

S. $\frac{13{\cdot}01}{32} = 0{\cdot}406.$

O. $\frac{26{\cdot}01}{16} = 1{\cdot}626.$

H_2O. $\frac{51\ 22}{18} = 2{\cdot}846.$

Dividing by the lowest number we have—

Mg. $\frac{0{\cdot}406}{0{\cdot}406} = 1.$

S $\frac{0{\cdot}406}{0{\cdot}406} = 1.$

$$O. \quad \frac{1{\cdot}626}{0{\cdot}406} = 4.$$

$$H_2O \quad \frac{2{\cdot}846}{0{\cdot}406} = 7.$$

The simplest formula for the compound is therefore—

$$MgSO_4, 7H_2O.$$

437. Application to Chemical Problems.—We have now considered the fundamental calculations which enter into chemical problems, and a few examples will be given to show how these bear upon questions involving chemical decomposition and interchange.

(15) What weight of caustic soda (NaOH) will be needed to just neutralise 10 c.c. of dilute sulphuric acid (sp gr. 1·155) containing 21 per cent. of H_2SO_4?

In all cases where a chemical reaction is concerned, involving considerations of weight or volume, it is well to state the reaction in the form of an equation at the outset—

$$2NaOH + H_2SO_4 = \underset{\text{Sodium sulphate}}{Na_2SO_4} + 2H_2O.$$

From this we see that 2NaOH neutralise H_2SO_4, the respective weight relations being—

$$2\ (23 + 16 + 1) \text{ and } (2 + 32 + 64) \text{ or } 80 : 94.$$

80 parts by weight of caustic soda serve to neutralise 98 parts by weight of sulphuric acid.

Now determine the actual weight of sulphuric acid that is to be neutralised—

10 c.c. of the dilute sulphuric acid (sp. gr. 1·155) weigh 11·55 grams.

21 per cent. of this is H_2SO_4, *i.e.* $\frac{11{\cdot}55 \times 21}{100} = 2{\cdot}426$ grams

Required amount of caustic soda is—

$$\frac{2{\cdot}426 \times 80}{98} \text{ grams, or } 1{\cdot}98 \text{ grams.}$$

(16) What volume of oxygen collected at standard temperature and pressure (0° and 760 mm.) is given off on heating 10 grams of mercuric oxide?

The equation representing the action of heat on mercuric oxide is—

$$2HgO = 2Hg + O_2.$$

First determine the *weight* of oxygen from the above equation, which shows that 432 parts of mercuric oxide yield 32 parts of oxygen, or, in simpler numbers, 27 parts yield 2 parts of oxygen.

10 grams therefore yield $\frac{2 \times 10}{27}$, or 0·74 gram.

Now 32 grams of oxygen occupy at standard temperature and pressure 22 22 litres, and the *volume* of oxygen corresponding to this weight is—

$$\frac{0\ 74 \times 22{\cdot}22}{32} = 514 \text{ cubic centimetres.}$$

(17) What weight of sulphur must be burnt so as to yield 1 litre of sulphur dioxide at standard temperature and pressure?

$$S + O_2 = SO_2.$$

Here we start from a known *volume* of gas and must work back to the *weight* in terms of which the result is to be expressed.

22·22 litres of SO_2 weigh 64 grams.

$\therefore$ 1 litre of SO_2 weighs $\frac{64}{22{\cdot}22}$ or 2 869 grams.

Also 64 grams of SO_2 contain 32 grams of S,

$\therefore$ 2·869 „ SO_2 „ 1·4345 „ S.

1·4345 grams of sulphur will therefore be required to produce 1 litre of SO_2.

Such a calculation may, however, be shortened by the consideration that as 32 grams of sulphur, according to the equation, yield 64 grams or 22·22 litres of SO_2,

$\frac{32}{22{\cdot}22}$ grams will yield 1 litre of SO_2.

The next example will be rendered more complex by introducing conditions of temperature and pressure differing from the standard. No further difficulty is really

involved, except that the correction for temperature and pressure must be made.

(18) $2\frac{1}{2}$ litres of nitrous oxide have been collected at 39° C. and 741 mm. pressure; what weight of ammonium nitrate has been decomposed in order to supply the gas?

First eliminate the irregularity introduced by the temperature and pressure, by determining what volume the gas would have occupied had it been collected at standard temperature and pressure. This will be—

$$\frac{2{\cdot}5 \times 273 \times 741}{312 \times 760} \text{ litres, or } 2{\cdot}133 \text{ litres.}$$

Now according to the equation—

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

80 grams of ammonium nitrate yield 44 grams (or 22·22 litres) of nitrous oxide, and hence

$$\frac{80 \times 2{\cdot}133}{22{\cdot}22} \text{ grams, or } 7{\cdot}681 \text{ grams, of ammonium}$$

nitrate have been decomposed.

(19) One gram of water is (*a*) converted into steam at 100° C., (*b*) decomposed by means of sodium and the hydrogen collected at 13° C.; what volume will each occupy, the barometer at the time standing at 750 mm.?

First, let us consider the case of the steam. This being water vapour has, at standard temperature and pressure, a density such that, as previously shown,

18 grams is the weight of 22·22 litres.

$$\text{Thus 1 gram occupies } \frac{22{\cdot}22}{18} \text{ or } 1{\cdot}234 \text{ litres.}$$

At 100° C. and 750 mm. pressure this occupies—

$$\frac{1{\cdot}234 \times 373 \times 760}{273 \times 750} = 1{\cdot}71 \text{ litres.}$$

Secondly, as to the hydrogen, the decomposition is represented by the equation—

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

from which we see that 36 grams of water yield 2 grams of

hydrogen, and therefore 1 gram of water yields $\frac{1}{18}$ gram of hydrogen.

The *volume* of hydrogen at standard temperature and pressure is thus $\frac{11{\cdot}11}{18}$ or 0·62 litre. Corrected so as to represent the volume at 13° C. and 750 mm. pressure this becomes—

$$\frac{0{\cdot}62 \times 286 \times 760}{273 \times 750} = 0\ 658 \text{ litre.}$$

The whole of the more important elements entering into the treatment of chemical problems have now been discussed, and it only remains to add some examples in further illustration of their application to chemical reactions.

(20) 10 grams. of mercury are heated with excess of concentrated sulphuric acid and the sulphur dioxide formed is collected at 15° C. and 765 mm. pressure; what volume does it occupy?

Here, as in most cases, it is best to commence by a statement of the reaction which takes place.

$$Hg + 2H_2SO_4 = \underset{\text{Mercuric sulphate}}{HgSO_4} + 2H_2O + SO_2.$$

200 grams of mercury give 64 grams of SO_2,
or 200 „ „ „ 22·22 litres of SO_2,
∴ 10 „ „ „ 1·111 „ „
at standard temperature and pressure.

Volume at 15° C. and 765 mm. pressure is then

$$\frac{1{\cdot}111 \times 288 \times 760}{273 \times 765} = 1{\cdot}164 \text{ litre.}$$

(21) 25 c.c. of marsh gas (CH_4) are mixed with 500 c.c. of air and exploded in a eudiometer; what volume of gas should there be (*a*) before the removal of the carbon dioxide formed, (*b*) after the absorption of the carbon dioxide by means of caustic potash? The temperature and pressure may be assumed to be the same when each of the readings of volume were taken.

The chemical reaction which takes place is

$$\underset{\text{2 vol.}}{CH_4} + \underset{\text{4 vol.}}{2O_2} = \underset{\text{2 vol.}}{CO_2} + 2H_2O,$$

the nitrogen of the air taking no part in the combustion.

It is further manifest on inspection that the 2 volumes of marsh gas and 4 volumes of oxygen, before explosion, give rise to 2 volumes of carbon dioxide, the space occupied by the water being negligible.

Thus 6 volumes are reduced to 2, and the diminution is 4 volumes.

But the marsh gas occupies 25 c.c , and is represented by 2 volumes.

The diminution in volume is therefore 50 c.c., and the 525 c.c. of mixed gases originally present in the eudiometer have been reduced to 475 c.c.

Similarly the carbon dioxide occupies the same volume as the marsh gas from which it was obtained, and is thus 25 c.c., and if this be removed there will remain 450 c.c. of gas in the eudiometer. The result is that the residual gas—

(a) before removal of CO_2 is 475 c.c.
(b) after ,, ,, ,, 450 c.c

(22) 10 c.c. of liquid carbon bisulphide (sp. gr. 2 63) are burnt in oxygen; find the volume of the resulting gases measured at standard temperature and pressure.

We must first ascertain the weight of the carbon bisulphide. Its sp. gr. being 2·63, the 10 c.c. will weigh 26·3 grams.

The chemical change during combustion is represented in the equation—

$$CS_2 + 3O_2 = CO_2 + 2SO_2.$$

76 grams of CS_2 yield 44 grams or 22·22 litres CO_2
,, ,, ,, ,, 128 ,, ,, 44·44 ,, SO_2
,, ,, ,, ,, 66·66 litres of CO_2 and SO_2 together.

$$26\ 3 \text{ grams of } CS_2 \text{ yield } \frac{66{\cdot}66 \times 26{\cdot}3}{76} = 23{\cdot}08 \text{ litres.}$$

(23) Considering air as a mixture of 79 per cent. by volume of nitrogen with 21 per cent. by volume of oxygen

(*i.e.* neglecting argon), find the density of air compared with hydrogen. Also find the density of the vapour of carbon bisulphide compared with air.

79 vol. of nitrogen are as heavy as 79 × 14, or 1,106 vol. of H.

21 vol. of oxygen are as heavy as 21 × 16, or 336 vol. of H.

100 vol. of air are as heavy as ... ... 1,442 vol. of H.

∴ Density of air is 14·42. §

Density of the vapour of bisulphide of carbon is $\frac{12 + 64}{2}$ or 38, compared with hydrogen.

Compared with air it is therefore $\frac{38}{14{\cdot}42} = 2{\cdot}635$.

QUESTIONS.—CHAPTER XXX.

[N.B.—In the following calculations use the atomic weights in the table at the end of Chapter IX.]

1. The volume of a permanent gas at 0° C. is 3 litres; at what temperature would it occupy 4 litres, the pressure remaining unaltered?
2. Two samples of gas occupy the same volume, but one is at — 20° C., and the other at 20° C.; what is their relative volume when both are at 0° C.?
3. The volume of a gas at 13° C. is 100 c.c.; find its volume at — 130° C., at — 13° C., and at 130° C.
4. A gas under standard atmospheric pressure measures 209 c.c.; what volume will it occupy under a pressure of $\frac{1}{10}$, $\frac{1}{2}$, 2, and $5\frac{1}{2}$ atmospheres respectively?
5. What volume will half a litre of gas measured at 750 mm. pressure occupy when subjected to a pressure of 850 mm. of mercury?

§ Actual density at normal composition is taken as 14·435.

6. A rectangular vessel 10 cm. long, 5 cm. wide, and 3·5 cm. deep, is filled with gas at 100° C. and 770 mm. pressure; what volume will the gas occupy at standard temperature and pressure?

7. A sample of gas is collected in a eudiometer, and it is found that the level of the mercury in the eudiometer is 257 mm. above that in the trough; also the height of the barometer at the time is 745 mm.; under what pressure is the gas?

8. A sample of gas is collected at standard temperature and pressure, and the pressure is then doubled and the temperature gradually raised until the volume of the gas is the same as it was originally; at what temperature does this occur?

9. Under how many atmospheres pressure will steam have the same density as water (1 c.c. weighs one gram), if the contraction takes place in accordance with Boyle's law, and the temperature remains at 600° C.?

10. If the temperature remains at zero, at what pressure will hydrogen have a density equal to 0·62 of that of water?

11. One cubic centimetre of bromine (density 3·2) is transformed into vapour at 78° C.; determine the volume occupied by the vapour.

12. The sp. gr. of pure nitric acid being 1·522, find the weight of 100 c.c. of it, and the volume that you must take to weigh 100 grams.

13 What volume of such acid will be required to just neutralise 100 grams of caustic potash (KOH), and what weight of potassium nitrate will be formed?

14. Calculate the percentage composition of calcium carbonate; what percentage of carbon dioxide does it contain?

15. Chlorine forms with water a solid hydrate, having the composition $Cl_2, 8H_2O$; calculate the percentage of hydrogen, chlorine, and oxygen contained in this body.

16. Find the empirical formula of a compound consisting of 46·66 per cent. of iron and 53·33 per cent. of sulphur.

17. An oxide of iron contains 72·3 per cent. of iron; determine its empirical formula.

18. Determine the simplest formula for a salt having the following percentage composition:—

Sodium,	29 36
Phosphorus,	26 38
Oxygen,	44·26
	100 00

19. A solution of caustic soda having the sp. gr. 1·32 contains 28·8 per cent. of NaOH; what weight of sulphuric acid is required to be just sufficient to neutralise a litre of such a solution?

20. What volume of sulphuretted hydrogen at 13° C. and 798 mm. pressure is required to effect the complete precipitation of one gram of corrosive sublimate, $HgCl_2$?

21. What weight of pure antimony sulphide, Sb_2S_3, should yield a litre of sulphuretted hydrogen collected at 10° C. and 760 mm. pressure?

22. Determine the volume of chlorine required to convert 10 grams of phosphorus into the pentachloride.

23. A gram of common salt is dissolved in water and excess of silver nitrate solution is added; what weight of silver chloride should be precipitated?

24. Calculate (*a*) the volume, (*b*) the weight, of carbon dioxide in the air of a room 6 metres long, 4 metres wide, and 3 metres high, if there is 1 volume of this gas present per 1,000 volumes of the air.

25. Dumas determined the relative amounts of nitrogen and oxygen in air by passing it over heated copper. He found—

Weight of tube and copper before experiment, 120 grm.
" " " after " 121·15 "
" globe when exhausted ... ... 852 "
" " and nitrogen ... ... 855·85 "

From these numbers calculate the percentage composition of air by weight, and deduce its percentage composition by volume.

26. Dumas determined the composition of water synthetically by passing hydrogen over heated copper oxide, and found—

Weight of tube and copper oxide before experiment, 334·598 grm.
" " " " after " 314·238 "
" drying tubes before experiment... ... 426·358 "
" " " after " ... ... 449·263 "

Calculate the percentage composition of water by weight.

27. Ten grams of steam are passed over red-hot iron; what volume of hydrogen at 26° C. and 741 mm. pressure will be obtained if one-third of the steam undergoes decomposition?

28. Fifteen cubic centimetres of ammonia are completely decomposed by electric sparks, and then 40 c.c. of oxygen are added and the mixed gases exploded; state the gases present and the volume of each (*a*) just before exploding, (*b*) after exploding.

29. A mixture of ten litres of oxygen with one litre of carbon dioxide is shaken up with 100 c c. of water; determine the volume of each gas that will be dissolved—the barometer at the time standing at 760 mm. and the thermometer at zero.

30. Make the same determination with a mixture of one litre of oxygen and 10 litres of carbon dioxide.

31 A litre of sea-water (sp. gr. 1·03) is evaporated to dryness, and found to leave as residue 36·4 grams of salts; find the percentage of solid matter in the sea-water.

32. Given that a metre is equivalent to 39·37 inches, calculate the number of cubic inches in a litre, and the number of litres in a cubic foot.

33. Determine the percentage of carbon in cane-sugar ($C_{12}H_{22}O_{11}$) and the volume of carbon dioxide that results from the combustion of 0·2 gram of sugar.

34. A mixture of 20 c.c. of ethylene and 200 c.c. of oxygen is exploded in a eudiometer; what volume of gas remains after the explosion, and what volume when the carbon dioxide is subsequently removed by absorption with potash?

35. What quantity of crystallised oxalic acid ($C_2H_2O_4 + 2H_2O$), heated with excess of sulphuric acid, will yield 5 litres of gas at standard temperature and pressure?

36. If 50 c.c. of sulphuretted hydrogen be mixed with excess of chlorine, what volume of hydrogen chloride will be formed, and what weight of sulphur liberated?

37. A gram of a substance containing carbon is heated with lead monoxide, and found to form 10 grams of metallic lead; what percentage of carbon was present?

38. What weight of iron must be dissolved in dilute sulphuric acid in order to yield sufficient hydrogen to fill a balloon having a capacity of 100 cubic metres?

39. Ten grams of carbon are burnt in 1,000 litres of air (taken as consisting of 79 vol. of N and 21 of O) at 15° C. and 700 mm. pressure; find the percentage of nitrogen, oxygen, and carbon dioxide in the air after the combustion is complete.

ANSWERS TO QUESTIONS

Chap. xiv	2.	11·2 grams of hydrogen. 88·8 grams of oxygen.
,,	3.	19·95 grams, 127·5 grams.
,,	4.	Standard pressure (*a*) 449·75 c.c. (*b*) 225·25 c.c. 76 mm. pressure (*a*) 44·975 c.c. (*b*) 22·525 c.c. 3 at. pressure (*a*) 1349·25 c.c. (*b*) 675·75 c.c.
,,	5.	44·975 c.c. of carbon dioxide and 19 475 c.c. of oxygen.
Chap. xvi.	6.	19·6 per cent.
,,	7.	Nitrogen 78·49 per cent. Argon 0·68 ,, Oxygen 20·83 ,, 100·00 ,,
,,	8.	22·97 per cent.
Chap. xix.	7.	4399 tons.
,,	16.	0·57 per cent.
,,	17.	1146·7 c.c.
Chap. xx.	5.	30 c.c. 20 c.c.
,,	15.	60 c.c. of oxygen.
,,	16.	85 c.c. 55 c.c. of oxygen; 20 c.c. of carbon dioxide; 10 c.c. of water vapour.
Chap. xxi.	13.	8550 c.c., 2020 c.c.
Chap. xxii.	14.	Disodium hydrogen phosphate, Na_2HPO_4. 88·75 grams.

ANSWERS TO CHEMICAL CALCULATIONS IN CHAPTER XXX.

1. 91°.
2. 293 : 253.
3. 50 c.c., 90·9 c.c., 140·9 c.c.
4. 2090 c.c., 418 c.c., 104·5 c.c., 38 c.c.
5. 441 c.c.
6. 129·7 c.c.
7. 488 mm.
8. 273° C.
9. 3,947 atmospheres.
10. 6,888 atmospheres.
11. 571·4 c.c.
12. 152·2 grams; 65·7 c.c.
13. 73·9 c.c.; 180·4 grams.
14. Ca = 40 per cent.
    C = 12 „
    O = 48 „
    44 per cent.
15. H = 7·44 per cent.
    Cl = 33·02 „
    O = 59·54 „
16. FeS_2.
17. Fe_3O_4.
18. $Na_6P_4O_{13}$.
19. 465·7 grams.
20. 81·8 c.c.
21. 4·86 grams.
22. 17·91 litres.
23. 2·45 grams.
24. 72 litres; 142·6 grams.
25. Oxygen, 23; Oxygen, 20·7. Nitrogen, 77; Nitrogen, 79·3.
26. Hydrogen, 11·1. Oxygen, 88·9.
27. 4·622 litres.
28. (*a*) N = 7·5 c.c.
    H = 22·5 c.c.
    O = 40·0 c.c.
    (*b*) N = 7·5 c.c.
    O = 28·75 c.c.
29. Oxygen = 3·73 c.c.
    Carbon dioxide = 16·36 c.c.
30. Oxygen = 0·37 c.c.
    Carbon dioxide = 163·6 c.c.
31. 3·534 per cent.
32. 61·023; 28·317.
33. 42·1 per cent.
    0·157 litre.
34. 180 c.c.; 140 c.c.
35. 14·18 grams.
36. 100 c.c.; 0·072 gram.
37. 29 per cent.
38. 252·0 kilograms.
39. Nitrogen, 79·00 per cent.
    Oxygen, 18·88 „
    Carbon dioxide, 2·12 „

APPENDIX I.

THE METRIC SYSTEM OF WEIGHTS AND MEASURES.

The metric system has been found the most convenient for operations in which weighing and measuring are concerned, and it is universally used in scientific work.

The *unit of length* in this system is the *metre*, which is equivalent to 39·37 inches.

The *unit of volume* is that of a cube whose side is $\frac{1}{100}$ of a metre, equivalent to very nearly one-sixteenth of a cubic inch, and the *unit of mass* is the mass of this volume of water, the temperature being that at which water has its maximum density, viz. 4° C. This mass is termed the *gram*, and is equivalent to 15·432 grains.

The prefix *kilo* indicates the multiple 1,000, thus—

1 kilogram = 1,000 grams = 15,432 grains
= about 2·2 lb.

The prefixes *deci*, *centi*, and *milli* respectively indicate the fractional parts $\frac{1}{10}$, $\frac{1}{100}$, and $\frac{1}{1000}$.

1 decimetre = $\frac{1}{10}$ metre = 3·937 inches.
1 centimetre = $\frac{1}{100}$,, = 0·3937 ,,
1 millimetre = $\frac{1}{1000}$,, = 0·03937 ,,

One inch is thus slightly more than 25 millimetres.

1 decigram = $\frac{1}{10}$ gram = 1·5432 grains.
1 centigram = $\frac{1}{100}$,, = 0·15432 ,,
1 milligram = $\frac{1}{1000}$,, = 0·015432 ,,

A measure of volume very frequently employed is the *litre*, which is the volume occupied by a kilogram of water at 4° C.; it is therefore equivalent to a cubic decimetre, or, in English measure, 61·027 cubic inches.

APPENDIX II.

TABLES FOR REDUCTION OF MOIST GAS TO STANDARD CONDITIONS.

The volume of a moist gas having been measured at a given temperature and pressure it is necessary to first find what volume the *dry* gas would occupy at 0° C. and 760 mm. pressure. Allowance must be made (see Chaps. VIII., XIII.)—

(*a*) for the temperature of the gas (*i.e.* of the room);

(*b*) for the pressure to which it is subject (that of the atmosphere at the time of the experiment);

(*c*) the tension of water-vapour.

This involves a somewhat complex calculation, and a table has therefore been drawn up to enable the student to make the correction by using the factor given in the table.

Thus suppose the temperature of the laboratory to be 10° C. and the atmospheric pressure 740 mm.; the tension of aqueous vapour with which the gas is saturated is for 10° C., 9·1 mm. Now if v is the volume of the moist gas as observed, then V the volume of the dry gas at 0° C. and 760 mm. pressure is given by the expression—

$$V = \frac{v \times 273 \times (740 - 9{\cdot}1)}{283 \times 760} = 0{\cdot}928\ v.$$

To deduce the volume of the dry gas at standard temperature and pressure from the observed volume it is therefore only necessary to *multiply this latter by the factor* 0·928 as taken from the table, and so for any other temperature or pressure.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0·915	0·907	0·899	0·891	0·882	0·874
740 mm.	0·928	0 920	0 911	0·903	0·895	0·886
750 mm.	0·940	0 932	0 924	0 915	0 907	0·898
760 mm.	0·953	0·945	0·936	0 928	0 919	0 910
770 mm.	0·966	0·957	0·949	0·940	0·932	0·923

For intermediate temperatures or pressures, the value may be expressed with sufficient accuracy by taking the proportional mean; *e.g.* for 10° C. and 745 mm. we may use the factor 0 934, and for 11° C. and 750 mm. 0 936.

If we desire to know the *weight* of the hydrogen liberated, the following table may be used. Taking the weight of a litre of dry hydrogen under standard conditions as 0·09 gram the table gives the weight of hydrogen in a litre of the moist gas collected at the temperature and pressure given.

Pressure.	10° C.	12° C.	14° C.	16° C.	18° C.	20° C.
730 mm.	0 0824	0·0816	0·0809	0 0802	0 0794	0 0787
740 mm.	0·0835	0·0828	0 0820	0·0813	0·0806	0 0798
750 mm.	0·0846	0·0839	0·0832	0 0824	0 0816	0 0808
760 mm.	0·0858	0·0851	0 0843	0·0835	0·0827	0·0820
770 mm.	0·0869	0·0861	0 0854	0·0846	0 0839	0 0831

An example will make the method of using the table quite clear —

Thermometer 16° C.

Barometer 750 mm.

Observed volume of gas, 120 c c.

The factor under 16° C. and 750 mm. is 0 0824.

$$\text{Weight of hydrogen} = \frac{0{\cdot}0824 \times 120}{1{,}000} = 0{\cdot}00988 \text{ gram.}$$

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