A FIRST YEAR'S COURSE

OF

EXPERIMENTAL WORK

IN

CHEMISTRY

BY

ERNEST H. COOK, D.Sc.(Lond.), F.I.C.
ASSOCIATE OF THE ROYAL COLLEGE OF SCIENCE, DUBLIN
PRINCIPAL OF THE CLIFTON LABORATORY, BRISTOL

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PREFACE

To be successful in passing an examination is one thing, perhaps a good thing, but to have a sound knowledge of the subject is another and far more important matter. It is because the course of work set out in the following pages has been found, from personal experience, to give students a good foundation of elementary knowledge that it is now published.

Care has been taken to describe only those experiments which offer no particular difficulties in carrying out, and which give fairly accurate results.

The book is intended for those who are beginning Laboratory Work, and students should attend a course of Lectures on Elementary Chemistry at the same time. Careful descriptions of every experiment—failures as well as successes—should be written out by the student and shown to the teacher for his criticism.

In order that the descriptions may be in the student's own words, very brief accounts are given in the text, and the teacher is thus enabled to judge of the honesty of the work that is being done, as well as to discover want of care in observation.

Theoretical deductions and generalisations are left to the teacher, so as to avoid, as far as possible, what is very common among students—to generalise before a sufficiently wide knowledge of facts has been acquired.

The author desires to acknowledge his indebtedness to Dr. Tilden's *Hints on Teaching Chemistry* for some suggestions; and to his assistants, Messrs. Froude, Vaughan, and Doresa, for help in various ways.

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CHAPTER I.

INTRODUCTORY.

THE study of chemistry resolves itself into an investigation of the properties of matter, and of the changes which it undergoes when placed under the influence of natural forces, such as heat, etc., as well as the alterations which sometimes occur when different kinds of matter are brought into contact. It is a purely experimental science, that is, one which is founded upon systematic observation. Not that there are not theories in chemistry; there are plenty of them, some even think there are too many; but all these theories are founded upon observations, and very often, when more observations have been made, the theories are found to be unsupported by facts. Over and over again in the history of the science, we find that a theory which the most eminent chemists of the day believed to be true has been proved to be false by more extended or more careful observation.

Such being the case, it is evident that the most important thing for the practical chemist is to learn to observe correctly. And at the very outset, I cannot too strongly impress this upon the student. When making an experiment be careful to give your whole attention and thought to it. Do not consider anything which occurs—whether you see it, or smell it, or hear it—as too trivial or too common to be taken notice of. Also, when performing an experiment, especially if doing so for the first time, follow implicitly the directions laid down. Finally, keep very carefully written notes of the experiments made and the results obtained; and illustrate these whenever possible by neatly drawn sketches.

The chemist, therefore, like the engineer and the physicist, has to deal with matter, but the chemist's branch is more particularly concerned with the inner structure or constitution of matter, and how changes in this structure can be brought about. The engineer, on the other hand, is engaged in placing matter together so as to form some new arrangement suited for a particular purpose; while the physicist is studying the peculiar results observed when matter is subject to the action of certain forces. Now it will readily be believed that, since chemistry is a very old science, chemists have gradually made the apparatus which they use more and more perfect. And this is perfectly true. We employ the most complicated and delicate instruments, in order that we may be able to regulate with the greatest accuracy the conditions under which the experiments are made. But elaborate and costly apparatus is not essential for doing good work in chemistry. Some of our greatest chemists made their most important discoveries with very simple appliances. Probably the materials employed by Priestley, for example, would not be tolerated in any modern laboratory.

In an elementary course the simplest apparatus should be used; and in this book I shall therefore describe this kind only. Most of it could be easily made in an ordinary laboratory, but it is only the advanced student who can profitably employ his time in doing this. A student who enters a laboratory for the first time becomes disheartened at his failures if he is put to glass-blowing or soldering straight away. It is much better for him to acquire skill in such operations gradually, and to attempt only the fitting together of such trains of apparatus as can be done by glass tubes and india-rubber connections.

As the source of the heat which he employs, the chemist makes use of gas burners or gas furnaces, and, if a metallurgist, of coke furnaces. A spirit lamp is sometimes used, but very rarely. The commonest form of gas burner employed is that invented by Professor Bunsen and known as the Bunsen burner. The gas issues from a small orifice into a wider tube, from the end of which it is burnt. But during its passage through this wider tube it mixes with air which comes in through openings in the side of the tube. The result is that the flame at the end of the tube is intensely hot, and does not deposit soot on any surface placed in it. The openings in the wider tube for the admission of air must be adjusted so as to allow a proper amount of air to enter. This will easily be known, because if too much enters, the flame will "roar" slightly, while if too little, the flame will become luminous and blacken any article placed in it. The Bunsen burner is suitable for operations requiring great heat; when a gentle heat is required, it is not so useful, because if you turn it down too low, the flame will not burn at the end of the wide tube, but jumps back to the end of the small opening at the bottom of the wide tube, where it will continue to burn as a very small flame, making the wide tube hot and producing a very poisonous gas, which mixes with the air of the laboratory.

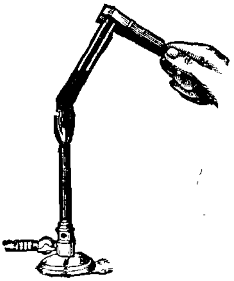
FIG. 1.

The burner employed for obtaining a gentle heat is an ordinary Argand burner fitted with a chimney. The substance or vessel to be heated is placed at a little distance above the top of the chimney but not in contact with the flame. In this way the substance is not blackened, but is made hot by the heat which is radiated from the flame. Argand burners are shown in several of the following figures.

Apparatus is usually fitted together and connected by glass tubes, *corks, and india-rubber tubing.* There are two kinds of glass tubing in common use—soft, and hard or combustion. The terms have reference to the effect of heating — the former being readily softened, while the latter requires the high heat of the blow-pipe to soften it. Test-tubes are made of the former kind, so that they should only be used for heating liquids, or such solids as require little heat to change them. Soft glass tube is the kind employed for connecting flasks, etc., together. The most convenient size for general work is called "quill" tubing, and is about 4 to 6 mm. in diameter. Combustion tubing is required of varying sizes, sometimes of about the same size as the soft, but frequently of larger diameter, so that a piece of small may be fitted into a piece of large by means of a cork. It is necessary that the student should be able to fit together simple pieces of apparatus, and we will therefore commence our work by learning how

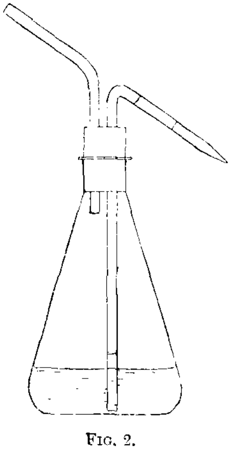
FIG. 2.

(1) *To fit up a Wash-Bottle.*—This is a bottle fitted with a cork with two holes through which two glass tubes pass, so arranged that the user can pour water from the bottle through one tube and blow it in a gentle stream through the other. Sometimes the water is required hot, and therefore the bottle must be made of a kind of glass that will stand water being boiled in it without its cracking. The best kind to use is a conical flask made of Bohemian glass, known as an Erlenmeyer flask, after the inventor. Select one of about half a litre capacity. (Most chemists use the Metric System of Weights and Measures. If you are not

familiar with the tables you must study them from some work on the subject. The flask here mentioned would hold a little less than a pint.) Find a cork to fit it. If the cork is hard it may be softened by wrapping it in a piece of paper and gently rolling it under foot on the floor. This cork must now be bored. This is done with cork-borers. These are pieces of brass tube with one end filed down until it forms a sharp edge all round. They are made of different sizes to correspond to the varying diameters of glass tube. Take the borer which is slightly smaller in diameter than the tube you are going to use. Hold the cork firmly between the thumb and fore-fingers of the left hand, place the sharp edge of the cork-borer flat upon the top of the cork, but nearer to one side than the other, and press firmly, rotating the borer while doing so. Be careful to keep the axis of the cork and that of the borer parallel to each other. In this way a clean-cut hole will be bored through the cork parallel to its axis. Now repeat the operation, but boring nearer to the opposite side of the cork. In this way, if the operations have been successfully performed, you will have two holes through the cork parallel to each other. It is, however, unlikely that success will attend the first effort, the holes will perhaps run into each other, or run out at the sides. If this happens, take another cork and try again until success is attained. It will help if you bore a single hole through the middle of a cork to begin with and then try the two.

Having successfully bored the cork, we have to fit the tubes in. For this purpose you must cut off a piece of glass tube. This is done by making a scratch with a three-cornered hard steel file across the place where you want the glass to break. If you use the size recommended above for your flask, you will want two pieces, one about 15 cm. and the other about 30 cm. long. These tubes must now be bent, one at an angle of about 130°, and the other at an angle of about 50°. To do this the glass must be softened in the flame. The best flame to use for this purpose is an ordinary gas burner, such as is used in our houses for lighting purposes ("fish-tail" or "bat's-wing" serves equally well). These burners heat a very much longer length of the tube than a Bunsen burner does, and consequently the bend produced is more regular and less liable to crack than one made with the latter. Moreover the soot deposited upon the tube by the luminous tube is not à disadvantage but an advantage, for it makes the glass cool more slowly and thus anneals it a little.

Take the shorter piece of tube first and hold it with one hand at each end, then place it in the flame so that the middle of the flame shall be about 5 cm. from one end. The flame will thus heat about 5 cm. of the tube. Keep the tube turning so that each side of it is equally heated. In a few minutes the glass will soften. When this is the case, bend the tube gently until it is at the proper angle. Then take it out of the flame and allow it to cool. Do the same with the other piece, but making the angle of the bend about 50°, and the bend about 12 cm. from one end. Now cut the shorter tube so as to have about 6 cm. from the bend on each side, and the longer one so as to have about 4 cm. on the shorter side of the bend. Next take a piece of the same-sized tube about 10 cm. long, and turn down the flame of the burner until the flame only heats about 2½ cm. of tube. Hold the middle of the tube in the flame until it is soft, keeping it turned whilst heating, then gently draw the two ends apart. The tube will thus be contracted. Remove it from the flame, and when cool, cut it across the narrow part; and also at the other end so as to make it about 4 cm. long.

You will now have three tubes: one about 12 cm., one about 22 cm., and a third about 4 cm. The ends of the tubes will be noticed to be very sharp. To round them off hold them in the flame of the Bunsen burner until the flame is coloured yellow just where it touches the glass. In this way the ends will be fused a little and the sharpness removed. The tubes are now put through the holes in the cork. They should fit tightly. The smallest tube is now connected to the short end of the longest tube by means of a piece of india-rubber tubing of the requisite size and about 3 cm. long. The apparatus when complete should have the appearance shown in the sketch.

An india-rubber bung for the flask is an advantage. These can be bought already bored; if, however, you have to bore them, it can be done in the same way as a cork, but the borer must be moistened with a little turpentine before use.

The making of a wash-bottle as above described will have given the pupil a little practice in cork-boring and in the bending of glass tubes. He will, of course, require a great deal more before he is able to set up apparatus with ease. Numerous examples will be given in working through the exercises that follow. We will therefore defer further illustration until we come to consider special cases in detail.

CHAPTER II.

CHARACTERISTICS OF CHEMICAL CHANGE.

So numerous and complicated are the changes which matter undergoes when it is placed under conditions which favour such changes, that any attempt at classification is almost impossible to be complete. We can, however, make a few broad generalisations which help to fix some of the peculiarities on the mind. The first of these has reference to what is called *chemical action* and *physical action.* By the latter is usually meant some action brought about by the operation of one or other of the natural forces, such as gravitation, electricity, magnetism, etc., which, while altering the relative position or condition of the substance, does not bring about any change which forms a new body, or bodies, from the original. Thus, for example, if we allow a stone marble to fall to the floor, or if we hold one end of a magnet near another suspended magnet, we bring about physical changes. We have in both cases caused forces to act which have altered the relative position of the bodies. It is true that instead of a marble we might have allowed an egg to fall, or be acted on by gravity, when it is equally true that "Not all the king's horses nor all the king's men could ever put" the egg together again. But, nevertheless, the whole of the parts of the egg are still there, and *if* we had the requisite skill we could gather them up and put them together. It would have been different if a chemical change had occurred; in that case no simple gathering together of particles would have sufficed; the only way would have been to have brought about another chemical change which would have exactly reversed the former. In only a comparatively few cases can such be done.

Now when these physical changes are carefully observed it will be seen that there is always an appreciable distance between the centre from which the force emanates and the substance acted upon. Thus, for example, we are warmed by a fire although at some distance from it; we are able to see a body which is illuminated by a light placed some distance away; and if we support a thin lath upon the bottom of an upturned flask and hold a dry and warm glass tube which has been rubbed with dry silk near it, it will attract the lath.

It is, however, different with chemical actions. For these to occur *the bodies must be brought into intimate contact with each other.* In illustration of this the following may be cited:—

Experiment 2.—Take about 5 grms. of tartaric acid and powder finely in a clean dry mortar. Now add about 5½ grms. of dry sodium bicarbonate, and rub the two substances together in the mortar. If both substances are quite dry, no effect will be noticed. Place the mixed substances in a beaker and pour in some water. A violent commotion will be observed to take place in the beaker accompanied by a fizzing or effervescence. A chemical action has taken place. The fact that no action occurred in the first case but it did in the second, *i.e.* when the water was added, is supposed to be due to the circumstance that the rubbing was unable to bring the particles into sufficiently close contact to enable them to act upon each other. When, however, the water is added the contact is much closer and a chemical action can take place. The effervescence is caused by the escape of some gas which is different from air, because if a lighted match or taper be held in the beaker above the substances it will be seen that the light is extinguished, showing that there is a colourless gas present which will not allow the taper to burn.

This experiment also illustrates what is found to be a very common thing, viz. that two solid bodies will seldom act upon each other so as to cause chemical action to take place; if, however, the bodies can be dissolved in some solvent and then the solutions mixed, chemical action will frequently occur. There are cases, however, in which solids apparently enter into union. For example:—

Experiment 3.—Place a piece of dry phosphorus, about the size of a small pea, in contact with a few crystals of iodine, and in a short time the phosphorus will burst into flame. But if you watched the experiment carefully, you must have observed that the phosphorus melted before it ignited, so that even in this case when ignition took place one of the substances was a liquid.

Again, it is found that chemical actions even of the same class vary in intensity. This is very well shown in processes which take place when bodies are heated in the air.

Experiment 4.—Take a piece of platinum wire, a piece of thin sheet tin known as tin-foil, and a piece of magnesium wire. Now hold them successively in the flame of the Bunsen burner. The platinum will become very hot and bright, but on taking it out of the flame it will be seen that no change has taken place in it. The piece of tin will become hot but will not give out light like the platinum, and will gradually crumble away to a powder. This powder when examined will be found to be white and rather heavy. The magnesium on the other hand will, directly it is put into the flame, burn with a most brilliant bluish-white light, forming clouds of a white powder. This powder will be observed to be much lighter than the former. Thus we see from this experiment that platinum is not affected when it is heated in the air, that tin is changed into a white powder but the change is not accompanied by any production of light, and that magnesium is so powerfully affected as to produce an extremely powerful light. In the second and third cases the shining metallic substances have been changed into white powders. This is one peculiarity of chemical change: *the products of the change are different from the substances which enter into it.* Also the experiment shows that under the conditions described, tin is less anxious to enter into change than magnesium is; whilst platinum will not do so at all.

Such experiments as those we have described up to the present take account only of the change produced in the appearance or quality of the bodies entering into the change. These changes are called *qualitative.* But chemical knowledge would not have progressed very far if the chemist had not studied his experiments *quantitatively, i.e.* by carefully weighing the substances before the change, and the products afterwards. In this way innumerable new facts have been discovered, and it has been found that all changes take place, not in a haphazard manner, but in strict accordance to the *amounts* of the materials which enter into the change as well as the *amounts* of those produced by it. In some cases, as for instance when a candle burns in the air, there is an *apparent loss* of matter, because it is evident that the candle does not weigh as much when nearly burnt out as it did at the beginning. But the loss in weight in such cases is caused by the circumstance that one or more of the products of the action are gases. These mix with air and thus escape weighing, but if special precautions are taken to prevent this, no loss of weight will be noticed. Abundant illustrations of such actions will be met with in the following pages.

Almost every *kind* of chemical action can be produced. In fact, if we omit the case of two solids, about which there is some doubt, we have examples of all other possible kinds. Thus:—

(1) Two gases can produce a solid, a liquid, a fresh gas, or mixtures of these.

(2) Two liquids may produce a solid, another liquid, a gas, or mixtures of these.

(3) A gas and a liquid may form a solid, a liquid, or a gas.

(4) A gas and a solid may form a solid, a liquid, or a gas.

(5) A liquid and a solid may form a solid, a liquid, or a gas.

Experimental illustrations of some of these require somewhat complicated apparatus, but many of them can be shown with simple materials.

Experiment 5.—Take a glass cylinder filled with the colourless gas ammonia and loosely covered with a glass circle, and invert it over another similar cylinder filled with the colourless gas hydrochloric acid. Slip out the circles, and thus allow the two gases to come into contact: a white solid will be formed which will quickly settle down upon the sides of the cylinders.[1]

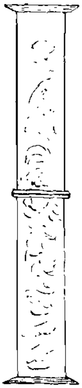

FIG. 3.

Experiment 6.—Take a piece of glass tube of about 1 or 1·3 cm. diameter and 40 cm. long and bend it at right angles at about 7 cm. from one end, draw the other end out to a jet (Experiment 1), and then bend this end around parallel to itself at a point about 7 cm. from the end. Now attach the first end to the gas supply to the laboratory by means of a piece of india-rubber tubing. Turn on the gas and light a small jet of it at the end of the tube. Take a clean *dry* gas cylinder and lower the burning jet down into it. Allow the gas to burn in the cylinder for a few minutes and then withdraw the tube. The sides of the cylinder will be found to be covered with a dew of some liquid substance which has been formed by the burning of the gas, *i.e.* the chemical action between the gas and the air—two gases.

Experiment 7.—To rigidly prove that two gases can

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[1] In this experiment as well as in Nos. 6, 7, 8, 10 (*b*), 10 (*c*), 11 (*a*), 11 (*b*), the teacher must provide the gases for the student to use.

combine and produce a new gas is not easy with simple apparatus, but a sufficiently accurate proof is afforded by repeating Experiment 5 but with the cylinders filled with oxygen and nitric oxide gases respectively. When they come into contact a reddish-brown gas or vapour will be formed.

Experiment 8.—To show that two gases may produce mixtures of gases, liquids, and solids. Take two cylinders as before, but filled—one with chlorine and the other with sulphuretted hydrogen. Mix them as described, when it will be seen that the sides become covered with a white coating—a solid; and on separating the cylinders they will be found to be filled with a gas that fumes strongly when allowed to come into contact with the air. Thus a solid and a gas have been formed by this change.

Experiment 9.—That liquids will react upon each other in the ways mentioned can be shown by the following:—

(*a*) Place about 5 grms. of calcium chloride in a small dish and add about 5 c.c. (cubic centimetres) of water to it. Stir and allow to stand. When all has dissolved, pour the liquid into a small beaker and add very slowly about 3 c.c. of strong sulphuric acid. Stir the liquids together with a glass rod; a large quantity of steam will be given off and a white solid substance will be left behind.

(*b*) Place a little distilled water in a beaker and cautiously add, drop by drop, a little strong sulphuric acid. The two substances will unite and form a liquid compound of sulphuric acid and water, and great heat will be produced by the action.

(*c*) Dissolve a small quantity of carbonate of sodium in distilled water, and allow to stand until all has dissolved. Now drop in a little sulphuric acid. An abundant evolution of gas will take place. Two liquids have produced a gas.

(*d*) Place a few drops of mercury in a small dish and pour on it a little strong nitric acid. Immediate action will take place, and a reddish-brown gas will be evolved.

Allow to stand for a little time, when the whole mass will become converted into a white solid. Thus the two liquids have formed a gas and a solid.

Experiment 10.—The modes of change mentioned above between a gas and a liquid may be illustrated by the following:—

(*a*) Crush a crystal of sulphate of copper in a mortar, place the powder in a beaker, and dissolve it in distilled water. When all has dissolved, attach a glass tube to the sulphuretted hydrogen apparatus and allow the gas to bubble through the blue liquid. After a little time the whole tube will appear to be filled with a black substance. This is a solid body and can be separated from the liquid by filtration through filter-paper, and then dried.

(*b*) Into a cylinder full of sulphur dioxide pour a solution of potassium permanganate and shake. The highly-coloured liquid will become quite colourless, in consequence of the action of the gas upon it. Another liquid has been formed.

(*c*) The cases where a gas and a liquid act upon each other and produce a gas are somewhat rare. The following experiment is an example of this mode of change. Into a jar of chlorine gas plunge a piece of paper moistened with a little turpentine. Chemical action will immediately occur between the gas and the hydrogen of the turpentine, and the heat will be so great as to ignite the paper. Before this happens, however, a gas will be produced which fumes very strongly in the cylinder. This gas is hydrochloric acid.

Experiment 11.—The changes between a solid and a gas may be shown as follows:—

(*a*) Place a small piece of dry phosphorus in a dry deflagrating spoon, set it on fire, and then place it into a gas cylinder filled with dry air or with dry oxygen. The phosphorus will continue to burn for some time, producing dense white clouds, and on allowing to stand, a white solid will be found to be deposited on the sides of the cylinder.

(*b*) Repeat the preceding experiment, but with the cylinder filled with dry chlorine instead of air, and do not light the phosphorus; it will ignite itself. After the phosphorus has burnt out, small oily drops will be observed on the sides of the cylinder.

(*c*) Place a little powdered lead acetate at the bottom of a dry test-tube and pass on it from the Kipp's apparatus (see Fig. 17) some sulphuretted hydrogen. The white salt will immediately be turned black. Place your thumb over the end of the tube and shake; the smell of the sulphuretted hydrogen will have disappeared and the smell of acetic acid will be noticed.

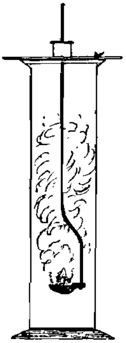

FIG. 4.

Finally, the actions between a solid and a liquid are illustrated by:—

Experiment 12.—(*a*) To a small quantity of solid caustic soda (sodium hydrate) placed in a dish, add a few drops of strong sulphuric acid. Steam will be given off and a white crystalline solid substance will be left behind.

(*b*) Into a small beaker containing hydrochloric acid add a small quantity of mercuric oxide; on warming, the mercuric oxide will dissolve, forming a clear liquid.

(*c*) Place some carbonate of sodium at the bottom of a tall beaker and drop on it a few drops of sulphuric acid. A violent frothing and effervescence will take place and a gas will be produced. To show that this is the case, place a lighted taper down into the beaker, after the action has gone on for a little time; the taper will not burn because the gas has driven out the air and now fills the beaker.

The foregoing experiments are samples of the different ways in which chemical action can occur, but it must not be supposed that all bodies can be made to act upon each other; we find that some substances cannot be made to act upon each other at all. Even in the case of some that do react, very great difficulties are experienced in causing the change. In endeavouring to bring about the changes the chemist uses every artifice that is known. He employs every degree of heat from the very lowest temperature known (below that of liquid air), up to the very highest—that of the electric arc. He also makes use of light, electricity, as well as every variety of pressure, both enormously great and exceedingly small. From his study of the behaviour of certain classes of bodies when treated in a particular manner he is sometimes able to predict that a certain substance belonging to a class will behave in a manner similar to the other bodies of that class. This is often quite true, but it is not invariably so, and it must be carefully remembered that all such predictions must be verified by actual experiment before they can be received as true.

Among the large number of chemical changes there are many of a similar character. These can be placed into classes. Two of such classes are of great importance; they are—first, those in which a substance consisting of two or more different kinds of matter can be resolved into less complex combinations; and secondly, those in which a complex substance can be made by uniting less complex ones. The first kind is essentially a splitting up and is called *analysis;* the second is essentially a building up, and is called *synthesis.* By both methods we are enabled to find the composition of a substance. When analysis is carried as far as it can possibly be, it is found that we arrive at certain kinds of matter out of which we can make nothing else. There are at present about seventy of these different kinds of matter known, but many of these are of extreme scarcity, and only seldom met with. Also more powerful means of breaking up matter are being introduced, and fresh discoveries are therefore constantly being made, so that this number is increasing. Each of these different kinds of matter is called an *element.* These elements are, as it were, the stones with which the chemist builds. Out of these, combined with each other in all kinds of proportions, every substance is formed. Chemists employ certain symbols to represent these elements. A list of these will be found in any work upon theoretical chemistry. The student is expected to make himself acquainted with these, as well as with the formulæ of the commoner chemical substances. He is also expected to make himself familiar with the use and significance of chemical equations. If this has not been already done, the student should do so while he is working through the experiments detailed in the next chapter.

CHAPTER III.

ACTION OF HEAT, WATER, ACIDS, AND ALKALIES UPON VARIOUS SUBSTANCES.

THE changes which bodies undergo when they are heated are some of the most important which the chemist has to study. There are practically two ways in which substances can be tested by this agent: first, they can be heated in a closed vessel or out of contact with the air; or they can be allowed to come freely into the presence of the air whilst being warmed. As will be abundantly proved later on, there is an essential difference in the two cases. Perhaps the simplest illustration of this is a matter of common knowledge. When we burn coal in an open fire we get, when it is completely burnt, ashes left behind which are gray, red, or white according to the kind of coal used; but when the same coal is strongly heated in a closed fire-clay tube, as in the making of ordinary gas, we get coke left behind; which coke when again heated in an open fire will burn away to the same kind of ash.

The source of heat usually employed by the chemist is the Bunsen burner, but very often the blow-pipe is employed, and when great heat is required furnaces of various kinds are used. The use of the blow-pipe will be treated of in a later chapter, but it is not proposed to touch upon experiments requiring the use of the furnace.

Almost every variety of vessel for holding the substance is used, but when examining the effect of heat upon it alone, either glass tubes, or porcelain crucibles, or dishes are employed. When the heat required is moderate, *i.e.* only two or three minutes in the Bunsen flame, ordinary glass test-tubes may be used; but when a longer exposure to the heat is necessary, tubes of harder glass are required. These do not melt so easily as ordinary test-tubes, and they would be better to use in every case except that they are more expensive and are very apt to crack when a liquid is heated in them. The best size of test-tube to use is about 12 mm. diameter and 10 cm. long.

When testing the effect of heat upon the dry substance, the tube is first made thoroughly clean and dry. A little of the substance is placed in it and heat applied. This must be done carefully. Hold the tube in a slightly slanting position and, at first, just about 1 cm. above the top of the flame. Move the tube into and out of the hot space continuously and note any change which may occur. Gradually lower the tube until it is fully immersed in the flame, keeping up the movement all the time. By proceeding in this way there is very little liability to cracking, and it can be seen whether moderate or strong heat is required to produce the changes.

The following experiments have been selected in order to give the student examples of some of the typical changes which take place when substances are heated, and to give him an opportunity of cultivating his powers of observation. Careful notes of all the effects produced should be made. These must be neatly copied into a note-book and handed to the teacher for examination. In order that an idea may be obtained of the way the notes should be kept, the earlier experiments are described in some detail.

Experiment 13.—*Effect of Heat upon Iodine.*—Place a few crystals at the bottom of a test-tube. Notice the colour of the crystal and the shape. Warm gently as directed. The crystals will be observed to become liquid (this is spoken of as *fusing*), and at the same time a beautiful violet vapour will be given off. This vapour will gradually fill the tube and run over the side, when it will be observed to fall through the air, showing that it is a much heavier vapour than air. As the heat is continued, more and more of the substance vaporises until the end of the tube which has been in the flame becomes quite clean and the whole of the iodine has vaporised. Now allow the tube to cool down. The violet vapour will become less, but on looking at the sides of the tube they will be seen to be covered with fine crystals of the same shape, but perhaps smaller than those originally taken.

This experiment might be entered in the student's notebook in the following manner:—

EFFECT OF HEAT UPON IODINE.

Appearance.—A crystalline substance.

Crystals.—Flat plates of a black colour and with a metallic lustre. They have an unpleasant odour and stain the skin of a dark brown colour.

As soon as a moderate heat is applied, the substance melts and violet-coloured vapours are given off. These gradually fill the whole tube and run out at the top, falling through the air, thus showing that they are heavier than air. When the tube is allowed to cool, the vapour gradually disappears, and small crystals of the same shape and colour as those originally taken are seen sticking to the sides of the tube. After the heating, the bottom of the tube is quite clear, showing that all the material has volatilised.

This process of heating a solid body until it vaporises, and then condensing the vapour upon a cold surface, is called "Sublimation."

Experiment 14.—*Effect of Heat upon Potassic Chlorate.*—Place in a dry tube (preferably of hard glass) a few crystals of this substance. Heat as directed. Notice that very little effect is caused with a gentle heat, but that a greater causes the substance to melt and then to boil. Hold a glowing wooden match in the tube when the boiling has commenced and notice that it is rekindled, thus showing that a gas is evolved which aids combustion more than air does.

Note appearance on cooling, and write full details in note-book.

Experiment 15.—*Effect of Heat upon Lead Nitrate.*—Substance decrepitates with loud noise, fuses and gives off reddish-brown fumes which rekindle a glowing match; on cooling, a brown mass is seen to be left in the tube.

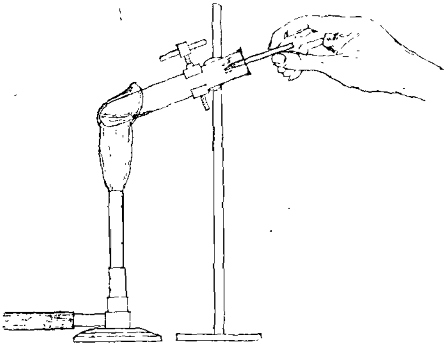

FIG. 5.

These experiments show the necessity of testing for any gas which may be given off. This should always be done. The tests to be made should be :—

1. Colour and odour.
2. Whether gas will burn or support burning.
3. Whether gas or fumes are acid or alkaline.
4. If carbon dioxide is the gas produced.

The second of these can be done by holding a wax match in a small piece of bent copper wire of such a shape that it can be lowered into the tube, but at the same time allow the match not to touch the sides. No. 3 is done by holding a small piece of moistened litmus-paper in the tube. If gas is alkaline, red paper will be turned blue. If acid, blue paper will be turned red.

The testing for carbon dioxide is best done as follows. Make a fine jet on a piece of glass tube. Dip the end into clear lime-water. The lime-water will run up inside the tube. Allow all liquid to run away that will. Now place tube inside the test-tube and gently suck the gas into it. If carbon dioxide is present, the lime-water will be made milky. (Tilden.)

There are frequently other gases given off; *e.g.* sulphur dioxide (recognised by its suffocating smell of sulphur), but many of these require special tests and are less common than the above. The following substances may be given for practice :—

Mercuric Oxide (HgO); Ammonium Chloride (NH_4Cl); Ammonium Carbonate; Ammonium Nitrate (NH_4NO_3); Sugar ($C_{12}H_{22}O_{11}$); Red Lead (Pb_3O_4); Sulphur; Potassium Hydrogen Sulphate ($KHSO_4$); Calcium Carbonate ($CaCO_3$) (hard glass tube and great heat); Lead Nitrate ($Pb(NO_3)_2$); Mercuric Nitrate ($Hg(NO_3)_2$); Ferrous Sulphate ($FeSO_4$); Alum; Magnesia (MgO); Acetate of Lead (Sugar of Lead).

Action of Water upon Substances.

The effects produced may be studied in either test-tubes, beakers, or porcelain dishes. They are very various: sometimes the substance is not altered, sometimes it dissolves either wholly or partially, sometimes chemical action resulting in the production of great heat is brought about, or a new substance differing in colour or appearance is produced. The following experiments will illustrate the changes. (The crystallisation of salts from water will be treated of in the following chapter.)

Experiment 16.—*Action of Water on Calcium Oxide* (*Lime,* CaO).—Place a piece of common quick-lime in a dry beaker, and pour a little water upon it. After a minute or two the hard lime will begin to crumble to powder, and an abundant evolution of steam accompanied with a hissing noise will take place. The hard stone will become a white powder. In this case a chemical action has taken place between the oxide (CaO) and water, and a new substance, the hydrate (CaH_2O_2), has been formed. Now add a much larger quantity of water and stir well together. Allow to stand, stirring from time to time. A white substance will be observed to settle to the bottom, showing that the hydrate has not entirely dissolved. Has any of it dissolved? To answer this question we must separate the solid from the liquid. This is done by filtration or decantation. In this case decantation is better. When the whole has stood for some time without disturbance, pour off a little of the perfectly clear liquid into a clean porcelain dish. Place the dish over a flame and boil off the water. A small amount of a white solid will remain in the dish, showing that a little solid was dissolved in the liquid.

Experiment 17.—*Action of Water upon Sodium.*—Half-fill a dish with distilled water. Dip pieces of blue and red litmus-paper into it and observe that neither is changed. Now cut off a small piece of sodium and drop it on the water. It will run over the surface very rapidly, accompanied with a hissing noise. Sometimes when it is nearly all used up a yellow flame will burst out. This flame can be produced if a lighted match be held near the rolling sodium. After the action has ceased, test the water again with litmus-paper; it will be found that it is now alkaline. If the sodium before putting into the water had been wrapped round with a dry piece of wire gauze and this thrown into the water, it would sink, and bubbles of gas would be observed to be given off. Thus water acts upon sodium, producing a colourless gas and forming an alkaline liquid; if this liquid be evaporated, a white solid body will be left.

The action of water can be studied with the following:—Sodium Chloride (salt) entirely dissolves (ordinary samples sometimes leave a slight residue owing to impurities); Sodium Hydrate, NaHO (caustic soda); Potassium; Anhydrous Copper Sulphate (white substance dissolving to form a blue liquid); Ammonium Nitrate (solution accompanied with lowering of temperature); Calcium Sulphate (use Plaster of Paris and notice the "setting" when a small quantity of water is used, and the partial solution when a large quantity); Phosphorus Pentoxide (rise of temperature and acid solution); solution of Antimony Chloride (use large quantity of water and notice the formation of a white precipitate); solution of Bismuth Nitrate (similar to Antimony Chloride).

ACTION OF ACIDS UPON BODIES.

In chemical changes which occur between acids and other bodies we find a difference owing to the nature of the acid as well as its strength and temperature. Many actions are common to all acids, but some are peculiar to the individual acid. This is especially the case with sulphuric acid, which in addition to its acid properties has added on, as it were, its remarkable avidity for water. If, therefore, this substance comes into contact with anything from which it can take water, or the elements of water, it will exert this power in addition to those properties which may be regarded as more particularly connected with acids. The detailed study of the effects of acids is a very extensive one; we shall therefore only illustrate the most important modes of action.

A very common result of the action of an acid upon a substance is to produce a gas as one of the products; this gas may be collected and examined separately. When this is done, however, different apparatus from that for simply testing the action of acids is required. Directions for preparing gases are given in Chapter VIII.

Experiment 18.—*Action of Acids upon Carbonates.*—Repeat Experiment 11 (*c*), using some other carbonate, such as a little powdered marble, and some other acid, such as dilute hydrochloric.

Experiment 19.—*Action of Acids upon Metals.*—Into a small flask of about 50 c.c. capacity, place a few pieces of granulated zinc, now pour in about 20 c.c. of dilute sulphuric acid (made by mixing one part of acid with four of water). A rapid disengagement of gas will take place. After the action has gone on for a few minutes, hold a light to the mouth of the flask; the gas will burn with an intermittent flame which is almost non-luminous, but tinged slightly yellow. The zinc will gradually dissolve (the addition of a little more acid will sometimes be necessary), but frequently a little black residuum will be left behind; this is due to some impurity (principally lead) in the zinc, which is not soluble in the dilute acid. In order to show the influence of the strength of the acid in modifying the change, repeat this experiment, but place the zinc in a dry test-tube and pour on it a few drops of strong sulphuric acid. A very minute action will take place, and the zinc will become coated with a white substance which floats about in the acid; practically no gas will be given off. Now pour in a little water; immediately a violent action will occur and gas will be evolved. The explanation given of this is, that the acid acts on the zinc and produces zinc sulphate, which is insoluble in strong sulphuric, and thus it remains on the zinc, coating it, as it were, with a paint. The acid is thus unable to get to the zinc to act upon it and thus all action ceases. When the water is added, the sulphate is dissolved, and a fresh surface exposed for the acid to attack.

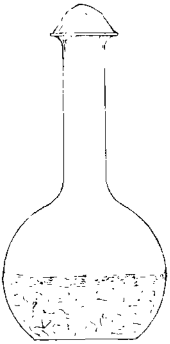
FIG. 6.

The following substances can be given for testing *with* acids:—Iron (filings or borings); Magnesium; Copper (turnings); Tin (granulated); Iron Sulphide; Sodium Sulphite; Tartaric Acid (with strong sulphuric, shows dehydrating action); Sodium Acetate (note odour and acid vapour); Oxalic Acid (strong sulphuric and heat); Salt; Potassium Iodide; Potassium Nitrate.

(*Note.*—The action on the metals should be studied with sulphuric, hydrochloric, and nitric, because the results are slightly different in each case.)

ACTION OF ALKALIES UPON SUBSTANCES.

In some cases these bodies act in a characteristic manner upon chemical substances. The term "alkali" is usually reserved for three substances:—caustic potash (potassium hydrate, KHO), caustic soda (sodium hydrate, $NaHO$), and ammonium hydrate (NH_4HO); but the action of the last is somewhat different from that of the potash and soda. This is partly owing to the fact that on heating the ammonium hydrate, it gives off ammonia. From this circumstance ammonium hydrate is sometimes spoken of as the "volatile alkali." The experiments may be studied in the same way as the previous ones, no special directions are required, and the following substances may be used to experiment upon:—

Ammonium Chloride (with potash and soda); Ferric Chloride (solution of, in water); Ferrous Sulphate (solution of, in water); Copper Sulphate (solution, note difference between ammonium hydrate and the others); Zinc Sulphate (solution); Lime (use the solid CaO, and drop the solution of the alkalies on to it, note difference with NH_4HO).

CHAPTER IV.

PREPARATION OF SUBSTANCES BY CRYSTALLISATION FROM SOLVENTS.

When a substance is dissolved in a solvent, and that solvent is slowly driven off either by heating or by spontaneous evaporation, it is usually found that the substance separates in the solid state in masses, which possess a certain definite shape. Each of these masses is called a crystal. The crystal may consist of the pure substance only, or generally of the pure substance united, perhaps chemically, with some of the solvent. Thus if copper sulphate be dissolved in water, and the water be gradually driven off by heat, the substance separates from the fluid in large blue crystals which consist of the sulphate united with about three-fifths of its weight of water. Chemists are undecided whether to regard such combinations as chemical ones or not. But it is certain that the water can be easily separated, for if we heat this substance to about 250° C., the water is driven off, and a white powder without any definite shape remains. Water which is combined in this way is called "Water of Crystallisation," and its presence seems to be essential to the existence of the definite shape of the crystal.

Different substances crystallise in different shapes; thus we have cubical crystals, octahedral crystals, etc. But many substances of an allied chemical nature crystallise in the same shape; thus, for example, salt, potassium chloride, potassium bromide, and potassium iodide, which are all of similar chemical constitution, crystallise in the same shape. It is found that one of the best ways of separating a substance from impurities is to crystallise it over and over again. Moreover we find that, generally, the largest and best-defined crystals consist of the purest material.

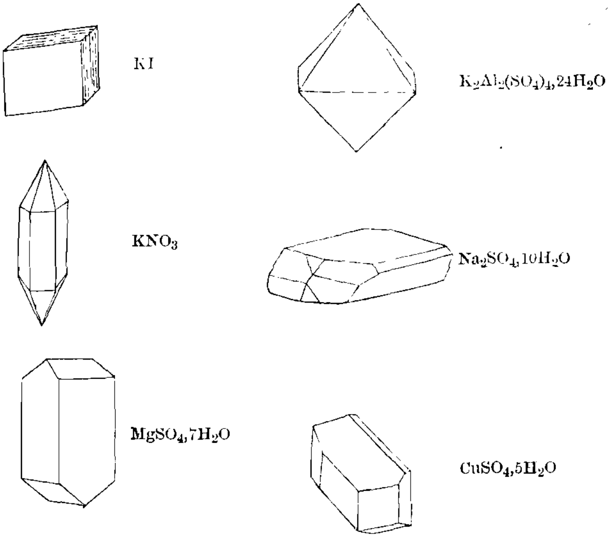

FIG. 7.

Crystals may be formed from any solvent, and in some cases the solvent unites with the substance just as water does; but the crystals obtained from one solvent frequently differ in shape from those obtained from another.

Very often the amount of water which is combined, and therefore also the shape, depend upon the temperature at which the crystal is formed. From this cause it is sometimes found that crystals of different shapes are mixed together in the same "crop." This is prevented by allowing the crystallisation to take place very slowly. This should always be done if regular and well-defined crystals are required.

The formation of crystals is considered to prove that at a certain temperature a solvent can only hold a certain definite amount of a substance dissolved in it. When it has this amount, the solution is said to be "saturated." If by any means a little of the solvent is withdrawn, or the temperature is altered, then the same amount of material cannot be kept in solution and some separates out, forming whilst doing so the crystal. Almost all substances are more soluble in hot than in cold liquids, and therefore crystals are usually obtained when a solution is warmed and allowed to cool. Occasionally a solution will cool down below the temperature at which it ought to deposit crystals without forming any. When this is the case the whole mixture is in a state of unstable equilibrium, and this condition is upset by the slightest cause, such, for instance, as shaking, or dropping into the liquid a small piece of the substance dissolved. When this is done, the formation of crystals will commence immediately, and frequently a great rise in temperature will take place. The solution in this condition is said to be "super-saturated." When the crystals are obtained, the student should make sketches of them. It is unnecessary to attempt to sketch the whole mass, and of little value when done. It is much better to fix the attention on one or two of the most regular ones and to sketch them. A little practice will reduce the difficulty.

Experiment 20. — Preparation of Crystals of Alum. — Powder about 30 grms. of alum in a mortar, and place in a beaker with about 40 c.c. of distilled water. Warm gently with constant stirring until all has dissolved. If the solution is not clear, it must be filtered. Pour the clear solution into an evaporating dish and warm until it is reduced to about five-sixths of its bulk. Cover the dish with a loose cover, and put it aside in a place where it will not be disturbed. After four or five hours a good crop of regular crystals will be obtained. If this is not so, drive off a little more water by heating, and again allow to stand. Now pour off the liquid from the crystals into another dish, evaporate a little more and obtain another crop. Drain the crystals as dry as possible, and then turn them out of the dish on to some dry blotting-paper, and complete the drying. Finally, select some of the most regular ones and sketch them.

In making *crystals*, remember that the more slowly the solvent is removed, and the quieter the solution is kept, the more regular and larger the crystal. Sometimes it is inadmissible to *warm the solution*. When this is the case the solvent is either allowed to spontaneously evaporate under a bell jar, under which is put at the same time some substance, such as strong *sulphuric* acid or fused calcium chloride, to absorb the water as fast as it evaporates, or the solution is put under the receiver of an air-pump along with the sulphuric acid and the air pumped out, when the solvent evaporates and is absorbed by the acid.

Most substances can be obtained in the crystalline state, and there is therefore no lack of material to experiment with. The following will be found to give good results :—

Potassic Iodide or Bromide ; Sodium Sulphate ; Potassic Nitrate ; Potassic Chlorate ; Copper Sulphate ; Lead Nitrate ; Ammonium Chloride ; Sodium Phosphate : Magnesium Sulphate ; Chrome Alum ; Potassium Ferrocyanide ; Ammonium Oxalate.

CHAPTER V.

THE BLOW-PIPE AND ITS USE.

THE employment of the blow-pipe as an aid in finding out the chemical nature of substances was made use of very early in analysis. The introduction of the *Bunsen burner* has somewhat curtailed its use, but it is still a most valuable little instrument, and is capable of yielding results in a few minutes which can only be obtained by long and tedious operations in any other way.

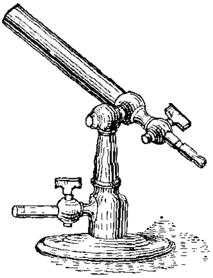
FIG. 8.

It is simply a tube through which a current of air can be sent into the interior of a flame. When a small quantity of substance is required to be heated this current is sent from the *mouth*, and the instrument is a "mouth blow-pipe." But when a large body of flame is required, the blast of air is usually obtained from a bellows which is worked by the foot; in this case we have a "foot blow-pipe."

The jet from which the air issues, and which is placed in the flame, is made of *metal*, and has a very fine opening—a pin-hole. The hole should be accurately bored, in order that the air may issue in a straight line, and it is advisable that the jet should be capable of replacement by a new one when it becomes corroded.

The proper use of the mouth blow-pipe requires a little practice. Beginners blow too hard and use too big a flame to blow through. A piece of metal tube which just fits inside the tube of the Bunsen burner, and which has its upper end squeezed in and cut off at an angle, is a great convenience. Turn down the flame until it is a little bigger than that of a candle. Hold the nozzle of the tube just within one side of the flame and blow gently across it. In this way the flame will assume the appearance shown in the sketch: there will be an outer portion, A, to the flame, and an inner portion, B. By altering the inclination of the jet, the flame can be directed in any required direction. When blowing, extend the cheeks and breathe through the nose. After a few trials this will be easy of accomplishment, and a long blast will be kept up with very little fatigue to the operator.

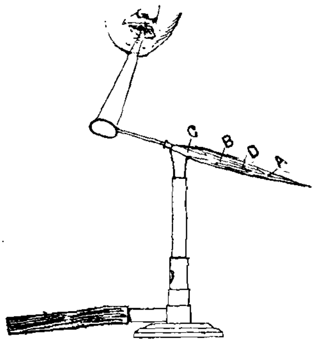

FIG. 9.

The blow-pipe affords us a means of putting substances under two distinctly different sets of conditions. In the first case, if the body be put at A, or anywhere *outside* the space CBD, it will be made very hot and surrounded on all sides by hot air. All the conditions will therefore be favourable for combination to occur between the body and the oxygen of the air. Such a combination we find very frequently does occur, and an "oxide" of the body, or of some constituent of it, is formed. This portion of the blow-pipe flame is for this reason frequently spoken of as the "oxidising flame." The case is quite different within the space marked DBC. Here we have not quite so much heat, but we have very little, if any, air; and instead we have a quantity of unburnt gases, which are anxious to unite with oxygen. This they will take from any substance with which they come into contact, and hence in this part of the flame bodies are deprived of their oxygen if they have any. This part of the flame is therefore called the "reducing flame."

The foot blow-pipe is used for glass-working, especially when hard glass is employed, and also for heating substances to a greater degree than can be obtained with an ordinary burner. In this case also there is a tendency to blow too hard. Remember it is quite easy to send more air through the flame than can combine with the gas; this excess of air only cools the flame. Make the up-stroke with your foot quickly, and the down-stroke slowly.

The substance to be heated is placed upon a suitable support. This is usually charcoal; but sometimes platinum foil or wire is used, and in others crucibles of platinum or porcelain. For ordinary work charcoal possesses many advantages: thus it is a much worse conductor of heat than the metals; it is infusible; its porosity enables it to absorb fusible substances which are heated on it, whilst infusible ones remain upon the surface; then, finally, it will assist operations conducted in the reducing flame because it is itself ready to combine with oxygen. Pieces which are compact and as free as possible from cracks should be selected. It is sometimes difficult to get good charcoal; in this case Griffin's substitute will be found to be excellent in every respect.

The following experiments illustrate the use of the blow-pipe:—

Experiment 21.—Make a little conical hole, about 4 mm. deep, in a piece of charcoal. Take a small crystal of silver nitrate and crush it to powder. Place some of the powder in the hole in the charcoal. Now hold the charcoal in the blow-pipe flame so that the substance shall be in the *reducing* part. As soon as the heat touches it, the nitrate will melt and then become red-hot and cause the charcoal to sparkle (called "deflagration"), and minute globules of white metal will be left. The nitrate has thus been "reduced" to silver.

Note.—In cases of reduction similar to the above, it is usual to mix the substance with three or four times its weight of sodium carbonate. This when heated is itself a reducing agent, and hence we have the effect of the flame, of the charcoal, and of the sodium carbonate all added together. Potassium *cyanide* is another substance used for the same purpose.

Experiment 22.—Place a small quantity of crushed alum in a cavity in a piece of charcoal. (A fresh hole must be used each time.) Heat it before the blow-pipe. (Some changes will occur equally well in either flame—this is one.) The mass will swell up (said to "intumesce"), and a large quantity of steam will be given off. Presently a white powder will be left, and no matter how long you heat, no change will be produced : the substance is infusible. Now allow to cool and then moisten the white mass with a solution of cobalt nitrate and again heat. The white mass will change to a fine blue one. This is due to a combination taking place between the oxides of aluminium and cobalt which are formed by the heating.

Experiment 23.—*The Borax Bead.*—Take a piece of platinum wire and bend one end round into a little loop. Dip the loop into powdered borax and heat. The salt will swell up, and give off steam, but presently will sink down into a colourless liquid filling up the loop. Now remove from the flame and allow to cool. This is a borax bead. Touch it with a very small quantity of potassium chromate and again heat. Then allow to cool, when the bead will be seen to be of a green colour.

Note the yellow colour given to the flame during these heatings. This is due to the sodium which is contained in the borax. Borax beads may be obtained, and the colours given to flames shown, by heating in a Bunsen burner as well as in the blow-pipe flame.

The following substances may be given for experimenting with:—Lead Acetate, Sodium Chloride, Copper Sulphate, Bismuth Nitrate, Ferrous Sulphate, Zinc Sulphate, Magnesium Sulphate, Barium Chloride, Calcium Carbonate, Tin Oxide.

In borax bead:—Cobalt Nitrate, Nickel Sulphate, Manganese Sulphate, Copper Sulphate.

Note.—Remember to moisten with solution of cobalt nitrate when a white residue remains, and to add sodium carbonate or potassic cyanide if results are difficult to obtain.

CHAPTER VI.

REAGENTS AND THEIR USE.

A VERY important part of practical chemistry is the testing of unknown substances in order to find out their composition. Many of the experiments already described will have shown the student that some bodies behave in such a characteristic manner when heated or acted upon by acids that they may be easily recognised. Other substances, however, are not so influenced. But almost all bodies can be made to show some peculiarity when tested, either in a particular way or with a particular substance. This peculiarity serves to distinguish the substance from others. Whenever the phenomena are brought about by the addition of known substances to the unknown, the substance causing the change is called a "reagent." Generally the reagent is in the liquid state, solids being dissolved in some solvent; but in some few cases the substance is in the solid form, and in still fewer in the gaseous.

The nature of the phenomena produced varies considerably. We have already studied the action of acids and water upon bodies, and we need not refer to that again. By far the larger number of "tests," as they are called, are made by adding to a solution of the unknown substance another liquid (usually a solution) of known composition, and observing the change produced. Some common kinds of change are:—an alteration of colour of the liquids, formation of a gas which bubbles out of the liquid, or the production of a "precipitate." This last is the name given to a solid substance which is sometimes formed when two liquids, or a gas and a liquid, are mixed. As a rule the solid sinks down to the bottom of the tube in which the liquids are mixed, hence the name; but whether it sinks or floats it is called a precipitate. The colour or appearance of this precipitate is very often sufficient to identify it, and as it was formed from the unknown substance by the addition of a certain reagent, the nature of the unknown substance is thus revealed.

Sometimes an additional test is required before the identity is completely made out. An example will make the process clear. The unknown substance is a clear liquid of a blue colour. I place a little of it in a test-tube and with great care drop into it about one drop of dilute ammonium hydrate. Immediately there is formed a light blue solid which sinks to the bottom of the tube. Now I add more ammonium hydrate. The light blue solid disappears and the fluid becomes quite clear, but of a deep blue colour. So far as we know at present there is only one chemical element with whose compounds ammonium hydrate will do this. That element is copper, and we therefore conclude that the unknown substance is, or is mixed with, some compound of that element.

As a result of careful study extending over many years, chemists have found that there are some substances which produce changes in a greater number of bodies than others. These are therefore used as the common reagents. These include the three important acids:— sulphuric, hydrochloric, and nitric; and the three alkalies:—potassium hydrate, sodium hydrate, and ammonium hydrate. In most cases the precipitate caused by an acid is a "salt" of that acid; *e.g.* sulphuric acid forms sulphates, hydrochloric acid forms chlorides; and in the case of the hydrates the precipitates formed are "hydrates." Thus the white precipitate formed when hydrochloric acid is added to a solution of nitrate of lead is chloride of lead; while that produced when sodium hydrate solution is added to a solution of ferric chloride is ferric hydrate. In addition to the acids and alkalies there are a large number of other substances useful as reagents. These sometimes produce precipitates themselves or act upon those produced by other substances. Sulphuretted hydrogen is one of the most valuable of these. It is used either as a gas, and made to bubble through the liquid, or it is dissolved in water and a little of the solution employed. The reason why it is so useful is because many of the sulphides which it forms possess characteristic colours, and others behave in a particular way when treated with certain reagents.

The formation of a precipitate in any liquid is a proof that that particular substance (that is, the precipitate) is insoluble or nearly so in the liquid. But it does not follow that the substance will not dissolve in other liquids. In fact it is necessary frequently to confirm the deduction drawn from the production of the precipitate in the first place by trying how it will behave with some other reagent. Thus if I add a solution of calcium chloride to one of ammonium carbonate, the white ppt. (used as an abbreviation for precipitate) which I shall obtain will be calcium carbonate; but if I were to conclude that whenever I got a white ppt. with calcium chloride it must be calcium carbonate, I should be very wrong, because calcium chloride will form white ppts. with a great many substances. In order to make sure that the ppt. was the carbonate I must add a drop or two of hydrochloric acid, when, if the solid dissolves and gas is given off with effervescence, it is a proof that the white ppt. was calcium carbonate.

CHAPTER VII.

SIMPLE QUALITATIVE TESTING.

In working through the foregoing chapters the student must have been struck with the peculiar appearance of some bodies, and with the way in which these or others behave when either heated or acted upon with acids or other reagents. He will therefore be prepared to commence qualitative analysis. This study has for its object the discovery of the kind of the constituents of which a substance is composed. Now, as we have said, there are only about seventy absolutely different kinds of matter; these are called elements; and therefore qualitative analysis is really the finding out how many and which of these elements are present in a given substance. But the problem is made more difficult because the elements do not simply mix together in the same way that sand and sugar would mix, but they chemically combine with each other and form substances in which the characteristic properties of the element itself are entirely altered. Thus, for instance, no one would be able to say from casual observation that ordinary table-salt contained the greenish-yellow gas chlorine or the white metallic substance sodium. The principle underlying the testing is, that every element possesses some properties which are possessed by no other, and that some of these properties are capable of being brought out, no matter with what other elements it is combined. Thus we find that the element sodium has the power of giving a bright yellow colour to an otherwise colourless flame. This colour is alike produced whether the element itself is put in the flame or any one of the innumerable compounds of sodium with other substances. If, therefore, we hold a small quantity of an unknown substance in a Bunsen flame, and it colours the flame of the bright yellow colour which we know is produced by sodium, we conclude that the unknown substance contains that element. It is, however, very seldom that a single experiment will enable us to prove the presence or absence of a substance ; in general we have to make a series of tests by which we gradually narrow the field and finally reduce the elements to one. For example, if we get a white ppt. by adding hydrochloric acid to a colourless solution, we know that we must have compounds of comparatively few elements present. But if we now take this white ppt. and pour on it a little ammonium hydrate and it is turned black, we are sure that we had present in the colourless liquid some compound of the element mercury.

It is of course evident that the difficulty of the problems depends upon the complexity of the substance to be analysed, because not only are more tests necessary, but very often the presence of one substance interferes with, and sometimes entirely prevents, the characteristic tests for another. In consequence of this, when we know that the material which we are analysing is a "simple" substance, *i.e.* consists of a single chemical compound and not a mixture of two or more, we can reduce the number of tests which we must make in order to identify the body. It is, however, most important that the prescribed tests should be made in the proper order, because a test which is characteristic of a certain substance when a certain other substance is absent, is not necessarily so when that substance is present.

But in many cases it is not necessary that we should test for individual elements, for we frequently find that groups of two or more enter into the composition of a large number of substances, and these groups can be tested for as groups. Thus every sulphate contains the elements sulphur and oxygen, and possesses certain definite properties which are characteristic of sulphates as a class. Therefore if we test for a sulphate and find it, we know that sulphur and oxygen are present and united in the same proportion as they are in sulphuric acid.

In inorganic chemistry, by far the larger number of substances which are met with are either acids, bases, or salts. It is somewhat difficult to define these with absolute accuracy, but for practical purposes we may say that an *acid* is a body which reddens vegetable colours, has a sour taste (when it has a taste at all), and is usually corrosive. A *base* is a body which will when a liquid, or soluble in water, turn vegetable colours blue, and will take away the acid characteristics from an acid. Some bases have a bitter taste. A *salt* will not affect vegetable colours (*i.e.* it is neutral); when it has a taste it is somewhat metallic, and it is formed when an acid and a base are brought together. Now it is found that acids and bases possess certain properties which hold good no matter how they are combined. In fact it is almost only those properties mentioned above which they lose when they form combinations with each other. Therefore we find that a salt has the properties of both the acid and the base from which it was formed. For example, nitrate of sodium shows the tests for nitric acid as well as for sodium. Thus in testing inorganic substances it is usual to test for the bases and then for the acids, and of course separate and distinct tests have to be applied for each. When a "simple" substance is being examined, only one base and one acid can be present. (In some rare cases we may have two bases and one acid.) We shall deal with simple substances only, and, moreover, only with the more important acids and bases. After working through this book, the student will be able to take up the study of qualitative and quantitative analysis in some of the larger manuals.

The most important acids are sulphuric, hydrochloric, nitric, carbonic, and hydrosulphuric.

The salts formed by these being known as sulphates, chlorides, nitrates, carbonates, and sulphides.

The selection of the most important bases is more difficult, but we may consider sodium, potassium, ammonium, magnesium, calcium, barium, zinc, aluminium, iron, copper, lead, and silver as being the most common.

We shall therefore study the principal tests for these substances, and finally give a scheme of testing whereby they may be detected if present in an unknown substance which is submitted to analysis.

As a rule the analyst treats a solid substance in two ways:—first, in the solid state, and secondly, when dissolved in some solvent. The former is spoken of as the "Examination in the Dry Way," and the latter as the "Examination in the Wet Way." Sometimes a dry-way test is the most characteristic, sometimes a wet-way one. It is always advisable to confirm your conclusion by as many tests as possible. The dry-way tests include the action of heat upon the substance as described in Chapter III., as well as the effect of heating before the blow-pipe. The wet-way tests consist in the addition of reagents as mentioned in the last chapter. The substance directed to be used for making the tests is in all cases one of the most abundant materials which contain the particular base or acid.

CHARACTERISTIC TESTS FOR BASES.

Silver.—Compound used:—Silver Nitrate, $AgNO_3$ ("Lunar Caustic").

(1) Mix a little of the substance with carbonate of sodium, and heat in the blow-pipe flame as directed in Experiment 21. A white globule of silver will be obtained. When cold remove the globule from the charcoal and

hammer it on an anvil. It will flatten out and not crack, showing that it is *malleable.*

(2) Place one or two small crystals in a clean test-tube, add a little distilled water (in chemical testing ordinary water must never be used), and shake until the crystals are dissolved. Now add a drop or two of hydrochloric acid (HCl). A curdy white ppt. will be produced. This is silver chloride (AgCl). Allow to settle, and pour off most of the fluid. Now add ammonium hydrate. The ppt. will dissolve, because AgCl is soluble in NH_4HO. If now nitric acid be added in sufficient quantity to more than neutralise the ammonium hydrate, the white ppt. is reproduced.

(The student should carefully think over what the various experiments which he makes teach him. Thus from the above he ought to learn that silver compounds readily yield their metal when heated with a reducing agent; that silver is a malleable metal; that $AgNO_3$ is soluble in water; that HCl forms AgCl when added to a solution of a silver compound; that AgCl is white, insoluble in water, hydrochloric acid, and nitric acid, but soluble in ammonium hydrate.

Corresponding lessons can be learnt from the other tests.)

Lead.—Compound used:—Lead Acetate, $PbC_4H_6O_4$ ("Sugar of Lead").

(3) Heated on charcoal with Na_2CO_3, a globule is obtained which is malleable, of a dull colour, and makes a mark on paper when rubbed across it.

(4) Dissolve in water and add HCl. A white crystalline ppt. is produced. Allow to settle, pour off most of the fluid, then add a large quantity of water and warm. The lead chloride (*i.e.* the ppt.) will dissolve. Now allow to cool; as the fluid cools, the ppt. will separate out again in the form of small white crystals. This is because lead chloride is much more soluble in hot water than in cold.

Copper.—Compound used:—Crystallised Copper Sulphate, $CuSO_4,5H_2O$ ("Blue Vitriol").

(5) Heated on charcoal with Na_2CO_3, a red globule of metallic copper is obtained.

(6) To the solution in water add a little HCl; no change except a slight alteration of colour is produced. Now bubble through the liquid a little sulphuretted hydrogen; a black ppt. will be formed.

(7) To the solution add one drop of ammonium hydrate; a light blue ppt. will be produced. Now add more NH_4HO; the ppt. will dissolve and a deep blue fluid will be formed. See Chapter VI.

Iron.—

Note.—Iron is one of those elements which form two distinct classes of compounds; one class containing more iron compared to the other substances combined with it, than the other. The compounds containing the larger proportion of iron are called "ferrous" compounds. They are usually easily converted into the other class called "ferric," by exposure to the air, or by being acted upon by some substance containing a large quantity of oxygen which it will readily part with, such as nitric acid. Ferric compounds are generally red or reddish brown; ferrous are green or white.

Compounds used:—(1) Ferrous Sulphate, $FeSO_4,7H_2O$ ("Green Vitriol"). (2) Ferric Chloride, Fe_2Cl_6.

(8) All iron compounds, whether ferrous or ferric, when heated on charcoal in the oxidising flame, leave a reddish-brown mass of ferric oxide, Fe_2O_3.

(9) A solution of a ferrous compound gives a white or nearly white ppt. with ammonium hydrate, rapidly turning green.

(10) A solution of a ferric compound gives a reddish-brown ppt. with ammonium hydrate.

(11) To convert ferrous compounds into ferric, take a small quantity of solution of ferrous sulphate, add two or

three drops of strong nitric acid, and warm gently. The solution will become brown, and a reddish-brown gas will be evolved. Allow to cool, and now add NH_4HO until a ppt. is obtained. This ppt. will be reddish brown, showing that the iron has been converted into the ferric state by the nitric acid.

Aluminium.—Compound used:—Alum, $Al_23SO_4,K_2SO_4,24H_2O$.

(12) When heated in the outer blow-pipe flame, aluminium compounds leave a white residue of Al_2O_3. If this be moistened with a solution of cobalt nitrate and again heated, it becomes of a fine blue colour.

(13) If ammonium hydrate be added to a solution of an aluminium compound, a gelatinous white ppt. of aluminium hydrate is produced. This ppt. is soluble in sodium hydrate.

Zinc.—Compound used:—Zinc Sulphate, $ZnSO_4,7H_2O$ ("White Vitriol").

(14) Zinc compounds when heated in the outer blow-pipe flame yield a mass which is *yellow* whilst hot, but becomes *white* on cooling. If this be moistened with solution of $Co(NO_3)_2$ and again heated, the mass becomes *green.*

(15) Solutions of zinc salts give no ppt. with NH_4HO, but if H_2S be passed through the solution, after the addition of the NH_4HO, a white ppt. of ZnS is produced. The same ppt. is formed if ammonium sulphide is added to the solution.

Barium.—Compound used:—Barium Chloride, $BaCl_2$.

(16) If a clean platinum wire be dipped into a little HCl, then into a barium compound, and then held in the colourless Bunsen flame, the flame will be coloured yellowish green.

(Platinum wire is called clean when, if it is made red-hot in the Bunsen, it imparts no colour to the flame. It is cleansed by repeatedly dipping it in strong HCl and heating it in the flame, and continuing this until the above is attained.)

(17) Solutions of barium compounds give a white ppt. with sulphuric acid, which is insoluble in HCl.

Calcium.—Compound used :—Calcium Chloride, $CaCl_2$.

(18) Calcium compounds colour the flame yellowish red when heated on platinum wire.

(19) Solutions of calcium compounds give a white ppt. with solution of ammonium carbonate.

Magnesium.—Compound used :—Magnesium Sulphate, $MgSO_4,7H_2O$ ("Epsom salts").

(20) When heated on charcoal in the blow-pipe flame, magnesium compounds leave a white mass. Moistened with solution of $Co(NO_3)_2$ and again heated, this becomes *pink.*

(21) The wet-way test for Mg is performed as follows :—Add a small quantity of a solution of ammonium chloride and ammonium hydrate and then solution of sodium phosphate; a white crystalline ppt. will be produced. If the solution is very dilute this ppt. may not form at once; it will, however, after standing, especially with shaking and stirring.

Ammonium.—Compound used :—Ammonium Chloride, NH_4Cl ("Sal-ammoniac").

(22) Heated in a clean dry test-tube all ammonium compounds volatilise. Many condense again on the cold part of the tube.

(23) Place a little of the substance in a test-tube, add a small quantity of a strong solution of sodium hydrate, and warm. Ammonia will be given off, and can be easily recognised by its odour and also by its turning a small piece of moistened red litmus paper blue.

Potassium.—Compound used :—Potassium Chloride, KCl.

(24) The most distinctive test for **potassium** is to heat a little of the substance on a clean platinum wire in the Bunsen flame. A peculiar pale lavender tint is given to it. If this flame is viewed through blue glass it appears red. By this means potassium can be detected in presence of sodium; for the power of sodium to colour the flame is so intense that when it is present the colour due to the potassium cannot be seen. But the blue glass prevents the yellow colour of the sodium flame being seen, and simply alters the appearance of the potassium flame to red.

(25) The tests for potassium when in solution are not very good. One of the best is to add to a *strong* solution of the substance, which should be neutral, a *strong* solution of tartaric acid. A white ppt. is produced. Both solutions should be cold, and the formation of the ppt. is promoted by shaking and allowing to stand.

Sodium.—Compound used:—Sodium Chloride, $NaCl$ ("Common Salt").

(26) Sodium compounds, as already stated, colour the flame an intense yellow. Sodium compounds are so prevalent that a yellow colour is almost always obtained when a substance is held in the flame. Even the yellow tint which a Bunsen flame possesses is due to the presence of sodium compounds in the dust, etc., in the air. The student must therefore remember that when he is testing an actual sodium compound he must get the flame *intensely* yellow.

(27) Since all sodium compounds are soluble in water there is practically no test for sodium in the wet way.

CHARACTERISTIC TESTS FOR ACIDS.

Sulphuric Acid.—Compound used:—Sodium Sulphate, Na_2SO_4.

(28) Sulphuric acid and sulphates are always tested for by adding to a solution a little hydrochloric acid and then

a solution of barium chloride. A white ppt. of barium sulphate will be produced. This substance is insoluble in all acids whether hot or cold, and hence its formation is a widely applicable test for sulphuric acid or sulphates.

Hydrochloric Acid. — Compound used : — Sodium Chloride, $NaCl$.

(29) Chlorides give a white curdy ppt. with a little nitric acid and solution of silver nitrate. The ppt. is insoluble even on boiling in nitric acid, but is readily soluble in ammonium hydrate.

Nitric Acid. — Compound used :— Potassic Nitrate, KNO_3.

(30) Most nitrates when heated in the dry state in a test-tube give off "nitrous" fumes (reddish-brown fumes with a disagreeable odour of strong nitric acid). Those which do not do this may be made to do so by adding one or two drops of strong sulphuric acid before heating.

(31) To a solution of a nitrate in a test-tube, which must be quite cold, add a clean crystal of ferrous sulphate and shake. Now hold the tube in an inclined position and pour down it very slowly a little strong H_2SO_4. If properly done, this will form a layer at the bottom of the tube. At the plane of contact between the acid and the liquid above, a brown colour will be formed. The principle underlying this test is that the H_2SO_4 decomposes the nitrate forming nitric oxide as one of the products. This dissolves in the ferrous sulphate solution, forming a brown-coloured compound.

Carbonates. —Compound used :—Sodium Carbonate, Na_2CO_3.

(32) All carbonates either in the solid state or in solution give off carbon dioxide, when an acid (hydrochloric) is added to them. This may be known by its producing a turbidity with lime-water (p. 22).

Sulphides.—Compound used :—Ferrous Sulphide, FeS.

(33) Most sulphides are insoluble in water. The test for a sulphide is to add an acid, when sulphuretted hydrogen is given off (sometimes with effervescence like CO_2), which may be recognised by its smell, and also by its turning black a piece of filter-paper which has been moistened with a solution of lead acetate. Some sulphides are only decomposed by boiling with the acid.

EXAMINATION OF AN UNKNOWN SIMPLE SUBSTANCE.

The student has now to use the knowledge he has acquired in working through the foregoing tests to discover the nature of a substance whose composition is unknown to him. In doing this he must make use of every observation he can. If it is a liquid, he must note its colour. If a solid, its colour; its state, whether crystalline or amorphous; whether soluble in water or in acids; and any other property which shows itself. In regard to solubility, the body should be first tried with water; then with dilute HCl; then with strong, hot HCl; then with HNO_3 dilute and strong; and finally with aqua regia (a mixture of HCl and HNO_3). In beginning analysis it is well to deal only with substances which are soluble in water or in dilute acid.

The solution of the substance in water, or the given liquid, should always be tested with litmus paper to discover whether acid, alkaline, or neutral. In this connection it must be remembered that some salts give acid and some alkaline solutions when dissolved in water. Therefore it must not be concluded if the solution is acid or alkaline that therefore no base or acid need be tested for.

The tests must be performed in proper order, and after each test a note of the result entered in the note-book. The best way to do this is by employing three parallel columns—one for the experiment, one for the observation, and the third for the inference (*i.e.* what the substance is).

If a liquid is being examined and it is shown to be acid by the litmus test, it may be only an acid. In order to prove this, some of it should be placed in a small evaporating dish and evaporated to dryness. If no residue remains, the substance was an acid and no base *need* be tested for. If a residue is found, the substance is an acid salt. The residue should be taken and examined in the same way as a solid.

An alkali or a base would be shown by the absence of every acid and by the solution in water being strongly alkaline.

EXAMINATION IN THE DRY WAY.

Experiment 1.—Heat the substance in a clean dry test-tube.

Observation.	Inference.[1]
(*a*) Substance becomes liquid . .	Easily fusible salt
(*b*) NH_3 is evolved	Ammonium compounds
(*c*) Nitrous fumes are evolved . .	Nitrates
(*d*) A *white* sublimate is formed .	Ammonium compounds
(*e*) A *yellow* sublimate is formed .	Sulphides

Experiment 2.—Heat the substance on charcoal before the blow-pipe.

Observation.	Inference.
(*a*) Substance deflagrates	Nitrates
(*b*) White, infusible residue remains .	Compounds of Mg, Ca, Ba, Zn, Al.
(*c*) Moisten this residue (*b*) with solution of $Co(NO_3)_2$ and heat again	*Blue* mass . Al *Pink* mass . Mg *Green* mass . Zn
(*d*) Residue coloured :—	
Black	Cu compounds
Red brown	Fe ,,
Yellow whilst hot, *white* on cooling .	Zn ,,
Yellow red, possibly with some metallic globules	Pb ,,

---

[1] It must be remembered that the inferences stated here are only for compounds of those metals and acids whose tests are given above. For other substances these inferences would still be true, but others would have to be added.

Observation.	Inference.
(*e*) Substance *melts and runs into charcoal*	Salts of alkalies and Al
(*f*) Substance forms white fumes . .	Am compounds
(*g*) If the white *residue glows strongly* when heated by the blow-pipe . .	Ca compounds

Experiment 3.—Heat substance on charcoal with Na_2CO_3 in the reducing flame of the blow-pipe.

Observation.	Inference.
Metallic globules are obtained . .	Ag, Pb, or Cu compounds
(1) White and malleable . . .	Ag
(2) Dull colour, soft and marks paper	Pb
(3) Red colour	Cu

Experiment 4.—Moisten a clean Pt wire with HCl, dip it in the powdered substance and heat in the colourless Bunsen flame.

Observation.	Inference.
(*a*) Flame an intense yellow . . .	Na compounds
(*b*) Yellowish red	Ca ,,
(*c*) Yellowish green	Ba ,,
(*d*) Green	Cu ,,
(*e*) Pale lavender or light violet, which appears red when viewed through blue glass	K ,,
(*f*) Full lavender, more intense than (*e*)	Pb ,,

Experiment 5.—Heat in borax bead in the oxidising flame of blow-pipe.

Observation.	Inference.
Bead is yellow when *very* hot, becoming green and then blue when cold . .	Cu compounds

EXAMINATION IN THE WET WAY.

The mode of proceeding in order to obtain a solution has already been explained. In order to see if anything has dissolved, evaporate a portion to dryness in a small porcelain dish. If no residue remains, none has dissolved.

When treating with acid, be careful to note any evolution of gas.

Experiment 1.—To a little of the cold solution add HCl; a white ppt. will indicate the presence of Ag or Pb compounds.

Allow the ppt. to settle, pour off as much of the fluid as possible, add water and warm. If the ppt. dissolves and reprecipitates on cooling, lead is the element present. If it does not dissolve, add ammonium hydrate; this will dissolve the silver chloride at once.

Experiment 2.—If HCl has failed to produce a ppt., attach a clean tube to the H_2S apparatus (see p. 70), and bubble the gas through the solution. Be careful to pass the gas slowly, but to pass enough. A black ppt. will be formed if copper compounds are present.

If lead compounds are present, a black ppt. is frequently obtained with H_2S due to the formation of PbS. The reason of this is, because chloride of lead, which is formed when HCl is added to the solution, is slightly soluble, and therefore the whole of the lead will not be thrown out of solution. In case of difficulty in deciding whether the ppt. is due to copper or to lead, filter it off, and dissolve it in a little dilute HNO_3, and then add an excess of NH_4HO; a blue colour will indicate Cu, a white ppt. Pb.

Experiment 3.—If neither HCl nor H_2S produces a ppt., take a little of the original solution and add a few drops of strong HNO_3 and warm; then add ammonium chloride, and finally NH_4HO, until the fluid smells of ammonia. A white ppt. will be formed if Al compounds are present, and a red-brown ppt. if Fe. Both these elements would have been found in the dry way.

Experiment 4.—If ammonium hydrate has failed to produce a ppt., pass H_2S through the ammoniacal solution. If a white ppt. is produced, zinc is the element present.

Experiment 5.—To the solution to which NH_4HO was added and H_2S passed without any result, add solution of ammonium carbonate. If a white ppt. is produced, calcium or barium compounds are present. Filter the mixture and collect the ppt. on a filter-paper. Pour over it a little dilute acetic acid; it will readily dissolve. To the solution thus formed add a solution of potassium bichromate; a light yellow ppt. will be formed if Ba is present.

If Ba is not present, to the acetic acid solution add solution of ammonia oxalate and NH_4HO; a white ppt. will show the presence of calcium.

Experiment 6.—If no ppts. have been formed with NH_4HO, NH_4HS (formed when the H_2S is passed through the NH_4HO), or $(NH_4)_2CO_3$, add a solution of sodium phosphate to the cold liquid. Shake well and allow to stand. A white ppt. will show the presence of Mg compounds.

Experiment 7.—The only elements now left to be tested for are ammonium, potassium, and sodium. There are no good wet tests for these. The colour given to the flame is relied on to prove the presence of sodium. Potassium is also tested for by the flame; its presence may be confirmed by the tartaric acid test, and also by adding a little HCl and solution of platinic chloride, and evaporating slightly, when large yellow crystals of the double chloride of platinum and potassium will be formed. This test is made more definite by adding a little methylated spirit before evaporating.

Ammonium compounds are tested for by heating the solid substance with a little NaHO when NH_3 is given off.

The acid is tested for as follows:—

Carbonic (carbonates).—Carbon dioxide is given off when the substance is brought into contact with an acid. The gas does not smell, but makes lime-water milky.

Hydrosulphuric (sulphides).—Place a little of the substance in a test-tube, add HCl and warm if there is no action when cold. H_2S will be expelled and can be easily recognised.

Sulphuric (sulphates).—To the solution add a little HCl, and then solution of barium chloride; a white ppt. will be produced if a sulphate is present.

Hydrochloric (chlorides).—To the solution add a little dilute nitric acid and then silver nitrate solution. A white curdy ppt. will be formed if chlorides are present.

Nitric (nitrates).—The dry-way test for nitrates is a very good one. The wet-way one is described on p. 48. When testing simple substances, it is well to remember that all nitrates are soluble in water; hence if a substance is insoluble in that liquid, nitrates need not be tested for.

If the foregoing tests are faithfully carried out, very little difficulty will be found in determining qualitatively the composition of any simple salt. The way in which the work is entered in the note-book is important, and an illustration may therefore not be out of place.

Date.........

ANALYSIS OF SIMPLE SUBSTANCE.

Appearance.—A white powder. Minute fragments, crystalline, therefore probably formed by crushing larger crystals.

Examination in the Dry Way.

1. Heated in a dry tube	Moisture was evolved, and substance fused	Water of crystallisation and fusible salt.
2. Heated alone on charcoal	Substance fused and then ran into the charcoal. Edges of the flame were tinged green	Running into the charcoal would indicate an alkaline salt. The green flame either Cu or Ba.
3. Heated in reducing flame with Na_2CO_3	Mixture fused and ran into charcoal. No globules	Absence of Pb, Cu, and Ag.
4. Heated on Pt wire moistened with HCl	Flame tinged yellowish green. The green colour did not disappear until after prolonged heating	Ba or Cu compounds. Probably barium.
5. Heated in borax bead	Bead colourless	Absence of Cu.

Examination in the Wet Way.

Solubility.—The substance was found to dissolve in water, forming a colourless solution. Solution was neutral to litmus paper.

1. Added HCl to solution	No effect . .	Absence of Pb and Ag.
2. Passed H_2S through solution	No effect . .	Absence of Cu and Pb.
3. To original solution added HNO_3, *then* NH_4Cl, and then NH_4HO in excess	No ppt. produced .	Absence of Fe and Al.
4. Through solution from (3) passed H_2S	No ppt. . . .	Absence of Zn.
5. To same solution added $(NH_4)_2CO_3$	A white ppt. was produced	Presence of Ca or Ba.
6. The ppt. from (5) was filtered off, washed and dissolved in acetic acid, and solution of potassium bichromate added	A yellow ppt. was produced	Presence of Ba.

Examination for Acid.

1. To a little of the substance a little HCl was added and then warmed	No gas evolved .	Absence of carbonates and sulphides.
2. Added dilute HNO_3 and $AgNO_3$ solution	A white ppt. was formed. Soluble in NH_4HO	Presence of chlorides.

Result.—Base found	Barium.
Acid found	Hydrochloric.

Note.—The student should carefully think over all his results for future use. For instance:—The formation of $BaSO_4$ is used as a test for H_2SO_4, therefore it is insoluble in water. It would therefore have been useless to test this substance for H_2SO_4, because we have found it to be soluble in water. Also $BaCO_3$ was ppted. when $(NH_4)_2CO_3$ was added to the solution, therefore our substance cannot be $BaCO_3$, for that would have been insoluble in water.

Also barium sulphide would not be a white crystalline substance. Hence we need only test for hydrochloric and nitric acids.

Thinking over the experiments in this way not only saves a large amount of time, but makes analysis an excellent subject for training the mind.

CHAPTER VIII.

PREPARATION AND PROPERTIES OF SOME COMMON GASES.

Many of the elementary substances of common occurrence are gases, and as these play a very important part in chemical work of all kinds, it is necessary to study them more fully.

The most abundant substance in the world is oxygen, but as hydrogen is used as the unit for atomic weights as well as of valency, we will begin with that element.

Hydrogen.—This element is an essential constituent of all acids, which have sometimes been called hydrogen salts. It is very easily prepared by replacing it in an acid by some metal. This can be done by many metals and with many acids; but the most convenient metals are zinc and iron, and the most convenient acid sulphuric or hydrochloric. The apparatus used is shown in the sketch, Fig. 10. The flask A, of about 500 c.c. capacity, is fitted with an india-rubber bung with two

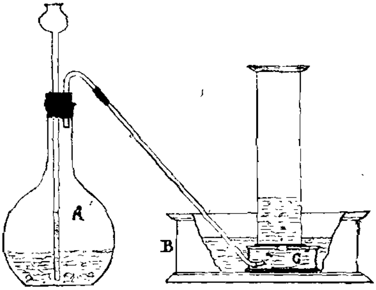

FIG. 10.

holes. Through one hole passes the thistle-headed funnel, and through the other the delivery tube to convey the gas to the pneumatic trough B. The "bee-hive" C is wholly immersed in water, and has one hole at the side through which the delivery tube passes, and another at the top to allow the gas to ascend into the cylinder. A small quantity of scrap or granulated zinc is placed in A along with some water. The cork is now put in, and a little sulphuric acid poured in through the funnel. Care must be taken that this latter dips below the liquid. The action commences almost at once. Allow the first portions of gas to escape, then put the end of the delivery tube under the bee-hive and collect the gas. When the cylinder is full, slip a glass cover which has been rubbed with a little grease under the end and remove it. Fill three cylinders.

Properties.—Take one cylinder and show that the hydrogen burns but will not support the burning of a taper, by putting a light to the end when it is open mouth downwards, then while the flame is still burning at the mouth, pass the taper up into the gas; it will be immediately extinguished. With the other two cylinders show the lightness of the gas compared to air. Hold one cylinder open mouth downwards, and the other mouth upwards. Simultaneously remove the covers, and keep them off for 1½ minutes, then replace them. Now try the two by a light. No hydrogen will be found in the one which was open mouth upwards, but the other one will be nearly full. Thus the hydrogen has gone up through the air and not down. (See also Experiment 19.)

The chemical change which has taken place may be represented by the following equation:—

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

Hydrochloric acid may be substituted for sulphuric in the above, and small scrap iron or iron filings for the zinc. When the latter is used the gas has a disagreeable odour. This is caused by impurities, compounds of carbon and hydrogen, contained in the iron. Hydrogen is odourless.

There are many other ways in which hydrogen can be made. It can be obtained from potassium or sodium hydrates by boiling them with zinc, but perhaps most important is its manufacture from water. Almost all metals will decompose water at some temperature or other; some, like sodium (see Expt. 17), decompose it at the ordinary temperature, but some require heat. Hydrogen is sometimes made on the large scale for filling balloons, by passing steam over red-hot iron.

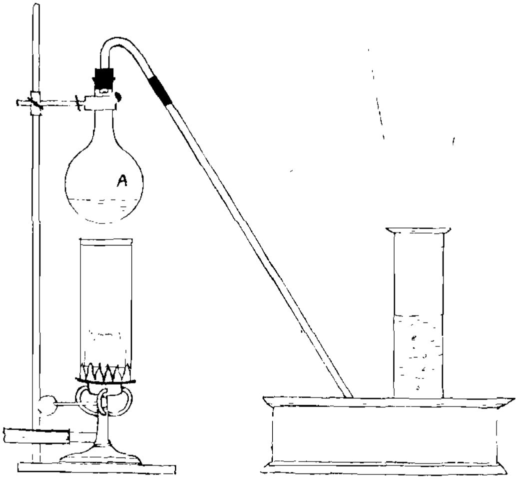

FIG. 11.

Oxygen.—This gas exists so largely in the air that it would be thought that it might be easily prepared from that source. It was from the air that Priestley first made it, and it is now made from it on the commercial scale, but not by the same process. But in the laboratory oxygen is almost always made from potassic chlorate. The apparatus is shown in Fig. 11. Into the hard glass flask A is placed a mixture of about equal parts of the chlorate and black oxide of manganese, both in powder. The mixture is heated by the Argand burner and the gas collected over water in the pneumatic trough.

It has been shown in Expt. 14 that potassium chlorate when heated alone will give off oxygen, but it is found that when mixed with the manganese dioxide it parts with its oxygen at a much lower temperature than when heated alone. The manganese dioxide is found unchanged at the end of the experiment, but the exact manner in which it acts is not well understood. However, practically, we find that when the dioxide is present we can get off the gas with the heat of an Argand burner, whereas without we have to use a Bunsen. On the first application of the heat the gas comes off very slowly, but after a time the mass inside the flask is seen to glow and the gas comes off with tumultuous violence. When this occurs the burner should be removed.

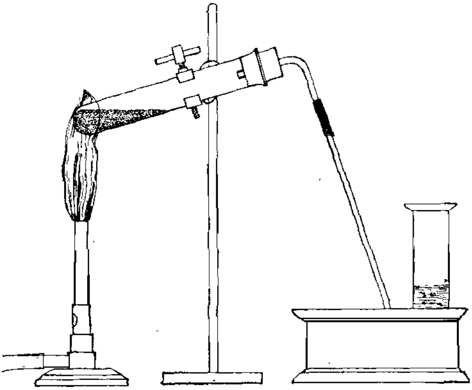

FIG. 12.

Oxygen can also be made by heating mercuric oxide or barium peroxide (as well as many other substances) to a red heat (Fig. 12). As these bodies can be made by exposing heated mercury in the one case and heated baric oxide in the other, to the air, these are methods for obtaining the gas from the air.

There are many other ways for making oxygen.

Properties.—Oxygen will cause a glowing match to burst into flame. Bodies that burn in air will burn with increased brilliancy in oxygen. This is easily shown by burning phosphorus and sulphur in cylinders of the gas, as in Expt. 11 (*a*). Also bodies which do not readily burn in air will burn in oxygen. Thus, tie a piece of steel watch-spring to the end of a deflagrating spoon by means of a piece of thin iron wire. Warm the extreme end of the spring and dip it into sulphur. Now light the sulphur, and while it is burning plunge the spoon into the oxygen. The heat of the burning sulphur will heat the iron so that it will burn with brilliant scintillations. The cylinder in which this is done should have about an inch of water at the bottom. In these cases of combination with oxygen, oxides are the bodies formed. Thus in the three cases above we have phosphorus pentoxide (P_2O_5), sulphur dioxide (SO_2), and triferric tetroxide (Fe_3O_4) formed. On coming into contact with water many of these oxides form acids. Thus, add a little water to the cylinders in which the phosphorus and sulphur were burnt, and shake, then test with litmus and it will be found that the liquids are acid; phosphoric and sulphurous acids have been formed. Noticing this, Lavoisier gave its present name ("acid-producer") to the gas. But acids are not formed when every substance burns in oxygen. Thus in the case of the iron an oxide insoluble in water is produced.

Oxygen combines with hydrogen with explosive violence. Take an ordinary soda-water bottle and one-third fill it with oxygen at the pneumatic trough. Then fill completely by passing in hydrogen. Now cork under water and remove. Wrap a cloth round the bottle, and then apply a light to the mouth. A violent explosion will occur, showing that combination has taken place. Steam will usually be seen on the sides of the bottle after the experiment.

Chlorine.—This gas is made either by acting on manganese dioxide with hydrochloric acid or by acting on a mixture of salt and manganese dioxide with sulphuric acid. The same apparatus may be used in both cases. It is the same as that used for making oxygen (Fig. 11), preferably using a little larger flask. Put the dioxide in first and then pour in the strong HCl in quantity a little more than sufficient to form a thin paste. Mix the two substances thoroughly, and apply a very gentle heat. The chemical change may be represented thus:—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2.$$

Chlorine is somewhat soluble in cold water, and therefore, by collecting in the way described, a loss of gas occurs. This may be largely avoided by employing warm water, or by collecting the gas by "downward" displacement, because it is a very heavy gas, being about 2½ times as heavy as air (for sketch of apparatus see Fig. 13). All experiments with Cl should be done in the "stink cupboard."

Properties.—Its colour is greenish yellow (hence its name). Its odour will probably have been observed while making it; if not, it may be *cautiously* smelt. It is very irritating and even dangerous when inhaled in large quantity.

Place a lighted taper in the gas; it will continue to burn, but with a very smoky flame and the production of white clouds; hold a piece of litmus paper in the clouds, they will be found to be acid. The hydrogen of the taper has combined with the chlorine to form HCl, and the carbon has been set free. Thus Cl has a more powerful attraction for hydrogen than it has for carbon. The same fact may be shown in a more striking manner by moistening a piece of paper with turpentine and quickly plunging it into a ar of chlorine; the heat of the combination of the hydrogen and chlorine will be sufficient to ignite the paper. Compare Experiment 10 (*c*).

Chlorine has a very powerful affinity for metals. This may be shown by crushing some antimony in a mortar, then quickly removing the cover of a cylinder of the gas and pouring the powdered metal in. The combination will be so vigorous that flame will be produced.

Cl also has a powerful affinity for other elements; see Experiment 11 (*b*). Moist chlorine will bleach vegetable colours. Into a jar of the gas place a piece of moistened rag which has been dyed with indigo or magenta or some such colour. Allow to remain for a few minutes, when the colour will be discharged.

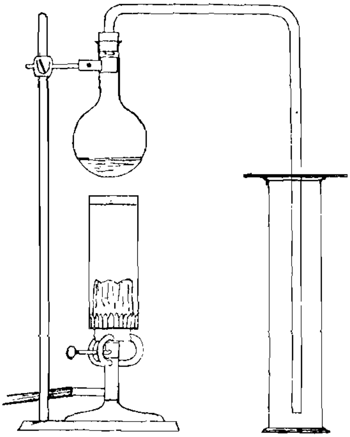

Fig. 13.

Hydrochloric Acid.—This acid is a gas, and can be formed by the direct combination of Cl and H. Invert a cylinder of chlorine over a cylinder of hydrogen. Remove the circles and mix the gases by turning the cylinders upside down two or three times. Now apply a light to the mouths. The gases will combine with a slight explosion. The gas is generally made by acting upon salt with sulphuric acid. The apparatus is shown in Fig. 13. It is better to fuse the salt. This is done by putting about 500 grms. (about half a pound) of ordinary salt into a fire-clay crucible and heating until completely melted, either in a furnace or in the middle of a clear coal fire. When quite liquid, pour the contents out on to a cold stone. When cold, break up into small pieces, and put into the stock-bottle. About 20 grms. of this is put in the flask and about 100 c.c. of dilute sulphuric acid (1 of acid to 1 of water) added. Gentle heat is now applied and the gas collected by downward displacement, because it is too soluble in water to collect over that liquid. It is, however, almost impossible to avoid getting air mixed with gases that are collected by displacement; if required free from air, this gas, as well as many others, can be collected over mercury. The chemical change is

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

Properties.—HCl is very soluble in water. Allow the gas to pass into a cylinder for a long time so as to fill it as much as possible, put on the cover and invert under water, remove the cover; the water will ascend and nearly fill the cylinder. Now pour a little neutral litmus solution into some of this water; it will be turned red, showing that the solution is acid. The liquid, which is known commercially as pure hydrochloric acid, is the strongest solution of the gas in water (about 33 per cent of HCl) which is commercially profitable to make. 1 volume of water at 0° C. will absorb about 500 volumes of HCl.

A taper will not burn in a jar filled with HCl, neither will the gas burn in air.

HCl fumes very strongly when it comes into contact with air. This is caused by the aqueous vapour which is present in the air. With this vapour the gaseous HCl combines, forming minute drops of *solution* of HCl. These minute drops form the cloud or fumes.

Nitrogen.—This gas is prepared by abstracting the oxygen from air. Up to the last few years the gas remaining after this was done was supposed to be nitrogen only; but it has now been shown that another gas, Argon, is also present, but only in small amount (about one per cent). The properties of argon are, however, so much like those of nitrogen that we can study the properties of the remaining gas and assume them to be the properties of nitrogen.

The apparatus is shown in Fig. 14. A small piece of phosphorus is ignited on the float A, and while it is burning a dry cylinder is inverted over it in such a way that the air is confined in it by the surface of the water. The phosphorus continues to burn inside, gradually combining with the whole of the oxygen and forming phosphorus pentoxide, which dissolves in the water, leaving nitrogen.

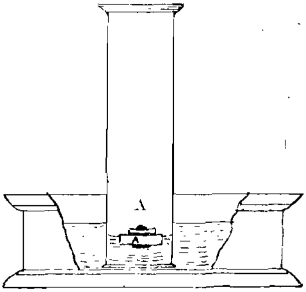

FIG. 14.

The float may be made by taking a cork of about 3 cm. diameter and 1 to 2 cm. deep, making a small hole in the top, and tying on by means of small binding wire the cover of a porcelain crucible. The ring on the top of the cover enables this to be easily done. The float must easily pass into the cylinder, and a small piece of lead must be tied on to the bottom so as to make it float upright and make it sink when full of water. When the phosphorus has ceased to burn, a slight jerk will fill the cover with water and make it sink, and thus enable the cylinder to be removed.

Nitrogen can be made in other ways free from argon and pure. Amongst these the easiest are by heating ammonium nitrite (or ammonium chloride and potassium nitrite), and by passing chlorine through a strong solution of ammonia.

Properties.—The properties of nitrogen that are capable of simple proof are negative. It will not support the burning of a taper, nor will it burn. It has no odour, no taste, no colour. It is practically insoluble in water, and is of very nearly the same weight as air.

Oxides of Nitrogen.—Although nitrogen possesses no active chemical properties it forms no less than five oxides with oxygen. Some of these are formed when electric sparks are sent through air. To show this, pass sparks from an induction coil through *dry* air contained in an ordinary flask. After a little time the air will acquire a brownish-red tint owing to the formation of some of these. The following experiments will sufficiently illustrate the properties of the most important.

Nitrogen Monoxide or Nitrous Oxide.—Into the flask of the apparatus shown in Fig. 11 place about 10 grms. of ammonium nitrate. Heat gently with an Argand until the salt melts and then boils. The gas is readily evolved and may be collected over water.

$$NH_4HO = N_2O + 2H_2O.$$

Properties.—It is colourless and odourless, but has a sweet taste. It will not burn, but a glowing match will be rekindled when plunged into it. This is just like oxygen, and the experiments mentioned under Oxygen may be repeated with nearly the same results. There is one point of difference, which serves to distinguish it from oxygen. It will be found that *feebly* burning sulphur is extinguished, but that when *strongly* burning it continues to burn more brilliantly than in air. This is explained by supposing that before combination with oxygen can take place the N_2O must be decomposed; the feebly burning sulphur is not hot enough to do this, and hence it goes out. When bodies burn in N_2O they only combine with the oxygen; the nitrogen is left behind.

Nitrogen Dioxide or Nitric Oxide.—This oxide is made by the action of dilute nitric acid upon copper. The same apparatus is used as was employed in making hydrogen, Fig. 10. Into the flask is put some copper turnings or small copper wire; water is then added in sufficient quantity to cover the turnings as well as to close the end of the thistle funnel; then pour in about an equal quantity of strong nitric acid. Red fumes rise in the flask and the gas is produced. Collect over water in the usual way. The chemical change is :—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO.$$

Towards the end of the reaction some N_2O is also produced.

Properties.—NO is a colourless gas, but when it is brought into contact with oxygen red vapours of nitric peroxide NO_2 are formed. The red fumes first formed in the flask were caused by the NO and the O in the air combining and forming this substance, which, however, dissolves in the water through which the gases pass to get to the cylinder.

Bodies will burn in nitric oxide, *but they must be very attractive for oxygen and at a high temperature.* Thus a glowing match will not rekindle, sulphur will only burn with great difficulty, and feebly burning phosphorus is extinguished. Nitrogen is left when bodies burn in NO.

The remaining oxides of nitrogen are of less importance, and *are too difficult to make for elementary students.*

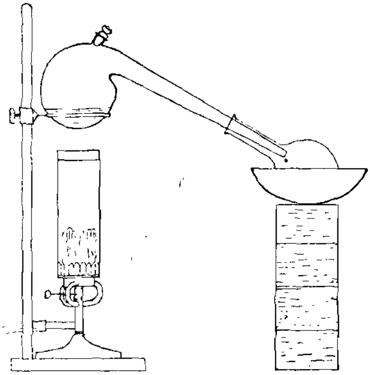

FIG. 15.

Nitric Acid.—The manufacture of this acid may be illustrated by making a small quantity in the apparatus shown in Fig. 15. Put in the retort about 30 grms. of potassic nitrate (KNO_3) and 25 c.c. of strong H_2SO_4. Apply a gentle heat by means of the Argand, and keep the flask into which the acid condenses cool by wrapping it round with a damp cloth or piece of blotting-paper. An almost colourless but intensely acid liquid will collect in the receiver. Note that the acid fumes slightly in contact with the air, and that it has a disagreeable odour like that of nitric peroxide.

Nitric acid is a very powerful oxidising agent. This may be shown by pouring a little of the strong acid upon a little dry and hot sawdust contained in a dish; the sawdust will ignite. Nitrates are also oxidising agents, for the deflagration caused when a nitrate is heated before the blowpipe on charcoal (see Chap. V.) is due to the oxidising of some of the charcoal by the oxygen of the salt.

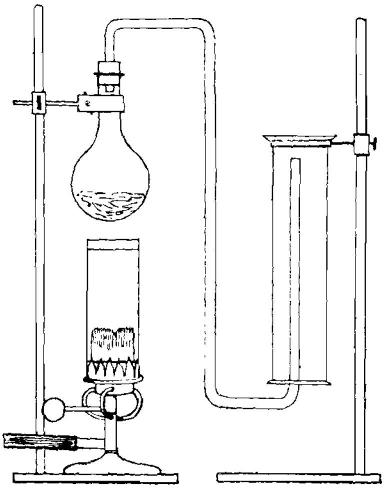

FIG. 16.

Ammonia.—This gas is very soluble in water and cannot therefore be collected in the usual way. It is also lighter than air and must therefore be collected by "upward displacement." The apparatus is shown in Fig. 16. The principle of the process for making the gas is that any ammonium compound when heated with a stronger alkali gives off ammonia. Into the flask is put a mixture of about 20 grms. of ammonium chloride and 15 of lime. Gently heat, and by cautiously smelling the end of the cylinder tell when it is full. The reaction in this case is :—

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

Properties.—Its odour is characteristic. Colourless. Place a lighted taper in a jar; it will not burn, nor will it allow the taper to burn (NH_3 will, however, burn in air if made hot before being ignited). Fill a jar as full as possible with the gas, and quickly invert it under water; the water will ascend and fill the jar. Test the water with litmus; it will be found to be alkaline.

Sulphur Dioxide or Sulphurous Anhydride.—The action of heat upon sulphur has already been described, as well as the burning of it in oxygen. In the latter case, as well as in the former, if any air be present sulphur dioxide is formed. On the large scale the gas is made either by burning sulphur in air or by roasting sulphides. For laboratory purposes, however, neither of these methods is practicable. In this case it is made by heating copper with strong sulphuric acid. The apparatus employed is shown in Fig. 13. Into the flask is put copper turnings or small pieces of thin sheet copper or copper wire, and sulphuric acid is poured in. The heat must be applied very carefully, as there is great danger of the flask cracking unless this is done. The gas is collected by downward displacement, as it is much heavier than air and very soluble in water.

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Properties.—Sulphur dioxide is a colourless gas. To show this, the cylinders must be allowed to stand for some time after they have been filled as described.

It is very soluble in water. Open a well-filled cylinder under water and allow it to stand for a short time; the water will gradually rise and almost fill it. Test the fluid;

it will be found to be acid. Sulphurous acid (H_2SO_3) has been formed.

Sulphur dioxide will bleach vegetable colours. To show this, suspend some red rose leaves which have been moistened with very dilute H_2SO_4 in a jar of the gas. The colour will slowly disappear from the leaves, and they will become whitish yellow.

Sulphuretted Hydrogen.—As already stated, this substance is one of the most useful reagents for qualitative analysis.

It may be made in the same apparatus as is used for the making of hydrogen. Instead of the metal which is acted upon by the dilute H_2SO_4 or HCl, we should use small lumps of ferrous sulphide. The gas is somewhat soluble in water, but it may be collected at the pneumatic trough in the ordinary way, if the water is warmed. The chemical change is:—

$$FeS + H_2SO_4 = FeSO_4 + H_2S.$$

But such a method of preparation would be unsuitable for laboratory work, where small quantities are required immediately and at irregular intervals. To meet such demands various plans and apparatus have been designed. One of the oldest and best of these is that of Kipp, shown in Fig. 17. The upper bulb A has a long stem which reaches almost to the bottom of the lower bulb C. This stem passes loosely through the contraction between bulbs C and B, but fits tightly into B.

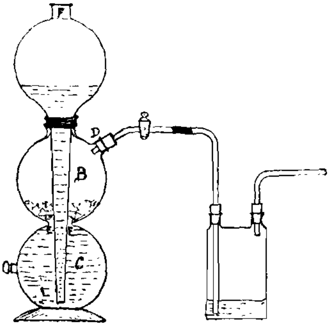

FIG. 17

It is essential that this joint, as well as the stopper at D and the stop-cock, should fit so perfectly that no escape of gas occurs even under a considerable pressure. Ferrous sulphide in lumps is put into B, through the opening at D. These lumps must be of such a size that they will not pass through the space at E. D is now closed, and a mixture of one part of HCl to one of water is poured in through F. This acid runs down into the lower bulb and rises in it, compressing by so doing the air in bulbs B and C. On opening the stop-cock this air is allowed to escape, and the acid rises and comes into contact with the sulphide. Immediately this occurs H_2S is evolved. If now the stop-cock be turned off, the gas evolved, having no place to escape, forces the acid back out of contact with the sulphide and up the stem of bulb A. The action thus ceases, but a supply of H_2S, under slight pressure, is ready for use when required. As the H_2S which fills bulb B is used up the pressure is removed, and the acid again comes into contact with the FeS, evolving more gas.

Whenever sulphuretted hydrogen is prepared by acting upon ferrous sulphide it always contains some hydrogen. This is because the sulphide itself is impure and contains iron. If the gas is required pure, it may be made by acting upon antimony sulphide with hot and strong HCl.

This could be done in a similar apparatus to that used for making SO_2, collecting the gas over hot water instead of by displacement.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Properties.—Sulphuretted hydrogen is colourless. Its offensive odour will soon make itself evident to those who make it. It burns with a pale blue flame. If the supply of air (*i.e.* oxygen) is abundant, as, for example, when it is burnt at the end of a tube, the products of combustion are water (of course in the gaseous form) and sulphur dioxide; but if the supply of air is limited, as, for example, when the light is applied to the end of a cylinder and the combustion extends down it to the bottom, then the hydrogen takes the oxygen, and the sulphur is deposited in the solid state. The two chemical changes are :—

$$(1)\quad 2H_2S + 3O_2 = 2H_2O + 2SO_2.$$
$$(2)\quad 2H_2S + O_2 = 2H_2O + S_2.$$

H_2S is somewhat soluble in water. To show this, bubble a little of the gas through some water. The fluid will smell strongly of the gas after. The solution will be found to be acid to litmus.

Chlorine decomposes H_2S, combining with the hydrogen and setting free the sulphur. To show this, bring a cylinder of Cl and one of H_2S together. Fumes of HCl will be produced and sulphur will be deposited upon the sides of the cylinders.

Sulphuretted hydrogen causes precipitates with many metallic solutions. This has been sufficiently illustrated in the chapter dealing with analysis, and need not therefore be repeated.

Carbon Dioxide or Carbonic Anhydride.—This gas is almost always made in the laboratory by the action of hydrochloric acid upon marble. The apparatus is the same as that used for making hydrogen. Marble is put in the flask in small pieces, and water and hydrochloric acid poured in through the funnel. The gas is collected over water, as its slight solubility in that liquid is of no importance in this connection. Sometimes carbon dioxide is required in quantity like H_2S. In this case it is prepared in a Kipp's apparatus in exactly the same way as that gas, using lumps of marble instead of ferrous sulphide. The chemical change is :—

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

Properties.—Carbon dioxide is colourless and odourless.

It will not burn and will extinguish a lighted taper if plunged into the gas. It is about 1½ times as heavy as air, and therefore may be poured from one cylinder into another just in the same way that water can. To show this, put the lighted taper into a cylinder full of air; it will burn. Now put it into a cylinder of CO_2 and it will not. Take the latter cylinder, remove the cover, and pour the gas, as if it were water, into the former. Now test again. The CO_2 will be found to have left one cylinder and gone into the other.

Carbon dioxide is slightly soluble in water. To prove this, take some distilled water, boil it for a few minutes, and then allow to stand until quite cold. Now pass CO_2 through it slowly for five minutes, and again allow to stand. Then warm (not boil) some in a large test-tube; bubbles of gas will be observed to form on the sides of the tube after the heating has gone on for a few minutes. Carbon dioxide produces a milkiness with lime-water. Pass a few bubbles through a little clear lime-water placed in a small beaker. A white ppt. of calcium carbonate will be formed. This will take some time to settle down, and until it does so the fluid remains milky. The ppt. thus formed will re-dissolve if more CO_2 be passed in. To show this, a long-continued passing of the gas is necessary, but when this is done the fluid will become quite clear. The calcium carbonate is, however, only held in solution as long as the CO_2 is present. Anything that gets rid of or takes up the CO_2 will cause the ppt. to re-form. To show this, take a little of the clear solution and boil it. The CO_2 will be expelled and a white ppt. will be formed.

Pass CO_2 through a neutral solution of litmus and note the change of colour produced.

Carbon Monoxide.—This gas is made for experimental purposes in the laboratory in two ways. *First*, by heating oxalic acid with strong sulphuric acid and passing the mixed gases thus produced through a strong solution of caustic soda or through milk of lime. The apparatus is sketched in Fig. 18.

Into A is put about 10 grms. of oxalic acid and enough strong H_2SO_4 to cover it. Heat is now applied, when the oxalic acid is decomposed, and equal volumes of CO_2 and CO are evolved. The CO_2 is removed by the soda or milk of lime in the wash-bottle B, and the CO is collected at the pneumatic trough over water. By this method, unless great care is taken to evolve the gas slowly and to have a series of wash-bottles, the monoxide will always contain some dioxide. Pure monoxide can be obtained by heating a mixture of powdered potassium ferrocyanide and strong sulphuric acid. These substances are mixed in a flask, heat applied, and the gas collected over water. The apparatus being the same as that used in preparing oxygen (see Fig. 11), except that a hard glass

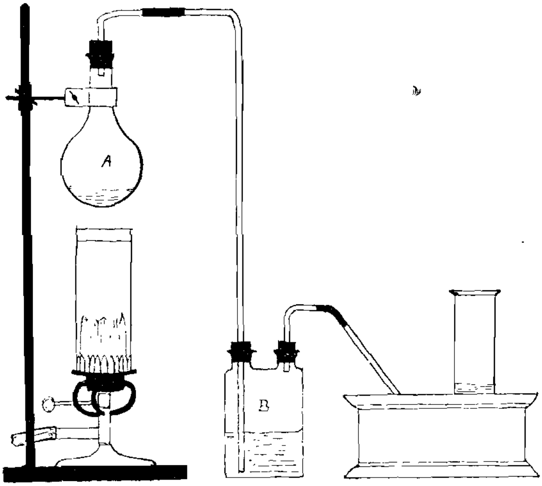

FIG. 18.

flask need not be used. The chemical changes which occur in the two processes are :—

$$(1)\quad H_2C_2O_4 = H_2O + CO_2 + CO.$$

The H_2O is retained by the strong acid, and the CO_2 by the substance in the wash-bottle.

$$(2)\quad K_4FeC_6N_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + FeSO_4 + 3(NH_4)_2SO_4 + 6CO.$$

Properties.—Carbon monoxide is a colourless gas. It burns with a blue flame, forming CO_2. It will not support the combustion of a taper. This is shown by lighting the gas at the mouth of a cylinder and quickly plunging the burning taper down into the cylinder below the flame. It will be extinguished.

Carbon *monoxide has no action upon lime-water.* To show this, some of the gas prepared by the second method given above must be employed. Pour a little clear lime-water into a cylinder which is filled with the gas, and shake. No change will be observed. Now set fire to the gas at the mouth of the cylinder, allow it to burn, and then shake up the lime-water; it will now turn milky, showing that CO_2 has been formed.

CHAPTER IX.

DETERMINATION OF THE BOILING POINT.

In our work hitherto we have dealt with experiments which took account of the *kind* of substance entering into the change and the *kind* produced. We have now to consider, in addition, the quantity of the materials used and products produced. So closely, however, is chemistry related to physics, and so definite are some of the physical constants of chemical substances, that in many cases these physical constants are the readiest means we have of deciding between two substances which have chemical characters that are very similar. Some of these determinations require elaborate apparatus and accurate instruments as well as a long experience in similar work. The description of such are beyond the scope of an elementary work. But there are two of these constants that are of more general application than the others, and which are moreover capable of fairly accurate estimation with moderate care. These are the boiling point of liquids and the melting point of solids. The measurement of both of these involve the use of the thermometer—an instrument for measuring the degree of heat to which a substance is exposed, and whose use is indispensable to every practical chemist. Thermometers are of various kinds, according to the uses to which they are put; but the chemical thermometer is one in which the liquid is mercury, whose bulb is of somewhat less diameter than the tube, and is cylindrical in shape, and in which the degrees are etched upon the glass. In ordinary work there are three thermometric scales in use—the Fahrenheit, freezing point 32°, boiling point 212°; the Centigrade, freezing point 0°, boiling point 100°; and the Réaumur, freezing point 0°, boiling point 80°. But in chemical work now almost universally the Centigrade only is employed. In some old writings, thermometric degrees may be stated in Fahrenheit. If so, and it be required to convert into Centigrade, all that is necessary is to subtract 32 from the number of degrees, and to multiply the remainder by 5 and divide by 9.

Thermometers can be purchased at almost any price, but it is well to remember that an accurate and thoroughly reliable instrument requires good materials and highly skilled labour, and is therefore worth a good price; cheap goods cannot be expected to be thoroughly accurate. When very good work has to be done, it is well to employ a thermometer which shows a small range of temperature, but which has large open degrees. Such instruments should always be read with a telescope, because the heat of the body when near during reading is quite sufficient to alter the temperature one or two degrees.

It is extremely difficult sometimes to be quite sure that a certain liquid is pure. To decide this, the determination of the boiling point is of the utmost importance. It is found that pure liquids boil at one definite temperature, whereas mixtures have a varying point. For example, pure alcohol will boil at 78°, whereas a mixture of equal parts of alcohol and water will commence to boil at 83°, and will gradually rise, until at last it will be necessary to heat it to nearly 100° C. before it will boil. It is therefore evident that if a liquid has a definite boiling point it is very strong evidence of its purity.

The boiling point of a liquid varies greatly with the pressure under which it is heated. For instance, by reducing the pressure, water can be made to boil at temperatures much below 100° C., whereas by increasing it it may be heated far above without boiling. Both these processes are adopted commercially. When a liquid boils and is transformed into vapour, it has to occupy a greater bulk, and therefore has to force back the pressure of the air upon its surface. The greater the pressure the greater the heat necessary in order to convert the liquid into the gas. Hence we may define the boiling point of a substance as *that point of temperature at which the pressure or elastic force of its vapour is equal to the pressure it supports.* Hence in all boiling-point determinations it is necessary to note the height of the barometer at the time of making the observation.

The apparatus employed is shown in Fig. 19. The distilling flask A containing the liquid has a somewhat long neck and side-way tube. The thermometer is fixed in through the cork, and is so placed that its bulb is not in the liquid but some little distance above the surface, but so that the whole of the stem up to the point to which the mercury rises shall be wholly immersed in the vapour. Sometimes this cannot be done, because the boiling point is so high that some portion of the thermometer stem will be outside the cork. In this case it is best to repeat the experiment with another thermometer with a smaller range, so that the heated thread of mercury can all be below the cork. But this again is not always practicable; in such a case it is usual to tie on another thermometer to the side of the

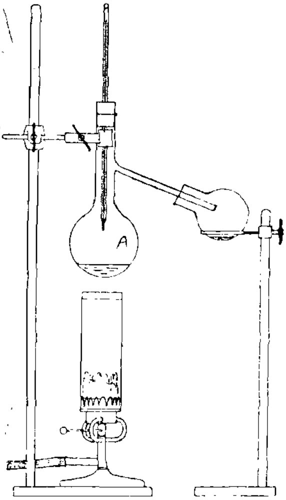

FIG. 19.

first, so that the bulb of this second one shall be about midway between the bottom of the cork and the top of the mercury. The temperature of this second thermometer gives the mean temperature to which the column of mercury outside the vapour is subjected. Then an addition must be made to the reading of the first thermometer, which is found thus. Let N be the number of degrees of the *first* thermometer above the under side of the cork, t_1 the temperature at which the mercury stands in it, and t_2 the temperature of the second thermometer. Then the addition to be added on is given by the formula

$$N(t_1 - t_2) \times \cdot 000155.$$

When this is done the temperature obtained gives the true boiling point.

While making the experiment it is usual to fit the sideway tube into a condenser or other vessel to receive the vapour which is expelled from the flask and condense it. This is simply done to avoid loss of material. An error may occur here unless care be taken to allow the tube to fit loosely into the condensing flask, so that there may be no increase of pressure upon the vapour. By employing a condenser freely open to the air, or a flask whose neck is much wider than the tube, there is no danger of this, and the pressure under which the boiling occurs is that of the outer air.

The following liquids are convenient ones to give for testing their boiling points:—Absolute Alcohol; Acetic Acid; Carbon Tetrachloride; Acetone; Benzene; Aniline; Ether (attach side-tube to a Liebig's condenser and pass well-cooled water through); Ethyl Acetate; Amyl Alcohol; Formic Acid.

Note.—As a rule, the purer the substance the sharper the point of temperature at which it boils.

CHAPTER X.

DETERMINATION OF THE MELTING POINT.

THE boiling point of a liquid is one of the most valuable indications of its purity; in like manner, the melting point of a solid affords a reliable indication of the same fact. The melting point is, like the boiling point, affected by pressure, but not to the same extent, and it is therefore not generally necessary to take account of the barometer when making an experiment.

There are several methods in use which differ slightly from each other. The commonest is probably that employing capillary tubes. A sketch of the apparatus employed is shown in Fig. 20. Small pieces of *thin* quill tubing are drawn out to a fine point. For example, the following sizes are appropriate:—length, 4 cm.; diameter, 5 mm. at one end, and drawn out at the other to 2 mm. The smaller end is either sealed or open. Some experimenters prefer them one way and some another; but it must be remembered that a difference is made in the results according to the method employed, and when an open tube is used it is found that the depth below the surface of the fluid in which the tubes are heated makes a difference. This is easily accounted for by remembering that the greater the depth the greater the upward pressure upon the material inside the tube; hence it will rise quicker in one case than in the other.

A small quantity of the substance is introduced into the little tubes, either by ordinary means or by melting a little in a small crucible and inverting the mouth of the tube under the surface and gently expelling the air by passing the flame over the closed end. On cooling, the liquid will rise in the capillary tube and there solidify. The tubes are now tied around the bulb of the thermometer, with a little wire or cotton as shown in the sketch. The thermometer and tubes are then placed in the liquid in the beaker. This is either water, strong sulphuric acid, or melted paraffin wax, according to the temperature at which the substance melts and whether acted on by the acid or water. A substance with low melting point would be immersed in water. The liquid is carefully heated and constantly stirred, and the point of temperature at which it becomes liquid noted. In the case of an open tube the temperature is taken, when the substance is released from contact with

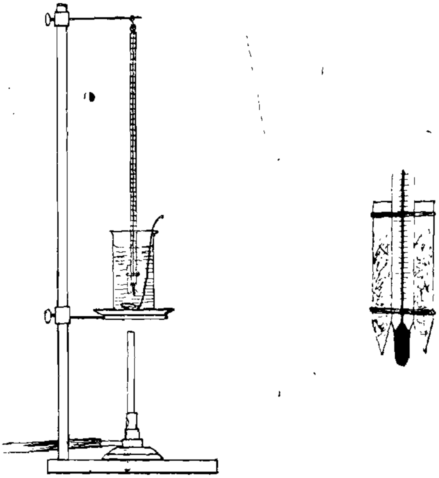

FIG. 20.

the sides of the tube and rises in the fluid. As stated above, it will be found that a slight difference is given by the two methods.

Sometimes after melting a solid so as to get it into the tube, and then taking the melting point at once, very abnormal results are obtained. This is probably due to the substance not having resumed its normal condition after the first melting. This error may be avoided by allowing some time to elapse between the filling of the tube and the taking of the melting point. Another method is as follows:—The apparatus (Fig. 21) consists of a beaker A filled to the brim with water; inside this and separated from it on all sides is a smaller one B. This smaller one is partly filled with mercury C, in which is placed the thermometer. A stirrer E is used to keep the water in the large beaker of uniform temperature. A cardboard or other disc covers the smaller beaker while the operation is in progress. The large beaker rests on a sand-bath G, which is carefully heated by a Bunsen or other burner. When the melting point to be determined is under 30° it is better to replace the sand-bath by an evaporating dish containing water. For temperatures between 100° and 200° the larger beaker is filled with paraffin wax.

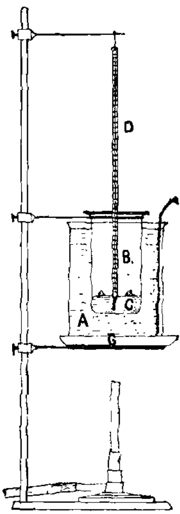

Fig. 21.

The process is conducted as follows. The material whose melting point is to be taken is placed on three or four small pieces of ferrotype plate or other thin metallic sheet, or on the cover-glasses which are used for microscope slides. If ferrotype slips are used, care must be taken to remove the varnish in order that good metallic contact may be had with the mercury. The slips with the substance on them are now placed on the surface of the mercury and the heat applied until the substance melts. The solidifying point is obtained by raising the temperature above the melting point and allowing the beaker to cool, noting the thermometer when the first solidification takes place. The following precautions are necessary:—(1) The temperature must be made to rise very slowly. (2) The liquid in the outer beaker must be frequently stirred. (3) Not less than 2·5 cm. in depth of mercury must cover the inner beaker. (4) Sufficient volume of water must be allowed between the two beakers. The minimum distances to give good results are 2·5 cm. laterally and 4 cm. at the bottom. (5) The inner beaker must be immersed a sufficient depth in the water. This point is of great importance, the least distance between top of mercury and top of water being 7 cm.; a greater distance, however, is to be preferred. (6) The whole apparatus should be protected from draughts. (7) The disc should be kept on the smaller beaker during the determination.[1]

It will be noticed that this method affords a means of taking the solidifying as well as the melting points. Theoretically these ought to be the same, but they differ slightly in some cases.

In commerce the substance whose melting point is most frequently taken is probably paraffin wax, or, as it is frequently called, "*paraffin scale*." In testing this, two plans are in common use—the "English test" and the "American test." In the former the wax is placed in a test-tube of about 18 mm. diameter and melted. A thermometer is now put in and the tube and contents allowed to cool slowly in the air, being stirred by the thermometer during the process. The temperature will gradually fall, but presently a point will be reached when the thermometer remains stationary for a short time. This is taken as the melting point.

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[1] E. H. Cook, *Proceedings Chem. Soc.* No. 177.

In the American test the substance is melted in a round dish of about 9·5 cm. in diameter, and a thermometer with a round bulb 12·5 mm. in diameter placed in the middle of the fluid, in such a way that three-fourths of the bulb is immersed. The fluid is now allowed to cool in the air, and the temperature is taken when a thin film covers the surface.

It will be noticed that in both these commercial tests it is really the solidifying points that are determined. The American test may be as much as 2½° to 3° Fahrenheit higher than the English.

The following substances may be given for determining the melting points:—One or two uniform samples of Paraffin Wax; Ortho-mono-nitro-phenol; Chloral Hydrate; Urea; Iodoform; Picric Acid; Mono-chloracetic Acid; Naphthaline; Diphenyl-amine; Camphor.

Note.—In this case, as in that of the boiling points, pure substances give sharper readings than impure.

CHAPTER XI.

SEPARATION OF TWO LIQUIDS BY FRACTIONAL DISTILLATION.

IN the foregoing we have seen how it is possible by filtration to separate a liquid from a solid which is mixed with it, and in some cases when two liquids which are placed together do not mix it is quite easy to separate them by decantation. But there remains the most common case of two liquids which mix with each other in all proportions, but which in many cases exert no chemical action upon each other. In this case a method known as "fractional distillation" is resorted to. The principle underlying the process is to take advantage of the difference of the boiling points which will probably exist between the two. If no such difference does exist, or if the difference is very small, the separation cannot be effected in this way, and is indeed very hard to bring about.

When a mixture of two liquids of different boiling points is heated it will begin to boil at some temperature near to the lower boiling point and some fluid will distil over. Then the temperature will gradually rise, more and more liquid distilling, until the upper point is reached, when the whole of the liquid will distil. Now suppose we had collected the distillate in several separate vessels, then we should have divided it into "fractions," hence the term applied to the process. The division into fractions is not done with regard to any idea of the *quantity* of liquid distilled, but is regulated by the rise in temperature. For instance, we might collect our fractions every 10° or so. Thus our first fraction, let us suppose, shall consist of all the liquid which distils over while the thermometer is rising from 80° to 90°; the second while it rises from 90° to 100°; the third while it rises from 100° to 110°; and so on. The quantities of these various fractions will generally be very different. Thus in a case mentioned by Perkin and Kipping in their *Organic Chemistry* the following numbers were obtained. The mixture consisted of 50 c.c. of benzene (b.p. 81°) and 50 c.c. of xylene (b.p. 140°). It was found to begin to boil at 87° and the thermometer gradually rose up to 140°. The receiver was changed five times and the following fractions were obtained :—

87°–100°	100°–110°	110°–120°	120°–130°	130°–140°
33 c.c.	16 c.c.	8·5 c.c.	8 c.c.	33 c.c.

It will be noticed that the amounts of the first and last are larger than the others. This is because the temperatures at which they are collected are very near the boiling points of the constituents. This is always found to be the case. The next step is to take these respective fractions and to repeat the process, thus successively "fractionating." In this way we shall ultimately get the pure constituents.

The apparatus employed differs somewhat in different laboratories. The simplest is to fit an ordinary distilling flask such as is used in determining the boiling point (see Fig. 19) to a Liebig's condenser and distilling. The only objection to this apparatus is that when it is used the fractionation has to be repeated several times in order to obtain a pure substance. Several attempts have been made to reduce the number of operations necessary. The principle upon which these work is to give the mixed vapours as they are boiled from the liquid a longer journey before they enter the condenser. In this way the portion of higher boiling point has a better opportunity of condensing and falling back into the flask. Thus the fractions which are collected near to the respective boiling points are much larger. The simplest improvement of this kind is the still-head suggested by Wurtz, which is shown fitted to the flask in Fig. 22, and which needs no further description. Two examples of more elaborate pieces of apparatus are shown at A and B. They are called "deflegmators." The first, A, is due to Henninger, and consists of a succession of bulbs with side-way tubes for the condensed vapour to run down into the flask. The second, B, has been recently introduced by Young and Thomas (*Chem. News*, lxxi. 177). It consists of a long glass tube about 120 cm. long, which has been *constricted* at several places along it. On each of these constrictions rests a small piece of platinum gauze, and through the platinum gauze a small piece of glass tube bent into the shape shown

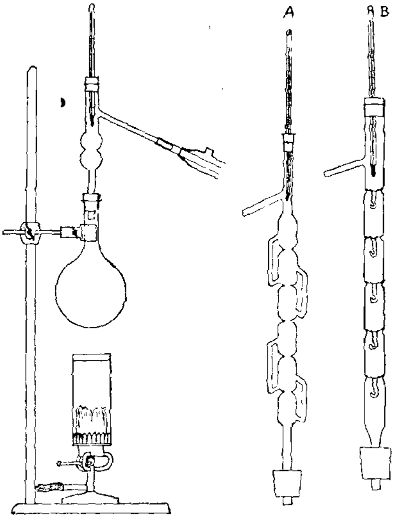

FIG. 22.

passes. The gauze becomes covered with liquid which runs down the tubes back into the flask. At the end of the operation the liquid in the tubes is forced back into the flask by blowing through the side-way tube.

The following mixtures may be given for practice in separating two liquids by fractional distillation. (1) Commercial "50 per cent" benzene. (2) Commercial "90 per cent" benzene. (*Note.*—These are mixtures of benzene and varying quantities of toluene and xylene.) (3) Rectified spirit (84 per cent by weight of alcohol), or Proof spirit (49·24 per cent by weight of alcohol).

CHAPTER XII.

DETERMINATION OF THE AMOUNT OF OXIDE FORMED FROM A GIVEN METAL.

One of the simplest kinds of chemical change which is capable of quantitative determination is that in which a metal is converted into an oxide by combination with oxygen. But it is only a very few metals which will combine with oxygen directly, in a sufficiently short space of time, to allow of experiments being made with them in the time available in a class. Practically, magnesium is the only one which can thus be used. In other cases we have to form the oxide in an indirect manner; viz. by first making the nitrate and then heating that salt, when the oxide will be formed.

The experiments require the use of the balance. But it is not necessary to have a very delicate and costly instrument when commencing work. One capable of weighing to half a centigramme is sufficiently delicate, and with a set of weights ranging from 50 grammes to 1 milligramme ought to cost about thirty-two shillings.

The student must be instructed in the proper use of the instrument and given a few articles to weigh before he begins to experiment. On no account should a student move a balance from its position or attempt to readjust it. All such alterations should be done by the demonstrator.

The operation of oxidising the metal is accomplished in a small porcelain crucible which is fitted with a loosely fitting cover. These are made quite clean and dry, and then carefully weighed. A small quantity of the metal is now put into the crucible and the whole again weighed; the difference between the two weighings gives the weight of metal taken. The crucible is now supported on a tobacco-pipe triangle which is placed on a tripod or a ring of a retort stand. (Tobacco-pipe triangles are very useful for supporting crucibles or other articles that have to be strongly heated. Being made of a non-conducting material the articles are not so liable to crack by the heat. They are made by cutting a piece of tobacco pipe into three equal lengths, and threading through each a piece of copper wire about two or three inches longer than the piece of pipe, then twisting by means of the pliers the ends of the wires tightly round each other. In this way the pipes will be drawn together and form a triangle, while the twisted ends of the wires will project from each angle.)

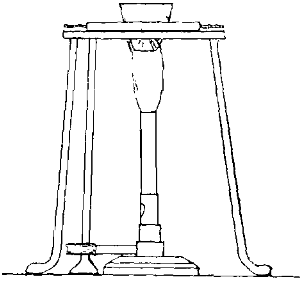

FIG. 23.

If we are dealing with magnesium we put on the cover of the crucible and gently heat with a Bunsen. The heating must be done carefully at first, but at the end the bottom of the crucible must be made red-hot. If we are dealing with other metals than magnesium we add to the metal about 1 c.c. of strong nitric acid. This must be done very carefully so as to avoid spurting. A brisk action ensues and reddish-brown fumes are evolved. When all action has ceased, heat is very carefully applied. When the contents are quite dry, the mass should be probed with a clean steel knife-blade to see if any metal remains unattacked; if it does, a little more nitric acid must be added and the process repeated. When it is thoroughly converted into the nitrate the heat must be raised to redness. After about fifteen or twenty minutes' heating, the crucible and contents are allowed to cool and weighed. After this it is heated to redness for five minutes and again cooled and weighed. If it has not altered in weight during the last heating, the experiment is finished and the weight of oxide formed is found by subtracting the weight of the crucible from the weight of the crucible and oxide together.

The metals which can be most readily converted into oxides are magnesium, tin, zinc, copper, and iron. Brass can also be used.

In all cases except that of magnesium it is better to act with nitric acid first. The metals should be as pure as possible and in small pieces. Magnesium and iron in wire, which must be cleaned before weighing; tin and zinc granulated, and copper and brass in the form of clean turnings or filings. As a rule about 0·2 gramme of the metal is a suitable quantity to employ, but it is better not to trouble to get *exactly* this amount.

In every case at least two determinations should be made with each metal, and the results obtained ought to agree within 2 per cent.

As some guide to the student to know when he has made a good experiment it may be mentioned that the final products in the cases of magnesium, tin, and zinc are white; and in that of copper, black; and of iron, red. With brass the colour varies very slightly according to the composition of the alloy, being of varying degrees of blackness.

The following example will show the amount of accuracy which may be expected by proceeding in the way described, and also the method of entering the results in the pupil's note-book.

Formation of Oxide from Metal.

(Write a short description of the process.)

Experiment 1.—Metal taken, tin.

Weight of crucible and cover alone	7·89 grms.
Weight of crucible and cover and tin . . .	8·14 ,,
Weight of metal taken . . .	0·25 grm.

Weight of crucible, cover, and oxide	8·205 grms.
Weight of crucible and cover alone	7·890 ,,
Weight of oxide formed . . .	0·315 grm.

Therefore 0·315 gramme of oxide of *tin* contains 0·25 gramme of tin. Thus 100 grammes of oxide of tin contain 79·36 grammes of tin and 20·64 grammes of oxygen.

Then follows a second experiment with the same metal.

One or two words as to the conclusions to be drawn from the experiments mentioned in this chapter may help the student. In the first place he must remember that they afford no absolute proof that he forms oxides at all. In order to prove this he would either have to make the experiments by heating in oxygen alone (synthesis) or he would have to take the substances and obtain oxygen from them (analysis). Both these would be very difficult of accomplishment with the metals mentioned; but Priestley discovered oxygen by first exposing hot mercury for a long time to the air and then collecting the red powder formed in this way and heating it more strongly, when it was broken up into mercury and a colourless gas which proved to be oxygen.

If, then, the experiments do not prove the formation of oxides, and that these oxides contain so much metal and so much oxygen, what do they prove? They prove this:

that by treating certain metals in this way *some compound of those metals is formed, and that this compound always contains the same amount of the metal united to the same amount of the other constituent or constituents.* This is the *Law of Definite Proportions.*

CHAPTER XIII.

DETERMINATION OF THE LOSS ON THE IGNITION OF A SUBSTANCE.

In an earlier chapter it has been shown that the effect of heat upon a large number of bodies is so characteristic as to serve to identify them when mixed with others. We have now to study some of the same experiments but from the quantitative side.

In the preceding chapter we have seen that the effect of heating a metal in the air is generally to produce an oxide, *i.e.* a more complex substance from a less complex; but the general effect of heat is just the opposite to this. As a rule, the effect of heating substances is to reduce them to bodies of less complex constitution. Thus potassic chlorate, a molecule containing fine atoms, is broken up into potassic chloride, whose molecule is supposed to contain two atoms, and oxygen.

The *loss* which a substance undergoes when strongly heated of course implies that there is something left which suffers no loss on further heating. That is, it is a "fixed" residue. Thus the great majority of organic compounds, which either volatilise or are first converted by heat into carbon, which afterwards burns away, are inadmissible for these experiments. Ammonium compounds also cannot be used because of their volatility.

It should here be mentioned that "ignition" means heating strongly, *i.e.* to a bright red heat. But it must be remembered that many compounds lose a definite proportion of their weight, which means that they undergo a definite decomposition, when heated to varying degrees of temperature. Thus crystallised copper sulphate loses about 29 per cent of its weight when heated to 110° C., and about 7·2 per cent additional when heated to 220° C. In such cases care must be taken to regulate the temperature, but in igniting the body this care is not required.

The apparatus used in this kind of experiment is similar to that employed in the formation of oxide, viz. a crucible; and the mode of weighing, etc., is the same as described in the last chapter, the reheating after the first weighing being never neglected. There are, however, some modifications which are sometimes necessary in consequence of the nature of the substance. Some salts when heated have a tendency to "decrepitate," *i.e.* to break up into smaller fragments with a crackling noise. This is frequently done so violently as to project some of the material from the crucible. This may be prevented by heating very slowly, and keeping the crucible closely covered. But in such cases the heating can be done in a hard glass tube, which is held in a nearly horizontal position and which is treated exactly like the crucible in regard to weighing.

Great care should always be taken in the first application of the heat, and in most cases this is best done by first using the Argand burner as the source of heat. The capability of turning down the flame enables the very smallest degree of heat to be applied. After heating with a gradually increasing Argand flame, the process is continued to redness by the Bunsen.

Sometimes the substances which are available for these experiments contain a slight amount of moisture, in no way chemically combined, but present as an impurity. In such cases it is well to get rid of this before weighing the salt. This may be done by putting the materials inside a water-oven and drying for about half an hour. Of course if the substance undergoes a decomposition at the temperature of the oven (approximately 100° C.), this is inadmissible.

It is not necessary for the teacher when giving the student the substance to experiment with to tell him what it is. But after the percentage loss is obtained it will be found advantageous to tell him, and explain the change or changes which are supposed to have occurred. The reason of this is, that it is important to impress on the student that he is making the reaction for himself, and that his work is an additional proof of its truth.

The following are the substances which may be used, duplicate experiments being always made:—Potassic Chlorate; Magnesium Carbonate; Zinc Carbonate; Copper Sulphate (crystallised); Lead Nitrate; Copper Nitrate; Calcium Sulphate (gypsum); Alum; Borax; Microcosmic Salt.

From ·5 to 2 grms. is a suitable amount to experiment with.

The following is an example of the mode of stating the experiment:—

Weight of crucible and cover alone	7·89	grms.
Weight of crucible and cover, plus substance	8·52	,,
Weight of substance taken	0·63	grm.
Weight of crucible, cover, and residue	8·27	grms.
Weight of crucible and cover	7·89	,,
Weight of residue	0·38	grm.

Therefore 0·63 grm. gives 0·38 grm. of residue. Therefore loss on heating, 0·25 grm. Thus percentage loss on heating = 38·14.

The substance taken was Potassium Chlorate.

CHAPTER XIV.

DETERMINATION OF THE LOSS OF WEIGHT ON DISSOLVING IN ACIDS.

WHENEVER a gas is produced by the action of an acid upon a substance, and that gas comes out of the apparatus and mixes with the air, a loss of weight occurs. This loss of course represents the weight of the gas produced by the chemical change. There are numerous cases in which gases are formed by chemical changes. Some of the commonest are the solution of carbonates of some metals, of sulphites and of sulphides. To accurately determine the loss of weight in every case would involve great care and the taking of numerous precautions. But in some instances simple apparatus will suffice to obtain approximate results. Many teachers will probably prefer to devise their own apparatus, and if not, there are numerous forms made and sold by the scientific instrument makers, more especially suited for the determination of the amount of carbon dioxide liberated from a carbonate when it is

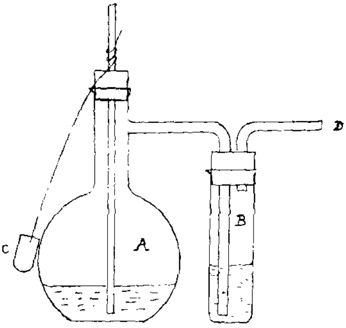

FIG. 24.

attacked by an acid. A very simple plan, which however works well, is that shown in Fig. 24.

A is a small flask of about 100 c.c. capacity fitted with a side-way tube which is bent at right angles at about 4 cm. from the flask; the vertical portion is about 7 cm. long, and passes through the cork of a small test-tube B of about $1\frac{1}{2}$ cm. diameter and $5\frac{1}{2}$ cm. long. A small tube D also passes through this cork. The small test-tube is about two-thirds filled with strong H_2SO_4. The flask A is closed by a cork through which a small tube passes nearly down to the bottom. C is a small glass capsule about 2 cm. long (the bottom end of a test-tube), to which is fused a thin platinum wire. The corks must fit tightly, and that of A must be somewhat soft, so that when the glass capsule is inside the flask and the wire passes out at the side of the cork there shall be no escape of gas.

The experiment is conducted as follows:—The cork of the flask with the tube passing through it, and the wire wound round it as in the figure, is removed, and enough dilute HCl (1 of acid to 3 of water) to cover the bottom of the flask to a depth of about 2 cm. is poured in. The strong H_2SO_4 is put in B, care being taken to pour it in so that none shall be left on the sides of the tube to come in contact with the cork when it is put in. The cork of the flask is now replaced and the whole weighed, the capsule resting against the *outside* of the flask.

The substance to be tested, in a powder if a salt, or small particles if a metal, is now put into the capsule (of course this must have been quite clean and dry). The apparatus is again weighed, and the former weight subtracted from this. The difference gives the weight of substance taken. The cork of A is again removed and the capsule lowered into the flask until it is about two-thirds covered by the acid. The cork being replaced, grips the wire and keeps the capsule in this position. The next step is to gently shake the flask, when a little acid comes into contact with the substance and action ensues. The gas liberated will first force air out of A, through the acid in B, and will then bubble through itself. The strong H_2SO_4 has a very powerful attraction for water, and the gas in passing through it will be robbed of any moisture which it has carried over from the dilute acid in A.

Thus the loss in weight will be only due to the escape of the dry gas. Shake the flask from time to time so as to bring more and more of the substance in contact with the HCl, and when it has all been acted on, warm the fluid in A for a short time so as to make the action complete. Allow to cool, and when at the ordinary temperature, suck the end of D. In this way air will be drawn in through the open end of the tube in A and replace the gas with which it has become filled. If a carbonate is being experimented with, and CO_2 is the gas evolved, the point when all has been sucked out can be told by the absence of the sweet taste of that gas. Finally, the apparatus is weighed and the loss of weight obtained. Care must be taken to regulate the action so that the gas shall pass slowly through the acid in B. If this be not done, the gas may escape being thoroughly dried, and some of the H_2SO_4 may be made to touch the cork.

The chemical changes which occur may be illustrated by the following equations:—

$$
\begin{array}{lll}
(1) & CaCO_3 & + 2HCl = CaCl_2 + H_2O + CO_2. \\
(2) & Na_2SO_3 & + 2HCl = 2NaCl + H_2O + SO_2. \\
(3) & FeS & + 2HCl = FeCl_2 + H_2S. \\
(4) & Zn & + 2HCl = ZnCl_2 + H_2.
\end{array}
$$

In the cases of carbonates, sulphites, and sulphides the gases evolved are of high specific gravity, and therefore a convenient amount of material to employ in each of these cases is about 0·5 gramme. But when hydrogen is evolved a larger quantity of substance is required. In this case about 2 grms. are necessary.

CHAPTER XV.

DETERMINATION OF THE VOLUME OF GAS EVOLVED ON TREATING WITH ACIDS.

In the preceding chapter we have determined the loss of weight which is caused by the evolution of a gas. In this chapter we shall describe a simple method of measuring the volume of this gas.

When dealing with the volumes of gases, it is necessary to remember that these volumes are very considerably altered by changes of temperature and pressure. It would therefore be necessary, if great accuracy is required, to correct the volume obtained by calculation. This is done by finding what the gas would measure at what is called "normal temperature and pressure." The normal temperature is taken as 0° C.; the normal pressure as 760 mm.

(*Note.*—This does not say that these are the *average* temperatures and pressures at any place. Obviously these depend on the place.)

The calculations are done by making use of two laws; one relating to temperature and the other to pressure. Both are experimental, and have been carefully investigated by many excellent experimenters. The first is known as Charles's Law, and may be stated thus:—

(1) *The volume of a gas is proportional to its absolute temperature.*

The only thing needing explanation in this is that by "absolute" temperature we mean the temperature reckoned from $-273°$ C. Thus to find the "absolute" temperature we must add 273 to the ordinary.

The second law is known as Boyle's, and is—

(2) *The volume of a gas varies inversely as the pressure upon it.*

Pressures may be measured as so much per unit of area, as so many pounds per square inch, or as so many millimetres or inches of mercury. The latter is almost always used in chemistry, and is given by the height of the barometer.

The calculations are very simple. First, correct for temperature by the first law. Thus, for example, 250 c.c. measured at 18° C. will become x c.c. at 0° C., where x is given by the proportion

$$273 + 18 : 273 : : 250 : x.$$

Then take this x and correct for pressure. Thus suppose the pressure at which the gas was measured was 750 mm. (*i.e.* this was the height of the barometer in the laboratory at the time), then the final volume V is given by

$$760 : 750 : : x : V,$$

because of the inverse proportion.

It is not usually necessary in rough experiments such as are described to make these corrections, especially that for pressure, but the temperature of the laboratory and the height of the barometer at the time of the experiment should always be stated.

Many different kinds of apparatus may be used for these experiments. That shown in Fig. 25 answers very well. A test-tube A, 15 cm. long and 1·6 cm. diameter, has a side-way tube about 20 cm. long fitted on at right angles. This tube is bent down so as to dip under the bottom of a burette, which is firmly held by a clamp under the surface of water contained in an ordinary mortar, or dish, or pneumatic trough. The tube is fitted with a cork, through which passes a thistle-headed tube with the bottom end bent sharply round as shown. This effectually prevents any gas rising up through the tube and escaping into the air.

The burette should be a large one; about 200 c.c. capacity answers very well. These may be bought graduated from the stop-cock downwards if desired, but one with the usual graduations may be made available in a simple manner. All that is necessary is to run in water from another burette, so as to fill the required one from the stop-cock up to the nearest graduation mark. With a 200 c.c. burette this will be, of course, at the 200 mark; with a 100 c.c. it will be at the 100 mark, and so on. The amount of water run in gives the capacity of the tube from the stop-cock to first mark. Then a label may be affixed to the burette stating this capacity, or the space may be further graduated and the divisions marked on a piece of paper which is gummed on the tube.

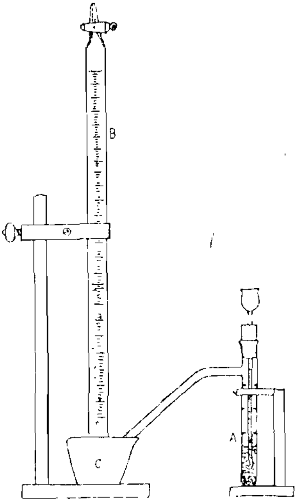

Fig. 25.

Smaller burettes may be employed, but in such cases it will probably be necessary to re-fill during an experiment. This is easily done by attaching a piece of india-rubber tubing to the stop-cock end of the burette, and when the volume of gas reaches the mark 0 on the burette, quickly turn the stop-cock and suck through the tubing. The water will thus be made to rise. If this is properly done, practically no loss of gas will take place. The burette is filled in a similar manner in the first place.

The substances to be acted on and the acid to act on them are placed in the test-tube, but in pouring in the liquid we necessarily displace some air, which ascends the burette and would be measured as gas evolved. To allow for this, a mark is made on the test-tube A where 10 c.c. of liquid stands in it, also where 15 c.c. and 20 c.c. At the conclusion of the experiment, when all action has ceased, water is poured in up to one or other of these marks before measuring. The number of c.c. of water put into A is subtracted from the number of c.c. of gas evolved.

The same substances may be used for these experiments as were employed for those mentioned in the last chapter. They should be weighed by being placed on a watch-glass, weighing both, and then subtracting the weight of the watch-glass. The substances are put into the test-tube by sweeping them in from the watch-glass with a camel-hair brush.

The weight of substance taken for experiment should be about ·5 grm., except in the case of metals. In these cases we may take, of magnesium about ·1 to ·2 grm., of zinc and iron about ·4 to ·5 grm. The larger the amount of substance used, the less the percentage error, but with the apparatus as described, about 150 to 200 c.c. of gas are convenient amounts to be liberated by the action.

The following example illustrates the method of entering in the note-book :—

Weight of zinc taken	0·53 grm.
Volume of gas evolved	192 c.c.
Temperature of laboratory	20° C.
Height of barometer	768 mm.

Therefore 100 grms. of zinc on being dissolved in acid evolves 36·23 litres of hydrogen measured at the above temperature and pressure.

The volumes thus obtained may be reduced to what they would be at normal temperature and pressure, and the results also entered in the note-book.

CHAPTER XVI.

DETERMINATION OF THE EQUIVALENT OF A METAL.

WHEN performing the experiments with metals which are described in the last two chapters, the student must have been struck by the differences in the weight and volume of the gas evolved on dissolving these metals in the same acid. For example, he cannot fail to have noticed that a much less quantity of magnesium is needed to give off the same volume of hydrogen than of zinc.

Suppose we calculate from our experimental data how much zinc is required to produce 100 c.c. of hydrogen and how much magnesium. We shall find that we shall require about ·291 grm. of zinc and ·107 grm. of magnesium. Thus, then, so far as the expulsion of hydrogen from the dilute acid is concerned, ·291 grm. of zinc is equal to only ·107 grm. of magnesium. We may therefore say that this amount of zinc is "equivalent" to ·107 of magnesium. Thus we get the idea of "equivalence" in chemistry. Obviously corresponding numbers may be obtained for other elements, and thus a list can be drawn up giving the relative weights of the various elements which are equal in chemical power to each other. But it is necessary to select some one element with which to compare the others. By universal consent this element is hydrogen, and hence we may define the "equivalent weight" or the "equivalent" of an element to be the *smallest weight of that element* *which is capable of combining with or replacing one part by weight of hydrogen.* It is found that when one element is replaced by another the weights are the same as when they combine.

The experiments we have been describing deal with the replacement of a metal for hydrogen, and therefore, in order that the definition may apply to these experiments, we may write it as "*the weight of the metal in grms. which will replace* 1 *grm. of hydrogen.*" It will therefore be seen that we have determined experimentally all the data necessary to calculate the equivalents of the metals we have been using. We can either dissolve a given quantity of the metal in dilute acid and estimate the loss, or we could collect the hydrogen, and if we knew the weight of unit volume we could find the *weight* of the volume collected. But hydrogen is a very light gas, and hence it takes a large bulk of it to weigh say ·1 grm. Therefore any slight inaccuracy in the weighing will make a great difference in the result. It is for this reason better for students to perform the experiment in the latter way, and to correct for temperature and also for pressure if desired. In order that the volume may be converted into the weight, we can make use of a constant which has been determined with very great care by numerous experimenters. This is, that at the normal temperature and pressure 1 *litre* (1000 *c.c.*) *of hydrogen weighs* 0·0896 *grm.* Thus, suppose a certain experiment gave 242 c.c. of hydrogen after allowance had been made for temperature (correction for pressure may be omitted in most cases), then the weight of this hydrogen is

$$\frac{242}{1000} \times \cdot 0896 \text{ grammes.}$$

The apparatus used is the same as that described in the last chapter. The metals should be pure, and made quite free from surface coatings of dirt or oxide by cleaning and rubbing with a little fine emery paper. The weighings should be made, if possible, correct to ·001 grm., and a thermometer hung near the burette which collects the gas. Of course all ordinary precautions should be taken; for example, burners should not be allowed burning on the bench during these experiments, as well as those in the last chapter. Sometimes the hot gases from these are allowed to ascend and surround the burette, thus expanding the gas inside and producing unnecessary errors.

After the volume has been read and the correction made for temperature, the weight of the gas must be ascertained as explained, and then the amount of metal necessary to give 1 grm. of hydrogen calculated. This is *the equivalent weight.*

As some guide to the student the following data may be stated :—

1 grm. of Mg will give 930 c.c. of hydrogen.
,, *Zn* ,, 343 ,,
,, Iron ,, 398·5 ,,
,, Tin ,, 189 ,,

The gases being measured at 0° C. and 760 mm. Bar.

Also we may state that 1 grm. of hydrogen will be evolved by the solution of 12 grms. of magnesium, 32·5 grms. of zinc, 28 of iron, and 69 of tin.

It must be remembered, however, that these numbers are obtained when every precaution to ensure accuracy is taken, and that when working with the *simple apparatus* such as described, only approximations can be hoped for.

The following example will illustrate the mode of stating the experiments :—

Weight of zinc taken	0·53 grm.
Volume of gas evolved (H)	192 c.c.
Temperature of laboratory	20° C.
Barometric pressure	768 mm.

$$\text{Corrected volume at N.T.P.} = \frac{192 \times 273 \times 768}{293 \times 760} = 180{\cdot}8 \text{ c.c.}$$

$$\text{This volume will weigh } \frac{{\cdot}0896 \times 180{\cdot}8}{1000} = 0{\cdot}0162 \text{ grm.}$$

Therefore 0·53 grm. zinc is equivalent to 0·0162 grm. hydrogen, or 1 grm. of hydrogen is equivalent to 32·7 grms. zinc.

CHAPTER XVII.

DETERMINATION OF THE VOLUME OF GAS EVOLVED ON IGNITION OF A SUBSTANCE.

VERY closely connected with the work treated of in recent chapters is that of the measurement of the volume of a gas given off on strongly heating a substance.

In many cases, however, when gases are produced in this way they contain small quantities of impurities, and as the separation of these involves special and sometimes complicated apparatus, the results obtained are vitiated by the presence of these impurities.

Again, we are collecting the gases over water, and as some of them are appreciably soluble in that liquid, another error is thus introduced. But with care and the use of pure materials, fairly concordant results may be obtained which have not a very great percentage error.

Very little is necessary to say in reference to the apparatus. For measuring, the same arrangement can be used as before and the same manipulation employed. The substance is heated in a hard glass tube similar to that described under the preparation of oxygen (Fig. 12) but perhaps a little smaller (15 cm. long by 1·5 cm. diameter answers very well). This tube is closed by a tightly fitting cork through which passes the delivery-tube.

It will be found on performing the experiment that at the end of it, when all the gas which the substance can yield has been evolved, and the heat is withdrawn, the water will ascend up the delivery-tube for a considerable distance. This is in consequence of the expansion of the air or gas by the heat, and an error in the volume of the gas to the extent of this expansion would be made if means were not taken to avoid it. It cannot be entirely avoided by the means at our disposal, but it may be reduced and practically corrected by applying the heat to the *part of the tube above the substance before any heat is applied to it, and allowing the expanded air to escape without entering the burette.* After the bubbles cease being evolved, place the end of the delivery-tube under the burette and then commence the decomposition of the substance.

A double result can be obtained from each of these experiments. Because we make the tube thoroughly dry and weigh it, then we put the *substance in the tube* and weigh both together, and finally we weigh the tube and residue remaining after the heating. Thus we obtain (1) the loss on heating of the material, and (2) the volume of gas evolved. Duplicate experiments must, of course, be made.

Substances suitable for igniting in this way are :—Potassic Chlorate; Potassic Nitrate; and Mercuric Oxide; while, if additional examples are required, any other chlorate may be used, or any bromate or iodate.

From ·5 to 1 grm. may be used.

Since the gas evolved has been heated very considerably, it is well to allow it to stand in the measuring burette for some time before reading its volume, in order that it may have time to acquire the ordinary temperature of the laboratory.

The following are details of an experiment made in this way :—

Weight of tube	16·20 grms.
Weight of tube and $KClO_3$ . . .	16·69 ,,
Weight of $KClO_3$	0·49 grm.

Weight of tube and residue	16·50 grms.
Weight of residue	·30 grm.
Volume of gas evolved	141 c.c.
Temperature of laboratory	20° C.

Therefore 100 grms. of $KClO_3$ will evolve 28·8 litres of gas at 20° C. on ignition; and leave 61·22 grms. of residue.

CHAPTER XVIII.

DETERMINATION OF THE AMOUNT OF ONE METAL THAT CAN BE REPLACED BY ANOTHER.

FROM the numerical data obtained by dissolving certain metals in acids we were able to calculate the relative amounts of those metals which were equivalent to one part of hydrogen, and then, by tacitly assuming the truth of Euclid's axiom that "things which are equal to the same thing are equal to one another," to calculate that a certain amount of one element is equal to a certain amount of another. Thus we found that 12 parts of magnesium were required to liberate 1 part of hydrogen from dilute acid, whereas 32·5 parts of zinc were required for the same purpose. Thus we can say that 12 parts of magnesium are equal to 32·5 parts of zinc. But in the vast number of chemical changes which can be brought about there are other and in some cases more exact methods of obtaining these same equivalent numbers. Moreover in numerous cases it is impossible to obtain any action upon an element with dilute acid in such a way that the result can be so easily measured. In these cases the equivalent numbers have to be obtained by different methods. In some cases even a special method has to be devised for the particular element.

The plan described in this chapter is applicable to a fairly large number of elements, and has the merit of being both simple and accurate. The principle of it is to take the solution of some compound of some one element and to place in that solution a second element. Sometimes under these conditions the second element will displace the first one from its combination and that first one will be liberated from its compound in the pure state. Thus if a small strip of zinc be placed in a solution of silver nitrate, immediate action will take place, some of the zinc will be dissolved, and the silver deposited in the finely divided metallic state.

Weigh out about ·3 grm. of zinc (foil or granulated) and place it in a clean beaker of about 10 cm. high by 5 cm. diameter. Pour on it about 50 c.c. of silver nitrate solution containing 20 grms. of the salt in the litre. The zinc will be dissolved and a black powder take its place. The mixture must be stirred from time to time with a clean glass rod, and when on stirring no hard metallic substance is felt, the action is complete. Care must be taken to have the silver solution "in excess," that is, to have more of the nitrate present than can be decomposed by the amount of zinc taken. When silver solutions are being decomposed, this can only be done by roughly calculating beforehand the quantity of silver which will be deposited by the zinc and then to be sure to take more of the solution than contains this amount of the metal. When copper solutions are being acted on, there is no such difficulty, because so long as the solution is blue there is copper in it. Therefore the experimenter has only to take care that the solution is blue during the whole time the action is going on. The solution is warmed towards the end of the action; it should, however, never be more than lukewarm.

When the action is complete, the deposited metal is pressed together by means of the stirring-rod and the whole allowed to stand for a few minutes. The clear fluid can then be poured off, and in order to wash out of the precipitate the whole of the nitrate of silver or nitrate of zinc with which it may be mixed, a little warm water is poured over it two or three times, the metal being allowed to settle down after each addition of the water, and then the water poured off. Care must be taken that during the pouring no metal is lost. The weight of metal deposited can be ascertained in two ways. Either the whole of it can be transferred to a small weighed crucible, then dried by driving off the water by careful heating, and then weighed; or the metal may be dried in the beaker itself and weighed in it. If the former plan be adopted, the transference to the crucible requires a little care. First, pour off as much water as you can and thus obtain the metal in a small mass at one side of the bottom of the beaker. Now take a camel-hair brush, and, holding the beaker in an inclined position over the crucible, brush the whole precipitate gently down into the crucible, washing the last particles in, if necessary, by blowing a little water from the wash-bottle. Swill the brush in the same way if necessary. The drying may be done over a sand-bath, but care must be taken not to crack the beaker in the one case, and not to dry so quickly as to cause any of the substance to be projected from the crucible in the other.

Unfortunately there are not many metals which are capable of being deposited and weighed in this way. Silver solutions can be decomposed by zinc, copper, iron, and magnesium; copper solutions by zinc and magnesium. (A strip of iron placed in a solution of copper becomes coated almost immediately with copper, but the solution of the whole of the iron takes so long that the experiment cannot be performed in the time usually given to a laboratory lesson.) Lead solutions can be treated in this way with magnesium and zinc.

In some cases the mixture of solution and metal may be carefully covered and put away in the student's cupboard so that the action may go on during the time between two meetings of the class.

The following numbers were obtained in an actual experiment:—

Weight of zinc taken	0·29 grm.
Weight of silver replaced . . .	0·96 ,,

Therefore 100 grms. of zinc will replace 331 grms. of silver

CHAPTER XIX.

DETERMINATION OF THE AMOUNT OF A SUBSTANCE THAT CAN BE FORMED BY A CHEMICAL CHANGE.

IT has been shown, when treating of the various ways in which chemical changes may occur, that almost every possible kind or class of change can be produced. Thus liquids produce solids, other liquids, or gases; gases produce solids, liquids, or other gases; and so on. The quantitative investigation of these changes is in many cases extremely difficult and in many instances has never been thoroughly done. One important factor in increasing the difficulty of such an investigation is that oftentimes secondary changes occur and go on side by side with the principal one; the final products being therefore the results of a complicated series of reactions. In other cases, however, the changes are so simple and definite that they may be easily and thoroughly investigated. It is these reactions which are relied on for proving the important fundamental laws in chemistry, as well as for ascertaining the quantity of an element which is present in any particular substance; *i.e.* making a quantitative analysis of that substance.

Of course, since the changes are of so various a character, the methods employed in proving them are also various. The complete study of the plans adopted for every element would involve the whole field of quantitative analysis, and is far beyond the scope of this book. There are, however, some typical operations and methods which are employed in numerous chemical investigations with which we are quite able to deal. The most common of these is the treatment of precipitates. We have already seen, in the chapter upon qualitative analysis, how the making of a particular chemical substance which at the time of its making forms a precipitate, enables us to prove that a certain element is present in a substance under analysis. In some cases these precipitates may be purified and weighed, and thus not only can we prove the *presence* of the element but also the *amount of it* present. As an example we will take the manufacture of aluminium oxide from alum.

Select some well-formed crystals. Powder them, and then place the powder between a couple of sheets of blotting-paper and press it. In this way any moisture which may have been adhering to the crystals is removed. Now take a little of the powder and test it to find whether it is "ammonia" alum or "potash" alum, *i.e.* whether its chemical formula is $Al_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, or whether it is $Al_2(SO_4)_3, K_2SO_4,24H_2O$. (This is mentioned because the two kinds of alum are so frequent in commerce and so much alike—both practically possessing the same properties—that when purchasing "alum" you are sometimes given potash and sometimes ammonia alum.) Having decided what alum is being experimented with, weigh out about 2 grms. and dissolve in distilled water in a beaker. Warm the solution and add to it ammonium hydrate as long as a precipitate is formed. After adding the $(NH_4)HO$, boil the fluid. The boiling can be done by placing the beaker either upon a sand-bath or upon wire gauze. After boiling for about five minutes, allow to stand for about the same time. In this way the aluminium hydrate will agglomerate into a mass and can be more easily filtered. Fold a filter-paper across a diameter and then across a

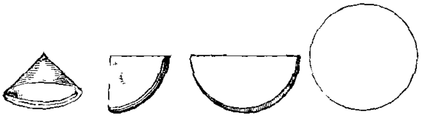

FIG. 26.

semi-diameter, thus obtaining four thicknesses of paper. Open one out and place the paper thus folded, corner downwards, into an ordinary funnel. If properly done it will fit the sloping sides of the funnel. Now pour the fluid and ppt. upon the paper, decanting as much of the clear liquid as possible before putting on the ppt.

Test the filtrate by adding to it a little more $(NH_4)HO$, to see that all the Al has been precipitated. If any further ppt. is obtained, more $(NH_4)HO$ is added to the filtrate until no ppt. is obtained and then the whole again filtered. In order to get the last portions of ppt. upon the filter-paper, wash it from the beaker by blowing through the wash-bottle, and, if necessary, gently rub it off the sides by means of a stirring-rod with a small piece of india-rubber pushed over the end. When all the ppt. is upon the paper, it must be washed thoroughly. This is done by blowing warm water from the wash-bottle over it, four or five times, allowing one lot to run through before adding the next. The precipitate and filter-paper is now dried. This is done by placing the funnel in a water-oven, or, more rapidly, by putting it over a slightly conical tube of thin sheet-iron which is supported on a sand-bath. In the latter case great care must be taken that the temperature does not rise so high as to char the paper. When quite dry, the ppt. is carefully removed as much as possible from the paper and put into a clean, dry crucible whose weight has just been determined. When dealing with ppts. in this way it is advisable to place down on the bench a piece of black glazed paper about 25 to 30 c.m. square, to put the crucible in the middle of this, and to transfer the ppt. over the crucible. In this way any small quantities which may be spilled can be readily seen and saved from loss. The filter-paper must now be burnt to an ash, for although we may have very carefully removed all that was possible from the surface of the paper some of the ppt. may have been drawn into the pores of it.

The burning is done by folding the paper tightly, wrapping it round with the end of a piece of clean platinum wire, and holding it in the flame of the Bunsen until it is burnt. The roll of paper is best held over the cover of the crucible, and the flame made to play upon it by inclining the burner. When burnt as completely as possible in this way, the ash is put upon the cover and burnt until it is quite white or light gray, the cover being placed on a tobacco-pipe triangle, and the heat carefully applied. The ppt. contained in the crucible is then heated in a similar manner, and when both cover and crucible have cooled they are weighed. The crucible and contents are again heated and this repeated, until, on cooling and weighing, the weight is not different from what it was before.

10 grms. of "ammonia" alum treated in this way will give, theoretically, 1·19 grm. of aluminic oxide (Al_2O_3); and 10 grms. of "potash" alum will give 1·13 grm.

Another kind of chemical action which can be easily tested quantitatively is to neutralise acids and alkalies by each other, to evaporate the liquid and obtain the salts thus formed, then to dry and weigh. If acids are neutralised by alkalies, care must be taken to only add just enough alkali to neutralise. If an acid be added to an alkali, care must also be exercised in the same way, but a very small excess of acid will not vitiate the result in the same way that a small excess of alkali will. In such experiments the point of neutralisation is shown by an "indicator" (see Chap. XX.). When evaporating, the heat must be very cautiously applied, to prevent any "spitting"; especially is this the case when the residue is almost dry.

The following are results obtained by students in the ordinary course of work:—

(1) FORMATION OF ALUMINIC OXIDE FROM ALUM.

Weight of potash alum taken	2·00	grms.
Weight of crucible and Al_2O_3	12·73	,,
Weight of crucible alone	12·52	,,
Weight of Al_2O_3 alone	0·21	grm.

Therefore 100 grms. of potash alum give 10·5 grms. of aluminic oxide.

(2) MANUFACTURE OF SODIUM SULPHATE BY NEUTRALISING CAUSTIC SODA SOLUTION WITH SULPHURIC ACID.

20 c.c. of standard caustic soda solution were taken and neutralised with reagent sulphuric acid, a little litmus being used as indicator. The liquid was evaporated to dryness in a small porcelain evaporating basin and weighed.

Weight of evaporating basin	24·26 grms.
Weight of evaporating basin and sodium sulphate .	24·97 ,,
Weight of sodium sulphate	0·71 grm.

Therefore 100 c.c. of solution would yield 3·55 grms. of sodium sulphate.

The following experiments can be given for practice.

The teacher can either give the student a known weight of the solid substance, and tell him to convert into a certain body whose weight he is to ascertain, or he can give him a known amount of a standard solution of the acid, or alkali, or substance. In this way the teacher is easily able to check the results obtained.

(1) Formation of sodium and potassium salts by adding acid to standard alkali, and alkali to standard acid. The acids most convenient to use are H_2SO_4, HCl, HNO_3, and oxalic.

(2) Formation of ferric hydrate by adding NH_4HO to solution of ferric chloride.

(3) Formation of silver chloride by adding HCl to solution of silver nitrate.

(4) Formation of barium sulphate by adding H_2SO_4 to solution of barium chloride. (*Note.*—Add the acid in small quantity at a time to the boiling solution.)

CHAPTER XX.

ESTIMATION OF THE AMOUNT OF ALKALI BY STANDARD ACID AND OF ACID BY STANDARD ALKALI.

THE measurement of the amount of acid present or of the amount of alkali is one of the most important applications of the principle which was treated of in the last chapter. But by a slight modification of the mode of proceeding we are enabled to avoid the necessity of evaporating the substance to dryness. This evaporation, unless very carefully performed, is liable to occasion error. The plan adopted is to have a solution of acid of known strength, and also a solution of alkali of known strength, and then to measure the unknown alkali by the known acid ("alkalimetry"), and the unknown acid by the known alkali ("acidimetry"). The process, it will therefore be seen, involves the measurement of the volumes of the liquids, hence it is an analysis by volumes. Numerous bodies can be accurately analysed in this way, the method of analysis being known as "Volumetric Analysis."

Evidently one of the essential requirements in this mode of analysis is to have solutions of accurate strength. Such solutions are called "Standard Solutions." These may be of any strength—1 grm. of substance dissolved in 1 litre of the fluid, or 100 grms., whichever is most convenient to use. But it has been found convenient to make use very largely of strengths which bear a simple relation to the molecular weight of the substance. In this way the chemical changes are more easily related to the volume of fluid and a large amount of calculation avoided. Solutions prepared in this way are called "Normal" solutions. The principle involved in the preparation of these normal solutions may be briefly explained.

When caustic soda and hydrochloric acid are brought together, the hydrogen of the acid is replaced by sodium, 1 atom of H being replaced by 1 of Na. Now we have seen that these replacements take place in certain proportions by weight, and we have experimentally determined these numbers in some few cases. In the case of Na it is found that 23 parts by weight of it are required to replace 1 part by weight of H. Therefore if we make our solutions of such strengths that 1 litre of one contains 1 grm. of H, and the other so that 1 litre contains 23 grms. of Na, then our two solutions are exactly equal, bulk for bulk. But 1 grm. of H is combined with 35·5 grms. of Cl in HCl, and 23 grms. of Na are combined with 16 of O and 1 of H in caustic soda. Therefore if we weigh out 36·5 grms. of HCl and 40 grms. of NaHO, and dissolve each of these in 1 litre of water, we have normal solutions of hydrochloric acid and caustic soda respectively.

This is exactly the way a normal solution of NaHO is made; but with HCl we must remember that pure HCl is a gas, and what is usually called hydrochloric acid in the laboratory is a solution of the gas in water. In this case, therefore, we must first find the specific gravity of the solution, then compare with a table giving the amount of pure HCl corresponding to the specific gravity found, and then to take the quantity of the solution which contains the *amount of pure* HCl *required*. The *actual preparation* of normal solutions does not come within our scope, and therefore details are not given. When the substance whose normal solution is being made contains two or more atoms of H which can be replaced, then we must divide the molecular weight by the number of such atoms, and then take the weight thus obtained, in grammes, of the substance and dissolve in a litre. Thus sulphuric acid (H_2SO_4) has two atoms of H in its molecule, and this molecule has a weight, compared to the atom of H, of 98; therefore the normal solution, in order to be equivalent bulk for bulk with the NaHO and HCl solutions, must contain 49 grms. of the pure acid per litre. The student may therefore define a normal solution of a substance to be "that solution which contains as many grms. of the reacting element in 1 litre as are equivalent to 1 grm. of hydrogen." The liquid should be measured at 15° C.

Very often such solutions are too strong for accurate work. In such cases it is customary to divide the strength by any suitable number. Thus we get decinormal ($\frac{N}{10}$), centinormal ($\frac{N}{100}$), etc., when we have one-tenth, one-hundredth, etc., of the normal strength.

The actual experimental work of the determination is very easy when once the solutions are made. Suppose we had to determine the strength of a commercial sample of sulphuric acid. Place a little of it in a stoppered burette, and then run into a beaker about 5 c.c. of the acid. Add water carefully, pour into a measuring flask of 200 c.c. capacity, and when at 15° C. fill up to the mark. Place this solution in another burette and run a measured quantity of it into a beaker. Now fill a burette with the standard solution of soda (this should be free from carbonate), add to the acid one or two drops of an alcoholic solution of phenol-phthalein, and then allow the soda solution to run into the acid drop by drop until the bright red colour produced where the drop of soda touches the liquid gives the faintest permanent colour to the fluid. The acid has then just been neutralised by the soda. The number of c.c. of soda solution required is then read off and the amount of actual soda calculated. Then from that amount the amount of acid can be found by remembering that 40 grms. of soda will neutralise 49 grms. of sulphuric acid. An example will make the mode of calculation clear.

Amount of acid taken, 5 c.c.

Made up to 200 c.c. with distilled water.

Took 25 c.c. of this dilute acid and neutralised with normal NaHO.

(1) Found 22·2 c.c. of soda required.

(2) Found 22·2 c.c. of soda required.

Mean, 22·2.

Amount of NaHO in 22·2 c.c. is 0·888 grm.

Amount of H_2SO_4 neutralised by 0·888 grm. of NaHO = 1·0878.

Therefore 25 c.c. of the dilute acid contains 1·0878 grm. of H_2SO_4.

Thus 200 c.c. of the dilute solution, or 5 c.c. strong acid, contains 8·702 grms. of H_2SO_4.

Therefore 100 c.c. strong H_2SO_4 contains 174·05 grms. of real H_2SO_4.

The substance which is used to tell when the solutions are just neutral is called an "indicator." There are many substances which may be employed for this purpose. Of these, litmus is one of the most useful. This forms a solution which, when exactly neutral, is of a purple colour, neither distinctly red nor blue, but of a mixture of the two. The slightest excess of acid will cause it to become distinctly red, and the smallest excess of alkali distinctly blue. These slight shades of colour are difficult to distinguish by gas light or electric glow-light; hence litmus solution should not be used at night.

Phenol-phthalein is another substance which is of great use in the testing of acids and alkalies. It gives no colour with acid or neutral solutions, but the faintest trace of excess of alkali instantly produces an intensely red colour, which is easily distinguished. Upon exposure to the air the colour, when very faint, sometimes disappears. This is probably due to the action of the atmospheric carbonic acid. Phenol-phthalein does not give very good results when titrating ammoniacal solutions, or even solutions of the other alkalies when ammoniacal salts are present. The colour can be distinctly seen by gaslight. This indicator is capable of being used with alcoholic solutions, or mixtures of alcohol with other fluids. It is therefore available for use with some organic acids which are insoluble in water but soluble in alcohol, etc.

A third indicator which is also largely used is methyl-orange, one of the aniline compounds. This substance is soluble in water, the solution possessing a very faint tint of yellowish red. When excess of alkali is present the colour becomes yellow, when acid it becomes pink. A few experiments are needed in order to become accustomed to the tints, but when this is once done the changes are very distinct. Methyl-orange is so useful because it is not affected by carbon dioxide and other bodies which give acid reactions with litmus. It is therefore available for use for the estimation of carbonates by acids, because the CO_2 evolved is without effect. The solutions in which methyl-orange is used should not be warm, because the tint-changes are more definite with cold than with hot solutions.

Convenient strengths of solution for these indicators are: for phenol-phthalein, 5 grms. in a litre of half alcohol and half water; for methyl-orange, 1 grm. in a litre of water. In all cases of the employment of indicators, a few drops only should be added to the solutions, and these must be kept stirred during the titration.

There are a large number of other substances which are available for use as indicators in alkalimetry or acidimetry, but they are of less extensive application than those mentioned, and it is therefore unnecessary to describe them here.

CHAPTER XXI.

ESTIMATION OF THE AMOUNT OF CARBONATE BY STANDARD ACID.

THE remarks made in the last chapter in reference to the use of methyl-orange will have indicated to the student the simplest method for estimating the amount of the carbonates of the alkaline metals which may be present in any substance or solution. It is simply to titrate the solution of the carbonate with standard acid, making use of methyl-orange as an indicator. The titration must be done when the solution is quite cold, and the method gives excellent results. But there are two other processes in common use which likewise give good results. In both these, litmus is used as the indicator. The first is a direct method. It consists in titrating the solution of the substance in the ordinary way, but adopting the precaution of boiling the solution towards the end of the operation in order that the carbon dioxide produced may be expelled and thus prevented from affecting the colour of the litmus. When CO_2 is present, it causes the litmus solution to become of a peculiar purple-red tint, very different from the proper pink-red which an excess of acid produces. The process adopted is to dissolve a known weight of the substance (if soda ash, about 10 grms.) in water in a beaker, then to filter (if necessary) into a graduated flask (for 10 grms. a 500 c.c. flask is required), wash the beaker and filter-paper, and make up the filtrate and washings to the mark. Take out of this solution about 50 c.c. and put into an evaporating dish of about 12 to 14 c.m. diameter. Add a few drops of litmus solution and run in standard acid from a burette. Presently the litmus will be coloured of a reddish purple. When this is the case, place the dish over a burner and boil. The colour will soon change back again to blue. Now add more acid, and again boil, and repeat this until the formation of the purple-red tint ceases and the neutral colour of the litmus is formed and remains constant during the boiling.

The second method referred to is an improvement upon this one. It will be found somewhat difficult to judge the difference of colour between that due to a very small quantity of CO_2 and the neutral tint, and a very common error is to add too much alkali. The present plan does away with all this kind of difficulty. It is a "reverse" method. The solution is made as before, and a measured quantity of it is taken and placed in a flask, and a known amount of standard acid run in. This amount must be greater than what is required to neutralise the quantity of carbonate taken. The addition of the acid will, of course, cause an immediate evolution of carbon dioxide, and the liquid is boiled until the whole of this is expelled. This will take about ten minutes. After this a few drops of litmus solution must be added and standard alkali run in until neutrality is reached. The amount of acid used up in decomposing the carbonate is then obtained by subtracting the amount neutralised by the standard alkali from the total amount added.

The following are actual experimental numbers obtained with a commercial sample of soda ash (impure carbonate of sodium).

Weighed out 10 grms. of soda ash and dissolved in 500 c.c. water.

1. Took out 50 c.c., placed in a dish, added a few drops of litmus solution, ran in normal H_2SO_4 till red colour

appeared, boiled, colour disappeared, ran in more H_2SO_4 and repeated till red colour was constant.

Required, 16·8 c.c.

2. Took 50 c.c. of solution, added 25 c.c. normal H_2SO_4, boiled for about ten minutes, and then titrated with normal NaHO after adding a little litmus solution.

Required, 8·2 c.c. NaHO.

Therefore number of c.c. H_2SO_4 required to decompose carbonate $= 25 - 8·2 = 16·8$ c.c.

3. Took 50 c.c. of solution, added a few drops of methyl-orange solution, and ran in normal H_2SO_4.

Required, 16·85 c.c.

4. Took 50 c.c. solution, added 25 c.c. normal H_2SO_4, boiled for ten minutes, added a few drops of phenolphthalein, and titrated with normal NaHO.

Required, 8·2 c.c.

Therefore number of c.c. of H_2SO_4 required to decompose carbonate $= 25 - 8·2 = 16·8$ c.c.

Weight of Na_2CO_3 neutralised by 1 c.c. normal $H_2SO_4 = 0·053$ grm.[1]
,, ,, 16·8 ,, ,, 0·890 ,,

This is the weight of Na_2CO_3 in 50 c.c. solution. Therefore weight of Na_2CO_3 in 500 c.c. or 10 grms. soda ash $= 8·90$ grms.

Or 100 grms. contain 89·0 grms. of pure Na_2CO_3.

---

[1] This figure is obtained from the reaction which occurs when neutralisation takes place, viz. :—

$$Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2,$$

from which we have that 106 parts of Na_2CO_3 are neutralised by 98 of H_2SO_4.

CHAPTER XXII.

SUMMARY.

HAVING now completed the task with which we set out, viz. to prepare for the use of students and teachers a scheme of experimental work in chemistry suitable for a first year's course of laboratory instruction, it may not be unprofitable to point out the principal laws which our experiments have illustrated.

In the first place, it must be clearly realised that what is called a "law" in chemistry is simply the statement of a general principle founded upon the results obtained from numerous experiments.

It is therefore possible that with extended observations the interpretations which we now put upon our experiments may be altered, and what we now regard as natural laws or truths prove to be false. But it is evident that before this is done a vast number of experiments will have to be made, which not only prove the falsity of our present notions, but also establish the truth of new ones. It is needless to say that up to the present no experiments which have been made give the slightest indication of any such revolution being likely to occur.

It must also be remembered that the experiments which have been described cannot be taken as "proving" the laws, but only of "illustrating" them. The rigid proof requires elaborate experiments conducted by experienced experimenters, and arranged with the utmost care so as to avoid the consequences of all known sources of error.

The earlier chapters are intended to give the student practice in manipulation and to train him in habits of accurate observation.

The preparation of chemical substances in a state of purity must of necessity precede any deductions drawn from their analysis, whilst the qualitative analysis of a body is required before a quantitative can be started. Hence up to the eighth chapter we deal with these subjects.

The next two chapters illustrate the use of the physical properties of bodies in proving their purity. The plans mentioned are more applicable to organic than to inorganic substances, but are very valuable in those cases also whenever it is possible to apply them. But it must be remembered that the behaviour of inorganic compounds with reagents, and when under the influence of heat, etc., affords a reliable criterion of purity.

Coming to the quantitative experiments, we are at once making use of and illustrating the fundamental laws. The first of these is concerned with the formation of new substances from others. We have studied the production of oxides, etc., as well as the decomposition of bodies when heated. We have found that these changes occur with absolute definiteness, and so long as we make the same substance, we require exactly the same weight of materials to produce the same quantity of it. Thus we deduce the *Law of Definite or Constant Proportions.* It may be stated thus :—"When two or more elements combine together to form a new substance, they do so in constant and definite proportions by weight, no matter in what way the combination is brought about." Thus whenever copper oxide is made and in whatever way, we always find that about 1 part of oxygen will combine with 4 parts of copper (more exactly, 16 parts of oxygen with 63·2 of copper) to form 5 parts of oxide of copper.

Other experiments, especially those relating to the formation of one chemical substance from a definite amount of another, illustrate another important law which may be stated as:—"The weights of the substances produced by any chemical change are exactly the same as those of the substances which entered into it." This may be called the *Law of Equality of Mass*. Expressed in another way it may be said that "Matter can neither be created nor destroyed." The constitution of any particular kind of matter can, however, be altered, and that is what the chemist is continually doing.

The third great generalisation which our experiments show is that relating to the equivalence or "chemical value" of the elements. There is perhaps no more important law than this one relating to equivalence. It may be put thus:—"A definite weight of every element is equivalent in chemical combining power to a certain definite weight of every other element." Thus we find that 8 parts by weight of oxygen are equivalent to 1 part by weight of hydrogen, 35·5 parts of chlorine to 1 of H, and so on. There is always a difficulty in understanding the difference between the "equivalent weight" of an element and the "atomic weight." The discussion of this would lead us too far, and therefore we cannot enter into it. But it may be briefly stated that the equivalent weight is that which is given by experiment, the atomic weight is some multiple of this; the number to multiply by being obtained from certain considerations, mostly theoretical, which a study of the compounds of the element in question gives us. Thus by experiment we find the equivalent of O to be 8; and in water we find nothing but hydrogen and oxygen. Therefore if this substance consisted of 1 atom of H, combined with 1 atom of O, the atomic weight of O would be 8. But experiments show us that we can separate the H from water in two equal portions; but we cannot thus divide the O. If we take away any O we take it all away. Thus we conclude that the number of atoms of O in the molecule of water is indivisible, but that the number of H atoms is divisible by 2. Therefore we conclude that the simplest formula for water is H_2O, and if this is the case, the atomic weight of O compared to the atomic weight of H must be twice its equivalent weight, *i.e.* it must be 16. Similar considerations are applied in the case of the other elements. We therefore see that the atomic weight of an element is equal to its equivalent weight multiplied by its valency.

The experiments described give several methods of determining the equivalents. Thus in one chapter we are told how to compare them directly with H, in another by replacement of some other element. It is needless to say that the results should be the same in every case, and the student should test the accuracy of his work by comparing the results obtained by the two methods. Thus in an experiment detailed in Chap. XVI. we found that 32·7 grms. of zinc are equivalent to 1 grm. of H, and in Chap. XVIII. we found that 100 grms. of zinc would replace, *i.e.* are equivalent to, 331 of silver. Thus we can calculate that 32·7 of zinc are equivalent to 108·22 of silver. But 32·7 grms. of zinc are equivalent to 1 of H; therefore 108·22 of silver are equivalent to 1 of H. This, then, is the equivalent of silver. The best determination of this number by Stas gave 107·92, and hence our rough determination is approximately correct.

Abundant opportunities for thus testing his accuracy will be afforded to the pupil in the course of his work.

Finally, in the last two chapters the application of the methods and principles used to commercial analysis is described.

It is hoped that after honestly working through this book the student will have such a desire for further knowledge as will induce him to carry on his studies until he has become acquainted with the natural facts upon which the science of chemistry rests.[1]

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[1] The whole of the apparatus described in this book is kept in stock by Messrs. Froude and Vaughan of Maudlin Street, Bristol.

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THE END

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