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INORGANIC CHEMISTRY

THEORETICAL & PRACTICAL

WITH AN INTRODUCTION TO THE PRINCIPLES OF CHEMICAL ANALYSIS
INORGANIC AND ORGANIC

AN ELEMENTARY TEXT-BOOK

BY

WILLIAM JAGO, F.C.S., F.I.C.

HEAD SCIENCE MASTER OF THE BRIGHTON SCHOOL OF SCIENCE AND ART



THIRTEENTH EDITION

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PREFACE

TO

THE NINTH EDITION.

IT was with some hesitation that I undertook the task of writing the first edition of this book, feeling as I did that a number of chemical works of a high character were already in existence. From the point of view of a teacher brought continuously into contact with large classes being taught under the regulations of the Science and Art Department, and also with other students preparing for various examinations, I felt there was still something wanting in the way of a text-book specially arranged to meet these requirements, and hence the first appearance of the present book. The work, when published, received a welcome both from teachers and the press far exceeding what I had ventured to hope or expect. Six years have now elapsed since that first edition was written; during that time considerable changes have been made in the chemical syllabus issued by the Science and Art Department. Among the most important of these was the publication in 1885 of an 'Outline of

Experiments suitable for illustrating Elementary Instruction in Chemistry,' prepared by Sir H. E. Roscoe and Dr. W. J. Russell. This Outline of Experiments was commenced with the significant remark that

> the following notes have been prepared as some guide to the teachers as to the general character of the course of instruction expected in the elementary stage. It includes instruction that should on no account be omitted, but must be considered rather as suggestive than exhaustive.

As a consequence of these alterations it became absolutely necessary that a text-book for the use of students of classes connected with the Science and Art Department should include the whole of the subject-matter indicated in this recent addition to the syllabus. In order to attain this end I have carefully re-written the whole book, and, disturbing the original plan as little as possible, have incorporated with it any additional matter required to make it fully meet the requirements of both students and teachers. A number of additional questions have been added to those given at the end of the book. In particular, greater attention is given to the exercises on chemical calculations: a number of typical examples are selected and worked out in detail, in order to illustrate the principles involved. In this edition the paragraphs are numbered and have side headings. The more important statements and definitions are printed in bolder type. These modifications will, I hope, be of assistance to the student.

A number of both students and teachers have pointed out to me that they have been using this work in preparing for the matriculation examination of the London University, but have been inconvenienced by its not covering the whole of the syllabus of that examination. In the present edition chapters have been added in order to supply this want; accordingly the book in its present form embraces the whole subject-matter necessary. At the discretion of their teachers, Science and Art Department students may omit this additional matter, which is contained in the following paragraphs: 108–110, 116–129, and 195 to end. I strongly recommend them, however, to read at least the intermediate paragraphs referred to, as by so doing they will gain a more complete elementary knowledge.

In conclusion I wish to tender my thanks to both reviewers and teachers for the kindness with which this book has been received in the past, and for the suggestions as to increasing its usefulness with which they have favoured me. Many of these have been of considerable value, and so far as practicable have been adopted.

WILLIAM JAGO.

SCIENCE SCHOOLS, BRIGHTON:
January 1888.

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TEXT-BOOK

OF

INORGANIC CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

1. Definition of Chemistry.—Phenomena are continually taking place around us to which we give the name of 'chemical actions.' For instance, a piece of bright iron speedily rusts when exposed to damp air; milk, as a result of exposure to the atmosphere, turns sour and acquires properties strikingly different from those possessed by that fluid when first obtained from the cow; coal, wood, and a host of other bodies, which are classed together as combustibles, burn on a light being applied to them, leaving in most cases no visible residue beyond a small quantity of ash. It is the function of the chemist to investigate these changes, and ascertain, as far as he can, the nature of the substances participating in the action and its causes. **Chemistry, then, may be defined as 'that science which treats of the composition of matter, of changes produced therein by certain natural forces, and of the action and reaction of different kinds of matter on each other.'**

The word 'matter,' which is here used, is employed scientifically to signify anything which has weight, *i.e.* which is acted on by gravitation. Stones, earth, water, and even gases, are matter.

2. Experimental Study necessary.—There is no science which is not better studied by the aid of experiments than without ; but while this is simply an additional advantage in some other sciences, it is *absolutely necessary* in the case of that of chemistry.

This book is intended, not only as a text-book for theoretical study, but also as a guide to practical work in the laboratory ; the experiments are, for this reason, not referred to descriptively, but, instead, practical directions are given for their performance ; except in some few instances, where they are of a nature more suited for the lecture table than to be tried individually by each student of a class.

It cannot be impressed too strongly at the outset that chemistry cannot be thoroughly and efficiently mastered without this work being actually performed by the student, and not merely seen performed. His own mind and hands should put the experimental question to nature, and his own powers of observation must learn to accurately interpret her answer.

The student will find at the close of this chapter some directions and hints for his use on first commencing work in the laboratory. He will, in all probability, have had the advantage of seeing the experiments performed by the teacher during the lecture preceding the laboratory lesson.

3. Characteristics of Chemical Action.—It is first necessary to carefully distinguish between what are merely alterations in the physical properties of matter and what are real chemical changes. This is best seen by an actual experiment.

Experiment 1.—Heat a piece of platinum wire in the flame of a Bunsen gas lamp ; it immediately becomes white hot ; re-

move it, and, as the wire cools, it once more regains its original brightness. It is not in the least altered, not even tarnished.

Next heat in the same way a piece of *bright* iron wire: this is tarnished, but otherwise will have undergone no great change.

Next place a piece of magnesium wire or ribbon in the flame: it burns with a dazzling white light, depositing a white, easily powdered body, composed of oxygen and magnesium, and known as magnesia.

In the first case the change produced is merely physical, and although the hot wire possesses properties which are absent in the cold, yet on the wire losing its heat it again regains its previous characters. With the iron wire a slight permanent change is produced on the surface: this is of a chemical character, but the main portion of the wire is unaltered. In the third instance a vigorous chemical change has occurred; the magnesium, as such, has entirely disappeared and a new body takes its place. The student hereby learns that **chemical changes are distinguished from those of a merely physical character by more or less striking permanent alterations in the appearance and properties of the substances involved therein.** The following are additional examples of changes produced by chemical action.

Matter occurs in three states, solid, liquid, and gaseous; chemical action is very frequently accompanied by a change from one of these to another.

Experiment 2.—Place in a test-tube some dilute sulphuric acid, in another about the same quantity of solution of calcium chloride; notice that each is a transparent, colourless liquid. Add the one to the other; in a few seconds the whole has become a solid mass, and the test-tube may be inverted with only a few drops of the liquid running out. In this case a new body has been produced, called calcium sulphate, which combines with a portion of the water present to form a solid.

Not only may liquids be converted into solids, but

solids in very many chemical changes are transformed into gases.

Experiment 3.—Light a piece of candle: it gets less by the act of burning, and ultimately would entirely disappear—the solid fat, composed of hydrogen and carbon, is being changed into gaseous compounds. Hold a cold surface, as the outside of a porcelain dish filled with water, in the flame: it gets blackened, owing to the separation of carbon as soot or lamp-black; and also becomes wet, through the deposition of water produced by the combination of hydrogen with the oxygen of the atmosphere.

Pour into a glass gas jar, or colourless glass bottle, of about a pint capacity, a layer of half an inch of clear lime-water; shake up the jar, the lime-water remains clear. Next take a small piece of candle and fix it in a deflagrating spoon; light it and place in the glass jar; it soon goes out; again shake the jar—the lime-water now becomes turbid through the formation of a compound of lime and the carbon dioxide produced by the oxidation of the carbon of the candle.

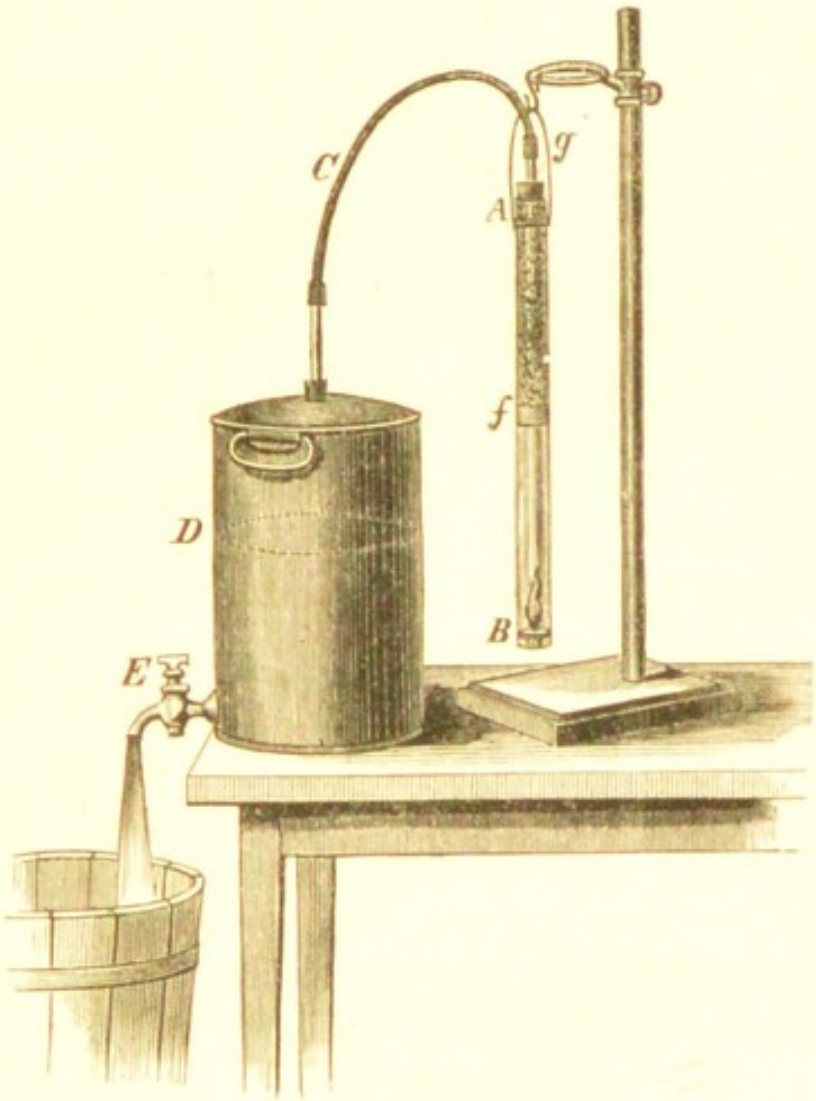
The small wax tapers used for lighting Christmas trees, &c., are very suitable for these experiments.

Although, in burning, the candle disappears, the bodies of which it is composed can thus be traced; for the disappearance of the candle is accompanied by the production of water, and also an invisible gas, which evidently differs from ordinary air, because it turns the lime-water milky, while, as the student will have seen, air is unable to produce this change.

4. Indestructibility of Matter.—By experiments similar in principle to that just described, but of a more exact character, in which **quantity** is estimated, it is found that the **whole** of the matter present before the combustion still exists after. **Matter is indestructible; and consequently the same weight of material remains after any and every chemical change as there was before its commencement.**

Experiment 4.—Take a glass chimney, such as is used for Argand lamps ; fit a cork to each end ; bore several holes in the lower cork, one being in the centre and of a size to fit a small taper, which must be inserted in it. Thrust a piece of wire gauze about two-thirds of the way up the chimney, so as to form a tight plug ; fill this upper chamber with fragments of caustic

FIG. 1.



soda ; bore a hole through the centre of the top cork and pass a piece of small glass tubing through. When complete, weigh the whole apparatus carefully ; next place it in a retort-stand and, by means of india-rubber tubing, connect with the short tube passing through the cork of a two-gallon can, filled with water, having a stop-cock at the bottom. Open this cock, and, as the water runs out, it causes a current of air through the

apparatus. Take out the taper, light, and quickly replace it; allow it to burn for three or four minutes, then turn off the cock —the taper goes out; disconnect the tubing from the top cork and again weigh; the weight has increased, owing to oxygen having been taken up from the atmosphere by the burning taper; it has combined with its constituents to form water and carbon dioxide respectively. These compounds are both absorbed and retained by the caustic soda. The apparatus is shown in Fig. 1. The student, working in a laboratory, will probably find these pieces of apparatus already prepared ready for use. As there is not likely to be a sufficient number for each student to try the experiment at the same time, it must be taken in turns.

So far from the burning of a candle being accompanied by any loss of its constituents, the weight of the resultant products is greater than that of the candle itself, because they contain in addition the oxygen removed from the atmosphere. Matter being indestructible, it follows that **when chemical combination occurs between substances, the weight of the products is exactly the same as that of the bodies previous to chemical action.** Proof of this statement will be afforded by experiments described in later chapters.

5. Distinction between Mechanical Mixture and Chemical Union.—The student who has carefully performed the preceding experiments will scarcely need to be told that **chemical combination is widely different from mere mixture.** In the latter case the resultant body is a mean in appearance, specific gravity, &c., between its constituents: they still each possess their individual properties, and the separate particles may be seen with sufficient magnifying power.

Experiment 5.—Take some finely divided copper; notice its colour; mix intimately with powdered sulphur; the mixture has a tint intermediate to that of the substances when separate. Place some of the mixed powder in an evaporating basin, and

wash with a gentle stream of water ; notice that the sulphur is carried away, and that the heavier copper remains behind. This and several other methods may be employed to effect their mechanical separation, which is easily done, as there is no union between them. Next, place some of the mixture in a dry test-tube, and heat ; observe that the sulphur first melts, and that shortly after the whole mass glows brightly. When cool, examine the resulting substance ; it is of a bluish-black colour, brittle, and one of its ingredients can no longer be separated from the other by the action of water or mere solvents. A new body has been formed by the union of the sulphur and copper, known as copper sulphide.

Not only does chemical combination produce bodies different from a mixture of the constituents, but it is also accompanied by an evolution of heat. In addition to the proofs of this statement afforded by previous experiments, the following shows the production of heat by chemical combination in a striking manner.

Experiment 6.—Place a few fragments of recently burned quicklime in a saucer or evaporating basin, and pour in sufficient cold water to just moisten the lime. In a short time the lime becomes very hot, and the water as such entirely disappears.

The heat in this experiment is due to chemical combination between the water and the quicklime.

The difference in appearance of bodies as a result of chemical combination and the production of heat are two of the principal characteristics by which a chemical union between substances is detected.

6. Element, Compound, Mixture.—It is well at this early stage of study to have accurate and concise ideas of the meaning attached to the terms, element, &c. Definitions are therefore appended :—

An ELEMENT is a substance which has never been separated into two or more dissimilar substances.

A COMPOUND is a body produced by the union of two or more elements in definite proportions, and consequently is a substance which can be separated into two or more dissimilar bodies. Compounds differ in appearance and characteristics from their constituent elements.

The term MIXTURE is applied to a substance produced by the mere blending of two or more bodies, elements or compounds, in any proportion without union. Each component of a mixture still retains its own properties, and separation may be effected by mechanical means.

7. Synthesis and Analysis.—In the experiments hitherto performed the operations have been of the kind known as 'synthesis,' that is, the putting together of elements and building up new compounds. Another most important mode of chemical investigation is 'analysis,' which consists of decomposing bodies, resolving them into their elements or simpler compounds.

Experiment 7.—Place some red mercuric oxide, about as much as could be held on a threepenny piece, in a dry test-tube; close the mouth *loosely* with the thumb and apply heat. Notice that the colour changes from red to black, the oxide gradually disappears, and minute globules of metallic mercury condense on the upper part of the tube. Next light a splinter of wood, a match will do very well; when well lighted blow out the flame, and introduce it while still glowing into the tube; it immediately again bursts into flame, thus showing the presence of the gas called oxygen.

In this experiment a compound has been separated into its two elements; or in other words its analysis has been effected.

8. Relation of Chemical Action to Force.—It has been already stated that when chemical combination occurs heat is generated; in order to effect the change

described in the last experiment heat has been used and has disappeared as such, being stored up in the elements in the form of the available or potential energy of chemical attraction or affinity. If the mercury and oxygen are again caused to combine the act of reunion will once more set free the exact amount of heat that was necessary to effect their decomposition. Many instances are known in which bodies that evolve a certain amount of heat on uniting may be again decomposed by being subjected to a more intense heat. In all such cases **the quantity of heat evolved during chemical combination is exactly equal to that requisite to effect the decomposition of the resultant body.**

Further, by proper appliances the chemical action of elements entering into combination may be caused to produce electricity ; and electricity in its turn is competent to dissociate the elements of compound bodies. There is in this case also a definite relation between the amount of chemical action and the quantity of electricity produced.

Force is defined as that which is capable of setting matter in motion; consequently chemical combination must be ranked among the forces; for such chemical actions, of which the combustion of coal is a typical example, generate heat, and thus indirectly, as in the steam-engine, constitute our most valuable means of setting matter in motion and overcoming resistances generally.

9. Relation between Gravitation, Cohesion, and Chemical Attraction.—Matter is maintained in its normal state through the Universe by the action of three most important forces—gravitation, cohesion, and chemical attraction. The first of these acts through all space, and exerts an attraction between all matter. Cohesion acts only across non-appreciable distances, holding together the particles of solids, and also, though to a much less extent, those of liquids.

Experiment 8.—Attach a clean glass plate about 4 or 5 inches in diameter to pieces of wire in the same way as a scale pan is suspended from the end of the arm; place it in a basin of water, so that the glass plate just floats on the surface; notice the pull necessary to tear it away from the water and overcome the cohesion existing between its particles. The amount of this cohesion may be approximately measured by suspending the glass plate from the arm of a balance, and counterpoising it in air; the plate is then floated on water and weights added to the pan until the two are separated.

By means of heat this force may be often overcome; thus solid ice may be converted into water; a further increase of temperature destroys the remaining cohesion and produces steam, which, in common with all other gases, is devoid of any cohesion between the particles. But, whether as ice, water, or steam, the substance is the same in chemical properties. By application of a more intense heat, however, the steam is decomposed into oxygen and hydrogen. Heat, therefore, not only destroys cohesion, but when sufficiently intense overcomes the force of chemical attraction which holds the elementary atoms of all compound substances together.

Summary.

Every-day instances of chemical action. Definition of chemistry. Experimental study is essential. Chemical action is accompanied by change of appearance, &c. Liquids into solids. Solids into gases.

Matter is indestructible; in no chemical change is it lost.

Chemical combination is essentially different from mere mixture; not only accompanied by change of appearance, but also by evolution of heat.

'Element,' &c., defined.

Two most important types of chemical action, synthesis and analysis.

Heat is capable of effecting the decomposition or analysis of compounds. The quantity necessary is reproduced when the elements recombine.

Chemical action may generate other forces, as heat and electricity; it is itself, therefore, a FORCE.

Chemical affinity holds together the elementary particles in compound bodies. Heat overcomes it, and dissociates them.

Laboratory Hints.

In the laboratory the student will either have to provide for himself, or be supplied with, a set of apparatus sufficient for the performance of the common experiments. Such a set should include—

Bunsen's burner and iron rose, with 2 feet of india-rubber tubing.

Retort-stand and spring clamp.

Two pieces of iron wire gauze 5 inches square.

Three flasks, respectively of 4, 8, and 16 oz. capacity.

Six test-tubes, 6 inches by $\frac{3}{4}$ inch diameter.

Test-tube brush.

Thistle funnel 18 inches long.

Glass funnel 2 inches diameter.

Dozen assorted corks.

Brass crucible tongs.

Small evaporating basin, about $2\frac{1}{2}$ inches diameter.

Small beaker, $4\frac{1}{2}$ oz. capacity.

Two books of litmus paper, red and blue.

$\frac{1}{4}$ lb. small glass tubing.

Two feet small india-rubber tubing.

Four gas bottles.

Four ground glass plates.

Messrs. Orme & Co., of 65 Barbican, London, E.C., supply the author with these sets of apparatus in boxes at 17*s*. They keep the sets in stock, and the apparatus is always reliable.

The following apparatus is generally supplied for common use:—

Earthenware pneumatic troughs and beehive shelves.

Deflagrating spoons and caps.

Deflagrating jars, open at top and bottom.

Retorts of various sizes.

Cork borers.

Pestles and mortars.

Aspirator, balance, weights, &c.

The more expensive pieces of apparatus must be obtained, when required, by application to the teacher.

The student should, in the first place, make himself familiar with the names and uses of his apparatus. Let him next carefully and thoroughly clean the glass and porcelain vessels. The chemicals required will be found as a rule in bottles and jars, so placed as to be readily accessible to the whole of the students. They should under no circumstances be removed from their places; the quantity required should be taken in a flask or test-tube, and the bottle immediately restored to its place. A strict adherence to this rule prevents the loss of a great amount of time which would otherwise be spent in searching over the laboratory for bottles, &c.

In getting the chemicals for an experiment, be sure the right ones are taken; see that concentrated acids are not used where dilute should be employed; never use pure substances when the commercial will answer the purpose; do not let the stoppers of bottles lie about or get mixed. Take no more of the substance than you require, and if you happen to have an excess do not return it to the bottle without express permission; much confusion has been caused by chemicals being replaced in the wrong bottles.

When directions are given that substances are to be *mixed*, solid bodies are to be first *powdered*, and then stirred together until the mixture is as uniform as possible.

Heat is applied to tubes, &c., by means of the Bunsen burner; before lighting it see that the holes at the bottom are open; the flame should be non-luminous; if smoky, it is a sign that the gas is burning at the lower end of the tube of the burner; it must be turned out and re-lighted. This catching fire at the bottom is the result of an excess of air entering; the remedy is to turn on more gas, or partly close the air-holes by turning the ring of the burner over them. In heating test-tubes, the heat must be applied gently at first, with a constant motion of the tube, or, if the tube be fixed, of the burner.

If heating a liquid, never let the flame play on the part of the tube above its surface. When a solid is being heated, if any moisture happen to be present, it condenses in the upper and cooler parts of the tube; when there is the slightest sign of this,

hold the tube almost horizontal, but with the hot part rather the higher: this prevents the condensed water running back on the hot glass.

The kind of balance usually employed in a laboratory is one having a long index-finger depending from the arm, with the point in front of a graduated scale. The swinging of the balance is shown by this index. When the weights placed in are equal to the body being weighed, it vibrates to an equal distance each side of the zero mark on the scale. The body to be weighed is placed in the left-hand pan, and the weights in the right. When not in use the pans are supported; by means of a handle they may be raised, and are then free to swing. The pans should always be dropped on their support when weights are being added or removed. The weights used for chemical purposes are those of the metric system; for their value, &c., the student should refer to the table given in Chapter III. Never touch the more delicate weights with the fingers, but use the forceps found in the box with them; great care must be taken that they are not soiled or otherwise injured.

A laboratory note-book should always be kept, and an account entered in ink of every operation as performed. This applies with special force to weighing.

At the close of the laboratory lesson wash the glass apparatus, and wipe with a dry cloth any water, &c., from the retort stand, and other articles which might rust.

CHAPTER II.

MODES OF CHEMICAL ACTION AND SEPARATION.

10. Heat, with other forces, acts over great distances.—Chemical attraction or affinity differs in one important particular from the other natural forces. These are capable of acting through distances which are, in many cases, enormous. Heat and light both reach us from the sun, and in doing so travel over ninety millions of miles, but chemical

action can only take place where there is absolute contact between the substances participating in it.

Experiment 9.—Hold a red-hot iron bar some inches from a piece of phosphorus about the size of a pea. Observe that the heat travels over the intervening space and the phosphorus is inflamed, *i.e.* takes fire. (In this and similar experiments the phosphorus, or other inflammable material, should be placed on a piece of iron or other substance which will prevent the heat injuring the work-bench.)

Magnetism and electricity, in common with heat, act over distances; a glass rod, when electrified, will cause the leaves of a delicate electroscope, which is some yards off, to diverge.

Experiment 10.—Electrify a piece of ebonite or a rod of shellac by rubbing with warm flannel; hold it near some fragments of paper or other light objects; they are attracted. If wished, a piece of glass rod or tube may be rubbed with silk, and used instead of the ebonite and flannel; when the same effect is produced. Place a magnet near a suspended magnetic needle; notice that the one end is attracted and the other repelled, though the two may be six or more inches apart.

11. Contact is required for Chemical Action.—Experiments of a most careful character have been made, in order to measure, if possible, the distance through which chemical action can take place; as a result it has been found that an interval unobservable to the naked eye is sufficient to prevent it.

Experiment 11.—Powder and mix together one part of loaf sugar and two of potassium chlorate. Take about as much of the mixture as can be held on a shilling and place on a stone slab. Dip the end of a glass rod in concentrated sulphuric acid; bring the rod as close to the mixture as possible, but not touching; notice that until actual contact ensues no action whatever occurs; the moment that they touch the whole mixture is inflamed.

In order that chemical action, once commenced, shall

continue, it is necessary that fresh portions of the substances should be brought into contact. The products of such action must therefore be removed as rapidly as formed ; the requisite mobility of particles necessary for this is best obtained by at least one of the bodies being in the liquid state. Liquidity may be effected in two ways : 1st, by the action of some solvent, of which water is the most common ; 2nd, by fusion.

Experiment 12.—Mix together some dry carbonate of soda and tartaric acid ; no action whatever occurs. Place the mixture in a test-tube and add water ; the substances are dissolved, and immediately a brisk effervescence ensues through the acid liberating carbon dioxide from the carbonate. Here chemical action is the result of the more intimate contact resulting from solution.

Experiment 13.—Mix together three parts by weight of nitre, two of dry carbonate of potash, and one of sulphur. Take a pinch *and no more* of this powder, and place in a small iron dish or ladle. Apply a gentle heat ; as soon as the mixture is fused it detonates violently. The face should not be held near this substance when being heated. The powder ready mixed is generally found in a laboratory. These substances may be preserved together in the solid state for an indefinite length of time, but combination immediately follows fusion.

12. Modes of Chemical Action.—Although chemical actions vary so much in their character, they can all be classified under the following five heads :—

I. Direct Union.—Several experiments already performed belong to this class, as heating together copper and sulphur ; many other examples will occur to the student as his knowledge of chemistry increases. The combination of hydrogen with chlorine or oxygen, producing hydrochloric acid and water respectively, are striking instances. Directions for the performance of these experiments are given in the chapters on the respective gases.

Experiment 14.—Place a small piece of phosphorus on an

iron plate and drop on it a very little powdered iodine. Combination at once occurs, iodide of phosphorus being formed; the heat evolved inflames the phosphorus, which continues burning.

II. Chemical Displacement.—The experiment of heating platinum and magnesium wires has already taught us that different elements have various degrees of chemical activity, for while the former is unaffected by such treatment, the latter combines with the oxygen of the air with great avidity. In certain cases a more active element, that is, one whose chemical attraction is stronger, is able to displace a weaker element from a compound, and itself occupy the vacant place.

Experiment 15.—In a solution of chloride or sulphate of copper, acidulated with a few drops of hydrochloric acid, place a bright iron rod; on removing it after a few seconds it will be seen to be coated with metallic copper, which has been displaced from its combination with the chlorine, chloride of iron being formed.

The chemical change may be thus represented :—

$$\text{Chloride of copper} \begin{cases} \text{Copper} \\ \text{Chlorine} \\ \text{Iron} \end{cases} = \begin{cases} \text{Iron} \\ \text{Chlorine} \\ \text{Copper} \end{cases} \text{Chloride of iron}$$

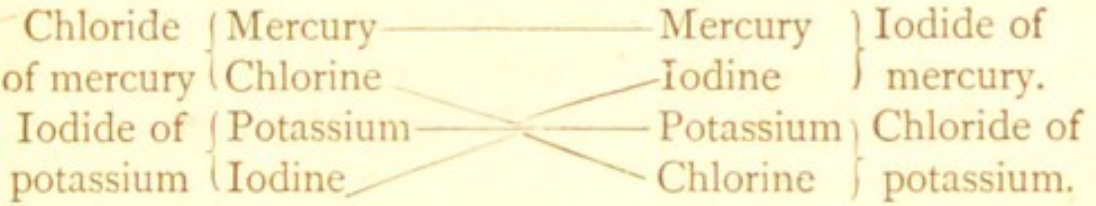
III. Mutual Chemical Exchange.—It frequently happens that when two compounds are brought together, an element of each may have a mutual attraction which results in their combination; the remaining elements also combine. An example will render this clear.

Experiment 16.—Place in a test-tube some solution of perchloride of mercury and add to it, drop by drop, iodide of potassium solution; a red powder is formed, which, from being suspended in the liquid, gradually falls to the bottom. This powder is iodide of mercury. Chloride of potassium remains in solution.

The mercury has exchanged its chlorine for the iodine

of the potassium, and the potassium in its turn combines with the chlorine.

The chemical change may be thus represented :—



If in this experiment an excess of iodide of potassium be used, it re-dissolves the iodide of mercury. Whenever a substance separates from a solution through the addition of another body, as the iodide of mercury has done in this instance, the term *precipitate* is applied to the separated body.

IV. Re-arrangement of Particles.—This is a mode of chemical action of which there are no good examples in inorganic chemistry ; from organic compounds many instances might be cited. In such cases a compound, consisting of certain elements combined in definite proportions, is converted into another in which the properties are different, and yet the composition is precisely the same. The change may be compared to the re-arrangement of letters of certain words ; thus the word 'art' may be transposed into 'rat' ; the two words are totally different, and yet the letters are identical.

V. Direct Decomposition.—The resolution of oxide of mercury into mercury and oxygen is an instance of this type of chemical action, which has already been described. The electrolysis, or separation by electricity, of water into its component elements is another example with which the student will shortly become acquainted.

13. Chemical Separations.—The chemist frequently finds, in the course of experiment, that it is necessary to separate bodies from each other ; the processes employed for this purpose are varied, depending on the nature of the substances. As in many future operations it will be necessary to use one or more of them, it is advisable that at this stage they should be studied. There is, as a rule, some par-

ticular property which one of the elements or compounds in a mixture possesses which the other does not : thus one may be soluble in water, the other insoluble; this at once affords a means of separating them. **The principal methods of separation employed are Solution, Decantation, Filtration, Crystallisation, Evaporation, Distillation, Sublimation, and Ignition.**

14. Solution, Decantation, and Evaporation.—A mixture of two bodies, one only of which is soluble in water, is separated by the action of that solvent.

Experiment 17.—Take some of a mixture of sand and salt, place in a test-tube, add water, and shake up ; allow the sand to subside ; the clear solution on the top is to be carefully poured off, without disturbing the sediment, into an evaporating basin. This process is known as *decantation.* Place a piece of wire gauze on one of the rings of the retort stand, adjusted at a suitable height above the Bunsen burner ; put the evaporating basin containing the solution of salt on the gauze and light the burner, keeping the flame small ; the water will gradually evaporate, and crystals of salt will form. The object of placing the wire gauze under the basin is to prevent the flame coming in actual contact with and cracking it. The water has been driven off by *evaporation.*

In cases where both bodies are insoluble in water, some substance must be selected which acts on the one without the other.

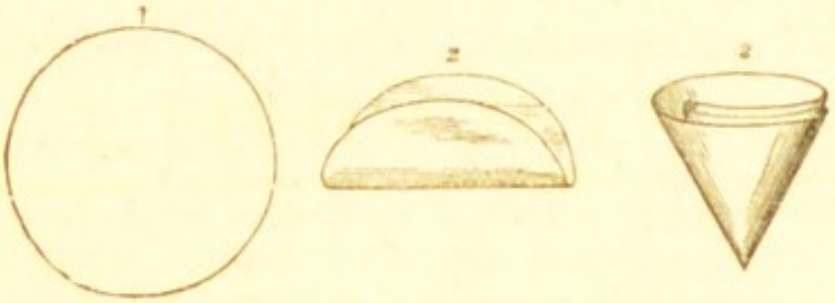
Experiment 18.—Place some of a mixture of sand and marble in a test-tube, add some distilled water, and heat. Take out a few drops of the water, and evaporate them on clean platinum foil ; they entirely disappear, or only leave the slightest stain on the foil. This is the usual test employed to ascertain whether a solvent has dissolved anything or not. Decant off the water and add dilute hydrochloric acid to the mixture ; effervescence occurs. When this is over, again take out a few drops of the liquid and evaporate on the foil ; a considerable residue will remain. The best plan to get a few drops out of a test-tube is to put in the end of a glass tube ; then close the top

with the finger, and withdraw it. On removing the finger the small portion it contains runs out.

The separation in this experiment depends on the fact that chalk is dissolved by hydrochloric acid, while sand is not affected by it.

15. Filtration.—There are many cases in which decantation is not suitable for the purpose of separating a liquid

FIG. 2.



and solid; the solid body may perhaps be so finely divided that it remains suspended in the liquid, giving it a muddy appearance. Under these circumstances, *filtration* is resorted to.

FIG. 3.



Experiment 19.—Take a filter paper about 3½ inches diameter, and double it twice; then open it into a cone, taking three folds of paper on the one side and one on the other, as shown in Fig. 2. Place this cone of paper in a glass funnel, which it will just fit, and moisten with water. Care must be taken that the point of the folded filter does not get broken. Next add to a solution of calcium chloride some ammonium carbonate; a white precipitate is formed. Pour the

whole on the filter, holding a glass rod against the lip of the beaker or test-tube down which the liquid runs (Fig. 3); the clear liquid known as the filtrate passes through and must be collected in a beaker; the precipitate, consisting of calcium carbonate, remains on the filter. Pour some clean water on it for the purpose of washing. After this has drained off, remove the beaker, push a hole through the bottom of the filter, wash the precipitate into an evaporating basin, and dry it. The filtrate contains ammonium chloride, which may be obtained by evaporation.

16. Crystallisation.—Where two bodies are mixed together, both of which are soluble in water, but in different degrees, another plan may be adopted for their separation.

Experiment 20.—Take a mixture of about equal parts of potassium chlorate and potassium chloride. Place some in a test-tube, and add just sufficient water to dissolve the whole on boiling; now allow the solution to cool; tabular crystals will separate out, consisting of the less soluble potassium chlorate. When cold, filter these off, just wash with cold water, and dry at a gentle heat.

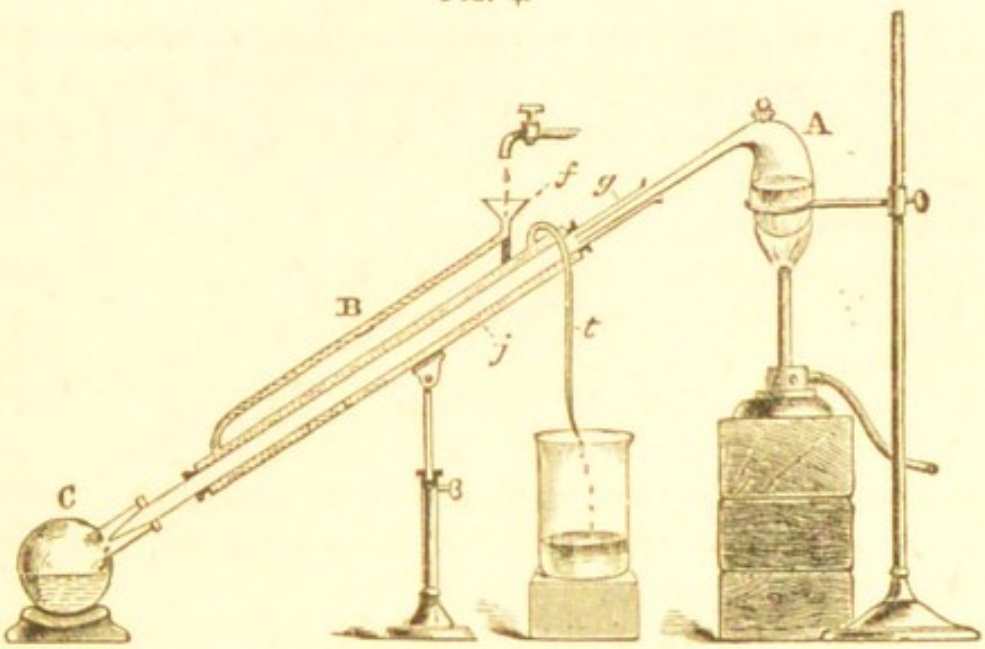
Separation by crystallisation is a process largely used for manufacturing purposes

17. Distillation.—In the experiments made by evaporation, we have only as yet dealt with the solids which remain, but in many cases the liquid is also required. In the laboratory, where pure water is an essential, it is obtained by this process of distillation, in which the steam is again condensed and collected.

Experiment 21.—Take a glass retort, or, what answers the purpose equally well, a copper vessel fitted with a cork and leading tube, and put some brine in it; fix it in the retort stand, and attach by india-rubber tubing to a Liebig's condenser, as shown in Fig. 4. The condenser consists of two glass tubes, one fitting inside the other; the steam passes through the inner one, and, as condensed, runs into the flask placed as a receiver. Through the outer tube a current of cold water is passed, which speedily condenses the steam. The pipe conveying the water

is attached to the lower end of the condenser. After some water has collected, taste it, and notice that it is perfectly free from salt.

FIG. 4.



The advantage of a copper vessel for this experiment is that there is no danger of breakage ; the required apparatus will be obtained in a laboratory on application to the teacher.

18. Sublimation.—This is a process somewhat analogous to distillation ; it is in fact distillation of substances which condense in the solid instead of the liquid state.

Experiment 22.—Heat a small portion of a mixture of sand and ammonium chloride in a test-tube ; dense white fumes are evolved, which condense as a white crust in the upper part of the tube, the sand remaining behind.

Bodies which distil or sublime are termed *volatile*, and those which neither distil nor sublime are said to be *fixed*.

19. Ignition.—Occasionally the chemist avails himself of the combustibility of bodies, and burns them off from others which are incombustible.

Experiment 23.—Place some of a mixture of sand and lampblack or soot on platinum foil, and keep at a bright red heat for some time with the Bunsen ; the lampblack will burn off, leaving the incombustible sand behind. It may be mentioned that when

directions are given to *ignite* a body, it simply means that it is to be heated intensely ; it does not follow that it will burn.

Summary.

Light, heat, electricity, and magnetism act over considerable distances ; chemical attraction only between bodies in actual contact. Liquidity of one at least of two bodies aids chemical action

Modes of chemical action :—

I. Direct union.
II. Chemical displacement.
III. Mutual exchange.
IV. Re-arrangement of particles.
V. Direct decomposition.

Methods of separation employed by the chemist :—Solution, decantation, filtration, crystallisation, evaporation, distillation, sublimation, and ignition.

Laboratory Hints.

Great care must be taken in the handling of phosphorus ; it is always kept under water because of its inflammability. If a small piece is wanted, take a stick out of the bottle with a pair of tongs, place it under water, and cut it while there. Dry it by pressing gently between folds of filter paper or a duster. It should not be touched with the fingers.

The student should not forget that sand and solid substances generally should *never* be thrown down the drains, but put into a box or other receptacle specially provided.

CHAPTER III.

WEIGHTS AND MEASURES, ETC.

20. The Metric System.—For the complicated system of weights and measures in use in England, most chemists substitute the very simple metric system. The unit of the system is the metre, a rod of platinum deposited

in the archives of France, which, when constructed, was supposed to be one-ten-millionth part of the quadrant of a great circle encompassing the earth on the meridian of Paris.

21. Measures of Length.—The metre measures 39·37 inches. It is multiplied and subdivided by 10 for the higher and lower measures of length.

Kilometre	= 1000	metres	= 39370	inches.
Hectometre	= 100	„	= 3937·0	„
Decametre	= 10	„	= 393·70	„
Metre			= 39·370	„
Decimetre	= 0·1	metre	= 3·9370	„
Centimetre	= 0·01	„	= 0·39370	inch.
Millimetre	= 0·001	„	= 0·03937	„

The Greek prefixes deca, hecto, and kilo are used to represent 10, 100, and 1000 respectively; and the Latin deci, centi, and milli signify a tenth, hundredth, and thousandth.

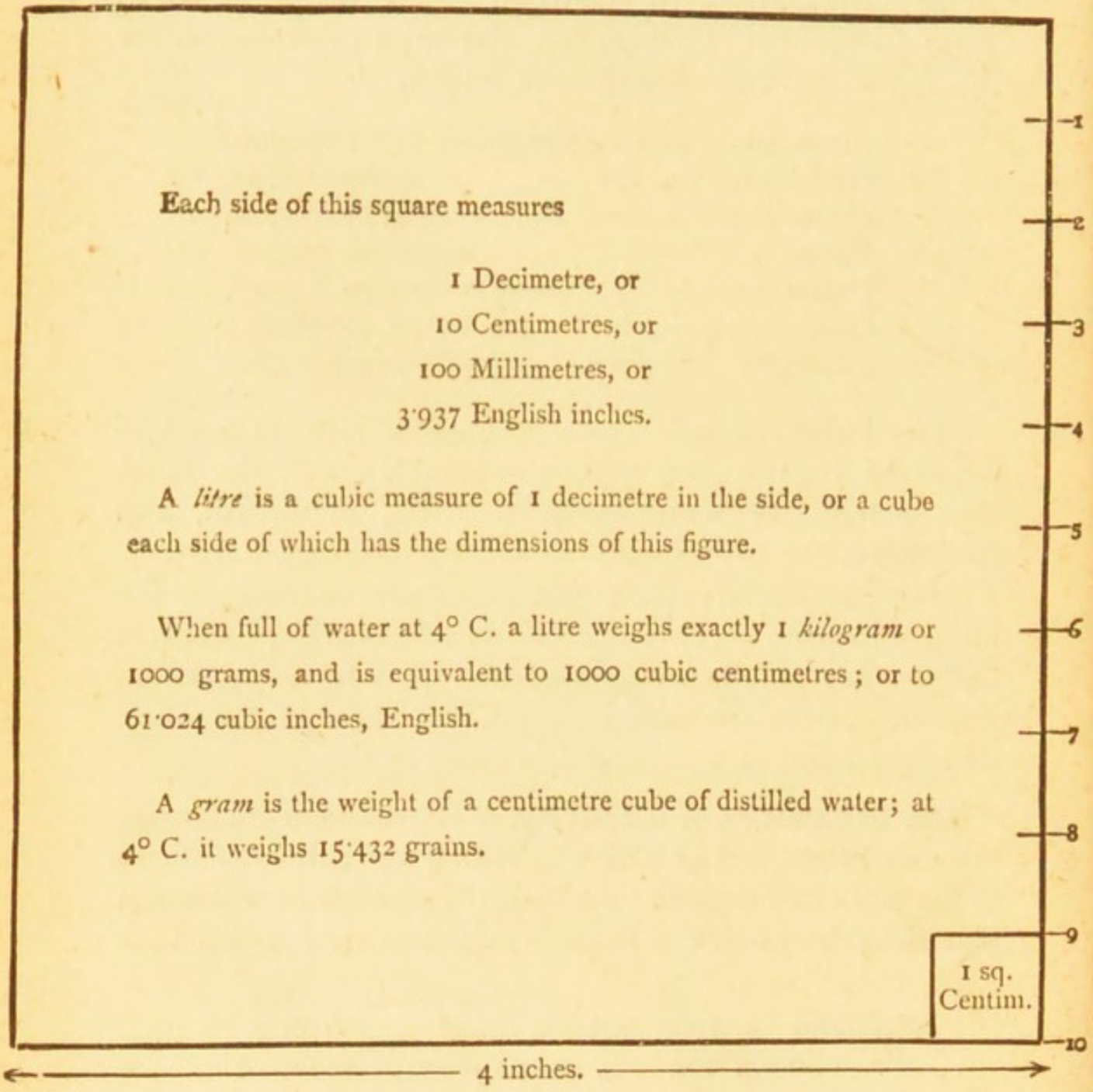
The prefixes are used with the same meaning in the other measures. The decimetre is very nearly 4 inches in length: this affords an easy method of roughly translating measures of the one denomination into those of the other. The actual size of a decimetre is given in Fig. 5.

22. Measures of Capacity.—The measure of capacity is derived from that of length by taking one cubic decimetre as the unit: this is named the litre, the capacity of which and that of its derivatives in English measures are appended:—

			Cubic inches.	Pint
Kilolitre	= 1000	litres =	61027	1760·7
Hectolitre	= 100	„ =	6102·7	176·07
Decalitre	= 10	„ =	610·27	17·607
Litre		=	61·027	1·7607
Decilitre	= 0·1	litre =	6·1027	0·17607
Centilitre	= 0·01	„ =	0·61027	0·017607
Millilitre	= 0·001	„ =	0·06102	0·0017607

The litre, being the capacity of a cubic decimetre, it is evident that the millilitre equals in volume a *cubic centimetre*; this latter term, or its abbreviation (c.c.) is very frequently

FIG. 5.



used in preference to millilitre; thus a pipette is said to contain 50 c.c., and a litre flask is often called a 1000 c.c. flask.

A cubic inch is equal to 16·38 cubic centimetres.

23. Measures of Weight.—The weight of one cubic centimetre of distilled water at its maximum density (4° C.) is taken as the unit of weight, and is called a gramme or gram. The subdivisions and multiples are again the same :—

			Grains.	Avoirdupois ounces.
Kilogram	= 1000 grams	=	15432·3	35·2739
Hectogram	= 100 „	=	1543·23	3·52739
Decagram	= 10 „	=	154·323	0·352739
Gram		=	15·4323	0·0352739
Decigram	= 0·1 gram	=	1·5432	0·003527
Centigram	= 0·01 „	=	0·15432	0·0003527
Milligram	= 0·001 „	=	0·015432	0·00003527

A kilogram is a little over 2 lbs. 3¼ oz., and a hectogram 3½ oz. An ounce avoirdupois equals 28·35 grams.

The relation between the weight and volume of water is seen to be a very simple one ; the volume being the same number of c.c. as the weight is grams. With other liquids the volume in c.c. × specific gravity = weight in grams.

Experiment 24.—Take either a half-litre or litre flask ; see that it is dry, and weigh carefully ; fill to the graduated mark with distilled water, and again weigh ; the weight of the water is either 500 or 1000 grams.

24. English Weights and Measures.—Familiarity with English weights and measures is assumed ; still the following particulars may be useful :—

One gallon of pure water at a temperature of 62° F. (16·6° C.) weighs 10 pounds, or 160 ounces, or 70,000 grains. The pint therefore weighs 20 ounces. The measure termed a 'fluid ounce' is derived from the weight of a pint of water. A fluid ounce is a measure of volume, not of weight, and equals one-twentieth part of a pint. The fluid ounce bears the same relation to the avoirdupois ounce as does the cubic centimetre to the gram. When directions are given to dissolve one part by weight of a solid in 5 or other number of parts by weight of water, either ounces in

fluid ounces, or grams in cubic centimetres, may be taken. A gallon is equal to 277·274 cubic inches. An ounce avoirdupois weighs 437·5 grains.

25. Heat Measurements.—The most important measures of heat are its temperature or intensity, and quantity.

26. Temperature.—The temperature of a body is a measure of the intensity of its heat, and is further defined as the thermal state of a body considered with reference to its power of communicating heat to other bodies. Temperature is, in fact, the measure of what is popularly termed 'how hot a body is.' It will be seen on consideration that this depends on the power the body has of imparting heat to another body. Thus, if when the hand is thrust into water the water is able to yield heat to the hand, it is said to be 'hot,' while if it robs the hand of heat it is said to be 'cold.'

27. The Thermometer.—The instrument used for measuring temperature is termed a 'thermometer.' The thermometer consists of a glass tube of very narrow bore, with a bulb blown at the end; the bulb and part of the tube are filled with mercury; all the air is then driven out, and the tube hermetically sealed by fusing its upper end. The thermometer is placed in contact with any body whose temperature it is desired to measure. If the body be the colder of the two the thermometer yields heat to it, or receives heat if it be the hotter. This transference of heat continues until the temperature of the two is equal. Mercury expands with an increase, and contracts with a decrease of temperature, but for the same temperature has always the same volume. From the construction of the thermometer any alteration of the volume of the mercury is readily observed; the height of the mercury in the tube is therefore a measure of its volume, and secondarily of its temperature, and that of any body with which it is in contact.

28. Thermometer Scales.—Subject to certain precautions, the temperature of melting ice and that of steam in contact with boiling water are constant. The height at which the mercury stands when immersed in each of these is marked on most thermometers. For the registration of other temperatures some system of graduation must be employed. The one most commonly used in this country is that of Fahrenheit, while for scientific purposes that of Celsius, or the Centigrade scale, is almost universally adopted. Fahrenheit divided the distance between the melting and boiling points of his thermometer into 180 degrees. Degrees of the same value were also set off on either side of these limits. At 32 degrees below the melting point he fixed an arbitrary zero of temperature from which he reckoned. On his thermometric scale the melting point is 32°, while the boiling point is $32 + 180 = 212°$. Degrees below the zero are reckoned as − (minus) degrees; thus − 8° means 8 degrees below zero, or 40 degrees below the melting point. Degrees above 212 simply reckon upwards: 213°, 214° F., &c.

The Centigrade scale is much simpler. The melting point is taken as 0° or zero, and the boiling point as 100°. Temperatures below the melting point are reckoned as − degrees.

The conversion from one to the other of the Centigrade and Fahrenheit scales may be easily performed.

180 Fahrenheit degrees = 100 Centigrade degrees

9 " " = 5 " "

1 " degree = $\frac{5}{9}$ " "

$\frac{9}{5}$ " " = 1 " "

There is this important difference between the two scales: Centigrade degrees count from the melting point,

while Fahrenheit degrees are reckoned from 32 below the melting point.

$$30° \text{ C.} = 30 \times \frac{9}{5} = 54 \text{ Fahrenheit degrees.}$$

Therefore 30° C. are equivalent to 54 Fahrenheit degrees above the melting point, but as the melting point is 32, that number must be added on to 54. The temperature Fahrenheit equal to 30° C. is 86°. By the reverse operation Fahrenheit degrees are converted into degrees Centigrade. The following formulæ represent the two operations :—

$$\frac{\text{C.}° \times 9}{5} + 32 = \text{F.}° \qquad \frac{(\text{F.}° - 32) \times 5}{9} = \text{C.}°$$

29. Quantity of Heat.—If two vessels, the one holding a pint, the other a quart, are both filled with boiling water, the temperature of the water in each will be the same, but the *quantity* of heat will be double as much in the quart as in the pint. **Quantity of heat is measured by the amount necessary to raise a certain weight of some body from one to another fixed temperature. The quantity of heat necessary to raise 1 gram of water from 0° to 1° C. is termed a Unit of Heat.**

30. Absolute Temperature.—There are certain reasons which lead us to suppose that at a temperature of − 273° C. bodies would be entirely devoid of heat. **This point −273° C. is therefore often termed the absolute zero of temperature, and temperature reckoned therefrom is termed 'absolute temperature.'** The absolute temperature of a body is its temperature in degrees C. + 273.

31. Expansion and Contraction of Gases.—All gases expand with increase, and contract with diminution, of temperature. The amount of expansion and contraction is the same for all gases between the same limits of temperature, provided the temperature is considerably higher than that

at which they condense to liquids. **The volume of all gases is directly proportional to their absolute temperature.** Because of this variation with temperature it **is necessary to fix a temperature which shall be considered as a standard in expressing the volume of a gas: 0° C. is commonly adopted for this purpose.**

Knowing the volume of a gas at any one temperature, its volume at any other may be easily calculated; thus, a vessel was found to contain 750 c.c. of air at 15° C.; it is required to find its volume at the standard temperature :—

$$15° \text{ C.} + 273 = 288° \text{ absolute temperature.}$$
$$0° \text{ C.} + 273 = 273° \quad \text{"}$$

As 288 : 273 :: 750 : 711 c.c. of gas at standard temperature.

The volume of a gas is also affected by the pressure to which it is subjected: this variation is governed by what is called Boyle and Marriotte's law. **The volume of any gas is inversely proportional to the pressure to which it is subjected.** This law also only holds good in strictness when the temperature of the gas is considerably above the liquefying point. The most important variations of pressure to which gases are liable are those resulting from the changes in pressure of the atmosphere. The height of the mercury column of the barometer is a direct measure of the pressure of the atmosphere; therefore that pressure is commonly expressed in the number of millimetres (m.m.) which that column is high. **For purposes of comparison it is also necessary to reduce all pressures to one standard; that selected is an atmospheric pressure which causes the barometer to stand at 760 millimetres.**

As an example of a calculation of the volume of a gas when the pressure is varied, the following may be taken: 1000 c.c. of gas is measured at a pressure of 750 m.m.; required its volume at the standard pressure of 760 m.m. :—

As 760 : 750 :: 1000 : 987 c.c of gas at standard pressure.

The temperature and pressure quoted as standards for gas measurement, 0° C. and 760 m.m., are often termed **normal temperature and pressure** : for this expression, the abbreviation 'N.T.P.' is frequently used.

Finally, the student is specially requested to bear in mind that, when sufficiently far removed from their liquefying points, **all gases expand and contract equally for similar variations in temperature and pressure, their behaviour in this respect being independent of their chemical properties.**

Summary.

Weights and measures ; the metric system ; English weights and measures.

Heat measurements ; temperature ; the thermometer ; thermometric scales ; quantity of heat ; absolute temperature.

Relation of volumes of gases to temperature and pressure.

CHAPTER IV.

ELEMENTS, SYMBOLS, AND ATOMIC WEIGHTS.

32. List of Elements.—Although the number and variety of bodies we see around us are practically infinite, yet we find that they are mostly compounds which contain only a few elements. All the compounds known to us are built up from between sixty and seventy elements. Of these but a small number occur plentifully, the rest being only sparingly distributed, while several are present in the earth's crust in only the merest traces. The following table contains a list of the known elements, their symbols, atomicities, where known, and combining or atomic weights. Those

printed in capitals are the non-metals or metalloids ; those in ordinary type are the commoner metals ; those in italics are the rarer metals. The combining weights given are those derived from the experiments of Stas. For most calculations the nearest whole number or whole number with ·5 may be employed. Thus chlorine may be taken as 35·5, oxygen as 16, and so on

Name.	Symbol.	Atomicity.	Combining or Atomic Weight.
Aluminium	Al	IV	27·3
Antimony (Stibium)	Sb	V	122·0
Arsenic	As	V	74·9
Barium	Ba	II	136·8
Beryllium	Be		9·0
Bismuth	Bi	V	210·0
BORON	B	III	11·0
BROMINE	Br	I	79·75
Cadmium	Cd	II	111·6
Cæsium	Cs	I	133·0
Calcium	Ca	II	39·9
CARBON	C	IV	11·97
Cerium	Ce		141·2
CHLORINE	Cl	I	35·37
Chromium	Cr	VI	52·4
Cobalt	Co	IV	58·6
Copper (Cuprum)	Cu	II	63·0
Didymium	D		147·0
Erbium	E		169·0
FLUORINE	F	I	19·1
Gallium	G		69·8
Gold (Aurum)	Au	III	196·2
HYDROGEN	H	I	1·0
Indium	In	III	113·4
IODINE	I	I	126·53
Iridium	Ir	IV	196·7
Iron (Ferrum)	Fe	VI	55·9
Lanthanum	La		139·0
Lead (Plumbum)	Pb	IV	206·4
Lithium	Li	I	7·01

Name.	Symbol.	Atomicity.	Combining or Atomic Weight.
Magnesium	Mg	II	23·94
Manganese	Mn	VI	54·8
Mercury (Hydrargyrum)	Hg	II	199·8
Molybdenum	Mo	VI	95·6
Nickel	Ni	IV	58·6
Niobium	Nb	V	94·0
NITROGEN	N	V	14·01
Osmium	Os	VI	198·6
OXYGEN	O	II	15·96
Palladium	Pd	IV	106·2
PHOSPHORUS	P	V	30·96
Platinum	Pt	IV	196·7
Potassium (Kalium)	K	I	39·04
Rhodium	Rh	IV	104·1
Rubidium	Rb	I	85·2
Ruthenium	Ru	VI	103·5
SELENIUM	Se	VI	78·0
Silver (Argentum)	Ag	I	107·66
SILICON	Si	IV	28·0
Sodium (Natrium)	Na	I	22·99
Strontium	Sr	II	87·2
SULPHUR	S	VI	31·98
Tantalum	Ta	V	182·0
TELLURIUM	Te	VI	128·0
Thallium	Tl	III	203·6
Thorium	Th		231·5
Tin (Stannum)	Sn	IV	117·8
Titanium	Ti	IV	48·0
Tungsten	W	VI	184·0
Uranium	U	VI	240·0
Vanadium	V	V	51·2
Yttrium	Y		93·0
Zinc	Zn	II	64·9
Zirconium	Zr	IV	90·0

33. Metals and Metalloids, or Non-Metals.—The elements are divided into two groups, termed respectively 'metals' and 'metalloids, or non-metals.' The line of

division between the two classes is not very marked, the one group gradually merging into the other. **The metals as a class are opaque bodies, having a peculiar lustre known as metallic; they are usually good conductors of heat and electricity.** Arsenic, which is here included among the metals, is grouped by some chemists among the metalloids: its properties are intermediate. Two of the elements are liquid at ordinary temperatures, mercury and bromine; four, viz. hydrogen, chlorine, oxygen, and nitrogen, are gaseous, but can be liquefied by intense cold and pressure. The remainder are solid. In 1877 MM. Cailletet and Pictet succeeded in effecting the condensation of hydrogen, oxygen, and nitrogen; hence, from these having before resisted all attempts at liquefaction, the name *permanent gases* was applied to them.

34. Composition of the Earth's Crust.—It has already been stated that of some elements mere traces only have been discovered; the great mass of the earth's crust is composed of even a more limited number than the remainder. It has been estimated that its average composition by weight is represented by the following table:—

Oxygen	480
Silicon	290
Aluminium	80
Iron	60
Calcium	30
Magnesium	20
Sodium	20
Potassium	15
Hydrogen	2
Other elements	3
	1000

35. Symbols and Formulæ.—For convenience of description **each element has an abbreviation of its full name, called its symbol.** This is, where practicable, the first letter of its Latin name: when two or more elements

have names commencing with the same letter, it becomes necessary to distinguish them from each other by restricting the initial letter to the most important element, and selecting two letters as the symbol of each of the others. Thus carbon, chlorine, and copper (*cuprum*) each commence with 'C'; that letter is chosen as the symbol of carbon, while those of chlorine and copper are respectively Cl and Cu.

As all compound bodies consist of elements united together, they may be conveniently expressed symbolically by placing side by side the symbols of the constituent elements: **the symbol of a compound is termed its formula.** Thus common salt consists of chlorine and sodium; its formula is accordingly written NaCl.

36. Further Uses of Symbols and Formulæ; Law of Chemical Combination by Weight.—Simply as abbreviations of the full names symbols and formulæ are of great service; this, however, is but a small part of their significance and value in chemistry. Their further use may best be explained by reference to certain information gained by experiment, to which careful attention is requested. On analysis it is found that 36·5 ounces of the substance known as hydrochloric acid consists of one ounce of hydrogen combined with 35·5 ounces of chlorine; also that in 58·5 ounces of common salt there are 35·5 ounces of chlorine to 23 of sodium. Taking water as another instance of a hydrogen compound, analysis shows that its composition may be expressed by the statement that 18 ounces of water consist of 2 ounces of hydrogen combined with 16 ounces of oxygen. In the table given in paragraph 31 there is a column headed 'Combining or Atomic Weight'; on referring to this it will be found that the numbers opposite hydrogen, chlorine, sodium, and oxygen are respectively (in whole numbers) 1, 35·5, 23, and 16, being (with one exception) identical with those that have just been given as the numbers obtained by analysis of the compounds under con-

sideration. **It is possible to assign to every element a number, which number or its multiple shall represent the proportionate quantity by weight of that element which enters into any chemical compound. These numbers are termed the 'combining or atomic weights' of the elements, and are deduced from results obtained on actual analysis.** In addition to its use as an abbreviated title of any element, **the symbol repesents the quantity of the element indicated by its combining weight;** where multiples of that quantity exist in a compound the fact is expressed by placing a small figure after the symbol and slightly below the line. A large figure placed before a symbol signifies that number of the whole compound.

As previously stated, the formula of sodium chloride is NaCl, and it contains 23 of sodium to 35·5 of chlorine. The formula of hydrochloric acid is HCl, and it contains 1 of hydrogen to 35·5 parts of chlorine. Water consists of 2 parts of hydrogen to 16 of oxygen; the fact that it contains twice the combining weight of hydrogen is expressed by writing the formulæ H_2O. Again, ammonia contains 3 parts by weight of hydrogen to 14 parts of nitrogen; consequently it has the formulæ NH_3. The gas termed carbon dioxide consists of 32 parts, or twice the combining weight, of oxygen to 12 by weight of carbon; the formula is consequently CO_2. **The quantity of an element represented by its combining weight is termed 'one combining proportion' of that element.**

37. Constitutional Formulæ.—In addition to simply showing the number of atoms of each element present, formulæ are frequently so written as to show the probable constitution of the molecule; such formulæ are termed 'constitutional formulæ.'

38. Chemical Equations.—Chemical changes are most conveniently expressed by what are termed 'chemical

equations': these consist of the symbols and formulæ of the bodies participating placed before the sign =, while those of the resultant bodies follow.

For example, the action of iodide of potassium and chloride of mercury on each other is thus expressed :—

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

Mercury chloride. Potassium iodide. Mercury iodide. Potassium chloride.

Having access to a table of combining weights, the chemist learns from this equation that one part of mercury chloride, containing one combining proportion of mercury weighing 200, and two combining proportions of chlorine, each weighing 35·5, together with two parts of potassium iodide, each containing one combining proportion of potassium weighing 39, and one of iodine weighing 127, together yield or produce one part of mercury iodide, containing one combining proportion of mercury weighing 200, and two of iodine each weighing 127, and two parts of potassium chloride, each consisting of one combining proportion of potassium weighing 39, and one of chlorine weighing 35·5. **As no chemical change affects the weight of matter, the weight of the quantity of a compound represented by its formula must be the sum of those of the constituent elements; so, too, the weight of the bodies resulting from a chemical change must be the same as that of the bodies before the change, whatever it may be, had occurred.** Also the same number of atoms of each element must appear on each side of the equation. Although from a chemical equation and table of combining weights it is possible to state what relative weight of each element is concerned in any chemical action, it must never be forgotten that **the combining weights were first determined by experiment, and then the table compiled therefrom.** The statement of premise and deduction is that hydrogen and chlorine have respectively the combining weights of 1 and 35·5 assigned to them, be-

cause analysis shows that they combine in those proportions; not that hydrogen and chlorine have as combining weights 1 and 35·5, and therefore they must combine in those proportions. The series of combining weights is simply a tabular expression of results obtained by practical analytic investigation.

39. **Atoms and Molecules.**—The fact that the quantity of every element which enters into combination is either a certain definite and unchangeable weight, or a multiple of that weight, led chemists to feel that this weight of a combining proportion of an element is in some way associated with its physical nature. The first step toward the explanation of this problem is due to Dalton, who enunciated what is termed the Atomic Theory. He assumed that all matter is built up of extremely small particles, which are indivisible, and that when elements combine it is between these particles that the act of union occurs. These ultimate particles of matter are termed 'atoms.' The name 'atom' is derived from the Greek, and signifies that which is indivisible. Atoms of the same element are supposed to be of the same size and weight. With the absolute weight of atoms the chemical student has but little to do; the principal point of importance for him is their relative weights compared with each other. For chemical purposes **an atom may be defined as the smallest particle of an element which enters into, or is expelled from, a chemical compound. For the phrase 'combining proportion,' hitherto used, the term 'atom' may be substituted. The combining weight then becomes the relative weight of the atom of each element compared with that of hydrogen, which, being the lightest, is taken as unity.**

In assigning an atomic weight to an element chemists are guided by several considerations: the study of these must be postponed until the student's knowledge is more advanced.

The little group of atoms represented by the formula of a compound is termed a 'molecule.' **A molecule is the smallest possible particle of a substance which can exist alone.** In the case of chemical compounds the molecules cannot be further subdivided, except by separation into the atoms of constituent elements or into two or more molecules of some simpler chemical compound or compounds.

40. Elementary Molecules.—There are not only molecules of compound bodies, but also **when elements are in the free or uncombined state their atoms usually combine together to form elementary molecules.** Thus in oxygen two atoms unite to form a molecule of oxygen; the formula of the oxygen molecule is written O_2.

The molecules of the following elements contain two atoms: hydrogen, chlorine, oxygen, sulphur, and nitrogen.

As all elements normally exist in the molecular state it is advisable always to use equations in which the lowest quantity of any element present is a molecule. Thus

$$H_2 + Cl_2 = 2HCl$$

should be written as the equation representing the combination of hydrogen and chlorine, rather than

$$H + Cl = HCl.$$

41. Further Explanation of Atomic Theory.—When the student's knowledge of chemical facts is more extended the atomic theory will be explained more fully, and also the experimental basis on which it is founded. It is necessary to have some idea of what it involves in order to understand the uses of chemical equations. An exact knowledge of these equations is of vital importance; the result of every experiment mentioned in this work will be so expressed, and the student must thoroughly master them.

The column headed 'Atomicity,' in the table of elements, will be referred to and explained in a subsequent chapter.

Summary.

Names, symbols, atomicity, and combining or atomic weights of the elements.

Division into metals and non-metals, into solids, liquids, and gases.

Approximate composition of the earth's crust. Symbols, formulæ, and equations.

Weight of atoms. Definition of 'atom' and 'molecule.' The atomic theory.

CHAPTER V.

OXYGEN AND OZONE.

Oxygen.—Symbol, O. Atomic weight, 15·96. Density, 15·96. Specific gravity, 1·1056. Molecular formula and weight, O_2, 31·92. Molecular volume,



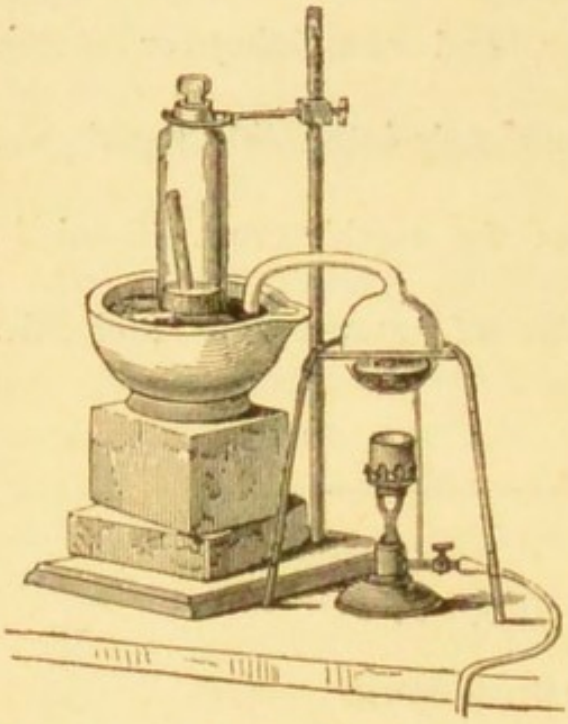
The density of a gas is its weight, volume for volume, compared with hydrogen taken as unity; the specific gravity is its weight compared with an equal volume of air. Molecular weight and volume are explained in Chapter X.

42. Occurrence.—Oxygen occurs plentifully in nature, both in the free state and in combination with other elements. About one-fifth of the atmosphere consists of this gas; it constitutes eighth-ninths by weight of water, and, as shown in the table given on a previous page, about 48 per cent. of the earth's solid crust.

43. Discovery.—Dr. Priestley, of Birmingham, discovered, in 1774, that by heating mercury in contact with

air in a closed vessel the volume of the air was lessened, and that red scales were formed on the surface of the mercury. An apparatus by means of which the experiment may be performed is shown in Fig. 6. The flask, containing the mercury over the gas-lamp, is connected with a jar of air inverted in a porcelain vessel filled with mercury. By this device the mercury in the flask, while in contact with the air in the jar, is shut off from the atmosphere. The mercury requires to be heated to a temperature just below its boiling point, and the heat maintained for two or three days. On allowing the apparatus to cool, at the close of the experiment the diminution of the air in the jar may be observed. The red scales produced consist of oxide of mercury. The chemical change may be thus represented :—

FIG. 6.



$$\underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Mercury oxide.}}{2HgO}$$

44. Preparation.—The student is aware from Experiment 7 that oxide of mercury is decomposed into oxygen and mercury by a strong heat—

$$2HgO = 2Hg + O_2.$$

This experiment should be again repeated and the gas evolved collected.

Before proceeding further prepare the apparatus for collection of gases, specified in the laboratory hints at the end of this chapter ; also read the whole of the directions there given carefully through.

Experiment 25.—In gas apparatus No. 1 substitute one of the combustion tubes for an ordinary test-tube; place in it about as much oxide of mercury as could be held on a sixpence; clamp it in the retort stand, or hold by means of a test-tube holder in the hand (it is preferable to use the retort stand); arrange the pneumatic trough and a small gas-jar for the collection of gas, as shown in Fig. 7. The quantity of mercury oxide is much less than that of potassium chlorate mixture which is shown in the figure. Carefully heat the mercury oxide with the Bunsen burner, and observe the evolution of gas. When the jar is full, take it out of the trough and introduce a glowing splinter; the rekindling shows that the gas is oxygen. A large test-tube may be used if a small gas-jar is not obtainable.

Most of the methods employed for the preparation of oxygen are instances of direct decomposition. The substance most frequently used by the chemist is potassium chlorate, which is composed of potassium, chlorine, and oxygen. At a comparatively low temperature the oxygen is driven off from this body, a compound of potassium and chlorine remaining behind—

$$2KClO_3 = 2KCl + 3O_2$$

Potassium chlorate. Potassium chloride. Oxygen.

Experiment 26.—Using the same apparatus as that employed in the last experiment, substitute an ordinary test-tube, placing it in about enough potassium chlorate to fill the bottom of the tube half an inch. As this liquefies on the application of heat, the tube must be inclined when fixed in the retort-stand. Heat gently; at first the salt crackles: this is owing to the crystals being split up by the heat, and is known as *decrepitation*. The chlorate soon melts, and then appears to boil: the salt is really being decomposed. Collect the oxygen over the pneumatic trough and test it.

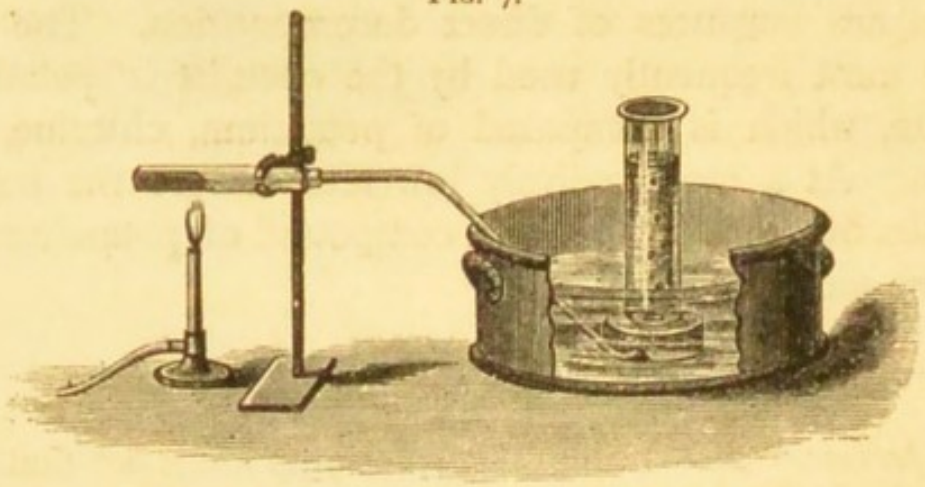
If instead of using potassium chlorate alone, a mixture of that salt with about one quarter of its weight of manganese dioxide (black oxide of manganese) is employed, the gas is given off much more rapidly and at a lower temperature. At the end of the experiment the manganese dioxide

is found unaltered. This mixture is almost always employed for the preparation of the gas, except when required in a condition of absolute purity.

The student will require seven jars of gas for the following experiments: it will be best to prepare them in two lots.

Experiment 27.—One-third fill a six-inch test-tube with the mixture of potassium chlorate and manganese dioxide in the proportions mentioned above: this amount is quite sufficient to evolve the quantity of gas required. Push a wire down to the bottom of the tube, so as to make a clear passage for the gas. Connect the test-tube to the rest of the apparatus used in the last experiment, as shown in Fig. 7, and, having three jars ready

FIG. 7.



inverted in the trough, proceed to fill them. Holding the Bunsen in the hand, commence warming the mixture gently at the *top*, *i.e.* the end nearest the cork, and slowly bring the flame nearer the bottom as the gas is evolved. The reason for this is that the mixture cakes on being heated: if heated first at the bottom, the upward current of gas would carry the loose dust of the mixture on with it, and probably choke the leading tube. Withdraw the source of heat when the last jar is about half full: the action will then probably cease as the jar is filled. Remove the end of the leading tube from the trough; otherwise, as the hot gas within cools, the contraction would draw up the water and crack the test-tube.

Experiment 28.—To one jar of the gas add some clear lime-water; replace the plate, and shake up: observe that the lime-

water remains clear. In the same jar make the usual test for oxygen.

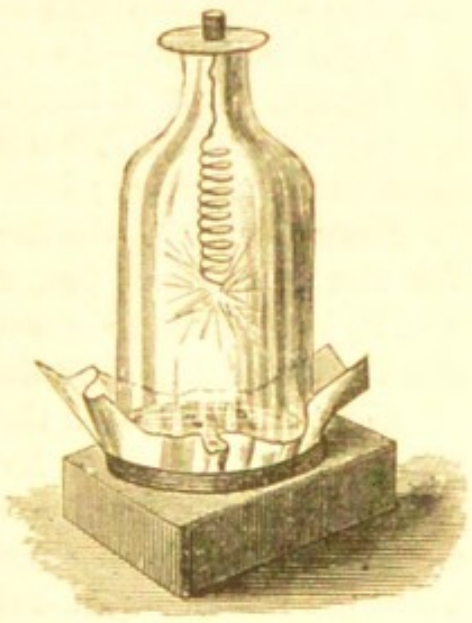
Experiment 29.—To another jar add some litmus solution, and shake up: notice that the blue colour is unchanged.

Experiment 30.—In the third jar burn a piece of charcoal. Get a deflagrating spoon and cap; see that it is clean by heating in the Bunsen. Push the spoon down through the cap, so that it will reach to about one-third the height of the jar from the bottom. Put the charcoal on the spoon and ignite with the Bunsen; when glowing, plunge in the jar of oxygen; it burns brightly. When the combustion is over remove the deflagrating spoon, pour in some lime-water, and shake up; the lime-water becomes milky.

For the remaining experiments two jars may be filled in the ordinary way; another must be wiped perfectly dry and filled by downward displacement. For the next experiment obtain a deflagrating jar, *i.e.* one open at the top and bottom. Cork up the upper opening and fill with gas; allow it to stand in the trough.

Experiment 31.—Take about four or five feet of fine iron binding wire; make it into a spiral by winding round a test-tube, and weigh it carefully. Next fix it to the cap of a deflagrating spoon, and attach a small piece of vegetable tinder (amadou) to the lower end; in the absence of this material, about a quarter of an inch of wax vesta may be used. The iron wire is now ready for burning. The deflagrating jar must be removed from the trough in a proper dish, in the bottom of which a piece of writing paper has been placed, and allowed to become saturated with water. There will thus be a layer of about half an inch of water at the bottom, then the paper, and underneath that another thin layer of water. Loosen the cork at the top,

Fig. 8.



light the tinder or vesta, and immediately place the wire in the jar (Fig. 8). It burns brilliantly, throwing out a number of sparks, while from time to time drops of molten oxide fall to the bottom : these are so hot that if allowed to come in contact with the porcelain dish they would fuse into the glaze even after falling through an inch of cold water. The writing paper momentarily arrests them, and thus gives them time to cool. When the burning is over, remove the unburnt end of wire ; collect very carefully the whole of the globules of oxide of iron, place them in a crucible or evaporating dish, and thoroughly dry them with a gentle heat. Weigh the oxide and the remainder of the iron ; there should be a sensible increase of weight over that of the iron alone previous to the burning : the increase is, of course, due to the oxygen, which is also present in the oxide.

Another modification of this experiment demonstrates that iron increases in weight as a result of oxidation. Procure some clean iron filings, dry thoroughly at a temperature about that of boiling water, or by placing them in a thin layer in an oven. Weigh out 25 or 50 grams, and raise to a red heat in a platinum or clean iron dish. Stir them from time to time, so as to expose a fresh surface ; in about half an hour allow to cool and weigh. There is a considerable gain in weight resulting from the combination of the iron with oxygen from the air.

Experiment 32.—In one of the jars of gas, collected over the trough, burn a fragment of sulphur in the deflagrating spoon ; notice the brilliant light. Add to the jar after the burning some litmus solution ; it is turned red.

Experiment 33.—In the other jar burn a piece of phosphorus the size of a small pea, remembering first to carefully dry it. The light produced is most brilliant. Add litmus solution, and observe that again the colour becomes red.

Experiment 34.—In the dry jar a piece of metallic sodium is to be burned. Sodium has such an affinity for oxygen that it requires to be kept in a liquid which does not contain that element : naphtha is usually employed. Cut off a little piece about the size of a pea, being most careful that the knife and everything which touches the metal is *perfectly dry*. Place in a clean and *dry* deflagrating spoon ; heat in the Bunsen until it

just glows, then put it in the jar of gas ; it burns brightly : the products of combustion which are solid remain in the spoon. Allow it to get quite cold, then place the spoon in a little water in a beaker and dissolve off the oxide of sodium. To some litmus solution in a test-tube add just a drop of dilute sulphuric or nitric acid. Pour the red solution thus produced into the beaker containing oxide of sodium ; the blue colour is restored.

Another method sometimes employed for the preparation of oxygen consists of heating to redness, in a closed iron tube, the black oxide of manganese. Unless large quantities of the gas are required this method is now rarely employed; the gas is always impure from the presence of traces of chlorine, &c., from foreign substances contained in the oxide. The decomposition is thus represented:—

$$\underset{\text{Manganese dioxide.}}{3MnO_2} = \underset{\text{Trimanganic tetroxide.}}{Mn_3O_4} + O_2$$

45. Properties.—Oxygen is a colourless, odourless, neutral, and non-inflammable gas, which until 1877 had never been liquefied. It is slightly soluble in water, one hundred volumes of water at 15° C. dissolving about three volumes of oxygen. Among its properties by far the most important is that it possesses the power of supporting respiration. The gas in the pure state, however, is so active, that a diluting agent is required; in the atmosphere this is supplied by the presence of nitrogen in large quantity. It also supports the combustion of inflammable bodies: substances which burn in air burn with increased brilliancy in this gas. Its chemical activity is so great that, with the exception of fluorine, it combines with all the elements. The class of bodies thus formed is an important one, to which the name of *oxides* has been given. The preceding experiments show the formation of several of these. The composition of the bodies produced is shown in the following equations:—

C	+	O_2	=	CO_2
Carbon (charcoal).				Carbon dioxide.
3Fe	+	$2O_2$	=	Fe_3O_4
Iron.				Triferric tetroxide.
S	+	O_2	=	SO_2
Sulphur.				Sulphur dioxide.
P_4	+	$5O_2$	=	$2P_2O_5$
Phosphorus.				Phosphorus pentoxide.
4Na	+	O_2	=	$2Na_2O$
Sodium.				Sodium oxide.

There is one important point of distinction between various oxides to which the student's attention will have been directed in the experiments already made: one group, of which sulphur dioxide is a representative, reddens a solution of litmus; another series, represented by sodium oxide, is characterised by the property of restoring the blue colour to litmus solution which has previously been reddened. The oxides of the first group, when dissolved in water, produce *acids*; those of the second group are known as *bases*.

Ozone (Allotropic Oxygen). — Density, 23·94. Specific gravity, 1·6584. Molecular formula and weight, O_3, 47·88.

46. Occurrence.—This gas, which has never been obtained in the pure state, is a curious modification of oxygen. Its density is exactly half as much again as that of oxygen. Traces of it are found in the air near the seaside and in the open country.

47. Preparation.—Ozone can be formed by the passage of a series of electric sparks through either air or pure oxygen, and may be recognised by its odour whenever an electric machine is worked. The quantity of oxygen thus changed is however very small, but if a *silent electric äischarge* be passed through the gas, care being taken to avoid sparks, a much larger proportion of oxygen undergoes

this transformation. In order to effect this, a special piece of apparatus is necessary, in which the arrangements are such that the discharge occurs between large surfaces placed very near each other. This end is best attained by the use of a device in which one tube is fixed inside another, so as to leave an annular (ring-like) space between. Through the outer tube two openings are made, so as to provide an inlet and outlet for the gas to be acted on. The surfaces of these tubes are coated with tinfoil, and are connected up to the terminals of an induction, or Ruhmkorf, coil. The discharge then takes place between the two tube surfaces, and through the annular space they enclose. If a slow current of oxygen be passed through this space it emerges containing ozone in considerable quantity. Ozone may also be prepared by the action of phosphorus on moist air.

48. Properties.—In properties ozone is much more active than oxygen, from which it is distinguished by its power of directly converting copper, mercury, and even silver into oxides. Iodide of potassium is decomposed by it, iodine being liberated and in the presence of water potassium hydrate formed. When substances are oxidised by ozone no diminution in volume of the gas takes place. The density of ozone shows that three volumes of oxygen condense to form two of ozone; during oxidation by its agency it is the extra volume of oxygen which enters into combination, the normal oxygen set free occupying precisely the same space :—

O_3	+	$2KI$	+	H_2O	=	$2KHO$	+	I_2	+	O_2
Ozone.		Potassium iodide.		Water.		Potassium hydrate.		Iodine.		Oxygen.

As ozone contains three atoms of oxygen in the molecule its formula is written O_3, thus distinguishing it from ordinary oxygen, whose molecule contains but two atoms, and is written O_2.

Free iodine combines with starch to form a deep blue coloured compound. Ozone may easily be detected by

exposing paper dipped in a solution of starch and potassium iodide; a trace is sufficient to develop a blue colour.

Experiment 35.—Carefully scrape a stick of phosphorus until quite clean, under water, then place it in a gas-bottle and cover with a plate. Put a piece of starch the size of a large shot into a test-tube and a quarter fill with water, shake up and then boil; add a fragment of about the same size of potassium iodide and allow it to dissolve. Dip some pieces of paper in the solution, and after the phosphorus has been in the jar for about twenty minutes or half-an-hour introduce the paper; ozone, if present, will immediately produce a blue tint. If the coloration does not at once appear, a piece of paper may be left suspended in the jar and will soon change colour.

Ozone is a colourless gas with a peculiar and characteristic odour, which it imparts to water, being soluble in that liquid. In virtue of its great oxidising power, ozone decolorises a solution of indigo, forming comparatively colourless compounds containing a higher proportion of oxygen.

Ozone very slowly decomposes into oxygen at ordinary temperatures. At a temperature of 237° C. the change is instantaneous, the gas, which contracted when the ozone was first formed, once more regaining its original volume. This change may be easily effected by passing the ozonised air or oxygen through a hot tube, when on its emergence all traces of ozone will have disappeared.

49. Allotropy.—Attention is directed to the fact that although oxygen and ozone are so different in many of their properties, yet they are simply modifications of one and the same element. The principal difference in constitution is in the numbers of atoms in the molecules, which are respectively two and three; in consequence of this the densities of the two gases are also in the ratio of these numbers. **When an element occurs in two or more distinct forms it is said to be allotropic:** for this reason ozone is sometimes referred to as 'allotropic oxygen.'

Summary.

Oxygen is widely distributed. Discovered in 1774 by Priestley. May be prepared by decomposition of mercury oxide, chlorate of potash, and manganese dioxide. Manganese dioxide assists the decomposition of chlorate of potash without itself undergoing change. Forms compounds called oxides, one group of which reddens litmus ; another restores the blue colour. Properties : a colourless, odourless gas, non-inflammable, supporter of respiration and combustion, neutral to litmus solution.

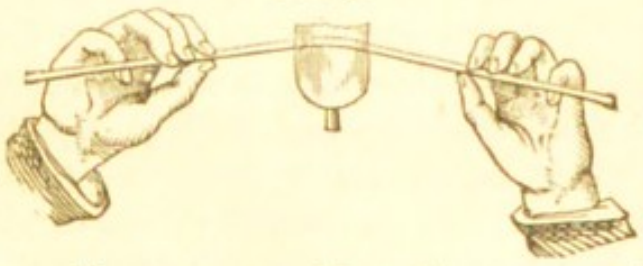
Ozone is a condensed form of oxygen, has a peculiar odour, is produced in the passage of electricity through the air, also during the oxidation of moist phosphorus, is even more active as an oxidising agent than oxygen, is decomposed by a temperature of 237° C. into oxygen.

Laboratory Hints.

The student will require the following pieces of apparatus before he proceeds with the preparation of the gases.

For generating apparatus No. 1, Fig. 7, take a test-tube three-quarters of an inch in diameter and 6 inches long. Select a cork which just fits it, after being rolled or squeezed in order to soften it. Take a piece of glass tubing 18 inches long, and bend it to shape shown in figure. The best way to bend glass tubing is to hold it horizontally in a gas flame (Fig. 9) from an ordinary burner, the long way of the flame. Keep twisting it round until it begins to soften, and then allow it to bend over to the right shape by its own weight. If this is done properly the tube will assume a long uniform curve. Next, by means of the blow-pipe, make the ends of the tube just red-hot ; this will round off the sharp edges. Should it be necessary to cut the glass tubing to the proper length, this may be easily done by cutting a notch in the tubing with a triangular file, and then breaking, by a kind of combined *pull* of the glass asunder and snapping it away from the notch. Next it will be necessary to bore a hole in the cork. For this purpose instruments called

FIG. 9.



cork-borers are provided : they consist of a set of thin brass tubes, the lower ends of which are sharpened. A rod is also contained in the set, in order to thrust out of the borers the pieces cut from the holes. The rod can also be pushed through two holes in the top of the borer, forming a handle to grasp when boring. Before commencing, see that the borer is clear : then, beginning at the *small* end of the cork, bore carefully by twisting the borer and pushing it through. Take care, while going on, that the hole is *straight*. Do not place the cork against the bench and bore into the wood, as this blunts the borer. The hole should be *cut*, not bruised through. When finished thrust out the boring with the rod. The borer selected should be one just a shade less in diameter than the glass tubing. Before pushing the glass tube into the cork it may be advantageously touched over with a little grease. Hold the glass in a duster so as to protect the hand in case it breaks. The cork and glass tube should fit perfectly air-tight ; lutings and cements of all kinds are unnecessary for the preparation of such apparatus, which the student should take the trouble to make properly in the first place, as so doing will save much time and vexation in after-experiments.

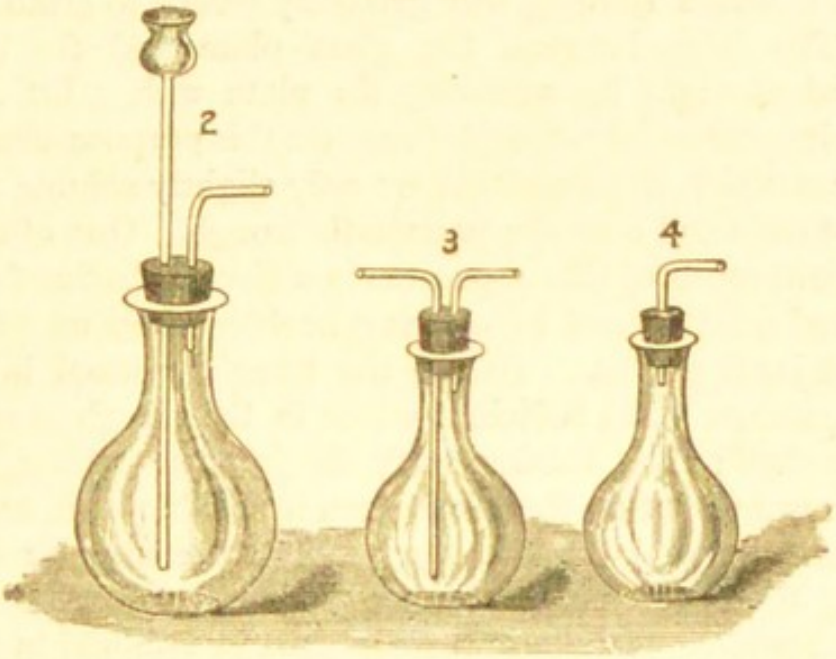
This completes apparatus No. 1, which is shown in use in Fig. 7. A couple of tubes should also be made of hard or combustion tubing, which stands a much higher temperature than the other kind. Take a piece of combustion tubing a foot long and warm it gradually in the middle over the flame of the foot-blow-pipe, at first without blowing ; keep turning it in the flame ; when warm, increase the heat slowly by blowing, until at last the whole strength of the blow-pipe is applied. The glass will shortly soften, and then the two ends must be drawn asunder. Break off the connecting thread of glass close to the end of the tube ; fuse up the small hole with the blow-pipe and the tube is complete, with the exception of rounding the edges of the open end in the flame, which must be done when the bottom is cool. Such tubes must be allowed to cool slowly, or else there is danger of their cracking ; for the same reason they must be heated when in use very carefully and gradually.

No. 2 apparatus should now be made. Fit a good cork to the 16 oz. flask ; take 6 inches of glass tubing and bend it in the

middle at right angles, always remembering to round off the ends. Bore two holes through the cork, one to fit this and one the thistle funnel. The glass bend should be just pushed through the cork, and the funnel should reach to within a quarter of an inch of the bottom of the flask.

No. 3 apparatus consists of an 8 oz. flask, to which a cork is fitted with two holes ; through one is passed a bent tube reaching the bottom of the flask, and through the other a short bend like that in No. 2 apparatus. This same flask should also be provided with a cork with one hole and a single glass bend. The three are shown in Fig. 10.

FIG. 10.



The whole of these should be constructed at the outset : they will be found sufficient for the preparation of most of the gases. If thoroughly cleaned immediately after use, they should last through the whole course of experiments.

In the special sketches subsequently given the student may often adapt bent glass tubes already made by the use of india-rubber connections, instead of making new ones of the exact shape shown.

The terms 'leading tube' and 'delivery tube' are applied to the tube by which a gas emerges from any particular piece of apparatus.

For the collection of gases by displacement and other pur-

poses a piece of glass tubing about 14 inches in length should be bent at right angles 3 inches from one end.

For experiments gases are usually collected in gas jars or bottles. For ordinary purposes of the student, wide-mouthed bottles do very well about the size of a common pickle bottle; they should however be of white glass. The gas is best retained in the bottle by placing a ground glass plate on the mouth, which must be ground flat. This is very easily and quickly performed in the following manner: Procure a piece of plate-glass about 6 or 8 inches square; place on it some emery of medium coarseness and water. Take the bottle, hold it firmly mouth downward on the plate, and rub with a circular motion. Half a minute's rubbing will generally suffice to grind the top true. The joint between the glass plate and the bottle is rendered air-tight by smearing the plate with a little grease. The resin cerate of the druggist answers this purpose admirably.

Gases which are insoluble or only slightly soluble in water are best collected over the pneumatic trough. One of the most convenient forms of this apparatus is a circular basin of earthenware, and a little stand known as a beehive shelf on which the inverted jar is placed. To use the trough proceed in the following manner: Put sufficient water in the trough to cover the beehive shelf; then, having ready the jars and plates, fill each jar with water, put on the plate, turn it upside down, and place the mouth of the jar under the water in the trough: on withdrawing the plate the jar remains filled from the pressure of the atmosphere. If there is room, all the jars should in this way be placed in the trough. Next place the leading tube from the generating apparatus under the shelf, and when the gas has driven the air out of the apparatus begin to collect by placing one of the bottles on the shelf. Have ready its plate; when it is full remove it and substitute another, taking care to keep their mouths under the surface of the water during the whole operation. Next close the mouth of a full bottle with a plate, and take it out of the trough. Fig. 7 shows a jar placed for the collection of gas, the front of the trough being removed in order to show the beehive shelf.

Gases which are soluble in water must be collected another way. They are sometimes collected in a pneumatic trough

over mercury. In general, however, the process of displacement is used. In this operation the gas is poured into the bottle and drives the air out. In cases where the gas is heavier than air, stand the bottles upright, and let the leading tube from the generating apparatus reach to the bottom of the bottle. Cover the top with a piece of cardboard, in order to prevent the escape of gas by diffusion. In order to find out if the bottle is full, test from time to time near the mouth. The test employed must depend on the nature of the gas ; oxygen may be recognised by its power of igniting a glowing splinter. When full close with a plate.

When the gas is lighter than the air the whole arrangement must be inverted : the gas is then said to be collected by upward displacement.

CHAPTER VI.

HYDROGEN.

Symbol, H. Atomic weight, 1. Density, 1. Specific gravity, 0·0691. Molecular weight, H_2, 2. Molecular volume,  .

50. Occurrence.—Hydrogen is chiefly found in combination with oxygen in the form of water, which contains one-ninth of its weight of hydrogen ; it is also a constituent of certain stars and nebulæ, in which it occurs in the free state. Hydrogen was discovered in the sixteenth century by Paracelsus ; but its properties were not thoroughly studied until 1781, when Cavendish subjected the gas to systematic investigation, and demonstrated that it was an element.

51. Preparation.—The attraction of the metals sodium and potassium for oxygen is so great that they readily decompose water, setting free the hydrogen, which, with sufficient care, can be collected.

Experiment 36.—Drop a very small piece of sodium into a trough of water; notice that it melts, and rushing round on the surface for some time becomes smaller and finally disappears.

Next, place a piece of either filter or blotting paper on the surface of the water, and drop a fragment of sodium on the paper; it soon melts, and then takes fire, burning with an intensely yellow flame.

Drop a piece of potassium in water; it at once takes fire, and burns with a flame of a characteristic violet colour. In this case the intervention of filter paper is unnecessary.

The combination of sodium and potassium with oxygen, even under these circumstances, is accompanied by considerable heat, which inflames the hydrogen gas displaced from the water by the action of the metal. It is this gas which produces the flame: the characteristic tint in each case is due to the presence of the vapour of each metal.

In any of these experiments with sodium or potassium and water in which the escaping gas should take fire, stand some little distance until it has burnt out, and then wait until the molten hydrate, which at first floats on the surface of the water, is dissolved; at this moment there is always a slight spit, and there is the danger, if a person is standing immediately over it, that portions of the hydrate may get into the eye. It would be wiser for the student to omit these experiments until he has first seen them performed by the teacher.

If the globule of metal, instead of being allowed to float on the water, is held under the surface, bubbles of gas are seen to arise: these consist of hydrogen, and may be collected in the following manner: First fold a piece of fine wire gauze into a cone in precisely the same manner as directed in Experiment 19 for the preparation of a filter paper. Have in readiness a pair of tongs, by which this may be held point upwards under the water. Place in the trough a small stout glass jar, inverted and full of water, ready for collecting the gas; be sure that not a bubble of air remains in it. Throw a piece of sodium about the size of a pea in the water, and at once depress it beneath the surface with the gauze cone, held in the tongs like a candle extinguisher. Wait until the first bubble of gas arises, then hold

the jar over the rising gas and thus collect it. Repeat this operation with fresh pieces of sodium, until the jar is filled. Apply a light to the jar of gas ; it burns with a pale flame tinged yellow by the sodium vapour.

The chemical change is thus represented :—

$$\underset{\text{Sodium.}}{2Na} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydrate, or hydroxide.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

Experiment 37.—Take another fragment of sodium and dissolve in a small quantity of water in an evaporating basin ; when the action is over observe the soapy feel which the liquid gives to the fingers : this is a characteristic of the class of bodies of which sodium hydrate is a member. Evaporate to dryness, and notice that a white solid substance remains.

Sodium hydrate is frequently called caustic soda, or soda only, for the sake of brevity. The formula of sodium hydrate shows that it contains hydrogen ; in fact, it may be regarded as water in which one of the atoms of hydrogen has been replaced by sodium. It is possible to also displace the second atom of hydrogen by sodium, thus forming sodium oxide, Na_2O, according to the equation—

$$\underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Sodium.}}{2Na} = \underset{\text{Sodium oxide.}}{2Na_2O} + \underset{\text{Hydrogen.}}{H_2}$$

This second atom of hydrogen may also be displaced by either zinc or aluminium, which elements have the advantage of being more easily manipulated than sodium.

Experiment 38.—Fit a four-ounce flask with cork and single delivery tube ; put in a small quantity of zinc and a piece of solid sodium hydrate about the size of a hazel-nut ; add just sufficient water to cover the bottom of the flask. Fix in the retort stand and apply heat ; at first bubbles of air come over, but when the sodium hydrate is melted, hydrogen is evolved, and may be collected over the pneumatic trough. The water takes no part in the chemical action, but is simply added to prevent the heat cracking the flask.

The following is the reaction which occurs :—

$$\underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Sodium zinc oxide.}}{ZnNa_2O_2} + \underset{\text{Hydrogen.}}{H_2}$$

The most interesting point about these two experiments is, that by means of them we succeed in obtaining hydrogen from water in two distinct instalments ; proving that at least two atoms of hydrogen are present in the molecule of water. The successive displacements of hydrogen from water may be shown more clearly by writing the equation in the following manner :—

$$\underset{\text{Two molecules of water.}}{H_2H_2O_2} + Na_2 = \underset{\text{Two molecules of sodium hydrate.}}{Na_2H_2O_2} + H_2$$

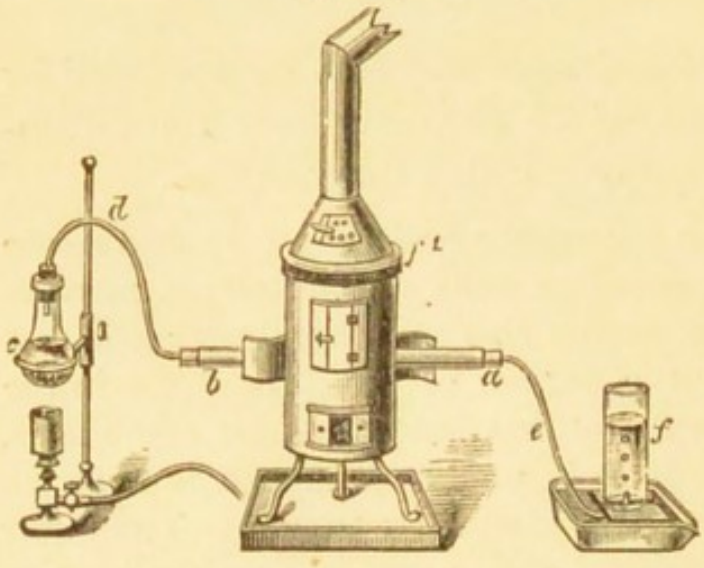
$$Na_2H_2O_2 + Zn = Na_2ZnO_2 + H_2$$

Na_2ZnO_2.

There are several other metals beside sodium which are able to decompose water ; some of them, however, require a higher temperature. Iron is one of these metals. The decomposition is most readily effected in the following manner :—

Experiment 39.—Take an iron tube about an inch in diameter ; fill it with loose iron turnings, and heat to redness in a furnace, as shown in the figure. The furnace may either be one arranged for the use of charcoal, or one of Fletcher's gas-tube furnaces answers admirably. Arrange a flask *c* for the generation of steam, and attach it by means of glass and india-rubber tubes and corks *d* to the iron tube *b*. The steam which enters *b* is decomposed; hydrogen escapes, and is collected in the jar *f*.

FIG. 11.



The change is thus represented :—

$$\underset{\text{Iron.}}{3Fe} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Triferric tetroxide.}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}$$

The oxide of iron, Fe_3O_4, produced in this experiment, is magnetic, and, unlike the oxide developed on iron by exposure to the atmosphere (Fe_2O_3), is *adherent*, and a protective from further rust. Barff's process for preventing articles from rusting is an application of this principle.

While certain metals are thus able to decompose water with the evolution of hydrogen, there are others, of which copper is an instance, that are unable to decompose water at any temperature.

The most convenient method for preparing hydrogen consists of acting on either commercial zinc or iron with dilute hydrochloric or sulphuric acid. As a rule, zinc and sulphuric acid are employed. The gas comes off readily and at the ordinary temperature :—

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

Experiment 40.—Place about half an ounce of granulated zinc in the flask of No. 2 apparatus ; to the delivery tube attach the bent glass tube of the apparatus No. 1 by means of a piece of india-rubber tubing, and arrange for the collection of the gas with the pneumatic trough. Pour about four ounces of water in the flask through the thistle funnel. Next add a very little concentrated commercial sulphuric acid ; about a teaspoonful is sufficient. Give the flask a shake ; immediately there is a brisk effervescence, and the gas may be readily collected over the trough. More sulphuric acid should be added as the action slackens. Apply a light to the first jar that comes over ; it detonates somewhat violently, from the fact that it contains a mixture of hydrogen and air, which is explosive. The second may very possibly also contain air ; the third jar will probably be filled with pure hydrogen. Collect now four jars for experiment.

Although hydrogen is thus readily evolved from sulphuric acid by the action of ordinary zinc, the pure metal is without

action on the dilute acid. Commercial zinc contains traces of other metals: these set up a voltaic (electric) action when placed in acid, and so cause its decomposition with evolution of hydrogen. This effect of the impurities of ordinary zinc may be avoided by first coating the zinc with mercury. This is done by first thoroughly cleaning the metal with sulphuric acid, and then rubbing mercury over the surface until thoroughly bright. This operation is termed amalgamation. That the effect is due to the presence of impurity is shown by adding a small quantity of a solution of either a lead or copper salt to pure zinc and dilute sulphuric acid, when hydrogen gas is at once evolved.

Experiment 41.—Add some dilute sulphuric acid to a little pure zinc; notice that no gas is evolved. Amalgamate a strip of ordinary zinc, and also observe its action when placed in dilute sulphuric acid. To the amalgamated zinc and acid add two or three drops of copper sulphate solution; gas is at once evolved.

The copper sulphate thus added is first decomposed according to the equation following; the liberated copper then forms a voltaic couple with the zinc:—

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Copper.}}{Cu}$$

52. Properties.—*Experiment* 42.—Hold a jar of gas mouth downward; apply a light: the gas burns at the mouth with a non-luminous and almost colourless flame. Thrust the taper up into the jar; the taper is extinguished, but the gas continues to burn.

The combustion of hydrogen in oxygen or atmospheric air produces water:—

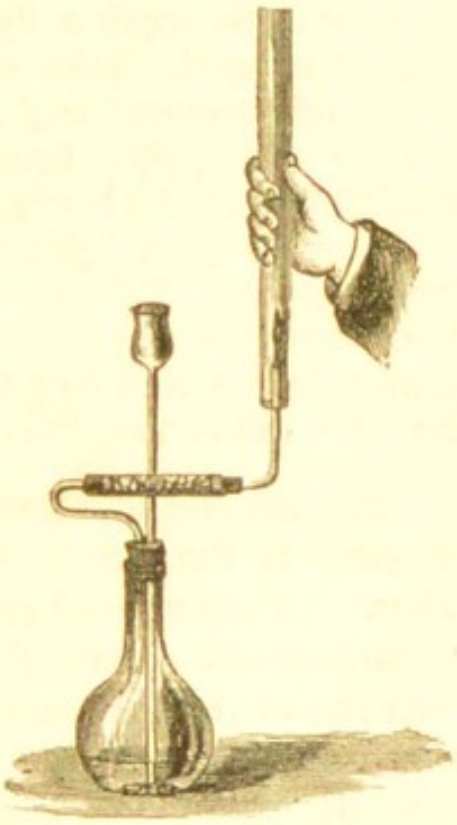
$$\underset{\text{Hydrogen.}}{2H_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Water.}}{2H_2O}$$

All gases evolved from mixtures, in which water is present, contain aqueous vapour; therefore, before attempting to prove the presence of water as a result of the com-

bustion of hydrogen, we should first *dry* the hydrogen itself. This is easily effected by passing the gas over some substance which has an attraction for water: the most important desiccating or drying agents used by the chemist are calcium chloride, sulphuric acid, and quicklime. Whichever of these is selected must depend on the nature and properties of the gas to be dried. Hydrogen may be dried by the use of either calcium chloride or sulphuric acid.

Experiment 43.—Select a piece of glass tubing of half an inch or five-eighths bore and about nine inches long, round off the ends with the blow-pipe and fit a cork to each. To the one cork fit a tube bent at right angles, with the end drawn out to a jet; through the other pass a piece of tubing bent to the shape shown in Fig. 12; or simply fit to it a straight piece of glass tube, and connect to the leading tube of the generating flask with india-rubber tubing: this part of the apparatus would then have to be supported by the retort stand. Fill the large tube with small fragments of calcium chloride, and place at each end, between the chloride and the cork, a plug of cotton-wool. A slow current of gas passed through this apparatus will emerge in the dry state. If necessary, place some more zinc and sulphuric acid in the generating flask; let the gas escape until a jar collected burns quietly without explosion; then attach the drying tube, and after a few seconds light the gas as it issues from the jet. *Too much stress cannot be laid on this injunction, to* FIRST *see* BEFORE *lighting the jet that a collected jar of the gas burns quietly. Want of attention to this direction will lead to* EXPLOSION *of the whole apparatus.* Take a glass tube eighteen inches or two feet long, and about half an inch

FIG. 12.



diameter; if necessary dry the inside by pushing a plug of cotton-wool through; hold it over the jet: the watery vapour condenses in the cooler parts of the tube.

This experiment is often accompanied by a peculiar musical note produced by a rapid series of small explosions within the long tube. The moisture which condenses on a kettle or other vessel of cold water heated over a gas stove, is the product of combustion of the hydrogen of the coal gas.

Hydrogen is the lightest substance known, and for this reason is conveniently chosen as the standard for comparison of other gases: its buoyancy has led it to be used for the purpose of filling balloons; coal gas, from its greater cheapness, is, however, usually preferred. The following experiments are illustrative of this property :—

Experiment 44.—Take a jar of the gas, and setting it down, mouth upwards, take off the glass cover; after the expiration of thirty seconds apply a light; the gas will be found to have entirely escaped. Take a second jar, and holding it mouth downwards remove the glass plate; let it also remain for thirty seconds and apply a light; the gas will take fire and burn as usual, but little of it having escaped.

From its great lightness this gas may be poured upward from jar to jar. Take an empty jar, invert it, and removing the plate from a full one pour the gas *up* into it. In ten seconds place a light to each jar; the gas in the inverted one will burn, the other will be found to contain no hydrogen.

53. Gaseous Diffusion.—One distinguishing property of gases is the readiness with which they mix with each other. This is noticed especially with those gases possessing a characteristic odour: thus, if a gas burner be left open for even two or three minutes, the smell of coal gas may be detected over every part of a large room. **The natural process by which one gas is thus disseminated through another is termed 'gaseous diffusion.'** It takes place between all gases, even though the heavier is first at the lower level. In other words, a heavy gas will diffuse up

into a superincumbent light gas, while the light gas will make its way downwards and mix with the heavier one. In this way different gases, when placed in the same space, rapidly produce of themselves a uniform mixture. This process of diffusion will also go on through a porous membrane, as, for example, a thin diaphragm of plaster of Paris or porous earthenware. Thus, if a vessel be divided into two parts by a thin partition of porous material, and the one half be filled with one gas and the other with another, they will be found after some time to have become thoroughly intermixed with each other. The rate of diffusion of all gases through such a diaphragm is not the same but depends on their densities. **The rate of diffusion of gases is inversely as the square root of their density.** Thus, hydrogen and oxygen have respectively densities of 1 and 16; hydrogen diffuses four times as rapidly as does oxygen. The rapid diffusibility of hydrogen is illustrated in a striking manner by the following experiment :—

Experiment 45.—Take a piece of glass tubing some ten or twelve inches in length, and proceed to close the one end with a layer of plaster of Paris in the following manner. First mix a little of the plaster with water, so as to form a thick cream ; spread this mixture uniformly on a plate to the depth of an eighth or three-sixteenths of an inch. Then press down in it one end of the clean dry glass tube, and allow it to remain undisturbed until the plaster has 'set' (become solid), which should take place in ten or fifteen minutes. Slide the end of the tube off the plate, and place it on one side for a day to dry.

Cover the plaster diaphragm with a cap of tinfoil and fill the tube with dry hydrogen by upward displacement. Place the inverted tube with its lower end in the water of a pneumatic trough, and about half an inch below the level of the surface. For this purpose put a beehive shelf in the trough and fill with water, until the level is a half-inch above the top of the beehive. Remove the tinfoil cap and immediately the water is seen to rise within the tube against the action of gravity until the tube is about two-thirds full of water. As a converse experiment,

the tube may be filled with carbon dioxide, when the level of the gas descends and displaces the water altogether from the tube.

In this experiment the hydrogen, being so much lighter than air, diffuses out through the diaphragm nearly four times as rapidly as the air diffuses in ; the consequence is that the volume of gas in the tube rapidly lessens and the water rises.

54. Reducing and Oxidising Agents.—A reducing agent is a substance which removes oxygen or elements similar to it from compounds; the word is most frequently used to signify a substance which enables us to obtain a metal in the free state from any of its combinations. Hydrogen is the typical reducing agent ; an illustration of its possession of this property is afforded by the action of the gas on copper oxide.

Experiment 46.—Take a piece of combustion tubing, about fourteen or sixteen inches in length, and fit a cork and piece of small glass tubing to the one end. Introduce some powdered oxide of copper into the tube, and about four inches from the corked end. Fix the tube horizontally in a retort-stand, and pass dried hydrogen through it. As soon as the whole of the air is expelled, apply heat by means of a Bunsen to the part of the tube containing the copper oxide. Notice after a time that water in considerable quantity condenses in the cooler part of the tube, and that the black oxide changes in colour to the characteristic red tint of copper.

In this experiment the following reaction occurs :—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Copper.}}{Cu} + \underset{\text{Water.}}{H_2O}$$

Hydrogen is also capable of effecting the reduction of iron oxide to the metallic condition. In addition to these instances of a reducing agent being employed in order to obtain a metal in the free state, there are other reactions in which bodies are simply reduced to lower degrees of oxida-

tion. Instances of these will from time to time be given. Carbon, carbon monoxide, zinc, sodium carbonate, and sulphurous acid are other examples of reducing agents.

An Oxidising Agent is one which imparts oxygen to a body, or otherwise causes it to combine with the substance. The term 'oxidising agent' is also sometimes used in a looser and more general sense; as when a body is caused to combine with a higher proportion of chlorine or some other element more or less similar in character to oxygen. Oxygen, chlorine, bromine, potassium chlorate, nitric acid, hydroxyl, &c., are instances of oxidising agents.

55. Nascent Condition of Elements.—Several elements are much more active in their properties at the moment of liberation from a compound than in the ordinary free state. As a consequence they under these circumstances produce chemical changes they are unable to effect when in their normal condition.

Experiment 47.—Take some solution of ferric chloride; notice that it has a sherry red tint. Bubble hydrogen gas through the solution; notice that no alteration in colour occurs. Next add to the solution a little sulphuric acid and then drop in a few fragments of zinc; the colour very quickly disappears.

In the second portion of this experiment the following chemical changes occur :—

$$\underset{\text{Zinc.}}{Zn} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Zinc sulphate.}}{ZnSO_4} + \underset{\text{Nascent hydrogen.}}{2H}$$

$$\underset{\text{Nascent hydrogen.}}{2H} + \underset{\text{Ferric chloride.}}{Fe_2Cl_6} = \underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

The hydrogen evolved within the solution has reduced the ferric chloride to a compound of chlorine and iron containing less chlorine and almost devoid of colour. It has been seen that free hydrogen passed into the solution is incapable of effecting this change. **At the moment of**

liberation from a compound an element is said to be nascent, a word signifying being born. Why under these circumstances an element is so much more active than ordinary will be better understood when the student's knowledge of chemical theory is more extended.

56. Properties of Hydrogen, *continued.*—The foregoing experiments show that this gas is colourless, odourless, tasteless, inflammable, and a non-supporter of combustion. It is of very low density, and consequently diffuses itself through other gases with great rapidity. Hydrogen is a powerful reducing agent, especially when in the nascent condition.

The gas prepared from zinc and sulphuric acid has generally a slight odour from the presence of impurities in the zinc and acid; when the gas is required in a state of absolute purity this is ensured by the use of pure reagents. Should iron be used instead of zinc for its production, the smell is much stronger, through the presence of compounds of hydrogen with carbon, carbon being an invariable constituent of common iron. The gas is not poisonous, but animals placed in it soon die from simple deprivation of oxygen. It is very slightly soluble in water, 100 volumes dissolving only 1·93 volume of the gas.

It will be remembered by the student that hydrogen, in common with oxygen, is one of the gases which have been liquefied by MM. Cailletet and Pictet. Hydrogen was even obtained in the solid form, appearing as a jet of solid steel-blue particles. In many of its chemical relationships it behaves rather as a metal than a non-metal; its appearance in the solid state tends to confirm this view.

Summary.

Hydrogen is principally found in water. May be prepared by the action of metals on that liquid, as sodium, iron, &c.; also by action of zinc or iron on various acids.

Hydrogen is a colourless, odourless, and tasteless gas, in-

flammable, a non-supporter of combustion ; it is also neutral to litmus solution. Is the lightest body known, and is a powerful reducing agent.*

Laboratory Hints.

It must not be forgotten in dealing with sodium that the fingers must be perfectly dry.

In collecting hydrogen from sodium hydrate and zinc, if the neck of the flask has been touched with the soda, there is frequently difficulty in keeping the cork in from its consequent soapiness. This may generally be prevented by just touching round the cork with dilute sulphuric acid.

Great care must be taken in mixing sulphuric acid and water ; if the directions given are followed there need be no fear ; on no account add the water to the sulphuric acid.

Never omit the precautionary measures given before lighting a jet of hydrogen.

In handling chloride of calcium, place it in the drying tube as quickly as possible, and *immediately* replace the cork in the jar containing it.

CHAPTER VII.

OXIDES OF HYDROGEN.

THERE are two oxides of hydrogen known :—

Hydrogen monoxide, or water . . .	H_2O.
Hydrogen dioxide, or hydroxyl . . .	H_2O_2.

Water.—Formula, H_2O. Molecular weight, 17·96. Density, 8·98. Specific gravity as steam, 0·622.

57. Occurrence.—Water is found so largely distributed in nature, and its uses are so well known, that a description of its occurrence and many of its properties is superfluous. It is found in the three distinct forms of ice, water, and steam.

58. Properties.—There are very few substances which are not more or less soluble in it; hence we never find water in a state of purity in nature. Even rain water contains traces of gaseous bodies dissolved from the atmosphere, while river water and spring water hold a considerable quantity of saline matters in solution.

The soluble matter of river water is carried to the sea, and there left behind, as the water again evaporates to form clouds. In this way rivers are constantly adding to the saltness of sea-water, the principal solid ingredient of which is common salt, or sodium chloride, NaCl. The sea contains in addition smaller quantities of magnesium and other salts, of which the compounds of bromine and iodine are of most importance

Experiment 48.—Evaporate to dryness on a clean piece of platinum foil a few drops of common water; notice that a perceptible residue remains; contrast with that obtained from distilled water.

The method of purification of water by the process of distillation has been already referred to (p. 20).

Experiment 49.—Take an eight-ounce flask fitted with cork and single bent tube, as shown in Fig. 10; attach with india-rubber a glass tube, leading into the pneumatic trough; fill the flask to overflowing with cold spring or rain water; push in the cork; the water displaced will drive the air from out the leading tube. Heat the water with the Bunsen, and place a large test-tube to collect in the ordinary manner the gas which is evolved; let the water boil until no more gas is disengaged.

In this way an estimate may be made of the quantity of air, and other gases, the water, when cold, held in solution. This quantity, though small, is of great importance, being the supply from which fishes derive the oxygen necessary for the support of respiration, and aquatic plants the carbon dioxide requisite for their growth and development. The experiment also shows that gaseous impurities are not sepa-

rated from water by distillation, being carried over by the steam.

59. Effects of Heat on Water.—The study of the effects of heat on water belongs rather to the domain of physics than chemistry, but it is important that the chemical student should know the principal changes produced by heat.

In common with other bodies water is expanded by the action of heat: this is readily observed in the following experiment :—

Experiment 50.—Fill an eight-ounce flask with cold water to within one inch of the mouth ; apply heat, and notice that before the boiling point is reached the water expands until the flask is entirely filled ; set aside to cool, or cool more rapidly by placing the flask in a trough of cold water ; notice that the original volume is regained.

If a piece of ice be taken at a temperature considerably below the freezing point, and subjected to heat, an interesting series of changes may be observed. The ice first expands as heat is applied ; at 0° C. the temperature remains stationary until the whole of the ice is melted. The heat necessary to melt a given weight of ice at 0° C. would raise the same weight of water from 0° to 79° C. A considerable diminution of volume accompanies the change of ice into water, 10·9 volumes of ice producing only 10 volumes of water. The whole of the ice being melted, a further application of heat raises the temperature steadily until 100° C. is attained. At first the ice-cold water *contracts* as it becomes hotter, until 4° C. is reached. At this point water expands on being either heated or cooled: this temperature is therefore termed that of the *maximum density* of water, as at this point the greatest weight of water is contained in the smallest space, maximum density being necessarily associated with *minimum* volume. The expansion proceeds regularly until 100° C. : at this temperature the water boils,

and is entirely changed into the gaseous state by a continued application of heat. The temperature remains constant while any water is left. The quantity of heat necessary to convert a given weight of water at 100° C. into steam at the same temperature is sufficient to raise 537·2 times the weight through 1° C.

Steam in cooling passes through a series of changes which are just the converse of those it experiences on being heated ; it gives out just the same quantity of heat in changing from steam to water as was required to convert the water into steam ; further, the water in solidifying evolves the same amount of heat as was necessary to effect its liquefaction.

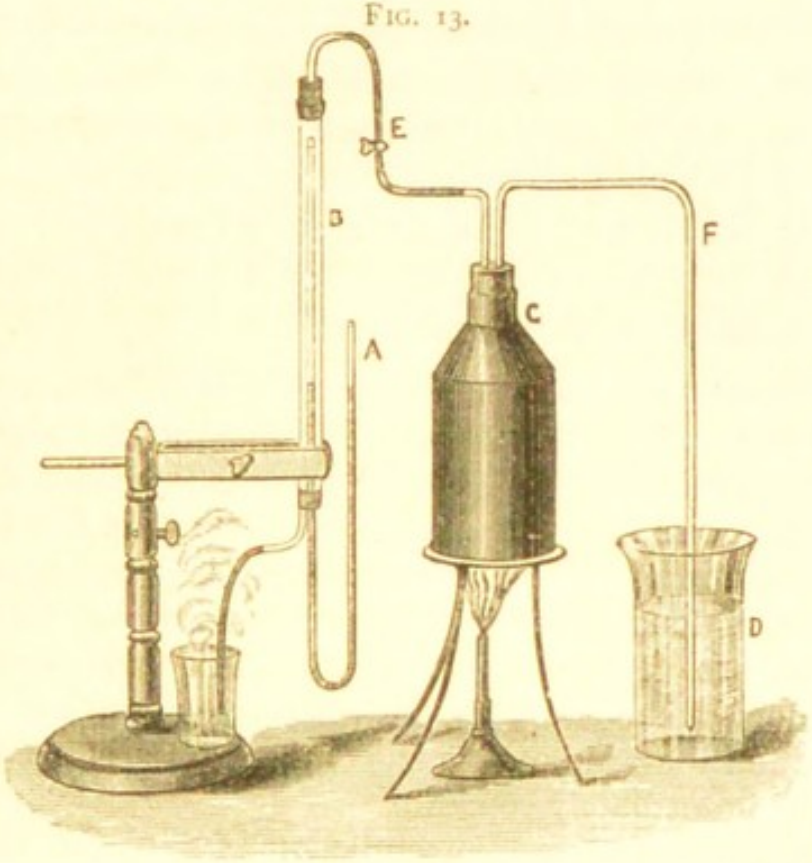
60. Tension of Aqueous Vapour.—Water gives off, at all temperatures, vapour, which exerts a definite pressure ; as the temperature rises the pressure of the vapour also increases. At the boiling point of water, or any liquid, the pressure or tension of its vapour is equal to that of the atmosphere. This fact may be easily proved by experiment.

Experiment 51.—Take a U tube A, as shown in Fig. 13, with one end sealed ; the limbs of the tube may be from about one foot to eighteen inches long and three-eighths of an inch diameter. Pour in a few drops of water, and let them run round to the sealed end ; next fill with mercury, so that the metal shall stand at the bottom of the straight portion of the open limb of the tube, the closed one being full ; the mercury is retained in position when the tube is upright by the pressure of the atmosphere ; on its surface in the sealed end a few drops of water will be seen floating. The sealed limb must now be enclosed in a jacket (B) composed of a glass tube sufficiently wide (about one inch diameter) to permit of the passage of steam between the two glass tubes. Fit the steam jacket with two corks ; fix a glass bend to the upper one ; and through the lower bore one hole in the centre for the U tube, and another in which must be introduced a glass tube to lead away the waste steam. Fix the apparatus upright in the retort stand, and pass steam through the jacket from water boiled in a flask ;

as the temperature of the jacket rises, the mercury is depressed, until it at last is stationary, and at a level in the two limbs of the U tube.

The mercury in the outer limb is subjected to the pressure of the atmosphere, that in the inner to the pressure of the steam; the surfaces being level with each other is a proof that the two pressures balance, and therefore the

FIG. 13.



boiling point of a liquid is that at which the tension of its vapour equals that of the atmosphere.

It follows that if the pressure on a liquid be varied, its boiling point also changes; if a few drops of water be placed in the vacuum at the top of the mercurial column of the barometer, where the pressure is *nil*, the boiling point falls below that at which water freezes. On the tops of mountains where the atmospheric pressure is comparatively low, water boils below 100°, while in steam boilers, where it is exposed to great pressure, the boiling point rises to 144° with a

steam pressure of 60 lbs. to the square inch (4 atmospheres) and to 180° at a pressure of 150 lbs.

61. Solution and Crystallisation.—The fact has already been mentioned that water acts as a solvent of very many substances; it usually so acts more powerfully when hot (except with gases which are more readily absorbed by cold water). Thus sodium sulphate is soluble in rather more than double its weight of water at usual temperatures; whereas the salt may be dissolved without difficulty in its own weight of warm water.

Substances differ very greatly in their degree of solubility: they may be roughly classified into (1) freely soluble substances, as sugar, washing soda, alum; (2) slightly soluble substances, as gypsum or plaster of Paris; (3) insoluble substances, as chalk, flint, and sand.

Experiment 52.—Take half an ounce of sodium sulphate, place in a test tube, and add the same weight of water; heat gently: the salt is dissolved. Now allow the solution to cool; as the temperature falls the water is unable to hold the whole of the salt in solution, and a portion separates in the solid state, as a series of long four-sided prisms: these are *crystals* of sodium sulphate. At times in this experiment the solution may be cooled down without any crystals whatever separating. Should this be so, add the minutest particle of the dry sodium sulphate; crystals will immediately separate.

Prepare crystals of sodium carbonate, and copper sulphate, in precisely the same manner.

A substance is said to be crystallised whenever it assumes a definite geometrical form; the same substance, as a rule, always crystallises in the same form or group of closely allied forms. When a body assumes two distinct crystalline forms it is said to be *dimorphous*: the study of even the more familiar elements includes some very important instances of dimorphism. A body which does not occur in crystals is termed *amorphous*, *i.e.* without (crystalline) form.

Many bodies require, in order to build up their crystals, a certain quantity of water ; on removing this the crystalline form is destroyed.

Experiment 53.—Pour the contents of the sodium sulphate tube from the last experiment on a filter, so that the liquid may drain off (mother-liquor) ; dry the crystals by gently pressing them between the folds of a dry filter. Remove the dry crystals into a test-tube which is also dry, and very gently apply heat ; the crystals melt, a quantity of water is given off, which condenses in the upper part of the tube, and ultimately a white, solid and amorphous mass remains at the bottom.

Such water is called *water of crystallisation*, and is always constant in quantity. Thus, crystallised sodium sulphate contains 10 molecules of water to one of the salt : this is represented in the formula, Na_2SO_4, $10H_2O$.

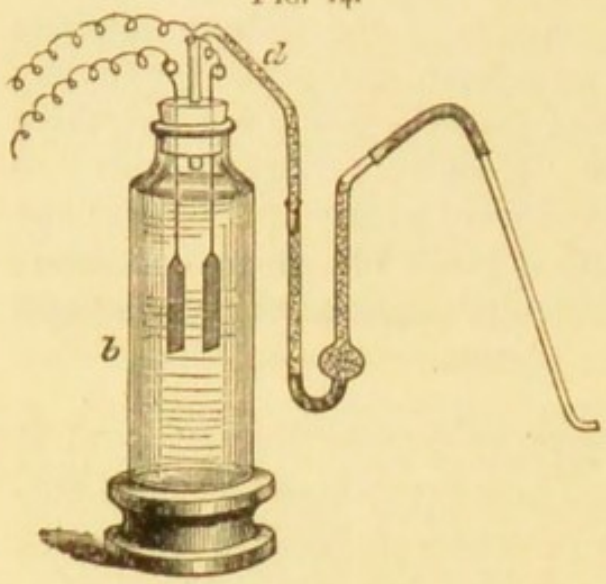
62. Composition by Volume.—Water, until within the last hundred years, was looked on as an element. The experiments described in the last chapter on hydrogen will have shown the student that its composition is compound, hydrogen having been obtained from it, and water again produced by the combustion of that gas in air.

By intense heat water may be separated into oxygen and hydrogen ; the most convenient force to apply for this purpose, however, is that of voltaic electricity. The following series of experiments on the analysis of water by electricity (electrolysis) and its synthesis should, if possible, be performed by the student ; failing this he should read the directions here given most carefully, and watch the results obtained when the experiments are performed by the teacher.

Experiment 54.—The electrolytic apparatus, shown in Fig. 14, is to be attached by means of the wires to a battery consisting of two or three Grove's or Bunsen's cells. Such an apparatus is readily constructed by taking a wide-mouthed bottle of six or eight ounces capacity, fitting it with a good cork, passing through it the delivery tube *d* and two platinum wires,

to which pieces of platinum foil are attached ; the bottle, being filled to the neck with water, to which twenty or thirty drops of sulphuric acid have been added, is ready for use. Instead of the platinum wires through the cork, as shown in the figure, pieces of glass quill tubing may be used, the platinum wires being fused into the ends of the tubes, which are to be filled with mercury ; the connection with the battery is then easily made by pushing the *clean* ends of the wires into the mercury. The leading tube *d* has a drying tube filled with chloride of calcium attached to it ; unless the issuing gas is required to be perfectly dry this may be dispensed with. The apparatus being in working order, connect the battery ; notice that a stream of bubbles of gas ascends from each piece of platinum. Collect the gas issuing from the leading tube in an egg-shaped soda-water bottle over the pneumatic trough. When full close the mouth either with a cork or the palm of the hand ; wrap up the bottle carefully in a duster and apply a light ; the gas explodes violently. Place the leading tube of the apparatus in a strong solution of soap, and thus blow some bubbles. Remove the apparatus and apply a light to the bubbles ; they detonate loudly.

FIG. 14.

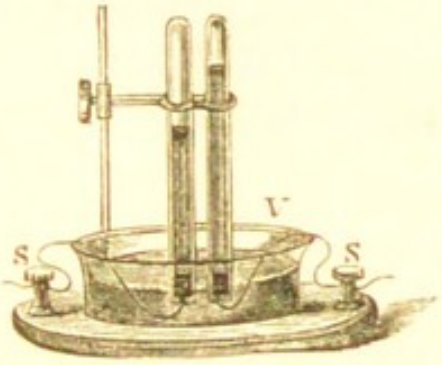


The pieces of platinum foil are called *electrodes* ; that connected with the zinc of the battery is the *negative*, the other the *positive* electrode.

Experiment 55.—Proceed again to electrolyse water, using this time an apparatus (Fig. 15) in which the gas evolved from each electrode is collected separately. Fill the vessel V with acidulated water, then fill the glass tubes with the same water, and invert one over each electrode. Connect the battery wires to the binding screws SS, to which the electrodes are attached. Gas immediately rises in each of the tubes ; it is soon noticed that in that inverted over the negative electrode

the volume is double that evolved from the positive electrode. When nearly full remove the inverted tube containing the larger quantity of gas, and apply a light ; it burns quietly with the familiar pale blue flame of hydrogen. In the second tube of gas plunge a glowing splinter ; it re-lights, the gas being oxygen.

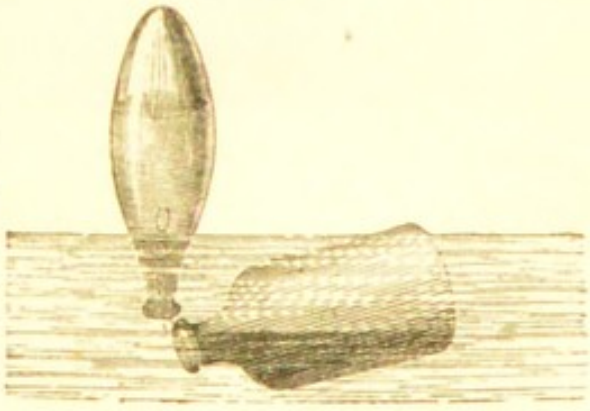
FIG. 15.



These experiments prove that water is capable of decomposition into oxygen and hydrogen in the proportions of one volume of the former to two of the latter. The student should also learn that the reunion of oxygen and hydrogen again produces water.

Experiment 56.—Take the soda-water bottle used for the collection of the mixed gases in the electrolysis of water ; fill it with water, and pour out into a graduated measure ; pour in again one-third of the quantity it holds, and mark the height by a file on the outside of the bottle ; pour in another third, and again make a mark. Now place the bottle in the trough, fill with water, and pour in, from a jar previously filled, one-third its volume of oxygen (Fig. 16). An easier way is to place the soda-water bottle on the beehive shelf, and place the mouth of the other underneath it ; or a funnel may be inverted in the mouth of the soda-water bottle. Next fill the remaining two-thirds of the bottle in the same way with hydrogen. Remove the bottle, give it one or two shakes, and, after wrapping in a duster or towel, apply a light ; it explodes in just the same manner as the detonating gas collected by electrolysis.

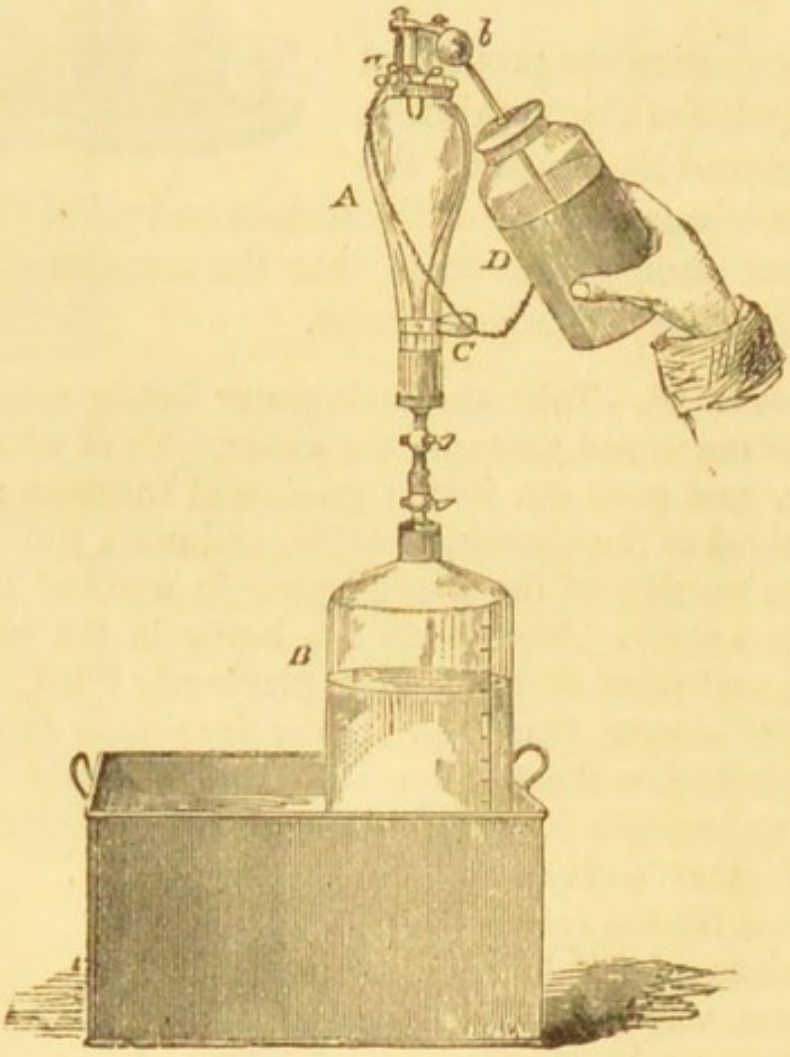
FIG. 16.



The recombination of the two gases may be also effected

by passing an electric spark through the mixture. Cavendish used in his investigations a strong glass vessel with two platinum wires inserted in it so that the electric spark might pass through the gases between their ends. A form of his apparatus is shown in A, Fig. 17. This vessel is first exhausted by the air-pump, then attached to the graduated

FIG. 17.



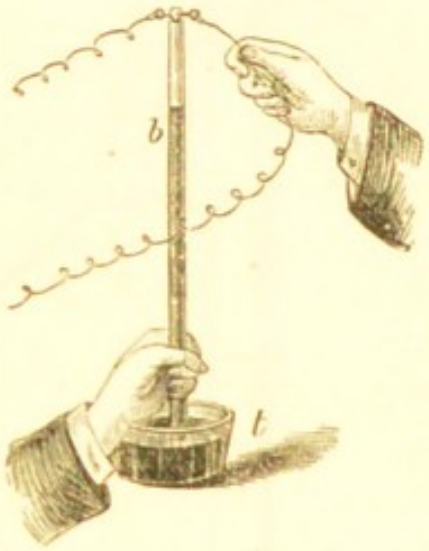
glass jar containing a mixture of two volumes of hydrogen and one of oxygen ; on opening the stop-cock C, the vessel fills with the mixture ; the stop-cock is closed and an electric spark passed ; drops of water condense on the sides of the vessel. The stop-cocks may be again opened and the vessel re-fills ; by the passage of a spark a second quantity of water is produced. This operation may be repeated until the whole of the gases have been caused to combine ; by this

time there is an appreciable quantity of water in the glass vessel.

A somewhat similar experiment to this, but performed on a smaller scale, may be tried by the student himself.

Experiment 57.—For this experiment procure a *eudiometer tube* (Fig. 18). This consists of a stout glass tube about twenty inches in length and half an inch diameter, closed at one end. Near the closed end two platinum wires are fused into the glass, their points being about a sixteenth or eighth of an inch apart. Fill this tube with mercury, and invert in a small trough, also containing mercury, and provided with an india-rubber pad at the bottom. Fill the tube about one-third full of the mixed gases evolved by the apparatus in Fig. 14; attach the wires to a small induction coil or an electrophorus; hold the eudiometer down firmly on the rubber pad, and pass a spark through the gaseous mixture; there is a bright flash of light at the moment of combination; lift the tube slightly; the mercury rushes in and entirely fills it.

FIG. 18.



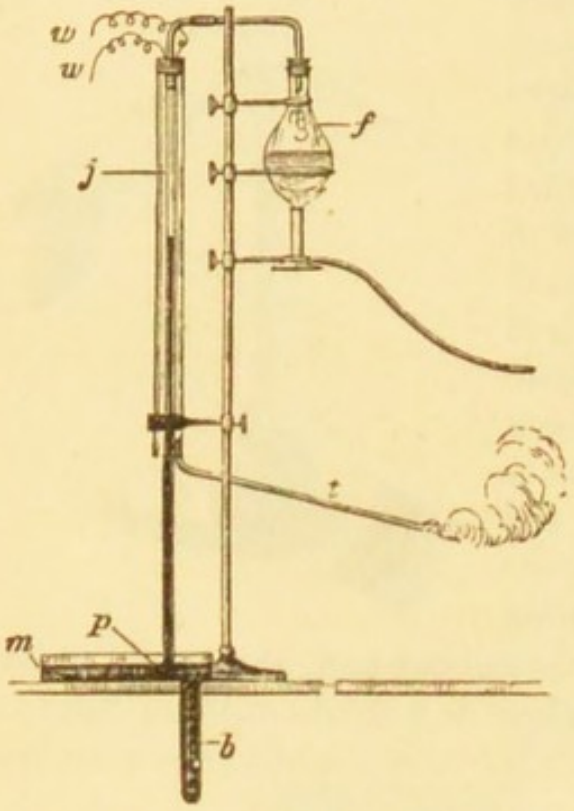
In this experiment the water vapour first formed immediately condenses. Another most important experiment, which the student should perform, if possible, consists of measuring the relative volume of the mixed gases, and the *steam* produced by their union.

The apparatus, usually described for this experiment, necessitates the use of means for maintaining the temperature of the eudiometer well above the boiling point of water. Vapour of amylic alcohol, which boils at 132° C., is passed through an outer tube in which the eudiometer is placed. There is an elegant modification of this apparatus devised by Professor Reynolds, in which use is made of the fact that water boils at a lower temperature under less

atmospheric pressure. The pressure on the water vapour inside the eudiometer being lessened, it is kept above its condensing temperature simply by the passage of steam through the outer tube.

Experiment 58.—Take a eudiometer tube about thirty inches long ; place over it the jacket *j*, which should be about fifteen inches in length and an inch in diameter. Each end of the jacket is fitted with a cork ; through the upper one a bent glass tube is passed, which is connected with the glass flask *f*, containing water heated by the Bunsen ; *ww* are the wires, also passed through it, connecting the eudiometer with the induction coil. The lower cork has one hole which fits the eudiometer ; through a second the tube *t* is fixed for waste steam. Two small india-rubber rings should be passed over the outer jacket. Fill the eudiometer with mercury and invert it in a mercury trough with india-rubber pad *p* and a well *b*. Pass into it some of the electrolytic gases, about sufficient to one-third fill the tube ; do not let the quantity exceed this. Connect the flask *f* and pass a current of steam until the gases inside the eudiometer, expanding with the increased temperature, once more attain a constant volume. Mark this point by sliding the lower of the india-rubber rings to the surface of the mercury. Measure also and note the height of the mercury above the surface of that in the trough. Pass an electric spark, holding the eudiometer meanwhile firmly on the india-rubber pad ; the gas after combination is seen to decrease in volume ; as soon as stationary, depress the eudiometer in the well *b* until the mercury stands again the same height above the surface in the trough as when previously measured. Now place the

FIG. 19.



second ring coincident with the surface of the mercury in the eudiometer. The amount of contraction thus measured will be found to be just one-third of the whole volume.

The current of steam must be maintained during the whole of the experiment. It may be found convenient to regulate the pressure by raising the mercury trough instead of lowering the eudiometer.

Three volumes of the mixed gases have produced two volumes of steam measured at the same temperature and pressure.

63. Composition by Weight.—The preceding series of experiments will have shown the student the composition of water by volume; it is necessary that he should also be acquainted with the means employed for the determination of the exact composition by weight. While iron and other metals decompose water, owing to their great attraction for oxygen, there is another group the oxides of which are decomposed by hydrogen, from their having a less powerful attraction or 'affinity' for oxygen than hydrogen has for that element. As seen in a previous experiment (No. 46), if oxide of copper be heated in a current of hydrogen, water is produced and copper liberated in the free state:—

CuO	$+$	$2H$	$=$	H_2O	$+$	Cu
Oxide of copper.		Hydrogen.		Water.		Copper.

With proper precautions this reaction enables us to ascertain with exactness the relative weight of hydrogen and oxygen which water contains.

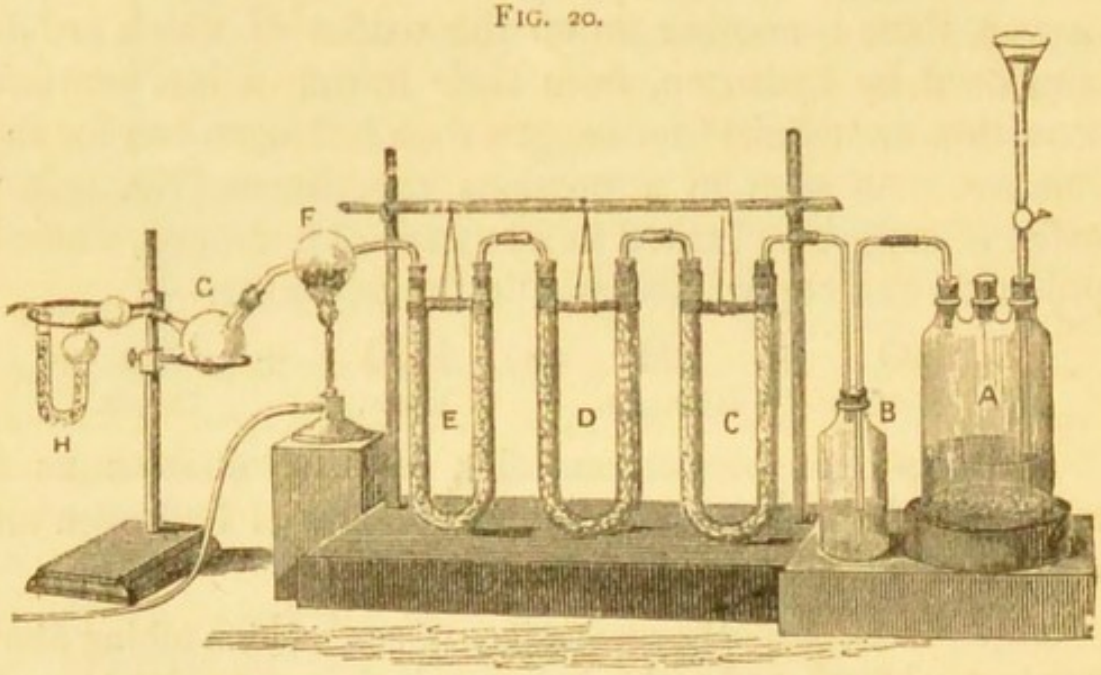
Experiment 59.—Procure a piece of combustion tubing about one foot in length, and with a bulb one inch in diameter blown in the centre. Partly fill this bulb with clean dry copper filings and weigh the bulb and its contents. Pass a gentle current of oxygen from a gas bag, or other holder, through the tube, and heat the bulb to redness by means of a Bunsen. In about five minutes disconnect the apparatus and weigh the bulb; notice that it has gained in weight. This is due to the formation of copper oxide.

Next pass hydrogen over the copper oxide thus produced and heat gently, using the same precautions as previously described in a similar experiment. Notice the production of water, which drive out of the tube by slightly warming it throughout its whole length. When no more water is being evolved, cease the passage of hydrogen, allow the tube to cool, displace any hydrogen it may contain by passing a current of air through; and again weigh the tube. The weight is the same as that of the tube originally, showing that the oxide is again reduced to the metallic state.

In order to utilise this chemical change for the determination of the relative proportions by weight of hydrogen and oxygen in water, the following modification of this experiment may be adopted:—

Experiment 60.—Fit up the apparatus shown in Fig. 20; by preparing first a generating flask or bottle A in which hydrogen

FIG. 20.



is evolved by the action of zinc and sulphuric acid. Attach this to the wash-bottle B, in which place a solution of caustic potash in order to retain any traces of sulphuric acid that may be carried over mechanically. Fit up the tubes C, D, E with corks and leading tubes, so that the gas may be conducted through the whole series. Fill C and E with fragments of pumice; moisten that in C with a solution of mercuric chloride ($HgCl_2$)

and that in E with strong sulphuric acid. Fill D with fragments of fused potash. The passage of the gas through the wash-bottle and these tubes removes all impurities, *dry* hydrogen only escaping from E. The globe F is a bulb blown on a piece of combustion tubing; attach this to E by india-rubber tubing and so arrange that a Bunsen may be placed underneath it. Arrange the bulb G for the collection of water, and for H obtain a drying tube and fill it with fragments of calcium chloride.

Having the rest of the apparatus in readiness, introduce about half an ounce of dry copper oxide in F and weigh accurately. Also weigh both G and H. Connect up the apparatus by india-rubber tubing and see that the joints are air-tight. By the addition of a small quantity of sulphuric acid to A, cause a slow evolution of hydrogen; allow this to expel the whole of the air from the apparatus and then gently heat the oxide of copper by means of the Bunsen under F; notice that water is formed, and collects in the receiver G; any traces of vapour are retained by the calcium chloride in H. In about ten minutes remove the Bunsen and allow the bulb to cool; disconnect the hydrogen apparatus A and draw air through the tubes in order to displace the hydrogen. Weigh the copper oxide globe; the loss represents the oxygen which has combined with hydrogen to form water. Weigh also G and H; their combined increase in weight is the weight of water which has been produced.

Supposing as the result of an actual experiment that the oxide of copper has lost 16 decigrammes of oxygen, the receiver and drying tube will be found to have gained 18 decigrammes in weight. We know, therefore, that water contains (very nearly) 16 parts by weight of oxygen and 2 parts by weight of hydrogen in 18 parts of water.

64. Hydrogen Dioxide, or Hydroxyl.—This second compound of hydrogen and oxygen differs from water in that it contains an extra atom of oxygen in the molecule; the second atom is, however, held somewhat loosely; hence this body is readily decomposed into water and free oxygen.

For a description of hydroxyl the student is referred to one of the larger treatises on Chemistry.

Summary.

Water is a widely distributed liquid; from its solvent powers it is never found pure. Heat changes its condition from solid to liquid and liquid to gas. The boiling point depends on pressure. Many crystals contain water as an essential constituent. Is decomposed by electricity into an explosive mixture of gases; each may be collected separately; the gases re-combine to again form water. By volume water consists of two volumes of hydrogen and one of oxygen, which condense on union to form two volumes of steam. By weight water contains sixteen parts of oxygen to two of hydrogen.

Laboratory Hints.

The U tube with jacket and eudiometer for the experiments of this chapter may be obtained from the general apparatus of the laboratory. The boiling flask shown in Fig. 13 is fitted with a safety tube F, which provides for the exit of steam until required to pass through the apparatus. The beaker D is nearly filled with water. When the screw-tap E is closed the steam must perforce adopt that way of escape; but if the tap be opened the steam passes through the apparatus in preference to forcing itself through some four or five inches of water in the beaker. This device may be dispensed with in this particular experiment, but frequently is of great use where a current of steam is required to be carefully regulated or alternately shut off and re-admitted.

In working with mercury, take care that none is lost. Failing a proper bench with a ledge round it, it is better to stand the whole apparatus in a shallow drawer or tray. Dirty mercury may be cleaned by folding a piece of writing paper as a filter and placing it in a funnel. Prick two or three holes with a pin through the bottom; pour in the mercury: it runs through perfectly bright and clean. To fill a U tube, pour in as much mercury as it will hold; then close the open end with the thumb; and turn it over: the mercury will run into the sealed limb. If necessary, turn it upright, pour in some more mercury, and turn flat: in this way the tube may be filled.

In the sodium sulphate experiment it is possible that when the liquid is cooled no crystals will separate. If this be the case, throw in a single small crystal of the salt: around this as a nucleus the crystals will rapidly form.

An electric battery of three or four of either Grove's or Bunsen's cells is most suitable for the decomposition of water; the only difference between these forms of battery is that Grove employs as the positive element a sheet of platinum foil, while Bunsen uses a rod of carbon. To use the battery, first see that the zinc plates are bright all over with mercury; if this is not the case, they should be re-amalgamated. Dip each plate in a dilute solution of sulphuric acid (1 of acid to 10 of water); after half a minute remove the plate, pour a little mercury on it, and rub over every part with a piece of flannel tied on to the end of a stick until the whole surface of the zinc is bright with a coating of mercury. Place the zincs in the outer cells with the ends to which the binding screws are attached, all looking the same way; put in the porous cells, and the platinum foil again inside the porous cell. Connect the end zinc of all to the conducting wire by means of a binding screw; connect together the platinum of that cell and the zinc of the next with a binding screw, letting the screw be on the zinc side and the flat part of the connection against the platinum. The platinum and zinc of each of the adjoining cells must be thus connected; the end platinum must have the second wire attached to it. At the end of the box in which the cells are supplied, there is a piece of sheet vulcanite, against which the platinum is fixed. All the connections, wires, &c., must be perfectly clean and bright. Next fill the porous cells by the aid of a funnel with the strongest commercial nitric acid, taking care that none overflows. The outer cells are to be filled with sulphuric acid of the same strength as that used to amalgamate the zincs. When the battery is finished with, unscrew the connections, wash the binding screws in a stream of water, and wipe dry with a duster. Pour the nitric acid back into a bottle kept for the purpose. The sulphuric acid may, as a rule, be thrown away; if used for only a few minutes it may, however, be employed once again. Rinse the porous cells and other parts thoroughly; before putting away, the porous cells will be all the better for soaking

in clean water for a few hours. Always keep them full of water when not in use.

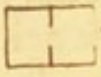
The most convenient apparatus for the production of an electric spark is a small induction coil. This is conveniently worked by a single bichromate cell; the advantage of this is that the cell is kept charged, the zinc being simply lifted out of the liquid. When required for use, connect by means of wires to the coil; connect also the terminals of the secondary circuit to the eudiometer; before filling it with gas, see that all is in working order; lower the zinc of the cell in the acid, tighten the binding screw, and turn on the current by means of the screw or handle fixed for that purpose on the coil; a rapid series of sparks should pass between the ends of the wires in the eudiometer. Do not let the zinc remain in the acid longer than necessary for the experiment.

In using ether, take care to keep any light at a distance; also replace the stopper and put the bottle in its proper place immediately. Ether is very volatile and very inflammable.

In Experiment 49 the reason for filling the leading tube with water is to lessen the amount of air which is mixed with the small quantity of gas given off. An easy way to do this is to attach some india-rubber tubing to the end of the leading tube; suck water into it from the trough or a beaker, and when full pinch the rubber tubing, fit the cork to the tube, and allow the end to remain under the water in the trough.

CHAPTER VIII.

CHLORINE.

Symbol, Cl. Atomic weight, 35·37. Density, 35·37. Specific gravity, 2·435. Molecular weight, Cl_2, 70·74. Molecular volume,  .

65. Occurrence.—This gas is not known in the free state in nature, but occurs in vast quantities in combination with sodium, forming rock salt.

66. Preparation.—The gas may be readily obtained from its compound with hydrogen (hydrochloric acid, HCl) by the action of manganese dioxide; on mixing these substances together a compound of chlorine with manganese is formed thus:—

$$\underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Manganese dioxide.}}{MnO_2} = \underset{\text{Manganese tetrachloride.}}{MnCl_4} + \underset{\text{Water.}}{2H_2O}$$

The manganese tetrachloride is an unstable compound, and, with an elevation of temperature, is decomposed into a chloride containing half the amount of chlorine, with the separation of the remainder in the free state:—

$$\underset{\text{Manganese tetrachloride.}}{MnCl_4} = \underset{\text{Manganese dichloride.}}{MnCl_2} + \underset{\text{Chlorine.}}{Cl_2}$$

In the actual preparation of the gas these two actions go on together, the tetrachloride being decomposed as rapidly as formed. Chlorine is manufactured in large quantities by this process for various uses in the arts. Chlorine is sometimes prepared from common salt (sodium chloride) direct, by the action on it of manganese dioxide and sulphuric acid; the gas is disengaged in the cold, but more rapidly with the application of heat. The whole of the chlorine is liberated:—

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Manganese dioxide.}}{MnO_2} =$$

$$\underset{\text{Hydrogen sodium sulphate.}}{2NaHSO_4} + \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{2H_2O}$$

Chlorine may also be obtained by the electrolysis of a solution of hydrochloric acid.

For the study of the properties of chlorine the gas may be prepared from hydrochloric acid and manganese dioxide

Experiment 61.—Take the apparatus No. 1, consisting of a sixteen-ounce flask, fitted with thistle funnel and leading tube.

Pour into the flask sufficient strong commercial hydrochloric acid, to just cover the bottom; then add about an ounce of powdered manganese dioxide; next pour in three or four ounces of the hydrochloric acid and shake the mixture well up; fix in the retort stand and introduce the cork. A, Fig. 22, is a flask arranged for the preparation of chlorine. The gas, being soluble in rather less than half its volume of cold water, cannot well be collected over that liquid. The process of downward displacement must be employed, or the water used must be hot. Eight jars of the gas will be required for the following experiments; it will be, as a rule, convenient to fill the jars twice. Having the four jars and well-greased plates ready, proceed to collect over hot water, if obtainable; if not, by downward displacement. In the latter case, the colour of the gas will indicate when the jars are full. Light the Bunsen and apply a gentle heat; the gas is readily disengaged. Having filled three bottles, remove the Bunsen, and the action will almost cease until the flame is re-applied. Under any circumstances, take care that as little gas as possible escapes in the room. Where possible, chlorine should be made in a stink-closet—*i.e.* a closet provided with a sliding glass door and flue for the removal of obnoxious gases. If there is no other alternative but to make it in the open laboratory, have every window possible open. It must be remembered that when a flask is heated a piece of wire gauze is to be interposed between it and the flame.

67. Properties.—*Experiment* 62.—Introduce into one jar a lighted taper: the gas does not take fire; the taper continues burning, but with a dull, smoky flame; notice that in addition to the soot there is an abundance of white fumes produced.

Experiment 63.—Put a small piece of phosphorus in a deflagrating spoon, and, without lighting it, place in a jar of the gas; notice that it commences to burn spontaneously, but does not evolve a very bright light.

Experiment 64.—Powder very finely some metallic antimony and drop a pinch into a bottle of the gas; it immediately takes fire. Into another jar drop a sheet of thin copper foil, or else a leaf of Dutch metal (a mixture of copper and zinc): it also immediately takes fire.

For two of the following experiments dry jars are re-

quired; they must, therefore, be wiped dry with the duster and filled by displacement:—

Experiment 65.—Take a small piece of sodium in a *dry* and clean deflagrating spoon; heat in the Bunsen flame until it is quite melted; plunge it in the *dry* jar of gas: it burns with the production of great heat, and white fumes of common salt are deposited.

Experiment 66.—Take the other dry jar of gas and introduce into it a piece of *dry* red cloth or blotting-paper. Notice that the colour does not disappear.

Next pour into the jar of gas a solution of some vegetable colouring matter, as litmus or indigo; shake up: the colour is instantly destroyed and cannot be restored. Introduce also a moistened piece of red blotting-paper: the colour is discharged. It will be observed that the presence of water is necessary in order that the operation of bleaching may proceed.

Experiment 67.—Fit up the eight-ounce flask for the generation of hydrogen from zinc and sulphuric acid; attach to it a jet thus (Fig. 21), with a piece of india-rubber tubing. After taking the usual precautions, light the jet and introduce it into a jar of chlorine; notice that the gas continues to burn, and that copious fumes are formed. At the same time, the yellow tint due to chlorine disappears.

FIG. 21.



The affinity of hydrogen and chlorine for each other is so great that many organic bodies containing hydrogen are decomposed by chlorine gas.

Experiment 68.—Take a piece of tow, pull it out as loose as possible, wet with turpentine (a hydrocarbon with the formula

$C_{10}H_{16}$); drop this into a jar of chlorine: it is decomposed, usually with heat and light. The carbon is deposited as soot; the hydrogen again produces fumes of hydrochloric acid.

The student will now have verified many of the properties of this gas for himself in the preceding experiments. Chlorine is of a yellowish green colour, and has a most pungent and disagreeable odour, which, when much diluted with air, somewhat resembles that of seaweed. It acts as an irritant poison when in the pure state, or even when present in considerable quantity in air.

It is soluble in cold water, which, at a temperature of 15° C., dissolves 2·368 volumes of the gas. Chlorine can be liquefied by a pressure of six atmospheres at 0° C., but has not yet been frozen.

Experiment 69.—Pass some chlorine from the gas-evolving apparatus for some time into water. Note that the gas imparts a yellow tint to the water, which at the same time acquires the characteristic odour of chlorine.

Add a little of this chlorine solution to solutions of litmus and indigo; notice that the solution possesses the same bleaching properties as the gas.

Add some of the chlorine solution to silver nitrate solution; a white precipitate of silver chloride is formed.

To solutions respectively of potassium bromide and iodide add chlorine solution; notice that in each case a deep coloration is produced, which is due to the liberation of bromine or iodine. To prove the presence of free iodine in the potassium iodide solution, add a few drops of a solution of starch, when the characteristic deep blue coloration is produced. If wished, the potassium iodide and starch solutions may be mixed prior to the addition of the chlorine.

Like oxygen, chlorine supports combustion, and is non-inflammable; it is a most active element, forming bodies called chlorides with the whole of the elements. It has a remarkable affinity for hydrogen; on exposing a mixture of those gases to diffused daylight, they slowly combine: bright

sunlight effects their immediate union with explosion. Intense artificial light, such as that of burning magnesium, produces the same effect. Carbon does not burn in chlorine, and if bodies containing it are burned, the carbon is deposited in the free state. One important peculiarity of the combustion of bodies in chlorine is that they often spontaneously ignite. As a rule, although a lower temperature is sufficient for the commencement of the formation of chlorides, the heat evolved during the union is less than that evolved in the production of the corresponding oxides.

The chemical actions occurring in the previous experiments are represented in the following equations:—

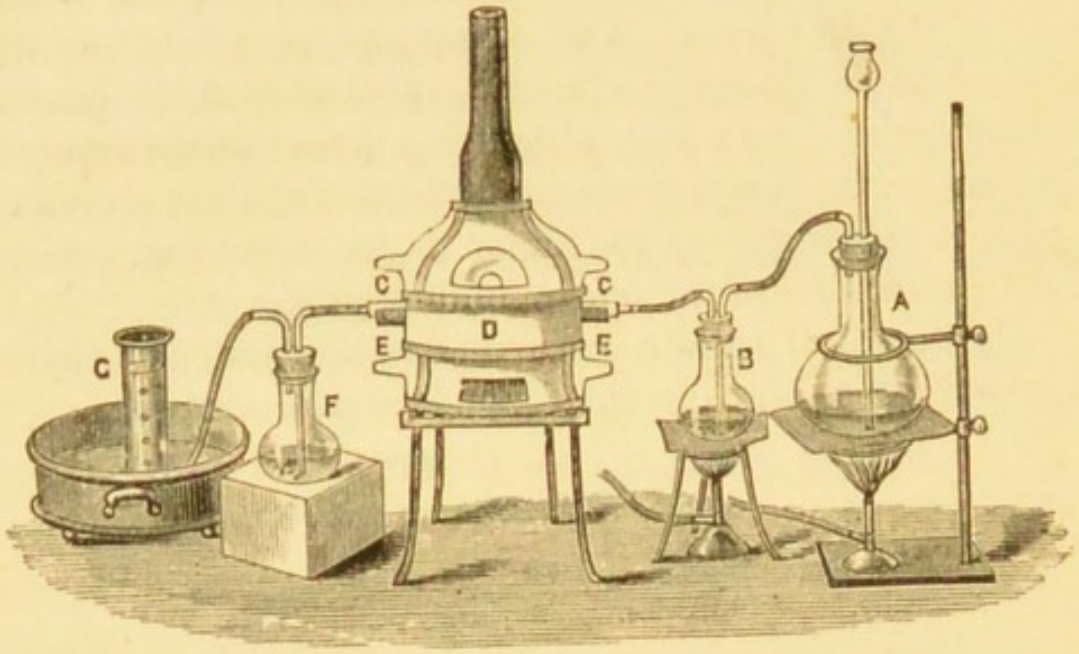
P_4	+	$10Cl_2$	=	$4PCl_5$		
Phosphorus.		Chlorine.		Phosphorus pentachloride.		
$2Sb$	+	$5Cl_2$	=	$2SbCl_5$		
Antimony.		Chlorine.		Antimony pentachloride.		
$2Na$	+	Cl_2	=	$2NaCl$		
Sodium.		Chlorine.		Sodium chloride.		
H_2	+	Cl_2	=	$2HCl$		
Hydrogen.		Chlorine.		Hydrochloric acid.		
$C_{10}H_{16}$	+	$8Cl_2$	=	$16HCl$	+	$10C$
Turpentine.		Chlorine.		Hydrochloric acid.		Carbon.

Water must be added to the list of hydrogen compounds capable of decomposition by chlorine. If a solution of chlorine in water is exposed to the sun's rays, bubbles are seen to rise to the surface, which, on examination, are found to be oxygen. At the same time the solution loses its yellow colour. The experiment is best performed by inverting a gas jar filled with the solution in a small trough also containing saturated chlorine water. At a higher temperature the decomposition takes place more rapidly.

Experiment 70.—Connect a flask, A, Fig. 22, fitted for the preparation of chlorine, to the second flask, B, which contains water; the leading tube from A dipping beneath the water level. Through the charcoal furnace, D, or one of Fletcher's gas-tube furnaces, pass a porcelain tube, C, filled with fragments of porce-

lain or flint, and fitted at each end with corks and glass tubes. The danger of cracking the porcelain tube is lessened by placing it in a semicircular iron trough, E, just large enough for the

FIG. 22.



tube to lie in. This is conveniently made from a piece of sheet iron, which can readily be turned up into a semicircle one inch internal diameter by any smith. F is a wash-bottle, containing a solution of caustic potash, for the purpose of removing the hydrochloric acid and any excess of chlorine; the oxygen passes over, and is collected in the trough G. B and F are connected to the porcelain tube by india-rubber tubing. The furnace must first be lighted and the tube raised to redness; then light the Bunsens under both the chlorine and water flasks: a mixture of chlorine and steam enters the furnace, decomposition ensues, and oxygen and hydrochloric acid escape.

The reaction is thus represented:—

$$\underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Oxygen.}}{O_2}$$

This experiment is an important one as showing the presence of oxygen in water; unlike hydrogen, by no known means can the oxygen of water be displaced in two instalments.

Chlorine is one of the most powerful bleaching or de-

colorising agents known; there are few vegetable colouring matters which are unattacked by it: ink, litmus, &c., are rapidly changed into colourless bodies. Mineral ink or printer's ink is not changed. Chlorine has no bleaching action in the absence of water; in its presence that compound is decomposed with the formation of hydrochloric acid. The nascent oxygen combines with the colouring matter and produces a compound containing a higher proportion of oxygen, and devoid of colour. Free oxygen has little, if any, bleaching power.

Chlorine decomposes silver nitrate with the formation of insoluble silver chloride, and hence causes a precipitate in a solution of a silver salt.

The action of chlorine on bromides and iodides is another instance of the great activity of this element. The following equations represent the chemical changes which occur :—

Cl_2	+	2KBr	=	Br_2	+	2KCl
Chlorine.		Potassium bromide.		Bromine.		Potassium chloride.
Cl_2	+	2KI	=	I_2	+	2KCl
Chlorine.		Potassium iodide.		Iodine.		Potassium chloride.

These reactions will be examined more fully when the elements bromine and iodine are under consideration.

Summary.

Chlorine is a heavy gas; does not occur in nature in the free state, but largely in combination with sodium. May be obtained from either hydrochloric acid or sodium chloride, or by electrolysis of hydrochloric acid. Possesses a yellow-green colour; odour somewhat like sea-weed, and acrid taste; non-inflammable; supports combustion; soluble in water; is a powerful bleaching agent; decomposes water with evolution of free oxygen.

Laboratory Hints.

Chlorine rapidly attacks corks; they may be protected by dipping them into melted paraffin; not *paraffin oil*, but the

solid substance melted in a small dish or pipkin. The reason for *first* adding hydrochloric acid, subsequently the manganese dioxide, and shaking up so thoroughly, is that otherwise the oxide is liable to form a cake at the bottom : this gets hot, and the liquid, finding its way through it after a time, cracks the vessel.

The fumes produced by burning both phosphorus and antimony in chlorine are poisonous, and should not be breathed.

The reason why such care must be taken to have dry jars for sodium experiments is that hot sodium accidentally coming in contact with water explodes violently. See also that there is no water spilled about the working bench. For the hydrogen experiment a second generating apparatus is required ; a second thistle funnel is a useful addition to the apparatus list given on page 11. Failing this, all other experiments with chlorine may be first tried, and then the apparatus cleaned and used for hydrogen. In the last experiment there is considerable danger of breaking the porcelain tube ; it is a good plan to incline it a little, so that the steam in passing through it has to rise ; this prevents any condensed steam running on to the red-hot porcelain. When the experiment is finished, disconnect the other apparatus, and allow the tube to cool slowly in the furnace.

Wash all apparatus used for chlorine immediately it is finished with ; this applies especially to corks and india-rubber tubing : the latter should have a stream of water sent through it.

CHAPTER IX.

HYDROCHLORIC ACID.

Formula, HCl. Molecular weight, 36·37. Density, 18·18. Specific gravity, 1·2474.

68.—This gas, called also muriatic acid, is the only known compound of hydrogen and chlorine. Its formation, by the union of these elements has been already described.

69. Preparation.—The gas is easily obtained by the action of sulphuric acid on almost any chloride; because of its cheapness, common salt is usually employed. Salt in its ordinary form is so finely divided that the action proceeds with almost unmanageable rapidity. This may be modified by first fusing the salt and then breaking the solid mass thus obtained into small lumps. The gas is extremely soluble in water, and therefore has to be collected by downward displacement.

The reaction is represented by the following equation:—

H_2SO_4	+	$NaCl$	=	$NaHSO_4$	+	HCl
Sulphuric acid.		Sodium chloride.		Hydrogen sodium sulphate.		Hydrochloric acid.

One atom of the hydrogen of the sulphuric acid is here driven out by the sodium. At a much higher temperature than could be used with a glass flask, the second atom of hydrogen is displaced :—

$NaHSO_4$	+	$NaCl$	=	Na_2SO_4	+	HCl
Hydrogen sodium sulphate.		Sodium chloride.		Sodium sulphate.		Hydrochloric acid.

Experiment 71.—Fill a clay crucible about five inches in height with common salt; melt over a bright red fire or in a furnace, and pour the molten mass on to a cold iron plate. When cold break up and store in a bottle, which must be kept corked. Place about half an ounce of the fused salt in the generating flask with funnel and leading tube arranged for downward displacement; see that the india-rubber and other tubes are dry. Fix in the retort stand and pour in sufficient concentrated sulphuric acid to cover the salt: the gas is evolved rapidly even in the cold. Thoroughly dry four gas jars and fill them; should the evolution of gas slacken, apply heat. Copious fumes emerge from the mouths of the jars as soon as full. Next place the delivery tube in a beaker, into which exactly 100 cc. of water have been poured; notice that the gas is absorbed as rapidly as formed, and that the water rises in temperature. After some minutes pour the solution back into a measuring tube. The volume will have increased.

70. Properties.—*Experiment* 72.—Take the plate off one jar of gas ; observe that although the gas itself is clear the fumes seen so frequently before again make their appearance when the gas comes in contact with the air. Introduce a lighted taper : the taper is extinguished, and the gas itself does not light.

Experiment 73.—Place the mouth of the second jar under water and slide off the glass plate ; the water rapidly fills the jar.

Experiment 74.—To the third jar add some litmus solution and shake up ; the colour is seen immediately to change to red.

Experiment 75.—Into another jar of gas hold a piece of paper which has been dipped in a concentrated solution of ammonia ; observe the production of dense white fumes of ammonium chloride.

Experiment 76.—Examine now the solution made by passing the gas into water ; it possesses the odour of the gas, evolves pungent fumes, and, like it, immediately reddens litmus.

Add some of the aqueous solution of the gas to litmus solution ; notice that the colour changes to red, but that no bleaching action results.

Add a portion of the solution of the gas to silver nitrate solution ; a white curdy precipitate of silver chloride is formed.

Add some of the hydrochloric acid solution to a mixture of potassium iodide and starch solutions ; no coloration is produced, showing that hydrochloric acid does not liberate iodine from its compounds.

In common with water, hydrochloric acid gas is decomposed by iron at a red heat, with the evolution of hydrogen.

Experiment 77.—Fit up the apparatus, consisting of iron-tube containing filings as shown in Fig. 11, except that a hydrochloric acid generating apparatus is substituted for the steam-flask. Pass the gas over the iron turnings and collect and test the hydrogen.

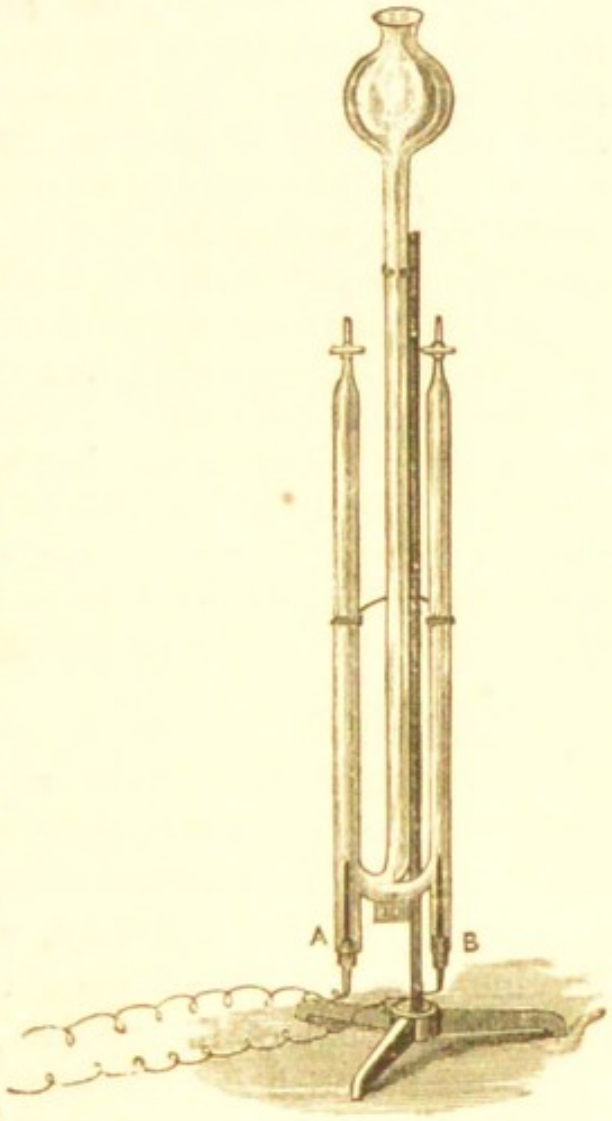
The following equation represents the change which occurs :—

$$\underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Iron.}}{Fe} = \underset{\text{Iron chloride.}}{FeCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

The same reaction takes place when iron is added to a concentrated solution of hydrochloric acid gas in water. Zinc and other easily oxidised metals displace the hydrogen in a similar manner.

Hydrochloric acid is colourless, but is rendered visible on coming in contact with air containing moisture by the formation of a compound with water which condenses to liquid globules; hence the dense fumes so often noticed. It has a sharp, pungent odour; its solution in water is intensely sour, and reddens litmus solution; it is a very powerful acid, and forms an important series of salts known as chlorides. Water at 15° C. dissolves 454 volumes of hydrochloric acid.

FIG. 23.



Hydrochloric acid in the gaseous form is distinguished by the dense fumes it forms with ammonia. In solution it produces a characteristic precipitate of silver chloride from the nitrate. It shares this property with the soluble chlorides, and also as shown by experiment with a solution of chlorine. It is distinguished from this gas by its having no bleaching power and being without action on a solution of potassium iodide and starch.

71. Composition.—The composition of the gas may be ascertained by exposing its solution to electrolysis, when it is resolved into equal volumes of hydrogen and chlorine.

The best apparatus to use for this experiment is Hofmann's, which, as shown in Fig. 23, consists of three tubes, connected at the bottom; through A and B are passed india-rubber corks with carbon electrodes (platinum cannot be used, as that metal is attacked by nascent chlorine).

Experiment 78.—Fill the apparatus with concentrated hydrochloric acid just to the level of the stop-cocks, leaving them open; connect with a battery of three or four cells, and allow the current to pass for an hour; the hydrogen rises rapidly from the negative electrode, but from chlorine being soluble in water, little gas is evolved until the solution is saturated. At the end of this time, turn off the stop-cocks; equal volumes of gas should collect in each tube. Should the chlorine be in too small a quantity, it is a sign that the acid in that limb is not yet saturated. The chlorine may be recognised by its colour; open the stop-cock and let the gas impinge on a piece of wet litmus paper; the colour of the litmus is discharged. Connect a small glass jet to the limb containing hydrogen by india-rubber tubing; open the stop-cock and apply a light to the issuing gas, which is recognised by its inflammability.

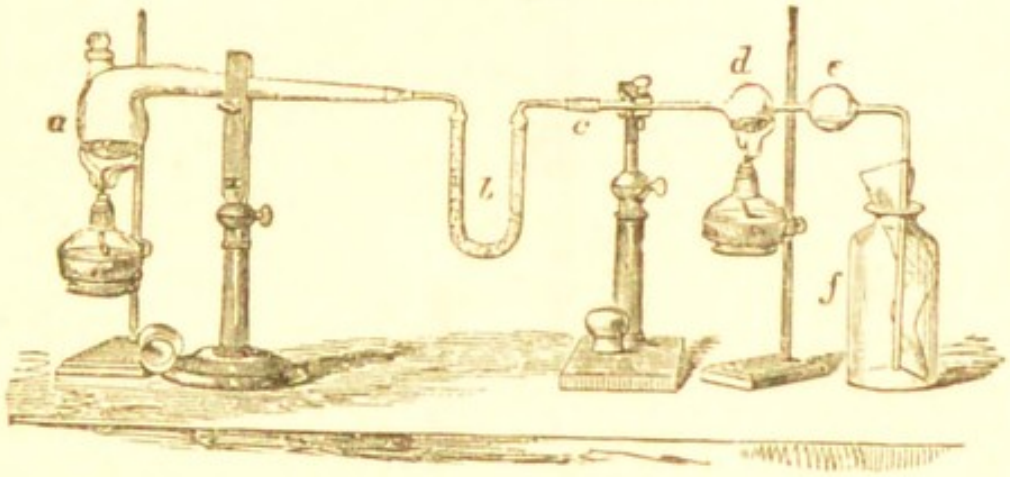
Chlorine, like oxygen, is liberated from the electrode connected with the copper or platinum element of the battery. The following eight elements are alike in this respect, and from their behaviour with an electric current are called negative:—oxygen, chlorine, bromine, iodine, fluorine, sulphur, selenium, and tellurium.

In the event of the apparatus for performing the last experiment not being obtainable, the presence of both chlorine and hydrogen in hydrochloric acid may be detected in the following manner:—

Experiment 79.—Fit to the generating flask, containing salt and sulphuric acid, the apparatus used for drying hydrogen in

Experiment 43 ; connect this to a tube in which two bulbs have been blown : in the first of these place some powdered manganese dioxide, which has been thoroughly dried by warming in an iron ladle over the Bunsen flame. Arrange a bottle to receive the escaping gas ; place in it a sheet of moist blue litmus paper. The hydrochloric acid evolved at once changes the colour. Apply heat to the bulb containing manganese dioxide ; the hydrochloric acid is decomposed ; water collects in the second bulb ; chlorine passes over into the jar, and is recognised by its odour and bleaching power. Fig. 24 shows

FIG. 24.

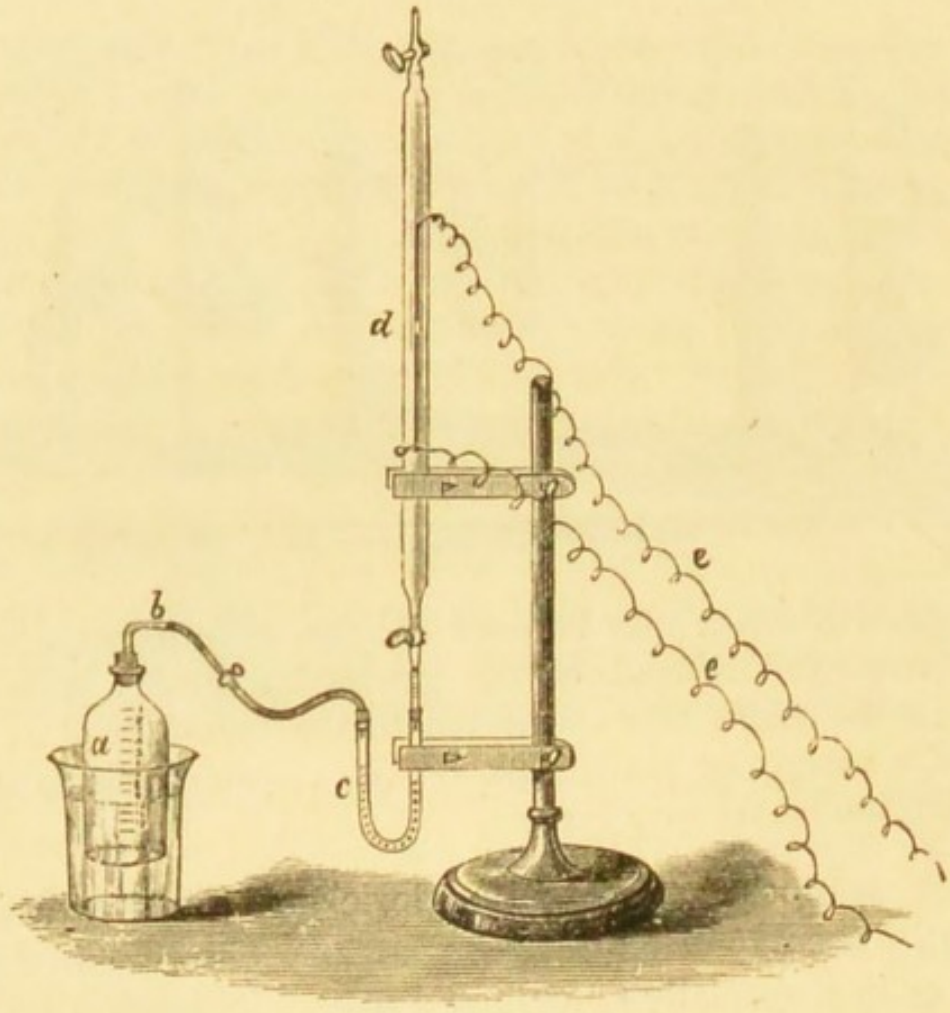


the apparatus which may be used for this experiment, a retort being employed instead of the generating flask : *a* is the retort ; *b* the drying tube connected to the bulb-tube at *c* ; *d* is the bulb containing manganese dioxide ; water collects in *e* ; and chlorine passes over into *f*.

The composition of hydrochloric acid by synthesis is shown by the explosion of hydrogen and chlorine in equal volumes in a specially constructed tube. The gases for the purpose are conveniently prepared by electrolysis ; or working by gas or diffused daylight, they may be mixed in a bottle over saturated chlorine water in a small trough or beaker and then transferred to the explosion tube : this simply consists of a glass tube about twenty inches in length, with a stop-cock at each end, and two platinum electrodes fused through the middle.

Experiment 80.—Procure a small gas jar *a*, Fig. 25, open at top and bottom; one holding 20 or 32 ounces is a convenient size. Close the upper opening with a cork which has been dipped in melted paraffin. Bore a hole and pass through it a glass tube with stop-cock. Failing this, a plain glass tube with a piece of india-rubber tubing and a pinch-cock may be used. Turn the jar *a* bottom upwards and exactly upright, and proceed to graduate it by pouring in successive quantities of 25 or 50

FIG. 25.



cubic centimetres of water, making a mark at the level of each on the outside of the jar either with a sharp file or a writing diamond. These marks should be numbered 1, 2, 3, &c., from the top of the jar downward. Having prepared the jar, stand it in a small trough or large glass beaker, filled with saturated chlorine water; pass the india-rubber tubing over *b*, allow the air to escape from the jars, and close the screw tap; next introduce through *b* 200 cubic centimetres of hydrogen, and then the

same quantity of chlorine, and agitate the jar, so as to mix the gases. Connect the glass tube *b* with the small U tube *c*, filled with calcium chloride, and attach the explosion tube *d* to the second end of the U tube. Open the whole of the stop-cocks sufficiently for the weight of the jar *a* to force the mixed gases *slowly* up into and through *d*. When nearly the whole of the gas has been allowed to escape, close the stop-cocks; *d* is now filled with a mixture of equal volumes of dry hydrogen and chlorine, which has expelled the air. Attach the wires *e e* from the induction coil to the electrodes, and pass an electric spark: combination takes place between the gases. When they have cooled down to the original temperature, place one end of the explosion tube under the surface of mercury and open the stop-cock; the mercury does not rise, showing that there is no alteration in the volume of the gas. Remove and open the stop-cock with the end immersed in water; the water rushes up and fills the whole of the tube.

These experiments show that hydrochloric acid is a gas produced by the union of equal volumes of hydrogen and chlorine without condensation. The composition by weight may be demonstrated by means similar in principle to those adopted in the case of water.

Summary.

Hydrochloric acid is the only compound known of hydrogen and chlorine; may be easily prepared by the action of sulphuric acid on a chloride. The gas is very soluble in water; is colourless, but fumes on exposure to air; has a sharp, pungent odour and sour taste; is non-inflammable and a non-supporter of combustion; reddens litmus. Is composed of equal volumes of hydrogen and chlorine united without condensation; this is proved both by analysis and synthesis.

Laboratory Hints.

Fused salt is as a rule kept in a laboratory; it is a convenient plan to get a working jeweller to melt down a good stock in one of the large crucibles used in the trade: the cost for melting would not be excessive.

It is not absolutely necessary in Experiment 79 that the tube containing manganese dioxide should have bulbs blown on it; bending it in the form of a W answers the purpose.

The graduated jar and explosion tube for Experiment 80 will, in most cases, be found among the general apparatus of the laboratory. Instead of using the graduated jar, and thus mixing the gases, they may be prepared electrolytically with the same apparatus used for obtaining the mixed gases from water; the bottle should, however, be a small one and the electrodes must be of carbon. The electric current must be passed for a sufficient time to saturate the acid with chlorine. Instead of graduating the jar in cubic centimetres, fluid ounces may be used as the unit; then 4 ounces in volume of each gas should be employed.

As it is possible that the explosion which takes place when the spark is passed through the tube containing the mixture of gases might shatter the tube, the precaution of placing it in a stink closet and shutting the door is advisable. The eudiometer in which oxygen and hydrogen were exploded over mercury cannot be employed, because mercury is rapidly attacked by chlorine. It is essential that the tube should be *dry* before being filled with the gases; to ensure this it should first be warmed in the hot-water oven and the water vapour sucked out.

CHAPTER X.

LAWS OF CHEMICAL COMBINATION BY WEIGHT AND VOLUME.

72. Combination in Definite Proportion.—The student is now in a position to appreciate the reasoning on which the atomic theory is based. The experimental work of the last few chapters will have furnished him with some specimens of the observations which are explained by this theory; he will do well, with this more intimate knowledge of experimental data, to go back to Chapter IV., and once more carefully read it through. It is there stated

that each element has a certain number given it, which represents the weight of that element which enters into a chemical compound, and that, of all the elements, hydrogen is represented by the smallest number. Proof of this law of definite proportion by weight is afforded in the experimental determination of the composition by weight of water. Proper precautions being taken, it is invariably found that in 9 parts of water there are 1 of hydrogen and 8 of oxygen by weight. Judging from this fact alone we might ascribe to oxygen 8 as its combining proportion.[1] This would give as the formula of water HO ; but from the experiments in which hydrogen is displaced from water in two distinct instalments, it is evident that there must be two combining proportions of that element present. Therefore, for this and other reasons, water is considered to consist of two combining proportions of hydrogen to one of oxygen ; consequently 2 parts of hydrogen by weight are looked on as combining with 16 by weight of oxygen ; and, as no less proportion of that element is ever displaced from a chemical compound, 16 is taken as the combining weight of oxygen.

73. Chemical Equivalent.—The weight of an element which combines with, or by displacement expels from a compound, 1 part by weight of hydrogen is termed its *chemical equivalent.* The number is in many cases the same as the atomic weight ; it must however be remembered that 'chemical equivalent' and 'atomic weight' are terms which have distinct and separate meanings.

74. Combination in Multiple Proportions.—In addition to water another compound of hydrogen and oxygen has been described, in which 2 by weight of hydrogen are in union with 32 of oxygen. This compound has accordingly received the formula H_2O_2. **Not only, then, does chemical combination invariably occur in definite**

[1] In these explanations, for the sake of simplicity, the nearest whole numbers are taken for the atomic weights.

proportions, but also, when two elements happen to combine in more than one proportion, they unite in multiple proportions. In the second compound of hydrogen and oxygen there is exactly *twice* as much oxygen as in the first. Although the number of chemical compounds is so vast, no deviation from this law has been observed.

The reason, according to the atomic theory, why combination occurs in multiple proportions is that when two elements combine one atom of the first may combine with one, two, or three atoms of the second, but combination with the *fraction* of an atom is necessarily a contradiction. Though the theory is not one which admits of absolute proof, yet it so amply and consistently explains all the phenomena of chemistry that its essential principles are universally recognised.

75. Chemical Calculations.—It is of the highest importance to the student that he should be able to make the various calculations necessary in analytic and other chemical work. It is now seen that the law of definite proportions underlies the whole basis of chemistry ; an explanation of the methods of chemical calculation naturally follows.

76. Proportion by Weight of Elements in a Compound.—The formula of a compound gives the number of atoms of each constituent ; those atoms each being of a definite weight, we are enabled to state the proportion by weight of each element in a compound. Thus the formula of potassium chlorate is $KClO_3$; assigning to each of these their atomic weight, we have —

$$\begin{array}{cccc} K & Cl & O_3 & \\ 39 & +35{\cdot}5 & +(16\times 3=)48 & = 122{\cdot}5 \end{array}$$

that is, the molecule weighs 122·5, this being the sum of the weight of the constituent atoms. As any weight taken of this salt must consist of a whole, though indefinite number of molecules, the proportion by weight of each element present is the same as that in the individual molecule.

This fact will be grasped more clearly when it is remembered that these very combining weights are numbers deduced from experiments made on the substances taken in quantity.

77. Percentage Composition from Formula.—From the molecular weight of a compound its percentage composition, or weight of each constituent in 100 parts, is easily found by a calculation in proportion. Thus, in the case of potassium chlorate, 122·5 contain 48 of oxygen; what quantity will 100 contain?

As 122·5 : 100 :: 48 : 39·18 per cent. of oxygen.
„ 122·5 : 100 :: 35·5 : 28·97 „ „ chlorine.
„ 122·5 : 100 :: 39 : 31·83 „ „ potassium.
99·98

Precisely the same method applies to any and every other compound.

78. Formula from Percentage Composition.—An important, but somewhat more difficult, type of calculation is that in which the percentage composition of a compound is obtained by analysis, and its formula is required. The results of analysis are almost always expressed as so much per cent.; suppose that the figures given above represent results obtained in the case of potassium chlorate, and that the formula is required.

As a first step toward obtaining the formula, we divide the number representing the percentage of each element by its atomic weight; the result is a series of numbers in the ratio or proportion of the number of atoms of each element.

$$\frac{39{\cdot}18}{16} = 2{\cdot}448 \text{ of O.}$$

$$\frac{28{\cdot}97}{35{\cdot}5} = {\cdot}816 \text{ of Cl.}$$

$$\frac{31{\cdot}83}{39} = {\cdot}816 \text{ of K.}$$

In this way we find that 39·18 by weight of oxygen in 100 parts is equivalent to 2·448 atoms of oxygen; and that of chlorine and potassium there are ·816 of an atom of each. But atoms are indivisible, and therefore, as explained, these numbers can only represent the ratio or proportion of the number of atoms to each other. The next step in the calculation is to find the smallest series of whole numbers which have the same ratio: dividing each of the numbers above by the lowest we have:—

$$\frac{2\cdot448}{\cdot816}=3 \text{ of O.} \quad \frac{\cdot816}{\cdot816}=1 \text{ of Cl.} \quad \frac{\cdot816}{\cdot816}=1 \text{ of K.}$$

The formula is therefore considered to be $KClO_3$. In assigning a formula to a compound, however, other considerations must not be overlooked; because the percentage composition will be the same whether we look on $KClO_3$ or $K_2Cl_2O_6$ as the formula. The above reasoning is conveniently summed up in the following rule for determining the formula from the percentage composition.

Rule.—Divide the percentage of each element by its atomic weight; divide each of the numbers thus obtained by the lowest one of the series; the quotients are generally whole numbers, or practically so. These represent the number of atoms of each element present in the molecule. In some cases the result of such division is that one quotient contains ·5, *i.e.* one atom of one element to a proportion of 1·5 or 2·5, &c. of another; the number of atoms in the molecule is then obtained by doubling every number, making 2 of one to 3 or 5 of the other.

The student is not expected at this stage to determine whether the formula is really $KClO_3$ or $K_2Cl_2O_6$. By the above method the simplest formula of any compound is obtained; other considerations, of which a knowledge of the vapour density is the most important, must determine whether the formula is or is not a multiple of this. As a matter of fact potassium chlorate, which has been taken as a

convenient instance, is represented by $KClO_3$; its vapour density cannot, however, be taken, as at a comparatively low temperature it is decomposed.

When chemical compounds are expressed by means of formulæ, the law of combination in multiple proportion is so evident that it seems impossible that it could have remained for any length of time undiscovered. But the following example will show that, until the use of formulæ, this law was not so clearly written, as it were, on the face of every series of compounds as it now is. There are two compounds of carbon and oxygen whose percentage compositions are respectively the following:—

	No. 1.	No. 2.
Carbon	42·857	27·273
Oxygen	57·143	72·727
	100·000	100·000

On the surface there is here no evidence of combination in multiple proportion; 42 is no simple multiple of 27, neither is 72 of 57. But let us in each case see what weight of oxygen is combined with 1 part by weight of carbon: this is determined by dividing the weight of oxygen by that of carbon in each compound:—

$$\text{No. 1.} \quad \frac{57{\cdot}143}{42{\cdot}857} = 1{\cdot}33 \text{ of O to 1 of C.}$$

$$\text{No. 2.} \quad \frac{72{\cdot}727}{27{\cdot}273} = 2{\cdot}66 \text{ of O to 1 of C.}$$

When stated in this manner it is at once seen that to the unit of carbon there is twice as much oxygen in the latter compound as in the former. As an exercise the student may determine the formulæ of these two compounds, when he will appreciate the greater simplicity and clearness resulting from the use of formulæ as a method of expressing chemical composition.

79. Calculation of Quantities.—The formula representing the weight of each element present in a compound, it is but going a step further in the same line of reasoning to say that an equation must represent the weight of each substance involved, and of each body produced, in a chemical change.

$$\underset{39+35{\cdot}5+48}{\underbrace{KClO_3}} = \underset{39+35{\cdot}5}{\underbrace{KCl}} + \underset{48}{3O}$$

$$\underset{122{\cdot}5}{\underbrace{\phantom{39+35{\cdot}5+48}}} \qquad \underset{74{\cdot}5}{\underbrace{\phantom{39+35{\cdot}5}}}$$

122·5 of potassium chlorate yield on decomposition 74·5 of potassium chloride and 48 of oxygen. It is most important that the student should remember that in every case the equations and atomic weights supply the data by which weights of bodies produced from certain weights of the substances which yield them may be calculated. On the other hand, given the quantity of a compound required, the weight of each body necessary for its production may be determined. Let this fact be once grasped, no difficulty should be found in making any of these calculations, the principles being always the same. It is scarcely necessary to remark that unless the student knows the equation representing the chemical change, and the atomic weights, he will be at fault.

The one example given below should make the whole subject clear to those who understand the *principles* involved.

From 3 grams of potassium chlorate what weight of oxygen may be obtained, and what weight of potassium chlorate will remain?

The equation shows that 122·5 of potassium chlorate yield 74·5 of potassium chloride, then:—

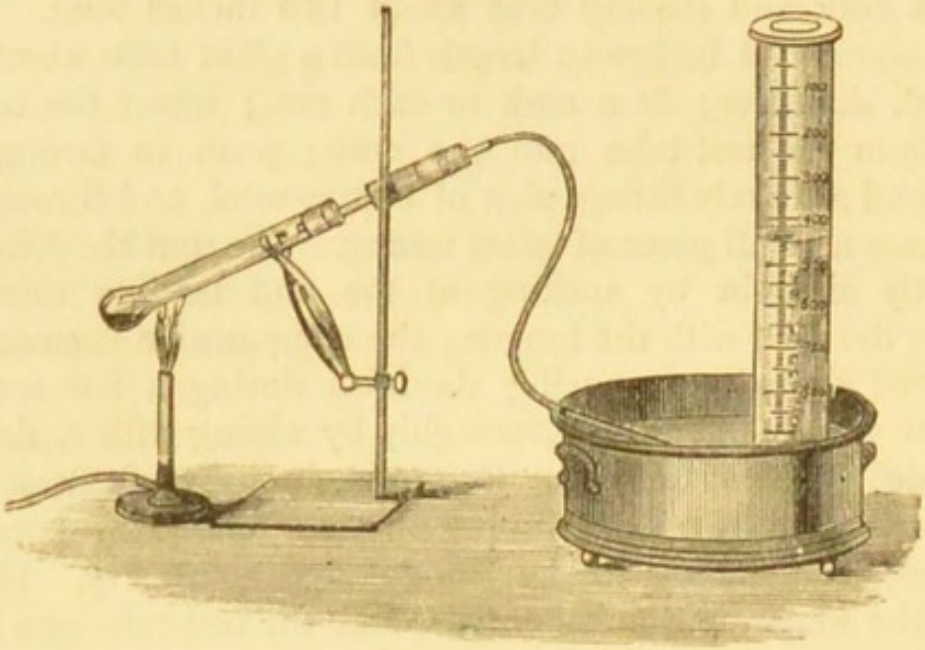
As 122·5 : 74·5 :: 3 : 1·824 gram of KCl remaining.
As 3 : 1·824 :: 100 : 60·8 = percentage of KCl.
3 − 1·824 = 1·176 gram of oxygen yielded.
As 3 : 1·176 :: 100 : 39·2 = percentage of oxygen.

The fact that the quantities calculated from this equation actually represent those obtained is proved by the following experiment :—

Experiment 81.—Take a test-tube made of combustion tubing six inches long and half an inch internal diameter; fit to it a cork and leading tube about two inches long. Cut a piece about two inches in length from a glass tube about half an inch diameter; fit a cork to each end; insert the leading tube from the test-tube into one cork; push in through the other end a loosely fitting plug of cotton-wool, and through the cork pass a small piece of glass tubing. See that the joints are perfectly air-tight by sucking at the end leading tube and closing the tube with the tongue; the comparative vacuum thus produced should not sensibly diminish during a few seconds. Dry the whole apparatus thoroughly by wiping with a dry and clean duster; next weigh it. Before beginning to fit these parts together, a small quantity of potassium chlorate should be powdered and placed in the hot-water oven to dry. Having noted the weight of the apparatus, take the test-tube and scoop into it three grams or thereabout of the dry potassium chlorate; give the tube a tap, so as to get all the salt at the bottom; wipe out any particles adhering to the side of the tube with a small brush or the corner of the duster; again weigh and note the weight. Connect the leading tube by india-rubber tubing to a glass tube placed in the pneumatic trough. Fix the test-tube in the retort stand, so that it is at an angle of 45°. Procure a tall graduated litre jar (a test-mixer), fill with water, and invert in the pneumatic trough to receive the gas. Fig. 26 shows the whole apparatus arranged for the evolution of oxygen. Warm the tube very gradually with the Bunsen; the salt melts and readily gives off oxygen. After a time, however, it becomes somewhat pasty, and the gas comes off less readily. At this point place the flame a little above the salt and heat carefully, working down toward the bottom. Toward the end heat the tube as strongly as possible with the Bunsen; turn it round, so that the whole of the salt is acted on; when no more gas is evolved disconnect the india-rubber and allow the apparatus to cool. The principal chances of failure are that the heat may so soften the glass that the gas may blow a hole through, and that

at the moment when the pastiness is produced the salt may bubble up into the higher part of the tube, and into the leading tube. This may be prevented by careful watching, using a tube of not less diameter than that given, and getting the tube hot

FIG. 26.



just above the salt; any which bubbles up is thus liquefied at the high temperature, and again runs back to the bottom. The little tube containing cotton-wool is fixed to retain any potassium chloride carried over mechanically with the gas. Remember that the plug must not be too tight, and that it must be at the end furthest from the generating tube.

When cold weigh the tube and potassium chloride, and find what weight remains. Observe the volume of oxygen in the measuring jar, when it is depressed until the level of the water inside corresponds with that in the trough. With a thermometer take the temperature of the water, and calculate what volume the oxygen would be at 0° C. Then find by calculation its weight. One litre of oxygen at N.T.P. weighs 1·4336 gram.

The following are results obtained in this experiment by a student working in the author's laboratory:—

Weight of apparatus and $KClO_3$.	43·68 grams
Weight of apparatus	40·68 „
Weight of $KClO_3$ . . .	3·00 „

Weight of apparatus and KCl	= 42·62 grams
Weight of apparatus	40·68 ,,
Weight of KCl	1·94 ,,

As 3·00 : 1·94 :: 100 : 63·7 per cent. of KCl.

Volume of oxygen collected at 20° C. = 900 c.c. Reduced to standard temperature, correction for pressure being neglected—

$$\frac{900 \times 273}{293} = 838 \text{ c.c. at } 0^\circ \text{ C.}$$

1000 c.c. of oxygen weigh 1·4336 gram.

As 1000 : 838 :: 1·4336 : 1·2013 gram of oxygen.

As 3·00 : 1·20 :: 100 : 40·0 per cent. of oxygen.

	Found	Theoretical
Potassium chloride	1·94 = 63·7 per cent.	1·824 = 60·8 per cent.
Oxygen	1·20 = 40·0 ,, ,,	1·176 = 39·2 ,, ,,

The potassium chloride is probably over-estimated through some of the chlorate remaining unreduced to chloride. The oxygen is so through the air in the test-tube expanding and being thus driven over. With care, however, results may be obtained which prove the general truth of the fact that the equation represents the weights of the various participating bodies; the error of experiment, even with a young student, should come within 4 or at most 5 per cent.

As further proof that the potassium chlorate is changed into another chemical compound by the action of heat, make the following experiment:—

Experiment 82.—In a clean test-tube dissolve the residuum of potassium chloride from the last experiment in a little distilled water. Add a few drops of a solution of silver nitrate, a curdy white precipitate is formed. In another clean test-tube dissolve a crystal of potassium chlorate, and again add silver nitrate solution; there is no precipitate. These tests show that

by the action of heat a substance is produced from potassium chlorate which was not originally present.

80. Elementary Molecules and Nascent Condition.—The student already knows that the term atom is applied to the smallest particle of an element entering into or leaving a chemical compound; thus, when hydrochloric acid is decomposed, we say that an atom of each element is liberated. He is also aware that the atoms of elements, when in the free state, are not supposed to remain single, but in most cases unite together to form molecules of the element; thus two atoms of hydrogen unite to form a molecule of hydrogen. This union is attended with loss of the chemical activity of the element. It has been explained that *nascent* oxygen, liberated by chlorine, is a powerful bleaching agent, while free oxygen is not so. Also nascent hydrogen acts more powerfully as a reducing agent than does the same element when in its normal free state. The theory on which this is accounted for is as follows: at the moment of liberation the oxygen exists as *atoms*, and these attack the colouring matter; failing anything else with which to unite, they unite with each other and form molecules. The activity of the oxygen molecule is less than the sum of that of the two atoms by the amount of energy with which they are held together. One striking experiment may be mentioned in which the affinity of oxygen atoms for each other is greater than that for the bodies with which they are combined:—

Experiment 83.—To a few drops of solution of nitrate of silver add, in a test-tube, an excess of sodium hydrate solution; a brown precipitate of oxide of silver is formed, which rapidly falls to the bottom. Wash two or three times by decantation; pour on it some hydroxyl and close the tube loosely with the thumb; rapid effervescence ensues. When the action is over, test the gas in the tube for oxygen by a glowing splinter.

The following equation shows the chemical change which has occurred:—

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

The affinity between the oxygen and silver is but small; so also is that between the water and second atom of oxygen which has changed it into hydroxyl. The attraction of the oxygen atoms for each other is sufficient to overcome these, and accordingly that element is liberated in the free state. Considerations of this kind have led the chemist to the conclusion that the atoms of elements combine together to form molecules.

81. Avogadro's Law. — The fact that all gases, whether elementary or compound, expand and contract at the same rate when subjected to variations of temperature and pressure has an important bearing on their probable molecular constitution. Their similarity in this respect has led to the assumption, expressed in the 'Law of Avogadro'—**'Under similar conditions of temperature and pressure equal volumes of all gases contain the same number of molecules.'** From this it follows that at the same temperature, and under the same pressure, the volume of any gaseous molecule is the same, whatever may be the nature and composition of the gas.

82. Constitution of Molecules. — The relative weights of equal volumes of hydrogen and hydrochloric acid are 1 and 18·18. These, according to Avogadro, are the relative weights also of the molecules. By experiment we know hydrochloric acid contains half its volume of hydrogen; it must therefore contain half as much of that element as an equal volume of free hydrogen. The molecule of hydrogen then contains double as much hydrogen as is contained by a molecule of hydrochloric acid, which occupies the same volume. As we assume that the hydrochloric acid molecule contains at least one atom of hydrogen, the molecule of hydrogen must necessarily be composed of at least two atoms. The fact that two atoms of hydrogen are present in water

was proved by its being removed in two successive portions; as the hydrogen of hydrochloric acid cannot be thus removed, this is strong evidence in favour of its containing *only* one atom; and as the quantity of hydrogen in the hydrogen molecule is double that in hydrochloric acid, it must be composed of two atoms, and no more than two.[1] As the molecule of hydrogen consists of two atoms, its weight must be taken as 2, and that of the molecule of hydrochloric acid as 36·37.

83. Combination by Volume.—The student has seen that two volumes of hydrogen combine with one of oxygen to form two volumes of water-gas. This is a necessary result of Avogadro's law, because the molecule of steam occupies the same space as a molecule of hydrogen: a still further condensation occurs in the production of more complex molecules. In the following equations the molecule is represented by two squares, indicating that the volume is double that of an atom:—

$$\boxed{H_2} + \boxed{Cl_2} = \boxed{HCl} + \boxed{HCl}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{O_2} = \boxed{H_2O} + \boxed{H_2O}$$

$$\boxed{H_2} + \boxed{H_2} + \boxed{H_2} + \boxed{N_2} = \boxed{NH_3} + \boxed{NH_3}$$

The first two reactions are already familiar to the student; the last represents the composition of ammonia gas; three volumes of hydrogen and one of nitrogen produce only two volumes of gaseous ammonia (NH_3). The gaseous volume of elements in a compound is not only definite, but the volume of each element present is represented by a whole number.

The comparative volumes of gases taking part in any chemical change may be always learnt from the molecular

[1] For further information on this point the student should consult Tilden's *Introduction to Chemical Philosophy*, from which the substance to this paragraph is taken.

equation by remembering that each molecule of a gas represents a unit of volume of that body. The error must not be made of writing an equation partly molecular and partly atomic.

84. Density and Molecular Weight of Gases.—The density of a gas has already been defined as the weight of any volume compared with that of the same volume of hydrogen, measured at the same temperature and pressure and taken as unity. (These conditions are always understood in speaking of the comparative weights of gases.) As the molecule of hydrogen contains two atoms, its molecular weight, expressed in terms of its atomic weight, is consequently 2. **The molecular weight of any gas is the weight of that volume which occupies the same space as do two parts by weight of hydrogen.** Conversely, as the molecular weight is the sum of the weights of the constituent atoms, the density of a gas may be determined from its formula. As the molecule of hydrogen weighs 2, **the density of any gas, whether elementary or compound, is identical with the half of its molecular weight.** For example, the molecule of steam weighs 18, and occupies the same space as the molecule of hydrogen, which weighs 2; the quantity of steam occupying the same space as 1 volume of hydrogen must weigh $\frac{18}{2} = 9$.

85. Absolute Weight of Hydrogen.—Hydrogen being taken as the unit of density, its absolute weight is of great importance. As a result of most careful weighing, it has been found that **1 litre of hydrogen at the normal temperature and pressure weighs 0·0896 gram, or 11·2 litres weigh 1 gram.** This figure 0·0896 gram is one which it is absolutely necessary that the student should remember: that the exact weight of 1 litre of hydrogen at 0° C. and 760 m.m. pressure is 0·0896 gram, must therefore be thoroughly imprinted on the student's mind. Knowing

this, there is no difficulty in calculating the weight of any other gas whose composition is known. **The weight in grams of a litre of any gas is its density × 0·0896. Further, the weight in grams of 11·2 litres of any gas is identical with the number representing its density.** The density of oxygen being 16, the weight of 1 litre at N.T.P.=0·0896 × 16=1·4336 gram. The weight of a compound gas is found with equal readiness. The density of hydrochloric acid is 18·18; therefore the weight of a litre = 0·0896 × 18·18 = 1·6289 gram, or 11·2 litres weigh 18·18 grams.

This amount 0·0896 is of such frequent occurrence in chemical calculations that it has been proposed to give it a distinct name 'Crith': the weight of a litre of any other gas is then expressed as so many criths.

Summary.

That elements combine in definite proportions is proved by experiments on the composition of water. When more than one compound of two elements is known the proportions present are multiples of the atomic weight. Dalton explained this by assuming that combination occurs between atoms. The weight of each element in a compound can be deduced from the formula and atomic weights of the elements present; the percentage composition may be calculated from these. From the percentage composition of a compound its formula may be obtained by calculation. An equation gives the weight of each element and compound participating in a chemical reaction. From these may be reckoned the weight of any one body necessary for the production of a certain quantity of another; as, for instance, the quantity of potassium chlorate necessary to produce a certain weight of oxygen, or the weight of oxygen that may be obtained from a certain weight of potassium chlorate. That the equation gives these weights may be determined by experiment. Atoms of elements in the free state unite to form molecules. The molecules possess less energy than the atoms; therefore a gas when nascent is more active. The affinity between atoms of the same element is in some cases sufficiently

great to cause the decomposition of unstable compounds. Molecules all occupy the same volume; the molecule of hydrogen contains two atoms. Even molecules containing a large number of atoms occupy the same space as a molecule of hydrogen; hence the union of hydrogen and oxygen to form water is accompanied by condensation. The density of all gases, both elementary and compound, is half the molecular weight. The weight of 1 litre of hydrogen at N.T.P. = 0·0896 gram; this number × density = the weight of 1 litre of any other gas.

CHAPTER XI.

NOMENCLATURE, ACIDS, AND ALKALIES, ETC.

86. Names of Metals.—The names given to the elements are, as a rule, in no way connected with their properties; the only attempt at system is that the termination *um* is reserved to the metals. Selenium and tellurium, however, are exceptions, as, when discovered, they were supposed to be metallic elements. It has been proposed to change the names to selenion and tellurion; this has not, however, met with general acceptance.

87. Binary Compounds.—Bodies which contain only two elements are called *binary compounds*. Their names are fixed by rule; but in the case of the more well-known compounds, the old or 'trivial' names are almost always used; no one would think, for example, of calling water hydrogen monoxide. The name of a body should, as far as possible, indicate its composition; this end is attained by making the name of a binary compound consist of derivatives of the names of the two elements. There are unfortunately several modifications of each name, different chemists using different methods of nomenclature; the student must make himself familiar with the whole, as, in the course of reading, he is

sure to meet with the same body under names different from one another. Very little practice is, however, sufficient to overcome this difficulty.

The most frequently occurring binary compounds are those composed of a metal and non-metal; the name of the metal is first written, and one or more syllables being removed the termination *ide* is added to the name of the non-metal. The compound of copper and oxygen is thus called *copper oxide*, that of copper and sulphur, *copper sulphide*, and so on for other compounds. These names are sometimes written *oxide of copper* and *sulphide of copper* respectively. Another plan consists or changing the Latin name of the metal into an adjective by substituting *ic* for its last syllable; the above names thus become *cupric oxide* and *sulphide*.

We frequently find that more than one compound of the same elements is known; it then becomes necessary to use names which shall discriminate the one from the other. Oxygen and copper combine in two different proportions, represented by the formulæ CuO and Cu_2O; the name oxide is common to both, but the second is called cupr*ous* oxide. The termination *ous* is applied to the compound containing the lower proportion of oxygen or other non-metallic element. Where there are two or more atoms of the metalloid present in a compound, the distinction is marked by the use of a prefix to the second name, indicating the number. The two oxides of barium, BaO and BaO_2, are thus known respectively as barium monoxide and dioxide. Occasionally the prefixes *proto* and *per* are attached to the second name; *proto* to the compound in which the lower proportion of the non-metallic element occurs, *per* to that containing the higher; barium monoxide and dioxide become barium protoxide and peroxide. There is one series of oxides in which there are two atoms of the metal to three of oxygen, as Fe_2O_3: these are sometimes termed sesquioxides: the name is however dying out. Where there are several binary compounds

of the same elements, or where the molecule is a complex one, the number of atoms of each element is indicated by a prefix thus, triferric tetroxide, Fe_3O_4. In binary compounds among the non-metals the termination *ide* is usually given in preference to oxygen, chlorine, and sulphur; thus we have carbon oxides and sulphides, phosphorus chlorides, and chlorine oxides.

88. Ternary and Higher Compounds.—The most important compounds containing more than two elements are those produced by the union of water with oxides, forming acids and hydrates.

In experimenting with oxygen the student will have observed that certain oxides dissolved in water turn litmus solution red, while others restore to the reddened solution its blue colour. This reaction serves to divide the various oxides into two important classes, to which attention must now be directed.

89. Acids.—The name acid is a familiar one, because it is continually applied in every-day parlance to anything which is sour. A number of bodies possess this distinction in common; to the chemist the sourness of an acid is but an accidental property, as, according to his definition of these bodies, substances are included as acids that are not sour to the taste. **An acid may be defined as a body containing hydrogen, which hydrogen may be replaced by a metal (or group of elements equivalent to a metal) when presented to it in the form of an oxide or hydrate (hydroxide).** As a class, the acids are sour; they are also active chemical agents. Most acids are characterised by the property of changing the colour of a solution of litmus, a naturally blue body, to a red tint. This, as the student has just been reminded, is one of the properties of the solution of certain oxides in water. In these instances chemical union occurs between the oxide and water, resulting in the production of an acid as a distinct

chemical compound; thus the addition of water to sulphur trioxide produces sulphuric acid:—

$$\underset{\text{Sulphur trioxide.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

Oxygen is a constituent of most acids, the members of this group being distinguished as 'oxy-acids.' The oxides, which by union with water form acids, are termed anhydrides, or anhydrous acids. They are in most cases non-metallic oxides, but sometimes consist of metals combined with a comparatively large number of atoms of oxygen. There are a few acids in which oxygen is absent: these are termed 'hydr-acids': hydrochloric acid, HCl, is an example of this class. According to the definition given (which is accepted by the great majority of chemists), hydrogen is an essential constituent of all acids. It should however be mentioned that some chemists apply the term acid to what are here termed anhydrides; consequently CO_2 (carbon dioxide, or carbonic anhydride) is sometimes described as carbonic acid gas. This name is now, however, being replaced by that more in accordance with the theories of modern chemical science.

90. Bases and Alkalies.—The oxides which, when dissolved in water, restore the blue colour to reddened litmus are called alkalies: they form a subdivision of a larger class of oxides, the whole of which combine readily with acids, and are known as bases.

A base is a compound, usually an oxide, or hydrate, of a metal (or group of elements equivalent to a metal), which metal (or group of elements) is capable of replacing the hydrogen of an acid when the two are placed in contact. The greater number of metallic oxides are bases. Bases, as well as acids, differ considerably in their chemical activity. As already mentioned, certain bases which dissolve in water are termed alkalies.

An alkali is a base of a specially active character, soluble in water, to which it imparts a soapy taste and touch. Alkalies restore the blue colour to reddened litmus. The principal alkalies are sodium hydrate, NaHO, and potassium hydrate, KHO. A solution of ammonia gas in water is also alkaline, and is often termed ammonium hydrate.

Paper tinted yellow with turmeric is also used as a test for alkalies, which give the paper a reddish-brown hue.

The hydrates are mostly compounds of metallic oxides with water; they are sometimes termed hydroxides, or hydrated oxides. Their formation is represented by the following equations:—

$$\underset{\text{Sodium oxide.}}{Na_2O} + H_2O = \underset{\text{Sodium hydrate.}}{2NaHO}$$

$$\underset{\text{Calcium oxide.}}{CaO} + H_2O = \underset{\text{Calcium hydrate.}}{CaH_2O_2}$$

91. Salts.—When an acid and base react on each other, the body produced by the replacement of the hydrogen of the acid by the metal of the base is termed a salt. Water is also formed during the reaction. The action of the stronger acids and bases on each other is very violent; the resultant salts are usually without action on litmus. This is, however, not always the case; for when a strong acid combines with a weak base, the salt is acid to litmus: nitrate of mercury is an example. When the base is a strong one and the acid weak, as in sodium carbonate, the salt has an alkaline reaction. Litmus is itself a salt of a vegetable acid and base possessing a blue colour. An acid, when added, displaces the weak vegetable one, and forms a salt with the base; the litmus acid, being red, gives the solution a red tint. On adding a base it combines with the acid; the litmus acid and base being liberated again unite with the restoration of the blue colour. The following are instances of the formation of salts by the union of acids and bases:—

HCl	+	$NaHO$	=	$NaCl$	+	H_2O
Hydrochloric acid.		Sodium hydrate.		Sodium chloride.		Water.
H_2SO_4	+	CaO	=	$CaSO_4$	+	H_2O
Sulphuric acid.		Calcium oxide (quicklime).		Calcium sulphate.		Water.
HCl	+	NH_4HO	=	NH_4Cl	+	H_2O
Hydrochloric acid.		Ammonium hydrate.		Ammonium chloride.		Water.

The acids are sometimes termed salts of hydrogen; thus sulphuric acid would be called hydrogen sulphate.

Experiment 84.—Take a dilute solution of hydrochloric acid; dip into it some paper coloured blue with litmus; notice that the colour immediately changes to red. Dip this reddened paper in a solution of soda; the blue colour is restored. Next add a few drops of litmus solution to the caustic soda in a large test-tube; add the acid very carefully until the blue colour changes to a port-wine tint; should this be overshot the mixture becomes red; a very small quantity of soda must then be added: this will bring the colour back to the intermediate tint. It may be that a single drop of either reagent changes the colour from full blue to red, or *vice versâ*; if so, dilute down some acid with four or five volumes of water, and add this drop by drop; with care the port-wine tint may be thus hit. Now dip in some red and blue litmus paper: the colour of neither is changed; neither free acid nor alkali is present; the whole of each has united to form the salt, sodium chloride. Evaporate to dryness: cubical crystals form.

Experiment 79, in which dry hydrochloric acid is passed over manganese dioxide, shows that water is formed as a secondary product by the mutual action of an acid and base. An interesting modification of the experiment may be tried by substituting lead oxide or litharge (PbO) for the manganese dioxide. On applying heat to the bulb the yellow litharge changes to white lead chloride, and abundance of water condenses in the second bulb according to the equation—

$2HCl$	+	PbO	=	$PbCl_2$	+	H_2O
Hydrochloric acid.		Lead oxide.		Lead chloride.		Water.

92. Names of Acids and Salts.—The names of acids are derived from those of their principal constituents by changing them into adjectives ending in *ic*; thus from sulphur we have sulphuric acid, and from nitrogen, nitric acid. The hydracids are distinguished by the prefix *hydro*, as hydrochloric acid. The names of the corresponding salts are derived from the same root by adding *ate*; the salts of sulphuric and nitric acids are respectively sulphates and nitrates.

When an element forms two oxides, both of which unite with water to form acids, the acid containing the higher proportion of oxygen receives the name ending in *ic*; for the other the termination *ous* is substituted. There are, for instance, two oxides of sulphur, SO_2 and SO_3: these are termed—

SO_2 Sulphurous anhydride.
SO_3 Sulphuric anhydride.

Both combine with water, becoming—

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

$$\underset{\text{Sulphuric anhydride.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

The salts of an acid whose name ends in *ous* have the termination *ite*:—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + 2NaHO = \underset{\text{Sodium sulphite.}}{Na_2SO_3} + 2H_2O$$

In describing the basic component of a salt, the simplest method is to mention the name as potassium sulphate. At times it is convenient to change this into the adjective form. When this is done, the same termination is used as is applied to the base itself; thus, salts formed by the action of mercuric oxide (HgO) on acids are called mercuric salts; those from mercurous oxide (Hg_2O), mercurous salts:—

$$\underset{\text{Mercuric oxide.}}{HgO} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Mercuric chloride.}}{HgCl_2} + H_2O$$

$$\underset{\text{Mercurous oxide.}}{Hg_2O} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Mercurous chloride.}}{Hg_2Cl_2} + H_2O$$

The salts of the hydracids, being binary compounds, have names ending in *ide.*

Summary.

Names of binary compounds end in *ide*; when the same elements form two, a separate name is given to each.

The most important compounds containing more than two elements are the acids; the names of these are derived from the principal element.

CHAPTER XII.

ATOMICITY, OR QUANTIVALENCE, AND BASICITY.

93. Atomicity.—The student already knows that the atom of chlorine combines with only one atom of hydrogen, while oxygen combines with two. From the following table he will see that certain elements may be classed together as combining with only one atom of hydrogen; those of another group combine with two atoms, those of a third combine with three, and those of the last with as many as four atoms. The chlorides may be similarly arranged into groups containing respectively one, two, three, and four atoms of chlorine. On comparing this classification of chlorine and oxygen compounds it is found that oxygen in these, and also in almost every other instance, combines with just double the number of the atoms of the other element as does chlorine. Oxygen, then, may be said to possess double the atom-combining power of chlorine.

HCl	H_2O	H_3N	H_4C
HBr	H_2S	H_3P	H_4Si
HI		H_3As	
ClH	Cl_2Ca	Cl_3B	Cl_4C
$ClNa$	Cl_2Ba	Cl_3Au	Cl_4Si
ClK	Cl_2Cu		Cl_4Pt
OH_2	OCa	O_3B_2	O_2C
ONa_2	OBa	O_3Au_2	O_2Si
OK_2	OCu		O_2Pt

The atom-combining power of elements varies. Atomicity, or Quantivalence, is the measure of the number of atoms of other elements with which one atom of each element can combine. Among the elements hydrogen, sodium, and chlorine are characterised by the fact that one atom of each never combines with more than one atom of any other element. Their atomicity is unity, and as every other element forms a chemical compound with one or more of these, the atomicity of an element can usually be determined by observing with how many atoms of one of these three elements an atom of the element in question can enter into combination. (This, however, does not invariably give the atomicity, as some elements unite with a higher proportion of oxygen than of hydrogen.) Thus the atomicity of oxygen which combines with two atoms of hydrogen is two, generally written in Roman numerals, II. Gold unites with three atoms of chlorine, and accordingly has an atomicity of III. Carbon combines with four atoms of hydrogen; its atomicity is therefore IV.

Elements, whose atomicity is one, are called monads; whose atomicity is two, dyads; three, triads; four, tetrads; five, pentads; and six, hexads.

The atomicity (as far as it is known) of the elements is given in the table in Chapter III.; that of the most important ones should be committed to memory.

94. Graphic Formulæ.—We are not acquainted with the reason why certain atoms possess a greater combining power than others, any more than we know the exact nature of the tie that holds elements together in a compound; but in order to have some tangible idea of atomicity it has been proposed to imagine that the atoms of various elements have a certain number of *bonds or links* by means of which they can unite themselves to other atoms. Hydrogen is thus assumed to have but one of these bonds, and can attach itself at most to only one atom of any other element, while oxygen, having two bonds, is capable of combining with two of the single-bonded hydrogen atoms. This is graphically expressed by the use of lines to represent the bonds in the formulæ; thus H—Cl shows at a glance that the two elements have each but one bond, and that these are united. Water is written on the same principles H—O—H. These are termed *graphic* formulæ.

The formula of a body can in many instances be written from a knowledge of the atomicity of the constituent elements. The atomicity of any element usually represents the number of atoms of a monad with which it combines; when two dyads unite there is one atom of each in the molecule, as Ca=O, calcium oxide. Two atoms of a triad combine with three of a dyad; thus, 

, boric anhydride.

One atom of a tetrad combines with two atoms of a dyad; as O=C=O, carbon dioxide. As a rule the number of active bonds of each element in a binary compound is equal.

95. Active and Latent Atomicity.—At times the same element forms two or more series of compounds in which its atomicity is different; nitrogen, for instance, is in some compounds a monad, in others a triad, and others a pentad. But when an element has more than one atomicity, they are almost always expressed by either a series of even

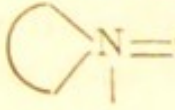
or of odd numbers, so that elements are sometimes simply classified into *artiads*, having an even atomicity, and *perissads*, in which the atomicity is odd. It is probable that this results from the bonds of atoms uniting in pairs, and thus satisfying each other. Taking nitrogen as an example, this is represented graphically thus:—



The highest atomicity an element possesses in any compound is termed the *absolute* atomicity. Where the element combines with a lower number of other atoms than is necessary to satisfy this, the number of its bonds entering into union is the *active* atomicity; the number which is inactive through mutual union represents the *latent* atomicity.

It is difficult in some compounds to trace out the manner in which the bonds are disposed, and at first sight the laws of atomicity are apparently set at naught. Still, even with these seeming discrepancies, the composition of bodies is rendered much plainer by a knowledge of the atomicity of the elements of which they are composed.

The laws above enunciated are followed in the great majority of compound bodies, which are known; there are, however, a few exceptions, and these, although not numerous, are very decisive. For instance the compound of nitrogen and oxygen known as nitric oxide cannot have its formula written graphically in conformity with the rules previously given. The molecule of that body contains 14 by weight of nitrogen and 16 of oxygen: this, therefore, must be expressed by NO. From a study of the great number of compounds of each of these gases, we must give them in almost all instances the absolute atomicities of V and II respectively. NO therefore can only be written



, which leaves one bond of nitrogen unsatisfied.

Some chemists explain this by assuming that the molecule of nitric oxide really contains two atoms of each element, and its formula, therefore, is N_2O_2; the graphic formula is then easily written O=N≡N=O. But this assumes that the molecule of this gas occupies double the volume of that of hydrogen, thus making it an exception to the law of Avogadro. The student will remember that that law is based on the similar behaviour of different gases when subjected to varying temperatures and pressures; nitric oxide, however, acts exactly like all other gases, and, therefore, must be considered as equally with those obeying Avogadro's law; consequently we must look on NO as its formula. Purely chemical considerations also point to its molecule being represented by the simple rather than the more complex expression.

Nevertheless the almost universal obedience to the rule which states that the atomicity of an element is represented by either a series of even or odd numbers causes us to look on it as much more than a coincidence; it is in all probability a *law*, the exceptions being ruled by a law within the law, of which we are as yet ignorant. The question of atomicity is a wide one, and its further consideration must be postponed until a more advanced stage of the student's studies.

96. Basicity of Acids.—In order to form salts, different acids require different quantities of a base; the measure of this quantity is termed the 'basicity' of the acid. **The basicity of an acid depends on the number of atoms of hydrogen it contains, that are capable of replacement by the metal of a base.** Those acids containing but one atom of replaceable hydrogen are termed monobasic acids; those with two and three are respectively termed dibasic and tribasic acids. In forming salts one atom of hydrogen is replaced by one atom of a monad metal, two atoms of a dyad, and so on. In consequence, two atoms of a monad metal are required in order to replace the hydrogen of a dibasic acid such as sulphuric acid, H_2SO_4; while an atom of a dyad metal, such as copper, displaces the hydrogen of two molecules of a monobasic acid such as

nitric acid, HNO_3. In the case of acids which contain more than one atom of replaceable hydrogen, salts are sometimes formed in which a part only of the hydrogen is replaced; such salts are termed 'acid,' or 'hydric,' salts, while those in which the whole of the hydrogen is replaced are termed normal salts. The following are typical examples of acids and the corresponding salts, sodium being a monad and calcium a dyad:—

Monobasic Acid.	Dibasic Acid.	Tribasic Acid.
HNO_3	H_2SO_4	H_3PO_4
Nitric acid.	Sulphuric acid.	Phosphoric acid.
$NaNO_3$	Na_2SO_4	Na_3PO_4
Sodium nitrate.	Sodium sulphate.	Sodium phosphate.
	$NaHSO_4$	Na_2HPO_4
	Acid sodium sulphate.	Hydric sodium phosphate.
$Ca(NO_3)_2$	$CaSO_4$	$Ca_3(PO_4)_2$
Calcium nitrate.	Calcium sulphate.	Calcium phosphate.

The above table shows that the dibasic acids require two atoms of a monad metal to displace the whole of the hydrogen, while a dyad metal requires two molecules of a monobasic acid to form its salt. The formulæ of such salts as $Ca(NO_3)_2$ are sometimes written CaN_2O_6; the former, however, shows more clearly its relation to nitric acid (HNO_3). The small 2 outside the bracket refers to the whole group within.

CHAPTER XIII.

CARBON.

Symbol, C. Atomic weight, 11·97. Specific gravity as diamond, 3·4.

The specific gravity of solids and liquids is referred to that of water, which is taken as unity.

97. Occurrence.—This element occurs in nature both free and combined. Like oxygen, it is found in more forms than one. The various modifications present striking differences in appearance and properties from each other, although chemically they are one and the same substance. The diamond and graphite are examples of native free carbon. In addition to these carbon is an essential constituent of all organic compounds; that is, such substances as wood, flesh, bones, &c., and the numerous bodies which may be derived from them. Coal, which is fossilised wood, must also be included among the carbonaceous bodies. It also largely occurs as carbonates, of which limestone is the most important.

98. Preparation.—By heating wood, coal, or bones in a closed vessel, carbon, in an impure state, may be obtained. Water and volatile compounds of carbon with hydrogen and oxygen are driven off; the excess of carbon remains, together with the non-combustible portions of the wood or other body.

Experiment 85.—Fit up the apparatus shown in Fig. 7 with a combustion tube; place in it some chips of dry wood; fix the tube in the retort stand with the mouth slightly lower than the other end, so that any liquid which distils may not run back on the hot glass. Place a bottle for the collection of the gas, and apply heat to the wood: some water and a tarry liquid condense in the cooler part of the tube; an inflammable gas passes over into the jar. When the action ceases a black mass remains of approximately the same shape as the original wood, and still retaining the grain and marks of woody structure: this body is charcoal.

This process of heating a body and causing its decomposition into gaseous and liquid products in part, which are collected, is termed 'destructive distillation.'

Charcoal is manufactured sometimes in this way, in large iron retorts, but more frequently by building a mass of wood faggots, covering them with peat, and making an opening at

the top and bottom. The pile is then fired, a portion only of the wood is allowed to burn, and its heat converts the remainder into charcoal.

Coal is subjected to destructive distillation on the large scale for the manufacture of coal-gas; the carbon which remains in the retort is known as 'coke.' It is denser and harder than wood charcoal.

Bones, on being similarly treated, yield 'animal charcoal.' This, when finely ground, is called 'ivory black.'

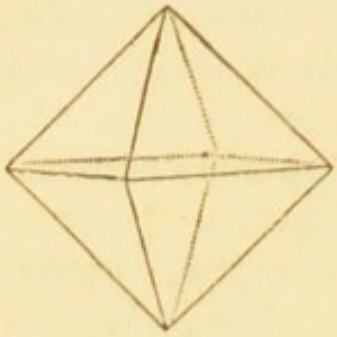
A purer form of charcoal is obtained by burning turpentine, resin, or other substances rich in carbon. With a limited supply of air the hydrogen burns and the carbon being liberated is deposited as soot in chambers arranged for its collection. In this way lampblack is made. It, however, still contains hydrogen, which is driven off by heating the lampblack intensely in a current of chlorine. Hydrochloric acid is formed, and carbon remains. The carbon obtained by the whole of these methods is amorphous; graphite and diamond are both crystalline. Graphite occasionally crystallises out in small hexagonal plates from the solution of carbon in fused cast iron. Chemists have long sought to obtain crystals of diamond by artificial means, but hitherto without success.

99. Properties.—The three forms in which carbon occurs differ remarkably in appearance and physical properties.

100. Diamond.—The diamond is usually found in rounded pebbles, but sometimes occurs in well-developed crystals of octahedral form, or shapes closely allied to it. Fig. 27 is an illustration of an octahedron. The lozenge-shaped outline of this figure, when viewed in certain directions, is familiar to all under the name of 'diamond-shaped.' The diamond is the hardest substance known, scratching or cutting all other bodies. Small crystals set in a proper holder are used by glaziers for cutting glass. When pure

the diamond is perfectly transparent and colourless; it takes a very high polish. Its index of refraction is high (that is, a ray of light which enters it obliquely is bent very considerably). Owing to this fact much of the light undergoes total reflection, and this is one cause of its great brilliancy when cut and used as a gem. The diamond neither conducts electricity nor heat. It may be made red hot without change; but in the intense heat of the voltaic arc it swells up, becomes opaque, and is changed into a black coke-like mass, and acquires the power of conducting heat and electricity.

FIG. 27.



101. Graphite.—Graphite differs from the diamond in almost every characteristic. It occurs in compact masses, which appear to be more or less crystalline. The more perfect crystals occur as hexagonal plates. This crystalline shape is totally distinct from that of the diamond. Graphite has a metallic lustre, and is of a leaden grey colour; it has consequently also received the names plumbago and black lead. It is very soft, and marks paper. The finer qualities are employed in the manufacture of black-lead pencils; it has a peculiar greasy feel, and is sometimes employed for lessening the friction between two rubbing surfaces. After the metals, graphite is one of the best conductors of heat and electricity.

102. Amorphous Carbon.—Amorphous carbon or charcoal possesses a remarkable property of absorbing gases and condensing them within its pores. Freshly burnt charcoal is in this way capable of absorbing about ninety volumes of ammonia. This property is demonstrated by experiment in the chapter on that gas. Owing to this peculiar property charcoal is a valuable antiseptic: it absorbs various putrefactive gases, and thus brings them into contact with oxygen, also condensed within it. Oxidation proceeds, and these

gases, which are mostly composed of hydrogen and carbon, are changed into harmless and odourless compounds, viz. water and carbon dioxide.

Charcoal also retains the colouring matter of liquids passed through it. Raw sugar is decolorised by being mixed in solution with animal charcoal and then filtered; the filtrate is found to be colourless.

Experiment 86.—Take some syrup of the brownest and coarsest sugar obtainable; shake up in a test-tube with coarsely powdered animal charcoal; allow the charcoal to subside and then filter off; the sugar solution will be much lighter in colour. The colour of the original solution may, if necessary, be heightened by the addition of a little burnt sugar.

103. Common Chemical Properties.—All forms of carbon are incapable of liquefaction or volatilisation at the most intense heats at our command. They are all combustible; the same weight of diamond, graphite, and charcoal yields the same amount of carbon dioxide when burned, thus establishing their chemical identity :—

C	$+$	O_2	$=$	CO_2
Carbon (diamond, graphite, or charcoal).		Oxygen.		Carbon dioxide.

The diamond may be burned by placing it on a connecting strip of platinum foil, between two copper wires passing through the stopper of a gas jar filled with oxygen. The passage of a voltaic current raises the platinum to a white heat, the diamond burns away, leaving only a minute trace of ash.

Graphite may be burned more easily.

Experiment 87.—Fill a jar with oxygen; place some powdered graphite in a clean deflagrating spoon; ignite to a bright red heat over the foot blow-pipe, and quickly plunge into the gas. Notice a brightening of the glow on entering the oxygen. When the action is over, take out the spoon, add lime-water and shake up; the lime-water becomes milky.

Charcoal burns in oxygen with readiness.

Experiment 88.—Place a piece of charcoal in the deflagrating spoon, kindle it, and introduce into a jar of oxygen; it burns brightly. Test the gas with lime-water and note milkiness.

Lime-water is prepared by adding a small piece of lime to water, and shaking up in a stoppered bottle. When the excess of lime has settled to the bottom the clear solution is poured off, and is ready for use.

Lime and carbon dioxide combine readily and produce an insoluble substance, carbonate of lime; hence the milkiness. After a time this falls to the bottom as a white precipitate.

$$\underset{\text{Calcium hydrate (lime-water).}}{CaH_2O_2} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Calcium carbonate (carbonate of lime).}}{CaCO_3} + \underset{\text{Water.}}{H_2O}$$

From this property lime-water is a most useful test for the presence of carbon dioxide. If the carbon dioxide is in considerable excess the precipitate will re-dissolve.

Bodies containing carbon also yield carbon dioxide when burned.

Experiment 89.—Light a taper and place it in a jar of air; when the light is extinguished, test with lime-water for carbon dioxide. Pour a few drops of methylated spirits in a deflagrating spoon; light and place in a jar of air; again test for carbon dioxide. Similarly pour a few drops of petroleum into the deflagrating spoon and heat until the liquid takes fire; introduce into a jar of air and test with lime-water.

Burn a small jet of coal gas in a jar of air, using the same apparatus as was employed for the burning of hydrogen in chlorine; as soon as the light goes out remove the gas jet and test with lime-water.

In each case carbon dioxide is found to be present. Water is also formed as a product of combustion of these bodies, all of which are compounds containing carbon and hydrogen. The formation of water is demonstrated by the quantity deposited when a cold body is placed above a gas

flame. This may be observed whenever a flask of water is heated over a Bunsen. Water would also be deposited on the outside of a flask held over the chimney of a petroleum lamp. The carbon compounds with hydrogen are so universally used as heat-producers that no fuel could be taken which did not give these reactions.

Further than this, animal heat is also a result of the slow combustion of compounds of carbon. That articles of food contain carbon may be easily demonstrated.

Experiment 90.—Take small portions of bread, sugar, and meat; dry them and heat to redness in test-tubes of combustion tubing; a mass of more or less pure carbon remains.

Finely powder each of these bodies in the dry state and mix each with powdered copper oxide. Heat each mixture to redness in a combustion test-tube, fitted with cork and tube leading into lime-water. A milkiness is produced in each case, showing that their oxidation had produced carbon dioxide.

Air is drawn into the lungs, and there oxidises certain constituents of the blood, which are obtained from food. Water and carbon dioxide are thus produced, and are exhaled continually from the lungs.

Experiment 91.—Breathe against any cold surface, as the outside of a bottle of water; it is covered with a film of dew. Breathe through a glass tube into some lime-water in a beaker; it rapidly becomes milky.

Carbon dioxide is always present in the atmosphere as a result of these changes. Its presence may be detected by means of lime-water.

Experiment 92.—Partly fill an evaporating basin with lime-water, and let it remain exposed to the air for a few minutes; a thin film of carbonate of lime will have formed on the surface.

That air contains far more carbon dioxide when exhaled from the lungs than when inspired may be proved by the following experiment:—

Experiment 93.—Fit up two wash-bottles such as are shown in No. 3, Fig. 10. By means of india-rubber tubing connect one end of a T or three-way tube with the long tube of one of the wash-bottles, and the second end of the T tube with the short tube of the other wash-bottle. About a quarter fill each wash-bottle with lime-water and insert the corks. Place the third limb of the T tube in the mouth and breathe; as each breath is drawn in, air enters through the short-limbed wash-bottle, bubbling through the lime-water. At each exhalation air passes out through the other bottle. The air is thus passed through lime-water before and after being breathed. The lime-water in the first bottle is only rendered very slightly turbid; that in the second rapidly becomes milky.

The functions of atmospheric carbon dioxide are treated more fully in Chapter XV.

Summary.

Carbon occurs in three forms: the diamond, graphite, and amorphous carbon as charcoal; the two first are native, the third is obtained from certain organic bodies by heating them in closed vessels. The diamond is extremely hard; graphite is soft and metallic-looking. Charcoal is used as a deodorising and decolorising agent. The whole three forms are combustible, producing carbon dioxide. This gas is detected by its turning lime-water milky. All bodies containing carbon produce carbon dioxide when burned; carbon dioxide is also formed by animals breathing; it is always present in air.

Laboratory Hints.

After Experiment 85 clean the leading tube at once by passing water through it; the tarry liquid is more difficultly removed after standing. Do not use any india-rubber tubing, but let the leading tube be entirely of glass.

In burning coal gas in a jar of air the jet must be removed as soon as the light goes out, because, if allowed to remain, the coal gas would displace the remaining air and carbon dioxide.

CHAPTER XIV.

OXIDES OF CARBON.

Two oxides of carbon are known :—

Carbon monoxide or carbonic oxide, CO.
Carbon dioxide or carbonic anhydride, CO_2.

The latter of these, being the most important. should be first studied.

Carbon Dioxide.—Formula, CO_2. Molecular weight, 43·89. Density, 21·94. Specific gravity, 1·527.

Graphic formula, O=C=O.

104. Occurrence.—The presence of carbon dioxide in the atmosphere is mentioned in the previous chapter ; it also exists in vast quantities in combination with lime, in limestone, chalk, marble, &c.

105. Preparation.—By the action of heat, limestone may be decomposed into lime and carbon dioxide, according to the following equation :—

$CaCO_3$	=	CaO	+	CO_2
Limestone (calcium carbonate).		Lime (calcium oxide).		Carbon dioxide.

Enormous quantities of limestone are 'burned' in properly constructed furnaces called kilns, for the purpose of obtaining quicklime, that substance being used in making mortar. The student may separate the two on the small scale in the following manner :—

Experiment 94.—In a test-tube of hard glass tubing place a little powdered marble or chalk ; close the mouth of the tube loosely with the thumb, and heat strongly for about a minute over the foot blow-pipe. Keep the tube closed, and pour into

another test-tube some lime-water ; the gas being heavier than air, pour it from the combustion tube into that containing the lime-water ; shake up : the lime-water becomes milky.

If the application of heat be continued, the whole of the carbon dioxide may be driven off ; but in the time mentioned a part only will probably be evolved.

A much readier method of separating the carbon dioxide from the base is by the addition of an acid, as hydrochloric. The following change ensues :—

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}$$

Experiment 95.—Add a drop of hydrochloric acid to lime-water which has been rendered milky by carbon dioxide ; it immediately becomes clear. Add some hydrochloric acid to some fragments of marble in a test-tube ; brisk effervescence occurs ; when over, pour the gas, and the gas only, into a second tube containing lime-water ; this, on shaking, becomes milky.

Experiment 96.—Prepare four jars of the gas in the following manner. Place some fragments of marble or limestone in the flask arranged as for the preparation of hydrogen ; add a little water, and then some hydrochloric acid ; collect over water in the pneumatic trough.

106. Properties.—Carbon dioxide is a colourless gas. It has a faint, sweetish, acid taste and smell, which are best described as being those of a bottle of soda-water when opened (so-called soda-water is a solution of carbon dioxide in water under pressure).

At a pressure of 38·5 atmospheres this gas condenses to a liquid at 0° C. : it may also be liquefied at ordinary pressures by a temperature of −78° C. Liquid carbon dioxide is colourless and transparent ; on being allowed to emerge in a stream from the vessel containing it, a part volatilises, and, in so doing, deprives the remainder of the heat necessary to maintain it in the liquid state ; it therefore freezes.

Solid carbon dioxide obtained in this manner is a white, snow-like mass, which evaporates comparatively slowly.

At 15° C. the gas is soluble in about its own volume of water, whatever the pressure; but as an increase of pressure increases the density of the gas, the *weight* absorbed is in direct proportion to the pressure to which the gas is subjected. Soda-water, lemonade, and other aerated beverages, are prepared by dissolving carbon dioxide in water, under the pressure of a force-pump. From the solubility of the gas in water directions are frequently given for its collection by displacement, but the gas is obtained so readily in large quantity that for most purposes it may as well be collected over water.

The weight of carbon dioxide permits many striking experiments to be performed with it.

Experiment 97.—Fill by downward displacement a bowl or some other vessel about eight inches diameter, and the same depth, with the gas. Make a soap solution, and blow some bubbles; detach them from the pipe used over the vessel of gas; they will descend and float on the surface of the carbon dioxide.

This gas is generated in brewing. The vats remain full for some time after the liquor has been drawn off; and many deaths have occurred through men incautiously descending in them. The same danger exists from accumulations of the gas in mines. A lighted taper is instantly extinguished by the gas, which does not itself take fire.

Experiment 98.—Immerse a lighted taper in a jar of the gas: it is immediately extinguished. Take another jar of gas and pour it over a lighted taper; notice that it extinguishes it: this shows the greater density of carbon dioxide. Take care that any drops of water remaining in the jar do not fall on the taper.

Several of the metals which have a great affinity for oxygen burn in the gas with the displacement of carbon. If a piece of brilliantly burning magnesium wire is intro-

duced in the gas, it continues to burn; the fragments of magnesium oxide falling to the bottom are found mingled with carbon. On the jar being rinsed with a few drops of hydrochloric acid, the oxide dissolves, and the carbon is readily distinguished:—

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Magnesium.}}{2Mg} = \underset{\text{Magnesium oxide.}}{2MgO} + \underset{\text{Carbon.}}{C}$$

The same reaction is also effected by potassium, potassium oxide being formed instead of that of magnesium.

Experiment 99.—Fill a four-ounce *dry* flask, by downward displacement, with carbon dioxide gas. Introduce a pellet of potassium, about the size of a pea, and heat gently until the potassium glows. When all action is over let the flask cool, and dissolve out its contents with water; observe that there is a residue of free carbon.

107. Carbonic Acid and Carbonates.—Carbon dioxide possesses feebly acid properties when combined with water, and therefore is sometimes called carbonic anhydride.

Experiment 100.—Pour a little litmus solution into a jar of the gas, and shake up; the colour is changed to a port-wine tint, very different from that produced by the stronger acids.

The solution of carbon dioxide in water is undoubtedly a true acid.

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbonic acid.}}{H_2CO_3}$$

It is, however, very unstable, and has never been separated from an excess of water. The gas is expelled entirely by boiling the water or by freezing it.

Being a dibasic acid it forms a double series of salts, one of which is normal, the other acid. Thus we have sodium carbonate, Na_2CO_3, and sodium bicarbonate, or acid carbonate of sodium, $NaHCO_3$.

The attraction of carbon dioxide for bases has been already utilised by the student in his tests for that gas by lime-water. Lime absorbs carbon dioxide slowly from the

atmosphere ; hence pieces of old mortar invariably contain it. It aids in 'setting' the mortar, which becomes harder with age.

Experiment 101.—Place some fragments of old mortar in a test-tube ; pour on them some hydrochloric acid ; notice the effervescence ; when over, pour the gas into another test-tube containing lime-water ; it is rendered milky.

This experiment is not, however, absolutely conclusive, as even new lime is never so thoroughly 'burned' as to entirely decompose the carbonate.

The carbonates are an important series of salts ; with the exception of those of the alkalies, they are insoluble in water. They are readily decomposed by almost any acid, with the liberation of carbon dioxide.

Several of the bicarbonates are soluble, the corresponding carbonates being insoluble. That of lime is an interesting and important example.

Experiment 102.—Boil some *hard* water from springs in chalk or limestone formations (if obtainable) in a small flask or beaker for about a quarter of an hour ; at the expiration of that time notice that the water has become slightly turbid by the separation of calcium carbonate.

The bicarbonate has been decomposed by heat, the carbon dioxide evolved, and the insoluble carbonate precipitated :—

$$\underset{\text{Calcium bicarbonate.}}{CaH_2(CO_3)_2} = \underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2}$$

The same experiment may be tried in another manner in which the formation of the bicarbonate may also be noticed.

Experiment 103.—Fit to the carbon dioxide apparatus a small wash-bottle with water ; pass the washed gas for some minutes into some lime-water in a beaker ; a precipitate at first forms, and is after a while redissolved. Then boil for some minutes ; calcium carbonate is again deposited.

108. Hard and Soft Waters.—In the preceding paragraph reference has been made to 'hard water'; the inference may be drawn that hardness is in some way connected with the presence of calcium salts in solution. It may be well to explain here what is understood by the terms 'hard' and 'soft' when applied to water, and to what these properties are due. Certain kinds of water when mixed with a very small quantity of soap immediately produce a lather, and the water acquires that peculiar feel to the hands known as 'soapiness.' Such water is termed 'soft.' Other waters when used with soap for washing purposes do not lather at all readily, and do not cause 'soapiness' until a considerable quantity of soap has been consumed. When a lather is actually formed, there will be found on examination a layer of scum on the surface of the water. Such water is termed 'hard.'

Without going into the details of the composition of soap and its reaction with water when used for washing, it may be explained that soluble salts of calcium and magnesium decompose soap, forming a precipitate which constitutes the previously mentioned scum found when washing with hard water. Consequently, if water containing calcium salts in solution is employed for washing, sufficient soap must first be added to precipitate these salts before any is available for cleansing; hence hard waters are neither so agreeable nor so economical for washing purposes.

The principal calcium and magnesium salts found in water are the carbonate and the sulphate. As seen from a previous experiment, the carbonates may be precipitated by the act of boiling, and any hardness due to their presence may be thus remedied. **Consequently any hardness produced by carbonates of calcium or magnesium is termed 'temporary' hardness, because such hardness is removed by boiling.**

The sulphates and chlorides of calcium and magnesium are not precipitated by boiling, as their solution is caused

by the water itself, and not by water plus carbon dioxide gas. **Therefore hardness due to the presence of sulphates (or chlorides) of calcium or magnesium is termed 'permanent' hardness.**

The hardness of most waters is partly temporary and partly permanent; the two together constitute the total hardness of the water.

The hardness of water is usually tested by taking a measured quantity of the water and adding thereto in a stoppered bottle a solution in alcohol of soap of a known strength. This is introduced in small quantities at a time from a measuring instrument, the water being well shaken after each addition. As soon as a lather is thus produced, which stands unbroken for five minutes, the quantity of soap solution which has been used is read off; from these data the total hardness is determined. A sample of the water is next boiled until the carbonates are precipitated; then after certain precautions the hardness is again determined with the soap solution. This gives the permanent hardness; the difference between the total and the permanent is the temporary hardness.

109. Processes of Softening Water.—Water may be softened to the extent of the removal of the temporary hardness by the act of boiling for some minutes. Potassium and sodium carbonates precipitate calcium and magnesium salts and themselves possess detergent or washing properties; therefore these salts will remove all hardness, whether temporary or permanent. One of the characteristics of potassium and sodium carbonates is the power they possess of imparting a soapy feel to pure water. Ordinary washing soda, or soda-crystal, is commercial sodium carbonate.

110. Clark's Water-softening Process.—A most interesting process for the softening of water is that bearing the name of Clark's Process. The process depends on two

chemical reactions with which the student is already familiar. First, that calcium carbonate is no longer soluble in water from which the carbon dioxide gas has been removed; secondly, that lime forms an insoluble compound with carbon dioxide gas. To soften water by Clark's Process, lime-water is added in sufficient quantity to exactly combine with the dissolved carbon dioxide gas. The whole of the lime, both that originally present in the water as carbonate and that added as hydrate, is precipitated, and the temporary hardness of the water is thus removed. The chemical reaction is represented in the following equations :—

$$\left\{\begin{matrix} CaCO_3 \\ H_2O,CO_2 \end{matrix}\right. + CaH_2O_2 = CaCO_3 + CaCO_3 + 2H_2O$$

$\left\{\begin{matrix} CaCO_3 \\ H_2O,CO_2 \end{matrix}\right.$: Solution of carbon dioxide in water (carbonic acid), holding calcium carbonate in solution.

CaH_2O_2: Lime water (calcium hydrate).

$CaCO_3$: Original calcium carbonate, and also that formed from dissolved carbon dioxide and added calcium hydrate. Both insoluble.

$2H_2O$: Water.

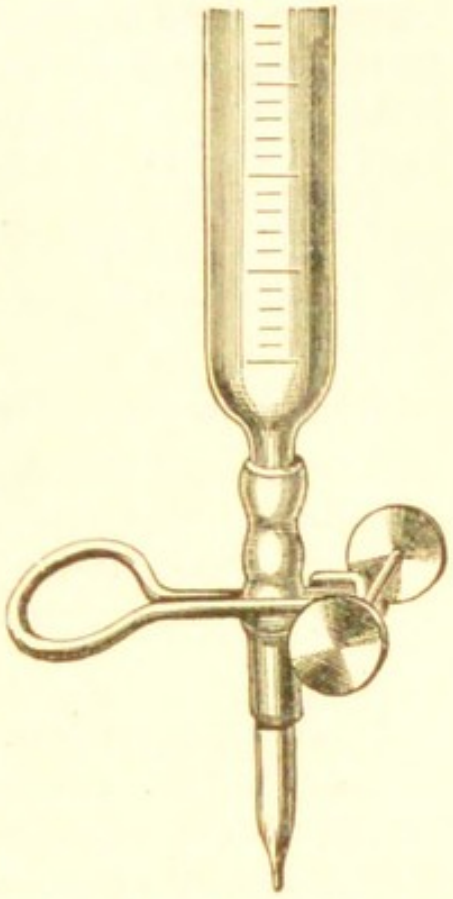
The precipitated lime is removed either by allowing it to subside or by filtration.

Experiment 104.—Procure some standard soap solution, such as is used for water analysis. (This may be prepared in the laboratory, according to directions given in works on analysis, or may be purchased from dealers in chemicals.) The following apparatus will be required; a burette, holding 50 c.c., and stand; the end of a burette is shown in the accompanying figure. The instrument consists of a glass tube, graduated throughout most of its length, and with a spring clip arranged at the bottom. A pipette, holding 50 c.c., and a stoppered bottle, of about ten ounces capacity, are also requisite.

Having cleaned the various apparatus, place the lower end of the pipette in some hard water and suck it up above the level of the graduated mark round the stem. Place the thumb on the top, and let the water drop slowly from the bottom until the graduation mark is exactly reached. Then, by removing

the thumb, allow the whole of the contents of the pipette to drain into the bottle. Rinse the burette with a few drops of the soap solution and then fill it above the zero mark at the top. Press the buttons of the spring clip and allow the solution to run out until the zero line is reached. Next run the soap solution into the hard water in the bottle in quantities of about 1 c.c. at a time, shaking vigorously between each addition, and noticing whether or not any signs appear of a permanent lather being formed. Continue this until, when the bottle is shaken and laid on its side, the lather does not break for five minutes. Make a note of the quantity of soap solution which has been used.

FIG. 28.—BURETTE WITH SPRING CLIP.



Next take a light flask of about 250 c.c. capacity; place it on a balance and fill with the water until the water and flask together weigh exactly 200 grams. Set the flask over a Bunsen and boil the water for half-an-hour. At the end of that time place the flask again on the balance and make up to the weight of 200 grams by adding recently boiled distilled water. This is done in order to replace the water lost by evaporation. Filter off the precipitated calcium carbonate, let the water cool, and determine the hardness in 50 c.c. precisely as before. The hardness now found is the permanent; that which has disappeared through boiling is the temporary.

To another portion of the hard water add sodium carbonate (washing soda) until the water feels soapy to the touch; then test with soap solution, and notice that a lather is produced by the addition of the first few drops.

Prepare a solution of phenolphthalein by dissolving 1 gram of the substance in 30 c.c. of strong alcohol. Take a litre of the hard water; add a few drops of the phenolphthalein solution

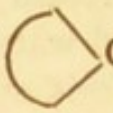
and then pour in lime-water until the water acquires a faint pink tint. From 80 to 100 c.c. of lime-water will probably be required. (The object of the phenolphthalein is to show the point when a sufficient quantity of lime has been added, as the slightest excess causes in the presence of this substance a red coloration.) The pink tint may be again discharged by the cautious addition of a little more of the water until the colour just disappears. Let the water stand for a few hours, and a precipitate of calcium carbonate falls to the bottom. Determine the hardness of the clear water; it should closely agree with that softened by boiling.

In softening water on the large scale the testing with phenolphthalein is performed, not on the whole bulk, but on small quantities taken out from time to time for the purpose of making the test.

Carbon dioxide is injurious when present in air in large quantity; all rooms should therefore have ample means of ventilation. Nine sleeping rooms out of ten are insufficiently furnished in this respect; a room should never be used for sleeping purposes without at least the register of the stove open.

111. Composition.—Carbon dioxide contains its own volume of oxygen; consequently carbon may be burned in that gas without its undergoing any change of volume. Its composition by weight is ascertained by burning a weighed amount of carbon in excess of oxygen, and collecting and weighing the resulting carbon dioxide.

Carbon Monoxide.—Formula, CO. Molecular weight, 27·93. Density, 13·96. Specific gravity, 0·967.

Graphic formula, 

112. Occurrence.—Everyone is familiar with the appearance of a coke or charcoal fire, or of a coal fire which has burned perfectly clear and smokeless; the whole mass glows with a bright red heat, and hovering over the top are lambent blue flames: the origin of these may be traced in this way:

in the lower parts of the grate, where air enters the fire, carbon dioxide is formed according to the following equation :—

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

This makes its way upwards through the red-hot carbon and becomes changed by reduction to carbon monoxide, and thus an inflammable gas is produced. The same effect is produced in the following manner :—

Experiment 105.—Loosely fill an iron tube with fragments of charcoal ; fit to each end corks with pieces of quill tube passed through ; place it in a furnace and raise to a red heat. Pass a slow current of carbon dioxide through the tube ; light the gas as it emerges : it burns with the same blue flame as is seen playing over the coke or charcoal fire.

Evidently, then, the gas is changed ; for carbon dioxide is non-inflammable. The change is thus represented :—

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

When carbon is burned without a sufficient supply of air, carbon monoxide is formed as one of the products of combustion. This gas may also be produced by the incomplete combustion of carbon compounds.

113. Preparation.—The gas is most conveniently prepared by heating certain organic compounds with concentrated sulphuric acid. This body has a very great attraction for water, in virtue of which it decomposes many substances containing hydrogen and oxygen, and assimilates the water ; the remaining atoms re-arrange themselves into whatever other compounds are possible. Oxalic acid, when thus treated, is split up into water, carbon dioxide, and carbon monoxide :—

$$\underset{\text{Oxalic acid.}}{H_2C_2O_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Carbon monoxide.}}{CO}$$

Equal volumes of carbon monoxide and dioxide are thus produced.

Experiment 106.—Place in an eight-ounce flask, fitted with either thistle funnel and leading tube, or with a leading tube only, half an ounce of oxalic acid (crystallised) and an ounce of concentrated sulphuric acid. Gently heat the mixture, and after the expulsion of air fill three jars with the gas over water in the pneumatic trough. As this gas is very poisonous it should be prepared in the stink cupboard.

Experiment 107.—Place a light to one jar ; notice that the gas burns with a blue flame.

Experiment 108.—Add some lime-water to a second, and observe that, on being shaken, it becomes milky.

Experiment 109.—Prepare a solution of crude caustic soda and pour it into a beaker sufficiently large to hold a jar and the glass plate. Invert a third jar in this solution ; hold the glass plate to the bottom of the beaker with a glass rod ; and thus remove it from the mouth of the jar. Let it stand in the soda for some time ; the liquid slowly rises, through the absorption of the carbon dioxide, until the jar is half filled. The quantity of soda solution to be taken should be roughly estimated from the size of the jar.

In this last experiment the soda and carbon dioxide unite and produce sodium carbonate :—

$$\underset{\text{Caustic soda.}}{2NaHO} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Water.}}{H_2O}$$

Carbon monoxide may be prepared free from the dioxide by the use of formic instead of oxalic acid. The following reaction then takes place :—

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

Another method is to heat potassium ferrocyanide (yellow prussiate of potash) with sulphuric acid ; the change occurring is complicated :—

$$\underset{\text{Potassium ferrocyanide.}}{K_4FeC_6N_6} + \underset{\text{Sulphuric acid.}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} =$$

$$\underset{\text{Potassium sulphate.}}{2K_2SO_4} + \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Ammonium sulphate.}}{3(NH_4)_2SO_4} + \underset{\text{monoxide.}}{6CO}$$

Experiment 110.—Take a sixteen, or preferably a thirty-two, ounce flask, fitted with thistle funnel and leading tube. Insert, in lumps, a quarter of an ounce of commercial ferrocyanide and about two ounces of sulphuric acid. Get three jars ready filled with water and inverted in the pneumatic trough. Fix the flask in the retort stand with the end of the leading tube in the trough ; apply heat carefully. As soon as the gas begins to be evolved remove the flame, as the action continues with extreme rapidity. When the whole of the air is expelled fill the three jars with gas. The end of the thistle funnel should be pushed down as near as possible to the bottom of the flask without touching. Sometimes, through lack of sufficient precautions, the gas is produced so violently that the pressure forces the boiling acid up through the funnel ; should this be the case remove the light, take the delivery tube out of the water, and stand out of the reach of splashes of falling acid. Throw whiting on any which is spilled on the working bench and then wipe off with an old duster.

114. Properties.—Carbon monoxide is a colourless gas ; it has a slight oppressive odour, and is extremely poisonous, producing a painful headache even when present in small quantities in air. It is but slightly soluble in water : 100 volumes dissolve 2·434 volumes of the gas at 15° C. It liquefies only under very great cold and pressure. Carbon monoxide is inflammable and a non-supporter of combustion ; when burned its own volume of carbon dioxide is produced, half of its volume of oxygen being required :—

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

Experiment 111.—Immerse a lighted taper in a jar of the gas ; it is extinguished, but the gas burns with a blue flame, as when made from oxalic acid.

This gas is devoid of acid properties, and consequently is without action on lime-water.

Experiment 112.—Add some lime-water to a jar of the gas and shake up ; no turbidity is produced. Inflame the gas, re-

place the plate, and then again shake ; the lime-water becomes milky through the presence of carbon dioxide.

Carbon monoxide acts as a powerful reducing agent, and is frequently used in metallurgical operations for the production of metals from their oxides.

Experiment 113.—Arrange a piece of combustion tubing about eighteen inches in length in the combustion furnace and connect by means of a cork, piece of quill tubing, and india-rubber tube with an apparatus evolving carbon monoxide gas. (The most convenient method of obtaining the gas for this purpose is from oxalic and sulphuric acids. The gas may be passed through a wash-bottle containing caustic soda, but the carbon dioxide takes no part in the reaction.) Partly fill the combustion tube with granulated copper oxide, expel the air by passing a slow current of carbon monoxide, and then light the furnace. On the tube becoming red-hot notice that the oxide is reduced to the metallic state.

If wished carbon monoxide, free from the dioxide, may be prepared and used for this experiment ; and the gas, after its passage through the red-hot copper oxide, passed into lime-water. The precipitate of calcium carbonate shows the production of carbon dioxide from the reaction of the monoxide and copper oxide on each other.

The following equation shows the chemical change which occurs during this experiment :—

$$\underset{\text{Copper oxide.}}{CuO} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Copper.}}{Cu} + \underset{\text{Carbon dioxide.}}{Co_2}$$

115. Composition.—The composition of carbon monoxide is determined by explosion with excess of oxygen in the eudiometer ; the volume of the monoxide and of the oxygen are observed. After the explosion potassium hydrate is introduced ; the diminution in volume represents the carbon dioxide formed which is absorbed. From these data the composition of the monoxide is readily deduced.

Summary.

There are two oxides of carbon—carbon monoxide and dioxide.

Carbon dioxide occurs in the atmosphere and in combination with lime in limestone ; may be prepared by heating limestone, or more conveniently by the action of an acid, as hydrochloric. It is a colourless gas, with a very faint odour and taste ; may be condensed by pressure ; is soluble in water ; is half as heavy again as air ; hence may be poured from vessel to vessel ; remains for a long time in the bottom of brewers' vats, &c. ; is non-inflammable and a non-supporter of combustion of most substances, but allows certain metals, as potassium and magnesium, to burn in it. The solution of the gas is slightly acid to litmus ; it forms a series of important salts, which are readily decomposed by a stronger acid. All the carbonates are insoluble in water except those of the alkalies ; certain others form soluble bicarbonates with excess of carbon dioxide : lime exists in this form in most hard waters. Carbon dioxide contains its own volume of oxygen.

Carbon monoxide is formed in the burning of coke by the deoxidation of carbon dioxide ; the same change occurs if carbon dioxide is passed over red-hot charcoal in an iron tube. The gas is more generally prepared by the action of sulphuric acid on some organic bodies, as oxalic or formic acids, or potassium ferrocyanide.

Carbon monoxide is a colourless gas with a faint oppressive odour ; is very poisonous ; slightly soluble in water. It is inflammable and a non-supporter of combustion ; it is devoid of acid properties. Carbon monoxide is a powerful reducing agent. Its composition is ascertained by explosion in the eudiometer.

Laboratory Hints.

A solution of crude caustic soda is conveniently kept for use in the laboratory ; the soda is very cheap, and the same solution can be used several times for such an experiment as No. 109. The solution which has been once used should not be replaced in the same bottle.

CHAPTER XV.

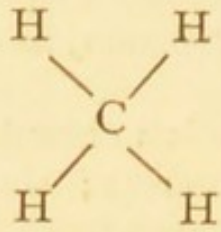
HYDROCARBONS AND COMBUSTION.

116. Hydrocarbons.—The compounds of carbon with hydrogen are known as hydrocarbons, or hydrides of carbon. These bodies are exceedingly numerous, and as most of them are distinctly of organic origin, their study is usually undertaken as a part of organic rather than inorganic chemistry. Only the following simple and important hydrocarbons will receive attention in this work.—

Marsh Gas, Light Carburetted Hydrogen, or Methyl Hydride . . . . . CH_4.
Acetylene . . . . . C_2H_2.
Olefiant Gas, Heavy Carburetted Hydrogen, or Ethene . . . . . C_2H_4.

Marsh Gas, Methyl Hydride.—Formula, CH_4. Molecular weight, 15·97. Density, 7·98. Specific gravity, 0·551.

Graphic formula,



117. Occurrence.—This gas is evolved during the decomposition of dead vegetable matter ; hence is found in marshy districts, and has thus received its common name of marsh gas. On watching stagnant water bubbles of the gas may be seen to arise, and may be collected by inverting a gas jar, filled with water, in the pool. During the changes which have occurred, as coal has been formed from vegetable growths, marsh gas has also been evolved, and has remained imprisoned within cavities of the coal itself. As the coal is removed by the miner the gas escapes from these

cavities into the mine, and mixing with the air forms the explosive mixture which has been the cause of so many terrible colliery accidents. The collier knows this gas as 'fire-damp.'

118. Preparation.—Marsh gas may be prepared by heating together a mixture of sodium acetate and caustic soda, when the following reaction occurs :—

$$\underset{\text{Sodium acetate.}}{NaC_2H_3O_2} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Marsh gas.}}{CH_4}$$

Experiment 114.—Arrange an iron tube closed at one end (a piece of inch gas-barrel) as a retort for the production of gas ; fitting a cork and delivery tube to the end remaining open. Introduce into this a mixture of two parts of sodium acetate with one of caustic soda. Apply heat and collect three jars of the evolved gas.

119. Properties.—Marsh gas is a light colourless gas, and has consequently received the name of light carburetted hydrogen. It is not a supporter of combustion, but burns with a non-luminous flame, something like that of hydrogen, but slightly tinged with yellow. Mixtures of either air or oxygen with this gas explode violently on ignition.

Experiment 115.—Apply a light to one of the jars of gas already prepared ; notice the nature of the flame. When the combination is over add some lime-water and shake up ; the lime-water turns milky. Notice also that a film of moisture is deposited on the sides of the jar. Mix in a stout explosion-tube one volume of marsh gas with two volumes of oxygen and apply a light ; the mixture explodes. Repeat the experiment with a mixture of one volume of the gas with ten of air. Test the gas remaining in the bottle with lime-water for carbon dioxide. Pour the gas upwards from one jar into another and set light ; in this way observe that, like hydrogen, it is much lighter than air.

The carbon dioxide remaining after the combustion or

explosion of marsh gas is known by the miner as 'choke-' or 'after-damp.'

Until recently, marsh gas was viewed as a permanent gas, but, in common with hydrogen and other gases, has now been liquefied.

120. Composition by Volume.—The composition of this gas may be ascertained by explosion with excess of oxygen in the eudiometer. If ten volumes of marsh gas be mixed with twenty-five volumes of oxygen there will be found after explosion, at a temperature above 100° C., thirty-five volumes of gas. On cooling to normal temperature the volume of gas contracts to fifteen; there must therefore have been present twenty volumes of water vapour. On introducing caustic potash a further absorption of ten volumes occurs, showing that ten volumes of carbon dioxide have been formed. The residual five volumes of gas are found on examination to be oxygen. One volume, therefore, of this gas requires for its combustion two volumes of oxygen, and produces one volume of carbon dioxide and two of water vapour.

Remembering that by Avogadro's law the molecular volume of all gases is alike, and that the molecule of hydrogen contains two atoms, then as two volumes of the gas yield two volumes of carbon dioxide, or one molecule yields a molecule of carbon dioxide, one molecule of marsh gas contains one atom of carbon. Again the two volumes of marsh gas produce four volumes of water vapour, that is, one molecule of marsh gas yields two molecules of water; and as each molecule of water contains two atoms of hydrogen, the molecule of marsh gas contains four atoms of hydrogen, the formula must consequently be CH_4.

121. Composition by Weight.—The composition by weight is ascertained by passing a known volume of marsh gas through a combustion tube containing red-hot copper oxide. Carbon dioxide and water are formed, and are

absorbed in weighed tubes containing respectively calcium chloride, which absorbs the water, and caustic potash, by which the carbon dioxide is retained. The increase in weight gives the amounts of these two bodies formed from the marsh gas. In an experiment a volume of CH_4, equivalent to 1000 c.c. at N.T.P., was passed over red-hot copper oxide ; there were produced 1·611 gram of water and 1·965 gram of CO_2. From these data the composition of the gas is thus calculated :—

Weight of 1000 c.c. = 0·0896 × 7·98 (density) = 0·715 gram.

$$\text{Weight of carbon} = \frac{1{\cdot}965 \times 12}{44} = 0{\cdot}536 \text{ gram.}$$

$$\text{Weight of hydrogen} = \frac{1{\cdot}611 \times 2}{18} = 0{\cdot}179 \text{ gram.}$$

From these numbers the percentage composition may be calculated in the manner already explained.

The simplest possible formula may be determined thus:—

$$\left.\begin{aligned} \frac{0{\cdot}536}{12} &= 0{\cdot}044 \\ \frac{0{\cdot}179}{1} &= 0{\cdot}179 \end{aligned}\right\} \text{Numbers in ratio of the number of atoms of carbon and hydrogen.}$$

$$\left.\begin{aligned} \frac{0{\cdot}044}{0{\cdot}044} &= 1 \text{ of C} \\ \frac{0{\cdot}179}{0{\cdot}044} &= 4 \text{ of H} \end{aligned}\right\} \text{Lowest number of atoms of C and H in the molecule.}$$

The simplest possible formula of marsh gas must be from this experiment CH_4. Whether or not this is the true molecular formula may be determined by calculating the density from the formula, CH_4.

$$\text{Density} = \frac{\text{Molecular Weight} = \text{C}, 12 + \text{H}_4, 4 = 16}{2} = 8.$$

This number agrees with the density as determined by experiment ; and therefore CH_4 is the correct molecular formula.

Acetylene.—Formula, C_2H_2. Molecular weight, 25·94. Density, 12·97. Specific gravity, 0·896. Graphic formula, H—C—C—H.



122. Occurrence.—Acetylene is produced during the combustion of many hydro-carbons in a limited supply of air. Thus, when a Bunsen burner lights at the bottom of the tube, acetylene is produced in considerable quantity.

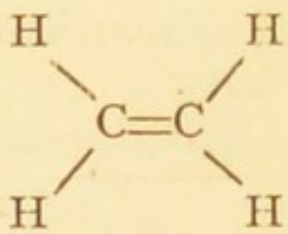
123. Preparation.—By the direct union of carbon and hydrogen at a high temperature acetylene may be formed. The most convenient method of thus preparing the gas is by passing a current of electricity, from a powerful voltaic battery, through two electrodes of carbon enclosed in a glass flask containing hydrogen.

124. Properties. — Acetylene is a gas possessing a peculiar and disagreeable odour ; it is a non-supporter of combustion, and burns with a bright and luminous flame.

125. Composition.—The composition, both by volume and by weight, of this gas may be ascertained in precisely the same manner as that of marsh gas. Acetylene consists of two volumes of carbon combined in the molecule with two of hydrogen, and therefore has the formula C_2H_2.

Ethylene, Ethene, Olefiant Gas, or Heavy Carburetted Hydrogen.—Formula, C_2H_4. Molecular weight, 27·94. Density, 13·97. Specific gravity, 0·965.

Graphic formula,



126. Occurrence.—This gas is one of the most important constitutents of coal-gas, being formed when the coal is subjected to destructive distillation.

127. Preparation.—Ethylene is most readily prepared by the action of concentrated sulphuric acid on alcohol, when the acid abstracts the elements of water from the alcohol.

$$\underset{\text{Alcohol.}}{C_2H_5HO} = \underset{\text{Ethylene.}}{C_2H_4} + \underset{\text{Water.}}{H_2O}$$

Experiment 116.—Mix in a large flask, fitted with a delivery-tube, one part of alcohol with five parts of concentrated sulphuric acid, and warm gently. Ethylene is readily evolved, and may be collected in jars over water. Collect two jars of the gas.

128. Properties.—Ethylene burns readily with a bright luminous flame, evolving at the same time considerable quantities of smoke. The gas, on being mixed with air or oxygen, explodes violently.

Experiment 117.—To one of the jars of gas already prepared apply a lighted taper; notice the bright flame with which the gas burns.

Mix in an explosion-tube one volume of ethylene with three volumes of oxygen and light; the mixture violently explodes.

Ethylene combines directly with chlorine to form an oily liquid of the composition $C_2H_4Cl_2$.

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

129. Composition.—The composition by volume of ethylene is determined by exploding the gas with excess of oxygen in a eudiometer. Thus if ten volumes of ethylene be taken and forty volumes of oxygen added there will be found after explosion, the temperature being maintained above 100° C., fifty volumes of gas; that is to say, the volume remains unaltered. On cooling, the volume contracts to thirty, showing that twenty volumes of water gas have been produced. The addition of caustic potash causes an absorption of twenty volumes, showing that that amount of carbon dioxide has been formed. The residual ten volumes of gas are found on testing to be oxygen. One

volume, therefore, of ethylene produces on combustion two volumes of carbon dioxide and two volumes of water. Applying, as in the case of marsh gas, Avogadro's law, one molecule of ethylene yields two molecules of carbon dioxide and two molecules of water; therefore the molecule of ethylene must contain two atoms of carbon and four of hydrogen, and its formula must be C_2H_4.

By passing a known volume of ethylene over red-hot copper oxide, and collecting and weighing the resultant water and carbon dioxide, the composition by weight may be determined. Thus 1,000 c.c. at N.T.P., having been thus treated, there will have been formed 1·609 gram of water and 3·934 gram of carbon dioxide.

Weight of 1000 c.c. = 0·0896 × 13·97 (density) = 1·2517 gram.

$$\text{Weight of carbon} = \frac{3{\cdot}934 \times 12}{44} = 1{\cdot}0729 \text{ gram.}$$

$$\text{Weight of hydrogen} = \frac{1{\cdot}6092 \times 2}{18} = 0{\cdot}1788 \text{ gram.}$$

The percentage composition may be readily calculated from these numbers.

The simplest formula may be thus deduced:—

$$\left.\begin{aligned} \frac{1{\cdot}0729}{12} &= 0{\cdot}0894 \\ \frac{0{\cdot}1788}{1} &= 0{\cdot}1788 \end{aligned}\right\} \text{Numbers in ratio of the number of atoms of carbon and hydrogen.}$$

$$\left.\begin{aligned} \frac{0{\cdot}0894}{0{\cdot}0894} &= 1 \text{ of C} \\ \frac{0{\cdot}1788}{0{\cdot}0894} &= 2 \text{ of H} \end{aligned}\right\} \text{Lowest number of atoms of C and H in the molecule.}$$

The simplest possible formula is therefore CH_2. Whether or not this is the true molecular formula may be determined by calculating the density according to this formula:—

$$\text{Density} = \frac{\text{Molecular Weight} = \text{C, 12} + \text{H}_2\text{, 2} = 14}{2} = 7.$$

But the density as determined by direct experiment is 14; therefore the molecular formula must be just double CH_2, that is to say, the molecule is represented by C_2H_4.

130. Combustion of Marsh Gas, Acetylene, and Ethylene.—The combustion of these three bodies affords some interesting examples of the laws of combustion by volume. Subjoined are the molecular equations representing the reactions which occur, together with those of some other examples of combustion already familiar to the student.

$$\underset{\substack{\text{Marsh gas.}\\ \text{One volume.}}}{CH_4} + \underset{\text{Two volumes.}}{2O_2} = \underset{\text{One volume.}}{CO_2} + \underset{\text{Two volumes.}}{2H_2O}$$

$$\underset{\substack{\text{Acetylene.}\\ \text{Two volumes.}}}{2C_2H_2} + \underset{\text{Five volumes.}}{5O_2} = \underset{\text{Four volumes.}}{4CO_2} + \underset{\text{Two volumes.}}{2H_2O}$$

$$\underset{\substack{\text{Ethylene.}\\ \text{One volume.}}}{C_2H_4} + \underset{\text{Three volumes.}}{3O_2} = \underset{\text{Two volumes.}}{2CO_2} + \underset{\text{Two volumes.}}{2H_2O}$$

$$\underset{\text{Carbon.}}{C} + \underset{\text{One volume.}}{O_2} = \underset{\text{One volume}}{CO_2}$$

$$\underset{\substack{\text{Carbon monoxide.}\\ \text{Two volumes.}}}{2CO} + \underset{\text{One volume.}}{O_2} = \underset{\text{Two volumes.}}{2CO_2}$$

$$\underset{\substack{\text{Hydrogen.}\\ \text{Two volumes.}}}{2H_2} + \underset{\text{One volume.}}{O_2} = \underset{\text{Two volumes.}}{2H_2O}$$

$$\underset{\substack{\text{Hydrogen.}\\ \text{One volume.}}}{H_2} + \underset{\text{One volume.}}{Cl_2} = \underset{\text{Two volumes.}}{2HCl}$$

These equations show very clearly the relation which exists between the volumes of gases and the respective volumes of oxygen required for their combustion. They afford additional illustrations of the method of deducing these quantities from the molecular equations. **As gaseous molecules are assumed** (at the same temperature and pressure) **to occupy the same space, it follows that the**

number of molecules of any gas participating in a chemical change represents the number of volumes of the gas concerned.

131. Nature of Combustion.—Everyone is familiar with the general idea of combustion as an act of burning. We may now inquire a little more closely into what is understood by this term. It has already been incidentally remarked that heat is produced when combination occurs between two substances; for instance, the addition of water to sulphuric acid causes a considerable elevation of temperature, because the water and acid unite with each other. There are many other cases in which the heat evolved is much more intense, as, for example, when phosphorus combines with oxygen. **Whenever the heat caused by chemical union is sufficiently intense to raise the resultant substances to a temperature at which they emit light, the act of union is termed 'combustion.'** The term has gradually come to receive a somewhat wider application; thus certain processes of decay, and also the chemical changes which produce animal heat, are cases of combination with oxygen. Such chemical actions are frequently termed instances of 'slow' combustion.

132. Inflammable Bodies and Supporters of Combustion.—The substances participating in the act of combustion are classified into inflammable bodies on the one hand, and supporters of combustion on the other. Thus, when hydrogen burns in oxygen, the hydrogen is said to be inflammable, and the oxygen a supporter of combustion. **The terms combustible and supporter of combustion are, however, purely relative.** We happen to live in an atmosphere of which oxygen is the active ingredient; when a jet of hydrogen is burned, what takes place is that at the orifice of the jet the hydrogen and the oxygen come in contact, and combination ensues. If the atmosphere consisted of hydrogen, then that element would be classified as

a supporter of combustion, and oxygen and similar bodies would be inflammable substances. Experiment readily demonstrates that oxygen burns in an atmosphere of hydrogen.

Experiment 118.—Fill a large globe, such as is used for the combustion of phosphorus in oxygen, with hydrogen gas : arrange the globe with its mouth downwards in a retort- or other stand, covering the mouth with a glass plate. Fill a bladder or small gas-bag with oxygen and attach to it by india-rubber tubing a piece of glass tube with the end drawn out into a jet. Place a weight on this bag and so arrange it as to produce a gentle stream of oxygen from the jet. Light the hydrogen at the mouth of the globe and steadily introduce the jet of oxygen. The oxygen will be ignited at the flame of the burning hydrogen, and as it is pushed up into the globe will continue to burn, showing clearly that oxygen burns in an atmosphere of hydrogen. The same experiment may be performed with coal-gas and air.

It is seen, therefore, that for combustion to occur, contact of the two substances is necessary. It is a matter of indifference which of the two envelops the other. But oxygen being so widely distributed, and the essential constituent of the atmosphere, it and like bodies are classified as supporters of combustion ; while hydrogen and bodies of similar character are termed inflammable.

133. Explosion.—When two substances, the one inflammable and the other a supporter of combustion, are intimately mixed with each other, on ignition combination occurs with extreme rapidity. The heat developed enormously increases the pressure of the gases produced as a result of the chemical action, and these give the surrounding air such a severe shock as to cause a loud detonation. **Extremely rapid combustion, attended with more or less noise, is termed explosion.** The mixture which thus explodes is termed an explosive body. If explosive mixtures be confined and then exploded, the resultant pressure may shatter the containing vessel. The explosive force of gunpowder is thus utilised for destroying large masses of rock. A hole is

bored in the rock, filled with the powder, and then ignited, with the result of shattering the rock into fragments. The great pressure exerted by exploding gunpowder is employed in guns for the purpose of propelling the bullet. Another interesting example of explosive force being utilised is that of the gas engine, in the cylinder of which a mixture of gas and air is caused to explode. The piston is driven forward by the force of the explosion.

134. Heat of Combustion.—Not only do substances in burning give out heat, but **the amount of heat evolved by the combustion (combination with oxygen) of a given weight of any substance is always the same.** Thus, whether the substance be burned slowly or rapidly, provided it is burned to the same products of combustion, the total amount of heat generated never varies. The following table gives the number of heat units evolved by the combustion respectively in oxygen and chlorine of one gram of each substance. The student is reminded that a heat unit is the quantity of heat necessary to raise one gram of water from 0° to 1° C.

HEAT DEVELOPED DURING COMBUSTION.

Substance.	In oxygen. Heat units.	In chlorine. Heat units.
Hydrogen . . .	34,462	24,087
Carbon . . .	8,080	
Sulphur . . .	2,220	
Phosphorus . .	5,747	3,422 (?)
Carbon monoxide .	2,634	
Marsh gas . . .	13,063	
Olefiant gas . .	11,942	
Alcohol . . .	6,909	

Of these bodies hydrogen develops by far the greatest amount of heat on combustion, the next place being taken by carbon. Of the various compounds of carbon it will be observed that carbon monoxide, during its further combus-

tion to the dioxide, evolves a considerable quantity of heat. It will be of interest to compare the amount of heat evolved in the two stages of oxidation of carbon. As carbon monoxide contains, according to its formula, but $\frac{12}{28}$ of its weight of carbon, it is evident that one gram of carbon would yield $\frac{28}{12}$ gram of carbon monoxide, and, consequently, that one gram of carbon as monoxide would, in its further oxidation to carbon dioxide, evolve

$$\frac{2634 \times 28}{12} = 6146 \text{ heat units.}$$

But the total number of heat units evolved by the complete combustion of carbon is only 8080. Therefore one gram of carbon evolves in oxidation to the monoxide

$$8080 - 6146 = 1934 \text{ heat units,}$$

and during further oxidation to the dioxide, 6146 heat units. The student is already aware that when the carbon dioxide formed in a fire of carbon passes upwards through red-hot carbon, it is reduced to the monoxide, which in its turn burns on the upper surface of the fire, where there is free access to air. Whenever carbon is burned with a limited supply of oxygen, as where a draught of air is drawn through a furnace containing large quantities of coke or other form of carbon, the monoxide is the chief product of combustion. This cannot burn until it reaches the air, and accordingly in the older forms of furnace used in metallurgical operations, particularly the blast furnace used for the smelting of iron ores, enormous quantities of carbon monoxide were formed and allowed to burn to waste on the tops of the furnaces. The value of this gas as a fuel is now recognised, and it is consequently drawn off from the upper part of the furnaces and utilised for heating purposes.

135. Temperature of Combustion.—Although the absolute amount of heat produced by the combustion of a unit weight of hydrogen, for example, is always the same, yet the temperature produced may vary within wide limits.

Thus, first of all, if within a given space, hydrogen is caused to burn in one instance at twice the rate of another, it follows that, as a greater number of units of heat are evolved in the same period of time, the temperature of that space will be raised proportionately higher. There are other causes which influence the temperature produced by combustion; for example, a jet of hydrogen, which burns the same number of cubic feet per hour, produces a flame of much higher temperature when it burns in oxygen than it does when burning in air. If 2 grams of hydrogen are burned in oxygen, the heat evolved has to raise the temperature of the 18 grams of water produced. But if the oxygen is obtained from air, then not only have there to be heated the 16 grams of oxygen, but also the 53·5 grams of nitrogen with which it is mixed. The same number of units of heat are in the one case spread over 18 grams; in the other over $18+53{\cdot}5=71{\cdot}5$ grams of gaseous matter; it follows that the temperature in the first instance must be very much higher than in the second.

136. Oxyhydrogen Blowpipe.—This instrument is a contrivance for utilising to the fullest extent the heating power of a flame of hydrogen fed with oxygen. The blowpipe consists of a platinum jet, leading from a small chamber, into which enter two pipes connected with gas bags or other vessels containing respectively hydrogen and oxygen under pressure. By means of a tap, hydrogen is first turned on and then lighted. In the next place the oxygen tap is also gradually opened, and there emerges from the jet a mixture of hydrogen and oxygen; the flame becomes smaller, and is scarcely more luminous than the ordinary flame of hydrogen itself. By means of this blowpipe, platinum and other most refractory substances may be reduced to the liquid state.

137. Luminosity of Flame.—The student will probably think it strange that, although the temperature of the

flame of hydrogen burning in oxygen is the highest due to combustion yet the flame is almost absolutely devoid of luminosity. The reason is that gases—and especially those of low density—radiate very little light even when intensely hot, while solids at a much lower temperature emit light most abundantly. This is strikingly illustrated by inserting some solid substance in the oxyhydrogen flame; if the flame from the oxyhydrogen blowpipe is caused to impinge on a piece of lime, the light emitted is one of the most intense known, and constitutes the well-known lime-light. It is here the solid substance which radiates so much light, although its temperature must be lower than that of the oxyhydrogen flame by which it is heated.

The various inflammable hydrocarbons burn with different degrees of luminosity; marsh gas and alcohol emit but very little light; olefiant gas, on the other hand, burns with a very luminous and smoky flame. As a general rule, the heavier hydrocarbons produce more light in burning than those which are less dense. During the combustion of such a body as olefiant gas, the hydrogen, being more inflammable, seizes first hold of the oxygen, and more or less of the carbon is liberated either in the free state or else as vapour of exceedingly dense hydrocarbons. The finely divided particles of carbon or dense hydrocarbons, as the case may be, are heated by the burning hydrogen and by abundantly emitting light impart luminosity to the flame.

138. Structure of Flame.—The actual structure of a flame may be studied by observing a jet of coal gas burning from the end of a round pipe, such as A in Fig. 29. In the interior of the flame there is a jet of unburnt gas, marked *a*, *a* in the figure, and appearing black by contrast with the surrounding brighter portions of the flame, by which it is enveloped. This bright or luminous zone, *f*, *e*, *g*, is that portion of the flame in which combustion of the hydrogen is proceeding, the unburnt carbon being thereby

heated to the point at which it emits light. In such a burner as is figured, there will be seen ascending from the upper portion of this zone a stream of smoke, consisting of carbon, which altogether escapes combustion. Outside *f*, *e*, *g* there may be distinguished another envelope, *b*, *c*, *d*, scarcely at all luminous, and much resembling the flame of burning hydrogen. This outer zone is that in which there is an ample supply of atmospheric oxygen, and consequently complete combustion : this is the hottest part of the flame, although the absence of solid particles causes it to be almost non-luminous.

FIG. 29.



The same divisions of the flame occur in a candle ; only in that case the dark interior portion consists of the solid matters of the candle, first melted, then drawn up into the heart of the flame by the capillary attraction of the wick, and finally vaporised by the heat of the flame.

139. Bunsen's Gas Burner.—When a gas flame is required for heating purposes only, it is desirable to attain the most perfect combustion possible. This end is accomplished by causing an admixture of air with the gas before it is burned. The gas burner invented by Bunsen is familiar to every chemical student. Examination shows that at the bottom of the upright tube are two or more holes communicating with the air ; on unscrewing this tube a small jet is seen within, from which the gas emerges. The air-holes may be wholly or partly closed by turning a ring which is fixed around them.

Experiment 119.—Take a Bunsen burner and examine its construction ; close the air-holes and light the burner. Place over it on a tripod stand a flask or other vessel containing a measured quantity of cold water ; observe the length of time before it boils ; notice also that the bottom of the flask becomes covered with soot.

Look at the flame and notice that the gas is evidently es-

caping but slowly from the top of the burner ; the flame is blown about readily by the most gentle air-currents. Holding the burner in the hand, turn it over in a horizontal position, the flame still remains vertical. Next slowly open the air-holes until the whole of the flame has acquired the pale blue tint of perfect combustion. Notice that a much more rapid current of gases emerges from the tube ; the flame is very little affected by gentle air-currents ; turn the burner over into the horizontal position ; the flame also lies horizontally. Take a piece of smouldering tinder and hold it near the air-holes ; the smoke is drawn in, showing that a current of air is entering. All these observations go to prove that the gas draws air up with it, and that a mixture of the two burns at the top of the tube.

Again place over the burner the flask of cold water, and with the conditions the same as before, except that air is being admitted, observe the length of time necessary to cause the water to boil. The boiling-point is reached in less time, and the flame is entirely smokeless, not causing the slightest mark of soot on the flask.

140. Blowpipe Flame.—The effect of converting a luminous flame into one devoid of light, but possessing considerable heating powers, is also obtained by blowing a current of air from a jet into the flame. The instrument employed for this purpose is termed a blowpipe, and is described at length in the analytic section of this work.

141. Lamp Chimneys.—The effect of the lamp chimney of a petroleum or Argand gas lamp is apparently just the opposite of that produced by the Bunsen burner. If either of these be lighted, it burns with a dull, smoky flame, but on fixing the chimney the flame becomes smokeless and much more luminous. The first result of the action of the chimney is to draw a current of air up around the flame (in the case of the Argand through the interior as well as the exterior). That this produces greater brightness is at first sight contradictory to what has already been seen of the effects of air in the Bunsen burner. But with the lamp chimney the air is drawn up, not into the flame, but

surrounding it ; the effect of this is more complete and intense combustion in the outside zone of the flame ; consequently the luminous envelope is heated more intensely and emits more light. The brisker current of air causes also the complete consumption of the smoke. If the current of air be too rapid, the brightness of the flame is thereby diminished, for with excess of air the envelope of complete combustion is unduly enlarged at the expense of that of luminosity ; the flame, in fact, partakes more or less of the character of that of the Bunsen. That in some cases the chimney causes too great a draught may be readily seen by partly closing the top by placing on it a small piece of tin-plate. This lessens the draught, and very frequently causes the flame to increase in size and emit more light.

Summary.

The compounds of hydrogen with carbon are very numerous. Marsh gas, acetylene, and olefiant gas are the simplest.

Marsh gas occurs as a product of decomposition of vegetable matter ; may be prepared by heating sodium acetate and caustic soda. The gas is of low density, colourless, inflammable, non-supporter of combustion, and produces carbon dioxide and water on burning. Composition is determined by explosion with oxygen in the eudiometer, and by passage over red-hot copper oxide.

Acetylene is formed when hydrocarbons are burned with limited supply of air, and also by direct union at high temperatures of carbon and hydrogen. The gas is colourless, possesses a peculiar odour, is inflammable, and a non-supporter of combustion. Composition is determined in a similar way to that of marsh gas.

Ethylene occurs as an important constituent of coal gas ; is prepared by heating alcohol with sulphuric acid. Possesses a pleasant odour, is inflammable, and a non-supporter of combustion. Composition ascertained in a similar way to that of marsh gas.

These three gases require different volumes of oxygen for their combustion ; this is seen by studying their formulæ.

Nature of combustion, inflammable bodies, and supporters of combustion: these terms relative. Nature of explosion, quantity of heat produced by combustion, temperature of combustion, oxyhydrogen blowpipe, luminosity of flame due to solid particles. Structure of flame effect of air as shown in Bunsen burner and use of lamp chimneys.

Laboratory Hints.

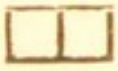
It is possible to use a glass flask for Experiment 114, but the heat is extremely likely to crack it.

In heating sulphuric acid and alcohol together, great care must be taken to avoid the alcohol taking fire. The flask used should be capacious, as the mixture froths.

In Experiment 118 take care that the hydrogen and oxygen used are pure, otherwise there is a risk of explosion.

CHAPTER XVI.

NITROGEN AND THE ATMOSPHERE.

Nitrogen.—Symbol, N. Atomic weight, 14·01. Density, 14·01. Specific gravity, 0·971. Molecular weight, 28·02. Molecular volume,  .

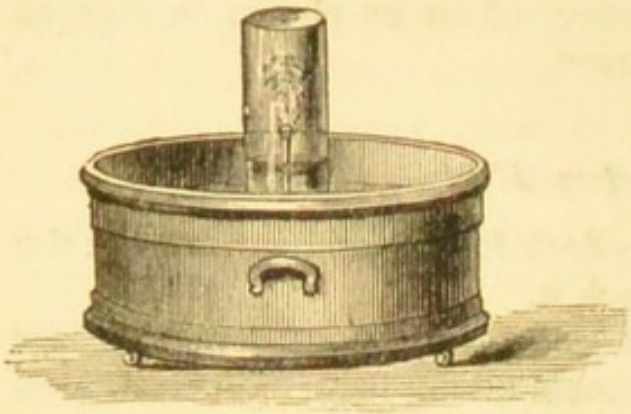
142. Occurrence.—Nitrogen exists in the free state in the atmosphere, in combination with oxygen and metals in certain native nitrates, and also is an essential constituent of many organic compounds.

143. Preparation.—There are several methods of preparing this gas, based on the removal of oxygen from the air by bodies having an affinity for that element; but in order that nitrogen only shall remain, it is necessary that the substance used be such that the resulting body can be easily separated from the gas. Phosphorus is very convenient

for this purpose, as the solid pentoxide produced is very soluble in water.

Experiment 120.—Procure an upright deflagrating spoon on stand ; place in it a small piece of dried phosphorus ; stand the spoon in the pneumatic trough with water ; ignite the phosphorus and immediately invert over it a gas jar: at first a few bubbles of air escape, owing to their being expanded by heat ; the phosphorus soon ceases to burn ; the fumes are dissolved by the water, and rather less than four-fifths of the original volume of gas remains : the loss is mostly oxygen, but there is in addition that resulting from the escape due to expansion.

FIG. 30.



A more accurate measurement may be made by removing the oxygen by the slow oxidation of phosphorus, which goes on at ordinary temperatures.

Experiment 121.—Take a piece of phosphorus about an inch long, and scrape off the oxide from it, holding it all the while under water ; fix this in the spoon and proceed exactly as before, except that the phosphorus is not lighted. If only a small piece is used, the phosphorus pentoxide first formed absorbs water, and so the whole piece, if it lie below the level of the top of the spoon, may be covered and prevented from undergoing further oxidation. At the end of from two or three days to a week observe and mark how far the water has ascended. Ascertain what proportion the whole contents of the jar bears to the gas remaining ; this is easily done by filling the jar with water and pouring it out into the graduated measure, then in the same way measuring its contents when filled to the mark indicating the absorption of oxygen. As the combination goes on in this case without any sudden heat, there is no loss by expansion.

By experiment it is also easy to demonstrate that the phosphorus, in the act of oxidation, gains in weight.

Experiment 122.—Select a light Bohemian globular flask, about 3 inches in diameter, and fit it with a good cork. To this cork fit two tubes, as in Fig. 31. The tube *a* must be bent and reach to the bottom of the flask; it may be very small; the second tube *b* must be of thin glass, and should be about four inches long and half-inch bore. Let its lower end protrude about an inch through the cork. Pack this tube with glass wool. Also pass through the cork a deflagrating spoon, *c*. This should reach as close to the bottom as possible. Fig. 31 shows the apparatus fitted up. Blow through *a* in order to see that air passes readily through *b* in the complete apparatus. Have also in readiness a gas-bag containing air. Thoroughly dry a piece of phosphorus and place it in the deflagrating spoon. Weigh the whole apparatus as accurately as possible and note the weight. Lift out the deflagrating spoon, light the phosphorus, and immediately replace it. Connect up the tube *a* with the air-bag. At first the phosphorus burns brightly, but soon the flame grows dim, through exhaustion of the oxygen in the air; at this stage pass a gentle current of air from the bag through *a* until the phosphorus is entirely burned. The nitrogen escapes through *b*, the phosphorus pentoxide being retained by the glass wool. When the apparatus is cool, again weigh. The experiment being properly performed, the increase of weight is due to the oxidation of the phosphorus.

FIG. 31.



The oxygen may also be removed by the action of metallic copper. If an iron tube be filled with copper turnings, and made red hot in a furnace, the copper immediately combines with the oxygen of any air which may be passed through, leaving the nitrogen—

$$\underset{\text{Copper.}}{2Cu} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Copper oxide.}}{2CuO}$$

Iron, likewise, removes the oxygen from air, especially if

it be caused to oxidise more readily by the addition of some ammonium chloride.

Experiment 123.—Introduce into a gas jar some iron borings, moistened with a strong solution of ammonium chloride (sal-ammoniac), and closely stop the jar with a glass plate or accurately fitting cork. Let it remain until the filings have rusted, then test the residual gas with a taper. It immediately extinguishes it, giving all the reactions of nitrogen.

There are several other methods of preparing nitrogen which are interesting from a theoretical point of view. For instance, the gas is evolved by passing chlorine into an excess of ammonia. The hydrogen and chlorine unite, and nitrogen is liberated.

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitrogen.}}{N_2}$$

A secondary reaction goes on between the acid formed and the excess of ammonia ; thus—

$$\underset{\text{Ammonia.}}{6NH_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Ammonium chloride.}}{6NH_4Cl}$$

The two equations may be grouped into one ; thus—

$$\underset{\text{Chlorine.}}{3Cl_2} + \underset{\text{Ammonia.}}{8NH_3} = \underset{\text{Ammonium chloride.}}{6NH_4Cl} + \underset{\text{Nitrogen.}}{N_2}$$

Experiment 124.—Prepare a flask for the evolution of chlorine ; arrange a second flask as a wash-bottle with the delivery tube very wide, and place in it two or three ounces of strongest solution of ammonia ; connect to the chlorine flask, and to the delivery tube of the wash-bottle attach a large diameter piece of tubing leading into the pneumatic trough. Heat the chlorine mixture ; as each bubble passes into the ammonia, dense white fumes of ammonium chloride are produced ; a wide leading tube is used, because a narrow one might be choked by accumulation of this salt. Considerable heat is evolved, and the action is so intense that flashes of light accompany the combination of the chlorine and hydrogen. Collect one small jar only of the nitrogen which passes over, and apply a lighted

taper : the light is extinguished, and the gas does not take fire. Unless strict attention be paid to the laboratory hints at the end of the chapter, this experiment becomes dangerous.

Another interesting method of preparing nitrogen is by the action of heat on the salt known as ammonium nitrite. This contains oxygen and hydrogen in the proportions necessary to form water : they combine and nitrogen is liberated.

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

It is usual to prepare the ammonium nitrite at the time of the experiment, that body being somewhat unstable. Ammonium chloride being added to potassium nitrite, the following decomposition takes place :—

$$\underset{\text{Potassium nitrite.}}{KNO_2} + \underset{\text{Ammonium chloride.}}{NH_4Cl} = \underset{\text{Ammonium nitrite.}}{NH_4NO_2} + \underset{\text{Potassium chloride.}}{KCl}$$

Experiment 125.—Take a four-ounce flask fitted with a cork, through which passes a single leading tube ; put in about a quarter of an ounce of potassium nitrite and an ounce of saturated solution of ammonium chloride in water ; arrange a jar for the collection of the gas, and apply heat ; the nitrogen comes over readily. The potassium chloride remains unaltered in the flask. Again test the gas by placing in it a lighted taper ; also introduce some litmus paper : notice that the gas is neutral.

144. Properties.—Nitrogen differs remarkably in properties from oxygen, with which it is associated in the atmosphere. The one is specially characterised by its great chemical activity ; the other is most inactive. It is a colourless, odourless, neutral, and tasteless gas, which is neither inflammable nor a supporter of combustion. It is not poisonous, but is unable to support life. Animals placed in it speedily die through suffocation. By the action of intense heat it may be caused to combine with oxygen, to form a ruddy-coloured gas, nitrogen peroxide, NO_2, which, by uniting with more oxygen and water, produces nitric acid. Small quantities of nitric acid are thus produced in the

atmosphere by lightning discharges. The effect may be imitated on the small scale by passing a series of sparks from an induction coil through moist air contained in a small glass globe. The air assumes a faint red tint, and litmus paper placed in the globe shows that it possesses an acid reaction.

Experiment 126.—Procure a globe properly prepared with platinum wires through the sides ; introduce a piece of moistened blue litmus paper ; cork up the vessel and pass through it for about ten minutes a current of sparks from the induction coil ; notice that the effects described above are produced.

Nitrogen is but slightly soluble in water : 100 volumes at 0° C. dissolve but 1·48 volumes of this gas.

The Atmosphere.—A gaseous mixture. Density, 14·47. Specific gravity, 1·00.

145. Occurrence.—This gaseous body, which envelops the earth, is of vast importance to us who live and breathe in it. Its existence is demonstrated whenever it is set in rapid motion, as we then have winds ; and these when sufficiently violent produce well-known and striking physical effects. That air among the other properties of matter possesses weight is capable of easy demonstration by experiment.

Experiment 127.—Procure a strong flask such as is sold by the instrument makers for the experiment ; screw it down to the air-pump and exhaust the air as completely as possible. Weigh the exhausted flask as accurately as you can. Then open the stop-cock ; allow it to fill with air and again weigh. The increase in weight is due to the air which has thus entered the flask.

146. Composition.—The composition of the atmosphere has been made the subject of many careful experiments, which show it to be a mixture of nitrogen and oxygen approximately in the proportion of four to one. A rough kind of analysis of air has been already made by the student, the oxygen being removed by phosphorus. In addition to these two elements there are also present varying quantities

of aqueous vapour, carbon dioxide, ammonia, nitric acid, and traces of other bodies. Its average composition over the land is shown in the following table :—

	Oxygen	20·61
	Nitrogen	77·95
	Carbon dioxide	0·04
	Aqueous vapour	1·40
	Nitric acid, Ammonia, Carburetted hydrogen	Traces
In towns	Sulphuretted hydrogen, Sulphur dioxide	,,

The proportion of nitrogen to oxygen in air is remarkably constant, but little variation from the above being found in air collected in the most varied localities ; still slight but marked differences are observed in samples collected from different sources. The results of careful analyses of air, freed from carbon dioxide and aqueous vapour, give the following average composition :—

	By measure.	By weight.
Nitrogen	79·19	76·99
Oxygen	20·81	23·01
	100·00	100·00

The composition by volume may be determined by using a eudiometer tube similar to that used in Experiment 57, Fig. 18, for showing the production of water by the union of oxygen and hydrogen. A measured quantity of air is placed in the eudiometer, and hydrogen added in excess of that necessary to combine with the whole of the oxygen present ; on the passage of a spark, union of the hydrogen and oxygen is effected, and on the gas regaining its original temperature, the volume is found to be much less. As water is composed of two volumes of hydrogen to one of oxygen the amount of oxygen present in the gaseous mixture is one third of the diminution observed. The eudiometer

employed for this pupose should be graduated. Supposing that 10 c.c. of air have been introduced and 5 c.c. of hydrogen added; after the explosion the volume will be found to be reduced from 15 to about 9 c.c.; 10 c.c. of air therefore contain approximately $\frac{6}{3} = 2$ c.c. of oxygen, the more accurate figures being those given above.

The composition by weight is ascertained by passing air over red-hot copper, due precautions being taken to avoid error. The copper is placed in a piece of difficultly fusible glass tubing, with which it is weighed; an exhausted receiver is also weighed and attached to one end of this tube; the other is connected with U tubes filled with caustic potash and sulphuric acid respectively, for the purpose of removing carbon dioxide and water. The glass tubing is raised to red heat, the stop-cock of the receiver is opened, and a slow current of air passes over the copper; its oxygen is removed and nitrogen only passes into the empty receiver. The gain in weight of the copper represents the weight of oxygen, and that of the receiver the weight of nitrogen.

147. Air a Mixture.—That air is a mixture and not a compound may be proved in many ways; in the first place the oxygen and nitrogen are not present in any simple multiple of their atomic weights, which is a necessity in all compounds. Air also differs remarkably from those compounds of the two elements with which chemists are acquainted. If a mixture be made of nitrogen and oxygen in the proportion in which they exist in air, no alteration of volume takes place, neither is there any increase of temperature; the mixture exhibits all the properties of air.

Experiment 128.—Mix in a gas jar in the pneumatic trough four volumes of nitrogen with one of oxygen; introduce a lighted taper: it continues to burn exactly the same as in air.

The most conclusive evidence of their being mixed, and not combined, is that they may be separated by the action

of water as a solvent. Oxygen is more soluble than nitrogen, and if water, which has been previously freed from gases by boiling be shaken up with air, and then again boiled, the expelled gas is found on analysis to be much richer in oxygen than was the air, the oxygen amounting to about 34 per cent. of the dissolved gases.

It will be interesting here to note the difference between air on the one hand and water on the other. In air the two most important constituents are not present in the same absolutely unvarying proportion. On oxygen and nitrogen being mixed in the same proportions as they exist in air, no alteration in volume occurs, and the mixture exhibits properties which are a mean of those of the two ingredients. Further they may be separated by the action of water as a solvent.

With water the hydrogen and oxygen are always present in absolutely unvarying proportions. When these gases are mixed and a light applied a violent explosion occurs ; the water produced condenses to a liquid possessing properties altogether different from those of its constituents. The explanation is that air is a mixture, and water a chemical compound.

148. Functions of Atmospheric Carbon Dioxide.—It has already in Chapter XIII. been pointed out that carbon dioxide is present in air, and that the breathing of animals and the burning of carbonaceous bodies are continually supplying this gas ; although this operation is proceeding without intermission, the quantity of carbon dioxide present in the atmosphere remains remarkably constant. Its amount varies betweeen 3 and 6 parts in 10,000 according to the locality where, and time when, the gas is collected. This quantity, though small, is of vast importance to the vegetable kingdom, as it is the source from which all organic carbon is derived in nature. Animals can only assimilate carbon from previously existing organic compounds. Vegetables decompose carbon dioxide using the carbon in the

formation of their tissues, and liberating the oxygen in the free state.

Experiment 129.—Take a beaker some ten or twelve inches high and arrange in it some sprigs of fresh mint or some other quickly growing plant, immediately after being cut; or preferably pulled up with the roots attached. In this latter case, first wash the roots in a gentle stream of water. Fill the beaker with water through which washed carbon dioxide gas has been passed to saturation. Fix an inverted funnel over the sprigs of mint, so that the top of the funnel is entirely submerged. Fill a test-tube with water, and place it over the funnel, so as to retain any gas that may be given off. Place the whole apparatus in direct sunlight. The growing mint decomposes the carbon dioxide dissolved in the water, the oxygen which escapes is caught as it rises by the funnel, and collects in the test-tube. After some hours, test the evolved gas with a glowing splinter; it gives the reaction of oxygen.

The effects, therefore, of animal and vegetable life on the atmosphere are opposite in character: the one removes oxygen and returns carbon dioxide, the other decomposes this compound, and again yields oxygen to the air (this return action is, however, partially balanced by the ordinary progress of decay); these two processes going on simultaneously keep the proportion of carbon dioxide in air within constant limits. The decomposition of certain rock-forming minerals, as felspar, by the action of the carbon dioxide of the atmosphere, which combines with the bases that they contain, is another important drain on the amount of that gas present in air.

149. Other Constituents.—The amount of aqueous vapour which the atmosphere contains varies considerably; but it is always present in more or less quantity. Its presence may be demonstrated by bringing a vessel of ice-cold water into a room: the aqueous vapour condenses on the outside as a film of moisture.

Ammonia is only found in air in minute traces. These,

however, are important, as from them plants obtain a great proportion of their nitrogen.

Summary.

Nitrogen exists in the free state in the atmosphere, and is also found in nitrates and different organic bodies. It is prepared either by the removal of oxygen from the air by the action of phosphorus or copper, or by the decomposition of bodies containing nitrogen, as ammonium nitrate and ammonia. Nitrogen is a colourless, odourless, and tasteless gas ; is neither inflammable nor a supporter of combustion ; is neutral to litmus paper ; by great heat may be made to combine with oxygen forming acid compounds.

The atmosphere is a mixture of nitrogen and oxygen, with small quantities of other compounds present. Its composition is determined by explosion with hydrogen and other methods. Air is a mixture, proved by different solubility of the two gases in water.

Carbon dioxide is produced by the breathing of animals and burning of substances containing carbon. The same gas is removed by the action of vegetable life and oxygen restored to the air.

The ammonia present in air supplies nitrogen to plants.

Laboratory Hints.

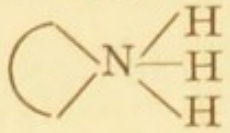
In preparing nitrogen by the action of chlorine or ammonia, strict attention must be paid to the directions *always to have excess of ammonia* : see accordingly that the solution used is the strongest, of specific gravity 0·88, and not the dilute solution employed in the laboratory for analytical purposes. Prepare but one jar of the gas by this method. These precautions are necessary because with excess of chlorine a most violently explosive compound of nitrogen and chlorine is formed. The wide leading tube is also an essential. The glass globe with platinum wires passed through, used in Experiment 126, should be obtained from the general apparatus of the laboratory ; they can be bought of any apparatus dealer ; the form sold is, however, somewhat fragile, and not well suited for the rough usage of a laboratory. One may be easily prepared by taking a three

or four ounce wide-mouthed bottle, fitting it with a cork through which is passed two pieces of quill glass tubing in which platinum wires are fused. The ends of the wires should be about an eighth of an inch apart, and reach to the middle of the bottle: the glass tubes are to be filled with mercury; the connection with the coil is made by dipping the *clean* ends of the leading wires underneath its surface. The cork should be soaked in melted paraffin. The apparatus as thus constructed bears some resemblance to that described for the electrolysis of water in Experiment 54, Fig. 14. Remember when the cork is taken out of the bottle to so place it that the mercury does not run out of the tubes.

CHAPTER XVII.

AMMONIA.

Formula, NH_3. Molecular weight, 17·01. Density, 8·5. Specific gravity, 0·59.

Graphic formula, 

150. Occurrence.—This, the only compound of nitrogen and hydrogen known in the free state, exists in small quantities in the atmosphere, and also in rain-water. It is probably a resultant product of the oxidation of different organic substances in the presence of moist air. The oxygen of the water acts as the oxidising agent, and the nascent hydrogen combines with nitrogen to form small quantities of ammonia It is produced in considerable quantity in the decomposition of animal and vegetable bodies which contain nitrogen. The urine and excreta of animals contain refuse nitrogenous matter. This after a time becomes changed into ammonia, and thus causes these substances to be such valuable manures, as plants are in-

capable of assimilating nitrogen while free, but are able to do so when that element is presented to them as ammonia.

The name ammonia is derived from that of Jupiter Ammon, because near a temple dedicated to him the Arabs extracted one of its compounds from camel's dung. If quills, horn, hair, &c., be heated in a closed vessel, various gases are evolved, among which ammonia is always present.

Experiment 130.—Heat in a test-tube some hair or quill cuttings ; place a piece of red litmus paper in the condensed moisture in the upper part of the tube : it is turned blue.

Coal contains about 2 per cent. of nitrogen, and in like manner evolves ammonia when heated. As this substance is subjected to destructive distillation on the large scale in the manufacture of coal gas, it affords a cheap and plentiful source of ammonia. The ammonia passes over with the gas, and is dissolved by the condensed moisture. This constitutes the gas or ammoniacal liquor of the works. From this ammoniacal salts are prepared by the addition of acids.

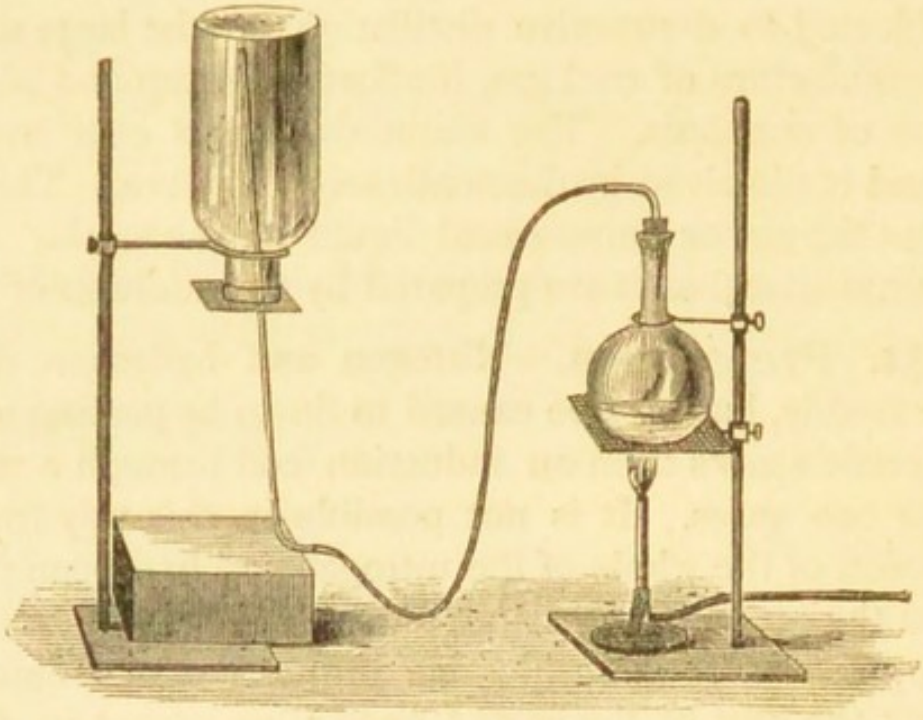
151. Preparation.—Nitrogen and hydrogen do not unite readily, but may be caused to do so by passing a series of electric sparks from an induction coil through a mixture of the two gases. It is not possible in this way to cause the union of the whole of the nitrogen and hydrogen present unless the ammonia is removed as rapidly as formed, because as soon as a considerable proportion of ammonia is present the heat of the sparks once more causes its decomposition into free nitrogen and hydrogen. The ammonia may be removed in this experiment by causing the reaction to take place over a solution of hydrochloric acid, which combines with the ammonia to form ammonium chloride.

Ammonia may be prepared from any of the ammoniacal salts by heating with a stronger base, as lime or soda. Of these lime is preferred because of its cheapness. If ammonium chloride and lime be heated together, the following reaction takes place :—

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Quicklime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Water.}}{H_2O} + \underset{\text{Ammonia.}}{2NH_3}$$

Experiment 131.—Fit to an eight-ounce flask a cork with single delivery tube, to which is attached, by means of a moderately long piece of india-rubber tubing, a glass tube about a foot in length. The flask, tubing, and all other apparatus must be perfectly dry. Dry separately some powdered lime and ammonium chloride (sal-ammoniac) ; the lime may be dried by simply heating in a sand-bath ; to dry the ammonium chloride, place it in an evaporating basin and heat gently either in the sand-bath or on a piece of wire gauze over the Bunsen flame

FIG. 32.



turned down very small ; the heat must not be sufficient to cause any fumes to be evolved. This may be set to dry before preparing the flask. They must be allowed to cool ; then take about half an ounce of the ammonium chloride and an ounce of the lime. The bath sand being cold, mix intimately in the mortar the chloride and about two-thirds of the lime ; notice that ammonia is given off by its smell ; pour the mixture into the flask, and then add the remaining lime in a layer over the top. Fix the flask in the retort stand with a piece of gauze underneath, arrange the leading tube upright so that gas

may be collected by upward displacement ; invert a dry gas bottle over the tube, the end of which must reach right up to the top. Fig. 32 shows the whole arrangement. The gas bottle is most conveniently held on the ring of a retort stand. Apply a gentle heat to the flask ; the gas is evolved readily. To test when the jar is full, hold a piece of reddened litmus paper outside the bottle just above the mouth ; it will be turned blue ; draw the tube out of the bottle, lift it from the ring and quickly place on the cover. Three jars of gas should be in this way collected.

Experiment 132.—Then place the end of the delivery tube in a little distilled water in a beaker ; notice that the whole of the gas is absorbed ; in two or three minutes remove the tube and withdraw the Bunsen from the flask ; the liquid smells of the gas ; to some litmus solution in a test-tube add a drop of sulphuric or hydrochloric acid so as to just redden it ; to this add the ammonia solution ; the blue colour is restored.

152. Properties.—Ammonia is a colourless gas with a most pungent and characteristic odour, which is pleasant when the gas is mixed with air ; but in the undiluted state the gas acts as a powerful irritant, bringing tears to the eyes, and if accidentally inhaled, even in small quantities, destroys the surface of the mucous membrane of the mouth, and may produce even fatal effects by its action on the lungs. The solution in water has a burning and disagreeable taste. The gas may be condensed to a liquid by a temperature of $-50°$ C., or a pressure of about 7 atmospheres at 15° C. Like other liquefied gases, liquid ammonia is very volatile, producing great cold in evaporating. This property causes it to be largely used in the manufacture of artificial ice. The gas is remarkably soluble in water, which dissolves at 0° C. 1050 times its volume of the gas ; at 15° C. 727 volumes. The concentrated solution readily evolves gas on being heated, and may frequently be used with advantage as a source of the gas. At ordinary temperatures the solution gives off gas, hence its pungent odour. A solution of hydrochloric acid in water has a higher specific gravity than

water, while that of ammonia is lower. The concentrated solution at 15° C. has a specific gravity of 0·880.

Experiment 133.—Place the mouth of one of the jars of gas under water and remove the glass plate; the water rushes up with violence and fills the jar.

It has been before mentioned that charcoal possesses the property of absorbing gases: ammonia is a striking example. Freshly burned charcoal absorbs about 90 volumes of this gas.

Experiment 134.—Take a dry six-inch test-tube, fill it with mercury in a mercury trough, and fix in a retort stand with the mouth under the surface. In a clean four-ounce flask place about an ounce of concentrated ammonia solution, fit to it a cork with single delivery tube, leading into the mercury trough, fix the flask in the retort stand, and apply a gentle heat; gas comes over almost immediately; wait until the air is all expelled, and then fill the test-tube with gas. Select a piece of charcoal of a size that will easily go into the tube; heat it in the Bunsen, and then by means of the tongs introduce it through the mercury into the gas; it rapidly absorbs it, and the mercury rises to the top of the tube.

Ammonia is a non-supporter of combustion, and non-inflammable at ordinary temperatures; but when heated it takes fire and burns with a greenish flame; water is produced and nitrogen set free.

$$\underset{\text{Ammonia.}}{4NH_3} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Nitrogen.}}{2N_2} + \underset{\text{Water.}}{6H_2O}$$

Experiment 135.—Place a lighted taper in a jar of the gas; the taper goes out, but just before doing so the flame slightly enlarges and becomes of a green colour.

Experiment 136.—Place in the furnace an iron tube fitted with corks and pieces of quill tube at each end; when the tube is red hot connect to it the four-ounce flask containing ammonia solution; apply heat and light the gas as it emerges from the iron tube; it burns with a green flame.

It has already been seen by experiment that ammonia

restores the blue colour to litmus. It neutralises the strongest acids, and forms a well-marked and most important series of salts. The composition of some of these is thus shown :—

NH_3	+	HCl	=	NH_4Cl	•	$NaCl$
Ammonia		Hydrochloric acid.		Ammonium chloride.		Sodium chloride.
NH_3	+	HNO_3	=	NH_4NO_3		$NaNO_3$
Ammonia.		Nitric acid.		Ammonium nitrate.		Sodium nitrate.
$2NH_3$	+	H_2SO_4	=	$(NH_4)_2SO_4$	•	Na_2SO_4
Ammonia.		Sulphuric acid.		Ammonium sulphate.		Sodium sulphate.

The salts of sodium are also written in a separate column for the sake of comparison. It will be seen that the group NH_4 and sodium occupy corresponding places. Further, this group may be expelled from one chemical compound and caused to enter another without decomposition.

153. Compound Radicals.—This is only one instance of a group of elements entering into the composition of a body, and performing functions very similar to those of an atom of an element. Such groups are not only found to form numbers of very definite compounds, but may be even transferred from one compound to another without undergoing decomposition. **Groups of atoms of different elements which possess a distinct individuality throughout a series of compounds, and behave therein as though they were elementary bodies, are termed 'compound radicals.'**

154. Ammonium and its Salts.—The group NH_4 is one of the best and most striking examples of a compound radical ; because it thus behaves in so many compounds as though it were an element, it has received a name *ammonium*, for which the symbol Am is sometimes used. Ammonium chloride is written either NH_4Cl or AmCl. Ammonium, however, cannot be isolated, but immediately

splits up into ammonia and free hydrogen. The solution of ammonia in water is sometimes conveniently represented as a hydrate of ammonium ; thus—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ammonium hydrate.}}{NH_4HO}$$

This, again, is analogous in composition to sodium hydrate, NaHO.

Ammonium hydrate produces in many cases the same chemical reaction as does either sodium or potassium hydrate. Thus all these bodies produce the same precipitate of ferric hydrate, $Fe_2(HO)_6$, from a solution of ferric chloride, Fe_2Cl_6. The student is referred to the analytic section of this work for an account of these reactions.

The principle of the preparation of ammonia is simply, therefore, to displace it from a salt by the action of a stronger and non-volatile base, as lime. The action is similar to that in which a volatile acid, as hydrochloric, is displaced by a less volatile and more powerful acid, as sulphuric.

The salts of ammonium are formed, as shown by equations, by the direct union of the acid with gaseous ammonia.

Experiment 137.—Fill a bottle with hydrochloric acid gas, place it over the remaining bottle of ammonia, remove the plates, bringing the mouths of the bottles together ; a dense white cloud of ammonium chloride is formed ; the bottles get sensibly warm to the hand.

Salts of ammonia with volatile acids may in some cases be sublimed without the production of any permanent chemical change, as with ammonium chloride. Others are decomposed, as ammonium nitrate ; those with non-volatile acids, as ammonium phosphate, are decomposed ; the acid remains, and free ammonia is evolved.

Experiment 138.—Heat a little ammonium chloride in a test-tube ; the salt, if pure, entirely sublimes, and recondenses in the upper part of the tube. In a second tube heat some ammonium phosphate : free ammonia is evolved and phosphoric acid remains.

155. Composition.—The composition of ammonia by volume may be ascertained by passing a series of electric sparks through the gas in a eudiometer. Any residual ammonia, which has escaped decomposition, must be absorbed by caustic potash. The volume of the remaining gas is double that of the ammonia from which it has been formed, two molecules of ammonia producing one molecule of nitrogen and three of hydrogen. The quantity of hydrogen is determined by adding excess of oxygen and exploding. It amounts to two-thirds of the diminution. The excess of oxygen is then removed by adding pyrogallic acid and caustic potash, by which it is absorbed; the residual gas is nitrogen.

The composition by weight may be ascertained by passing a measured quantity of dry ammonia over red-hot copper oxide; water is formed and may be collected by calcium chloride. Nitrogen passes over in the free state. The hydrogen is calculated from the water, and the difference of weight between that and the ammonia represents the nitrogen.

Experiment 139.—Pass a current of dry ammonia over copper oxide, heated to redness in a combustion tube. Note that water is formed and that the oxide is reduced to the metallic state.

Pass a mixture of air and ammonia over the red-hot copper remaining in the tube and collect the gas which escapes. On testing it is found to be nitrogen.

In this latter part of the experiment the oxygen of the air and the hydrogen of the ammonia unite to form water; the atmospheric nitrogen and that contained in the ammonia both escape together.

Summary.

Ammonia exists in traces in the atmosphere; is formed by the decomposition of nitrogenous organic matter; is manufactured from the watery distillate of the gaswork, by neutral-

ising with acid and subsequently treating the salt produced with lime and heating.

Ammonia is a colourless gas, with characteristic odour; may be liquefied by pressure or cold; is very soluble in water, and is also absorbed in large quantities by charcoal. The gas is a non-supporter of combustion, and is non-inflammable at ordinary temperatures; but when heated burns with a greenish flame. It is alkaline to litmus paper, and forms with acids a series of salts in which NH_4 occupies the place of a monad metal. This group has received the name ammonium and symbol Am; does not exist in the free state, but breaks up into ammonia and hydrogen. Ammonium salts are volatile if the acid be so; those with a fixed acid are decomposed; the acid remains and ammonia is evolved.

The decomposition is determined by decomposing the gas by electricity and estimating the hydrogen and nitrogen.

Laboratory Hints.

In preparing ammonia from the chloride and lime, unless both are dried, there is a danger of breaking the flask by water condensing in the upper parts and trickling down on the hot glass. It is a good plan to place two pieces of gauze under the flask, and to use a rose burner if you have one; otherwise keep the flame small. When collecting a gas by displacement, it is advisable to have a piece of cardboard closing the mouth of the jar, with a slit through it for the leading tube: this is kept on the mouth until the glass plate is exchanged for it.

When the end of the leading tube is placed in water, watch carefully to see that the gas is not absorbed so rapidly as to cause the water to rise in the tube; should it have a tendency to do so, increase the heat, and, if necessary, take away the beaker of water, and draw the cork from the flask. In any case remove the beaker *before* the flame.

There is a difficulty in filling jars in the mercury trough through not being able to see the end of the leading tube; this should be bent up at an acute angle, and may then be hooked into the mouth of the tube. A tube of stouter glass than that of the test-tube is much better, and may be made by drawing out a piece of glass tubing.

CHAPTER XVIII.

OXIDES AND ACIDS OF NITROGEN.

156. Nitrogen Oxides.—There are five compounds of nitrogen and oxygen known, two of which, by union with water, form acids : their names and composition are :—

Nitrogen monoxide, or nitrous oxide, N_2O.
Nitrogen dioxide, or nitric oxide, NO (or N_2O_2).
Nitrogen trioxide, or nitrous anhydride, N_2O_3.
Nitrogen tetroxide, or nitric peroxide, NO_2 (or N_2O_4).
Nitrogen pentoxide, or nitric anhydride, N_2O_5.

By the action of water we have—

$$N_2O_3 + H_2O = 2HNO_2, \text{ Nitrous acid.}$$
$$N_2O_5 + H_2O = 2HNO_3, \text{ Nitric acid.}$$

This series of compounds is interesting because it affords such a striking illustration of the law of multiple proportions ; 28 parts by weight of nitrogen combine respectively with 16, 32, 48, 64, and 80 parts of oxygen.

Nitric acid is by far the most important of these bodies, and as the whole of the others are prepared from it nitric acid is conveniently studied first.

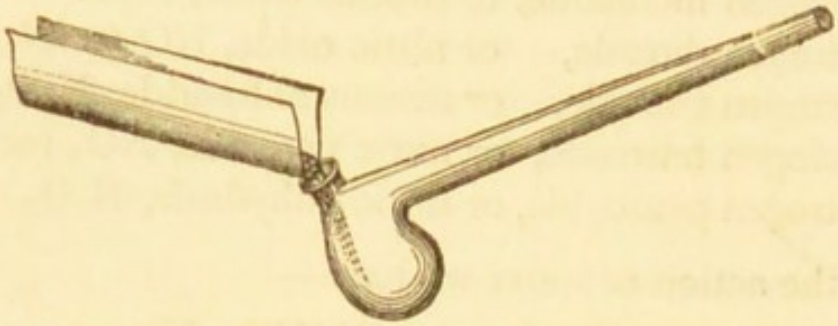
Nitric Acid.—Formula, HNO_3. Molecular weight, 62·89. Specific gravity of liquid, 1·52. Melting point, about −55° C. Boiling point, 84·5°.

157. Occurrence.—Nitric acid is produced in small quantities in the atmosphere, from which it is separated by rain, which therefore usually exhibits traces of this acid when subjected to analysis. The salts of nitric acid with soda and potash (sodium and potassium nitrates) are its most common sources. Layers of potassium nitrate are found incrusting the soil in India and of sodium nitrate in parts of Chili and Peru ; the latter of these is the more plentiful. These

nitrates are produced by the oxidation of nitrogenous organic matter in the presence of the bases potash or soda. Potassium nitrate is also known as saltpetre or nitre; sodium nitrate is frequently called Chili saltpetre or cubic nitre, from the shape of its crystals.

158. Preparation.—Nitric acid is always prepared by the action of sulphuric acid on a nitrate, usually either that

FIG. 33.

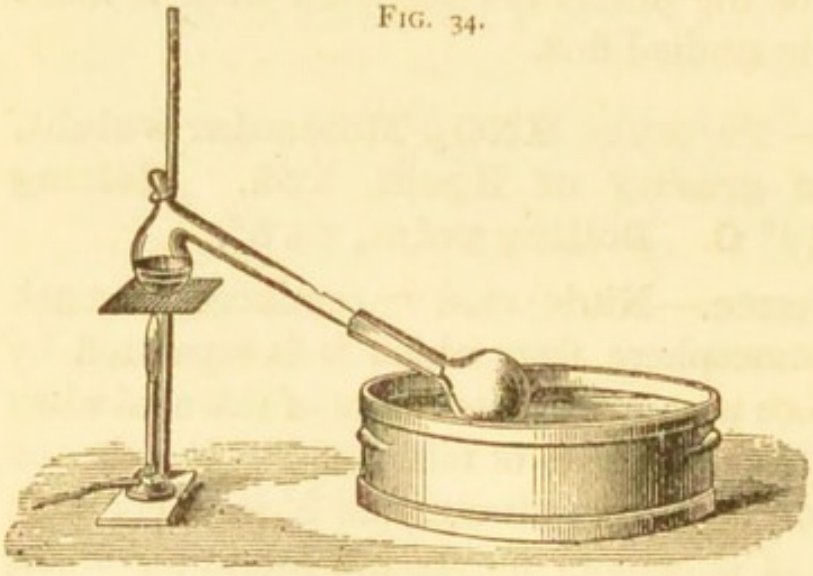


of sodium or potassium. The two are mixed in a retort, and on the application of heat nitric acid, being more volatile, distils over, leaving acid sodium sulphate :—

$$\underset{\text{Sodium nitrate.}}{NaNO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Acid sodium sulphate.}}{NaHSO_4}$$

Experiment 140.—Take a four or six-ounced stoppered retort, get it thoroughly clean, and pour in about an ounce of

FIG. 34.



sodium nitrate through the tubulure (*i.e.* hole for the stopper) : this is most easily effected by taking a piece of paper, and doubling it up as shown in Fig. 33 ; the nitrate is placed on this, and carefully transferred to the retort, which should be held as in the figure ; on no account must any of the nitrate get into the neck.

Next clean and drain a small flask or six-inch test-tube and introduce into it the beak of the retort as represented in Fig. 34. Arrange the apparatus in the retort stand with the test-tube or flask well under water in the pneumatic trough; the further under the better, so that the water does not run into the tube. The retort must be held securely by a ring passing over the neck; it may be necessary to raise the trough some little distance above the table; adjustments of this kind are best performed by pieces of blocking; the trough should be got to its right place *first*, and then filled with water. Next pour in an ounce of concentrated sulphuric acid, replace the stopper, and apply heat carefully with the Bunsen. The nitrate melts, brownish red fumes are seen in the retort, and a pale yellow liquid distils over into the tube or flask. Collect sufficient to about one-quarter fill a six-inch test-tube, then remove the light and disconnect the apparatus; pour the sulphate out of the retort into an evaporating basin while still liquid; it solidifies, being nearly pure acid sodium sulphate. Reserve the nitric acid for further experiments.

On the application of a more intense heat the acid sulphate of sodium is capable of acting on another quantity of the nitrate with the formation of the normal sulphate :—

$$\underset{\text{Acid sodium sulphate.}}{NaHSO_4} + \underset{\text{Sodium nitrate.}}{NaNO_3} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Nitric acid.}}{HNO_3}$$

The temperature necessary for this second reaction, however, partly decomposes the nitric acid produced.

159. Properties.—Nitric acid, when pure, is a colourless fuming liquid, but usually is of a faint yellow tinge through the presence of some of the lower oxides of nitrogen, produced by its partial decomposition. It is an extremely powerful oxidising agent, and rapidly destroys animal tissues; it stains the skin, horn, &c., a bright yellow colour. It attacks most of the metals, including copper, mercury, and silver, with great vigour; gold and platinum are unaffected by it, or any single acid (except that gold is oxidised by the rare compound, selenic acid).

Expreiment 141.—Fill an iron ladle with small fragments of charcoal, and heat to redness over a powerful Bunsen flame. Fasten a test-tube to the end of a rod and partly fill with concentrated nitric acid. Pour a little of the acid on to the red-hot charcoal. Vigorous combustion ensues, due to the rapid oxidation of the charcoal by the acid.

Vigorous combustion of this kind is termed *deflagration.*

160. Action of Acids on Gold.—*Experiment* 142.—Take a small piece of gold leaf and place it in a test-tube, add some nitric acid and heat gently; the gold is undissolved. Treat another piece similarly with strong hydrochloric acid; this also is without action; now mix the two together: the gold dissolves rapidly.

This mixture of acids is generally termed *aqua regia* (royal water), from its power of thus dissolving 'the king of metals'; its activity depends on the production of nascent chlorine, which combines with gold forming auric chloride; the reaction may be represented by the following equation, but varies with the different proportions of hydrochloric and nitric acids which may be used :—

$$\underset{\text{Nitric acid.}}{3HNO_3} + \underset{\text{Hydrochloric acid.}}{9HCl} + \underset{\text{Gold.}}{2Au} = \underset{\text{Nitrogen oxychloride.}}{3NOCl} + \underset{\text{Water.}}{6H_2O} + \underset{\text{Gold chloride.}}{2AuCl_3}$$

161. Action of Nitric Acid; and Nitrates.—The action of nitric acid on the metals generally is more complex than that of hydrochloric or sulphuric acids; the nascent hydrogen, displaced by the metal, attacks the remaining nitric acid and forms water, liberating one or more of the lower oxides of nitrogen; the particular one evolved, and the proportions of each present in a mixture, depend on the metal used, the degree of concentration of the acid, and other causes.

Experiment 143.—To some of the nitric acid distilled in a previous experiment add one or two pieces of copper clippings; notice that a violent action goes on, ruddy fumes are evolved, and a green solution of copper nitrate formed.

Nitric acid is a monobasic acid, its salts being known as nitrates; they may be prepared either by acting on the metal, as with copper, or by adding the acid to an oxide or a carbonate.

Experiment 144.—Take about half an ounce of strong nitric acid, place it in a beaker, and add solid ammonium carbonate in small quantities until it no longer causes effervescence; the liquid now has an alkaline reaction to litmus paper, add nitric acid drop by drop until the solution is neutral; place this away for a week in an evaporating basin; at the end of that time long needles of ammonium nitrate will have crystallised out; the salt must be reserved for a future experiment.

The nitrates, like the acid from which they are derived, are powerful oxidising agents; potassium nitrate is used as a source of oxygen in gunpowder, which is a mixture of that compound with sulphur and charcoal.

If charcoal be dropped into melting potassium nitrate, it burns with great brilliancy.

Experiment 145.—Melt some potassium nitrate in a test-tube, drop in a fragment of charcoal; it burns with evolution of carbon dioxide. The mouth of the tube should be held away from any person, as sometimes the red-hot piece of charcoal jumps out of the tube.

Nitric acid and all the nitrates are decomposed by heat, oxides of the metals remain, and oxygen and nitrogen oxides are driven off.

Experiment 146.—Procure a clay tobacco pipe with very long stem (churchwarden); pass the stem through a small gas tube-furnace, arranged obliquely so that the bowl of the pipe is upwards, and the mouthpiece just beneath the surface of the water of a pneumatic trough. Arrange a test-tube for the collection of gas evolved from the pipe. Pour concentrated nitric acid in the bowl drop by drop; in passing through the red-hot stem it is decomposed into water, nitrogen peroxide, and free oxygen. The peroxide is dissolved by the water, and oxygen collects in the tube. Test the gas by means of a glowing splinter.

The reaction in the above experiment is represented by the following equation :—

$$\underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen peroxide.}}{4NO_2} + \underset{\text{Oxygen.}}{O_2}$$

Experiment 147.—Arrange a test-tube with cork and delivery tube and one-third fill with potassium nitrate. Apply heat and collect the gas which is evolved. Continue the application of heat until the free evolution of gas ceases. Test the gas by means of a glowing splinter. Reserve the substance remaining in the test-tube for a future experiment.

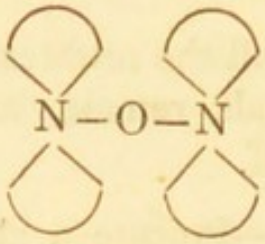
Potassium nitrate when heated undergoes the following change :—

$$\underset{\text{Potassium nitrate.}}{2KNO_3} = \underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Oxygen.}}{O_2}$$

162. Nitric anhydride is an unstable body, and is rarely prepared ; it readily unites with water and forms nitric acid :—

$$\underset{\text{Nitric anhydride.}}{N_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2HNO_3}$$

Nitrogen Monoxide.—Formula, N_2O. Molecular weight, 43·98. Density, 21·99. Specific gravity, 1·527.

Graphic formula, 

163. Preparation.—This gas may be prepared by the action of zinc on dilute nitric acid, the two being gently heated ; the reaction is a somewhat complex one, and may be represented by the following equation :—

$$\underset{\text{Nitric acid.}}{10HNO_3} + \underset{\text{Zinc.}}{4Zn} = \underset{\text{Nitrogen monoxide.}}{N_2O} + \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Water.}}{5H_2O}$$

The gas is frequently impure, portions of the nitric acid being reduced to free nitrogen.

Nitrogen monoxide is much more easily obtained by the action of heat on ammonium nitrate, which is decomposed in a manner similar to that in which ammonium nitrite, NH_4NO_2, is separated into water and nitrogen ; the nitrate, however, contains another atom of oxygen (its formula being NH_4NO_3), which is evolved in combination with the nitrogen :—

$$\underset{\text{Ammonium nitrate.}}{NH_4NO_3} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen monoxide.}}{N_2O}$$

This equation should be compared with that representing the decomposition of ammonium nitrite.

Experiment 148.—Take an eight-ounce flask, fitted with cork and single leading tube ; transfer to it the ammonium nitrate prepared according to directions previously given ; pour in the saturated solution of the salt as well as the crystals which have formed ; get ready a trough of *warm* water for the collection of the gas, fix the flask into the retort stand, place the end of the leading tube in the trough, and apply heat ; at first air escapes and bubbles through the water in the trough ; this is soon displaced by the steam resulting from the evaporation of the water present with the nitrate ; as this enters the colder water it is condensed, and no bubbles arise ; in a short time the whole of the water is driven off ; at this point the liquid becomes pasty and froths up ; watch carefully, and if necessary remove the light ; it soon again subsides and then evolves gas quietly ; use a flame not too large but just at such a height as to produce a steady and slow current of gas. Collect three jars for experiment ; take the leading tube out of the trough, remove the Bunsen, and allow the flask to cool : any ammonium nitrate which then remains readily dissolves if some water is placed in the flask.

164. Properties.—Nitrogen monoxide is colourless, has a faint sweetish smell and taste ; it is soluble in cold water ; 1 volume at 15° C. dissolves 0·77 volume of the gas. It may be condensed to a liquid by a pressure of thirty atmospheres at 0° C. or at ordinary pressures at a temperature of −99° C. Nitrogen monoxide supports combustion almost

as vigorously as oxygen, oxides are formed, and nitrogen liberated. Carbon thus forms carbon dioxide :—

$$\underset{\text{Carbon.}}{C} + \underset{\text{Nitrogen monoxide.}}{2N_2O} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Nitrogen.}}{2N_2}$$

Experiment 149.—Introduce into a jar of the gas a glowing splinter of wood ; it bursts into flame as though placed in oxygen.

The two gases, oxygen and nitrogen monoxide, may however be readily distinguished from each other by the much greater solubility of the latter gas, and also by the difference in their behaviour with nitric oxide, to which reference will again be made. In actual analysis the presence of a residue of nitrogen after combustion would also distinguish nitrous oxide from oxygen.

The decomposition of nitrogen monoxide into free oxygen and nitrogen is necessary before bodies can burn in this gas ; if the heat of the combustion is not sufficient to effect this burning does not go on. Thus feebly burning sulphur is extinguished by the gas, but when burning brightly it continues to do so almost as vividly as in oxygen.

Experiment 150.—Place a piece of sulphur in a deflagrating spoon, let it just take fire in the Bunsen, and plunge it into a jar of the gas ; the light is extinguished. Replace the cover of the gas jar and heat the sulphur in the flame until almost boiling, now again place in the gas ; it continues to burn.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Nitrogen monoxide.}}{4N_2O} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Nitrogen.}}{4N_2}$$

Nitrogen monoxide behaves as an anæsthetic when breathed (*i.e.* a substance which causes insensibility to pain). Some four or five gallons of the gas are sufficient in most cases to produce total insensibility ; before this stage it in many persons causes a kind of intoxication, often accompanied by violent fits of laughter ; because of this it has received the popular name of 'laughing gas.'

165. Composition.—The molecule of nitrogen monoxide yields a molecule of nitrogen ; therefore any quantity of the gas when decomposed produces its own volume of nitrogen ; the composition may be determined by exploding the gas in the eudiometer with excess of hydrogen—

$$\underset{\text{Nitrogen monoxide.}}{N_2O} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{H_2O}$$

A corresponding volume of nitrogen remains to that of the monoxide taken ; the diminution in volume consists of hydrogen which has combined with the oxygen ; it is necessary, however, to measure the excess of hydrogen which remains in order to deduce the composition of nitrogen monoxide from this experiment.

Nitrogen Dioxide, or Nitric Oxide.—Formula, NO (or N_2O_2). Molecular weight, 29·97. Density, 14·98. Specific gravity, 1·039.

166. Preparation.—This gas is readily obtained by the action of copper on moderately concentrated nitric acid; the reaction occurs without the application of heat : hydrogen is probably first liberated, and then reduces some of the remaining acid :—

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{6HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nascent hydrogen.}}{6H}$$

$$\underset{\text{Nascent hydrogen.}}{6H} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{4H_2O}$$

Or the two reactions may be stated in the one equation :—

$$\underset{\text{Copper.}}{3Cu} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water}}{4H_2O}$$

Experiment 151.—Take the flask and delivery tube used for the preparation of hydrogen, No. 2, Fig. 10, and place in it about half an ounce of copper clippings. Dip the cork of the apparatus in melted paraffin, and attach a glass leading tube to the delivery tube, so that the ends are in contact, by a

small piece of india-rubber tubing about two inches long. Nitric acid rapidly corrodes both india-rubber and cork, so that we avoid, as far as possible, exposing either to its influence ; the paraffin protects the cork, and the leading tube is practically of glass throughout ; arrange for the collection of the gas over cold water in the pneumatic trough. Pour on to the copper some of a mixture of strong nitric acid and water in equal volumes (about two ounces) ; bubbles of gas are evolved and the whole flask rapidly fills with red fumes. These soon become lighter in colour, and as each bubble of gas rises through the water in the trough into the air, it assumes a dark red tint ; the air is now expelled from the flask, and the gas jars may be filled ; four will be required for experiment. If the action slackens before the whole of them have been filled, add some more of the nitric acid ; as the action goes on with great rapidity, as many jars as possible should be filled with water and placed inverted in the trough before the acid is poured on the copper. Remember the order in which the jars are filled. This experiment should, if possible, be performed in a stink closet.

This gas may also be prepared by the action of sulphuric acid on potassium nitrite, when the following reactions occur :—

$$\underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Nitrous acid.}}{2HNO_2}$$

The nitrous acid, if slightly heated, immediately undergoes decomposition with the formation of nitric acid and nitric oxide :—

$$\underset{\text{Nitrous acid.}}{3HNO_2} = \underset{\text{Nitric acid.}}{HNO_3} + \underset{\text{Nitric oxide.}}{2NO} + \underset{\text{Water.}}{H_2O}$$

Experiment 152.—Place the residue from Experiment 147 in a flask fitted with thistle funnel and delivery tube. Add dilute sulphuric acid and heat gently ; collect the evolved gas over water in the pneumatic trough. On the admission of air the gas turns red, showing it to consist of nitric oxide.

167. Properties.—This gas is colourless, but immediately on coming in contact with air combines with the oxygen and forms higher nitrogen oxides of a ruddy tint ;

from its possessing these properties it is difficult to either taste or smell it. The strong odour observed during its preparation is that of these higher oxides.

Nitric oxide has until recently been considered a permanent gas, but was liquefied by Cailletet at -11° C. by a pressure of 104 atmospheres. It is much more stable than nitrogen monoxide, and may be subjected to even a red-heat without decomposition; consequently a lighted taper does not burn in it.

Phosphorus, when feebly ignited, is also extinguished, but if strongly ignited burns with almost as much brilliancy as in pure oxygen :—

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Nitric oxide.}}{10NO} = \underset{\substack{\text{Phosphorus}\\ \text{pentoxide.}}}{2P_2O_5} + \underset{\text{Nitrogen.}}{5N_2}$$

Experiment 153.—In the third jar of gas prepared introduce a lighted taper; notice that it goes out. If this is quickly done, a deflagrating spoon containing brightly burning sulphur may be placed in the same jar of gas; this also ceases to burn.

Experiment 154.—Place a piece of phosphorus in the deflagrating spoon, first thoroughly cooling it; get the second jar of gas ready and just kindle the phosphorus and *immediately* place it in the gas; it is extinguished. Remove it and again ignite and let it get to burn brightly; once more plunge it in the jar; it burns with extreme brightness.

A mixture of carbon disulphide vapour and nitric oxide burns with an intense bluish light.

Experiment 155.—Pour half a cubic centimetre of carbon disulphide into a test-tube; replace the bottle. Take the first jar prepared of nitric oxide, remove the cover, quickly pour in the disulphide, and as quickly re-cover the jar; shake it vigorously, in order to thoroughly mix the gas and vapour, holding the plate on firmly. Remove the plate and apply a light; the mixture burns quietly with a bright blue flame.

Nitric oxide is not itself combustible. One of its most striking properties is the power it possesses of spontaneously combining with oxygen on the two being brought together;

the resultant ruddy gas is a mixture of nitrogen trioxide and peroxide in varying proportions :—

$$4NO + O_2 = 2N_2O_3, \text{ Nitrogen trioxide.}$$
$$2NO + O_2 = 2NO_2, \text{ Nitrogen peroxide.}$$

As nitrous oxide does not possess this property, this reaction serves to distinguish the one gas from the other.

Experiment 156.—Take the fourth jar of gas prepared and invert it in the pneumatic trough. Having filled a jar with oxygen, pour the nitric oxide up into it bubble by bubble ; as each bubble enters, a red colour is developed ; this again vanishes, and the water rises in the gas jar. If the two gases be pure, the gradual addition of nitric oxide causes the oxygen to disappear entirely.

Prepare a jar of nitrous oxide, free from air ; add nitric oxide to it in a similar manner. There is no red coloration nor rapid absorption of the gas by the water.

The reason of the above reaction is that, while nitric oxide is but feebly soluble in water (water dissolves about one-twentieth of its volume), the higher oxides produced are very soluble, and are thus absorbed as rapidly as formed. This reaction is a most important one, as the whole process of manufacturing sulphuric acid is dependent on it. A description of its employment for that purpose is given in Chapter XXII.

168. Composition.—The anomalous composition of nitric oxide has been already referred to in Chapter XII. From the formula being written N_2O_2 by some chemists, the name *nitrogen dioxide* has been given it, and is still used, although but one atom of oxygen is contained in the molecule. It is a general rule that the more atoms a molecule contains, the more unstable it is. Nitric oxide is more stable than nitrogen monoxide, and this, therefore, is an additional reason for considering its true formula to be NO.

169. Nitrogen Trioxide is one of the products of oxidation of nitric oxide. It dissolves in a small quantity

of water to form nitrous acid. This is, however, so unstable that even the addition of more water causes its decomposition :—

$$\underset{\text{Nitrous anhydride, or nitrogen trioxide.}}{N_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitrous acid.}}{2HNO_2}$$

If the gas be passed into a solution of caustic potash or ammonia, it is absorbed, and a nitrite is formed :—

$$\underset{\text{Nitrous anhydride.}}{N_2O_3} + \underset{\text{Potassium hydrate.}}{2KHO} = \underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Water.}}{H_2O}$$

Nitrites are decomposed by stronger acids with evolution of nitrogen trioxide :—

$$\underset{\text{Potassium nitrite.}}{2KNO_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Nitrogen trioxide.}}{N_2O_3}$$

This represents the simplest action of acids, but the nitrous acid formed also undergoes decomposition into nitric oxide, and nitric acid produced by the extra atom of oxygen uniting with another molecule of nitrous acid.

170. Nitrogen Peroxide is of but little importance. Like nitric oxide, the formula is anomalous, being NO_2. At a low temperature, however, the density increases, when N_2O_4 may be considered a true representation of the molecule.

It may be prepared by the action of heat on certain nitrates, as lead nitrate :—

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

Summary.

Five oxides of nitrogen are known, two, at least, of which form acids.

Nitric acid is the most important ; is produced by lightning discharges. It is manufactured from nitrates by distillation with sulphuric acid. It is a powerful oxidising agent, attacks most

of the metals, but neither gold nor platinum; these may be dissolved by *aqua regia*, a mixture of hydrochloric and nitric acids. When metals are acted on by nitric acid, the lower oxides of nitrogen are evolved and nitrates formed; they are also produced by acting on metallic oxides or carbonates with the acid. The nitrates also are capable of powerful oxidising action.

Nitrogen monoxide is usually prepared by heating ammonium nitrate. It is colourless, has a faint, sweetish odour and taste, is somewhat soluble in water, non-inflammable, supports combustion, but requires for that purpose an initial heat sufficient to start its decomposition into nitrogen and oxygen. It also acts as an anæsthetic.

Nitric oxide is prepared by the action of copper on nitric acid. It is colourless, but on exposure to air immediately becomes red by combination with oxygen. It is more stable than nitrogen monoxide, and does not support combustion unless the heat of the burning body is sufficiently intense to separate it into oxygen and nitrogen. The red fumes formed by its combination with oxygen are soluble in water. The composition of the gas is anomalous.

Nitrogen trioxide and peroxide are comparatively unimportant.

Laboratory Hints.

Blocking for the adjustment of height of different pieces of apparatus is in constant requisition in the laboratory. Pieces six inches square are of a convenient size; the following thicknesses should be kept in stock: half-inch, one, two, three, and four inches.

Small pieces of gold-leaf are quite sufficient for the experiments with that substance; one leaf may be cut into nine pieces. Do not attempt to handle the leaf in a draughty room; a leaf should be removed from the book, placed on a pad, and cut with an old knife, the edge of which is quite smooth. When the leaf is cut, it may be taken on the point of the knife and scraped into the test-tube; it may then be washed down by a few drops of water from a wash-bottle.

In adding ammonium carbonate to nitric acid do not throw it in the form of a fine powder, as the action then is so violent

that it is likely to overflow the beaker. Pieces about the size of peas are the most convenient.

The flask used for the preparation of nitrogen monoxide should not be less than eight ounces, as otherwise some of the melting nitrate may froth up and choke the tube; should any do so, immediately remove the light, as the continued evolution of gas might burst the flask. If the heat is too great, the gas comes over impure; if it is cloudy in the jar, that may be looked on as a sign that the heat must be moderated.

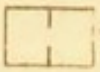
The action of copper on nitric acid sometimes does not start immediately; if so, apply a very gentle heat to the flask until the action commences. It is liable then to proceed with extreme rapidity; a large flask is therefore used. If coming over too fast, pour in a little water; this will render the reaction less violent. The cork and tubing used should be washed at once after use. The directions for the protection of the cork and tubing are important; if a long piece of india-rubber tubing be used, the tubing is not only destroyed, but also gets stopped with the products of corrosion. It is a good plan to have the leading tube bent out of one piece of glass tubing; but if there is a joint, provided the ends of the glass tubes touch one another, it will not matter.

The reason why the order of collection of the gas must be remembered is that that which first comes over is purer. At the last nitrogen monoxide and nitrogen are also present; the jars first filled are therefore used for those experiments in which the purest gas is required.

The phosphorus must be introduced into the gas *very quickly* when lighted, as otherwise it will be burning too brightly to be extinguished. Place the gas-jar close to the Bunsen burner, and loosen the glass plate *before* lighting the phosphorus.

CHAPTER XIX.

SULPHUR.

Symbol, S. Atomic weight, 31·98. Density, 31·98. Specific gravity of native crystals, 2·07. Molecular weight, 63·96. Molecular volume,  .

171. Occurrence.—Sulphur is a widely distributed element. In the neighbourhood of volcanoes it occurs plentifully in the free state. The ores from which many metals are derived are sulphides. Among these may be mentioned those of lead, copper, mercury, and zinc. Many of the native metallic sulphides are characterised by a bright metallic lustre. The most common sulphide is that of iron. From this large quantities of sulphur are extracted.

Experiment 157.—Heat a small quantity of powdered native sulphide of iron in a test-tube; yellow drops condense in the upper part of the tube.

The reaction is represented by the following equation :—

$$\underset{\text{Ferric sulphide.}}{3FeS_2} = \underset{\text{Triferric tetrasulphide.}}{Fe_3S_4} + \underset{\text{Sulphur.}}{S_2}$$

In the presence of a limited supply of air the whole of the sulphur is driven off, an oxide of iron remaining. In practice about half of the sulphur is also oxidised into sulphur dioxide, so that the yield of sulphur is not more than 50 per cent. of that present in the ore. The reaction in this case is thus represented, the oxidation of the sulphur being omitted :—

$$\underset{\text{Ferric sulphide.}}{4FeS_2} + 3O_2 = \underset{\text{Ferric oxide.}}{2Fe_2O_3} + 4S_2$$

Experiment 158.—Take a piece of combustion tubing six inches long and one quarter-inch diameter; place a small

quantity of the sulphide about half-way up. Hold the tube slanting and apply heat; an upward current of air is produced, in which the liberated sulphur burns. Smell the gas issuing from the end; it has the characteristic odour of burning sulphur.

The sulphates are another important class of natural bodies containing sulphur. Of these gypsum or calcium sulphate, $CaSO_4$, and barium sulphate, $BaSO_4$, occur in large quantity.

Many organic bodies contain sulphur as an essential ingredient, especially albumin. Hence, in their putrefaction, sulphur compounds are among the products, and are always present in sewage gases, &c. White of egg is an almost pure form of albumin, and owes its odour when rotten to the presence of a compound of sulphur and hydrogen.

172. Preparation.—The free sulphur, collected in volcanic districts, is contaminated with earthy impurities. These are removed on the spot by melting the sulphur from them; or, in the poorer samples, by the process of distillation. The crude sulphur thus obtained is further purified on its arrival in this country by being a second time distilled. The retorts employed are of iron; the necks lead into large chambers of brickwork. If the heat be applied slowly, the vapour, on entering the chamber, condenses to a solid, and falls as a fine dust to its floor. This constitutes 'flowers of sulphur.' At a higher temperature the walls are heated, the sulphur condenses to the liquid form on them, and runs to the bottom as a melted mass. This is drawn off into cylindrical wooden moulds and allowed to solidify. In this manner is produced the roll 'brimstone' of commerce.

173. Properties.—Sulphur is a lemon-yellow solid. It is insoluble in water, and therefore possesses no taste, but has a faint odour. The rolls of sulphur are extremely

brittle, and as it is also a bad conductor of heat the warmth of the hand is often sufficient to cause a roll to fall in pieces when held. It melts at a temperature of 113° C. to a limpid yellow liquid, which, if allowed to cool slowly, deposits long prismatic needle-like crystals. These are at first perfectly transparent, but after a time become opaque, through each breaking up into a number of minute rhombic octahedral crystals. The external form is still retained, but little coherence remains.

If sulphur be dissolved in carbon disulphide, and the liquid then allowed to evaporate, the sulphur is obtained in octahedral crystals of the rhombic system. These are permanent in air, and the form is that in which native sulphur crystals occur.

Experiment 159.—Take a clay crucible about three inches high, or, preferably, an iron ladle ; fill it with sulphur and heat very gently with a small flame, taking care that the sulphur and the flame do not come in contact. As soon as the whole of the sulphur is melted remove the Bunsen ; as it cools, a crust forms over the surface, crystals being seen to shoot out from the side. Immediately that this crust is formed, bore two holes through with a red-hot iron wire close to the edge and opposite each other ; pour the sulphur (which still remains melted) out, and then cut round the upper crust with a knife and remove it ; the interior is one mass of long transparent needles (prisms), belonging to the oblique system. Set the mass aside for a week, and then observe that the crystals have lost their transparency.

Shake up some flowers of sulphur with carbon disulphide so as to form a saturated solution. Decant off the clear liquid and filter into an evaporating basin. Set aside and allow the disulphide to evaporate spontaneously. A residue of more or less transparent octahedra of sulphur remains.

There are, then, two distinct forms in which sulphur crystallises ; the one from fusion, the other from solution. The latter are permanent, the former unstable, gradually changing into the latter.

In addition to these two varieties, there is another known

as plastic sulphur, whose properties widely differ from those of either. If, instead of allowing the limpid yellow liquid, produced as a result of melting sulphur, to cool, the application of heat be continued, a remarkable series of changes ensues. The colour gradually darkens as the temperature rises ; at the same time the liquid becomes thicker, until, at a temperature of 180° C., the mass is almost black, and so viscid that the vessel may be momentarily held inverted without the sulphur running out. With a further increase of temperature, the sulphur again becomes liquid, but remains of a much thicker consistency than it possessed on first melting. If while in this state it be poured into water, a soft, india-rubber-like mass is produced, of a yellowish-brown tint, which may be drawn out into long threads. The difference between these and the common brittle form of sulphur is very striking. In a few hours it loses its tenacity, becoming again opaque and brittle. At a temperature of 446° sulphur boils.

In addition to the three forms of sulphur described, there are some other varieties, which, however, are not of great importance.

Experiment 160.—Place some sulphur in a test-tube and heat gently, until the whole has melted down into a limpid clear liquid. Pour a portion out on to an iron plate or other cold surface. It solidifies to a brittle yellow mass possessing the same properties as those originally belonging to the sulphur.

Next heat the remainder very gently, and notice the successive changes, from a thin liquid of light colour to the almost black, treacly mass. When in this condition invert the tube ; the sulphur does not run out, or only very slowly. Continue the application of heat until the sulphur boils ; observe the dark orange-coloured vapour, which condenses to solid yellow particles in the upper part of the tube. Pour the liquid into a trough of cold water ; notice the plastic condition of the sulphur ; reserve some for a week, it will have become brittle.

Sulphur is highly inflammable, burning in air with a pale

blue flame, and emitting a suffocating odour, the reaction being represented by—

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2}$$

Traces of a higher oxide of sulphur are also formed, the formation of which will be subsequently described.

Sulphur also combines readily with other elements. Iron, copper, and others burn brightly when heated with it. Silver and sulphur combine at ordinary temperatures, giving the metal a black coating of silver sulphide.

Experiment 161.—Raise some sulphur to the boiling point in a test-tube. Insert a coil of fine copper wire in the vapour and notice the vivid combustion which ensues.

Two compounds of sulphur with hydrogen are known—SH_2 and S_2H_2—which are analogous in composition to the oxides of hydrogen, OH_2 and O_2H_2. The first of these is the only one of practical importance. The sulphides of the metals have usually corresponding formulæ to the oxides. Thus the sulphide of copper is CuS; the oxide, CuO. Sulphur in these compounds behaves as a dyad; but in sulphuric acid and the sulphates its atomicity is VI.

Summary.

Sulphur is found in volcanic districts, also in sulphides and sulphates, and several organic bodies; is purified by distillation; is a lemon-yellow brittle solid; occurs in two crystalline forms, one of which is unstable; may be also obtained in the plastic form by the application of heat. It is highly inflammable and combines with most of the metals, and also with many of the non-metals. Its absolute atomicity is VI.

Laboratory Hints.

For the first experiment in this chapter the native sulphide should be used; that employed in the manufacture of sulphuric acid is most suitable. To succeed in obtaining sulphur crystals by solidification of the melted body, bore the holes through the

crust *immediately* it forms, and drain the melted sulphur away *completely*.

In pouring sulphur from a test-tube there is danger of the tube cracking unless the upper part is thoroughly heated. The safest plan is, before pouring, to boil the sulphur until the whole tube is full of uncondensed vapour ; by this means the whole is uniformly heated and the danger of cracking is but little ; care should, however, be taken that the tube is so held that in the event of its breaking none of the sulphur should fall on the hands. The liquid will probably take fire as it leaves the test-tube : this, however, is of no importance. Should any fall on the bench at once throw a little water on it.

CHAPTER XX.

SULPHURETTED HYDROGEN.

Formula, SH_2. Molecular weight, 33·98. Density, 16·99. Specific gravity, 1·1912.

Graphic formula, 

174. Occurrence.—This compound, which is also sometimes known by the name of hydrosulphuric acid, is found free in volcanic districts, and also in the waters of certain mineral springs, as those at Harrogate.

175. Preparation.—It is formed when hydrogen is passed into sulphur vapour, but only in small quantities.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Sulphuretted hydrogen.}}{2SH_2}$$

Experiment 162.—Arrange a small retort with its stem just dipping beneath the surface of the water in a pneumatic trough.

Place some sulphur in the retort and heat to the boiling point; notice the sulphur which condenses in the stem. Withdraw the stopper from the tubulure of the retort and insert a cork through which has been passed a glass tube of such a length as to reach almost to the surface of the melted sulphur. Through this tube pass some pure hydrogen gas and collect it as it escapes from the stem of the retort. The gas possesses the odour of putrid eggs, and a piece of paper moistened with a solution of lead acetate is blackened when plunged into the gas.

Sulphuretted hydrogen is commonly prepared for use in the laboratory by the action of dilute sulphuric acid on a sulphide, that of iron being usually chosen. The reaction goes on readily, without the application of heat, the iron displacing the hydrogen, and the sulphur and hydrogen uniting.

$$\underset{\text{Ferrous sulphide.}}{FeS} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Ferrous sulphate.}}{FeSO_4} + \underset{\text{Sulphuretted hydrogen.}}{SH_2}$$

Experiment 163.—Fit up the apparatus used for the preparation of hydrogen, attach a small flask as a wash-bottle (Fig. 35), and place in it a little water; place in the flask some fragments of iron sulphide; add three or four ounces of water, and then a *small* quantity of sulphuric acid; the gas is rapidly evolved. Fill three jars with it over warm water.

Experiment 164.—In the next place attach a jet to the generating apparatus and light the gas; it burns with a feeble blue flame, producing water and sulphur dioxide. Hold just above the flame a rod which has been dipped in a strong solution of ammonia (ammonium hydrate); dense white fumes ascend.

The combustion of sulphuretted hydrogen is represented by the equation—

$$\underset{\text{Sulphuretted hydrogen}}{2SH_2} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Water.}}{2H_2O}$$

On holding above the flame the rod dipped in ammonia, the sulphur dioxide forms a solid compound named am-

monium sulphite. The fumes of this body are evidence of the presence of sulphur dioxide :—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Ammonium hydrate.}}{2NH_4HO} = \underset{\text{Ammonium sulphite.}}{(NH_4)_2SO_3} + \underset{\text{Water.}}{H_2O}$$

Sulphuretted hydrogen produces no fumes with ammonia. More conclusive evidence of the presence of sulphur dioxide as one of the products of combustion is afforded by holding the nose above the flame, when its characteristic odour is observed. The following experiment also illustrates a test frequently employed for the detection of sulphur dioxide :—

Experiment 165.—Hold over the flame a piece of filter paper which has been dipped in a mixture of potassium chromate and dilute hydrochloric acid ; the yellow colour is changed to green by the reducing action of the sulphur dioxide.

Prove also that water is produced, when sulphuretted hydrogen burns, by holding a beaker of cold water in the flame ; moisture condenses on the cold surface.

Sulphuretted hydrogen is soluble in cold water, one volume at 15° C. dissolving 3·23 volumes of the gas.

FIG. 35.



Experiment 166.—At the conclusion of the experiment with flame pass the gas into a little distilled water in a test-glass or beaker—the arrangement of the apparatus is shown in Fig. 35. If necessary, add a little more sulphuric acid to the ferrous sulphide in flask A. Continue the passage of the gas for about ten minutes, and then notice that the water has the odour of the gas.

While the above experiment is proceeding, examine the three jars filled with the gas in the following manner :—

Experiment 167.—Remove the cover from one jar and introduce a lighted taper ; the gas burns, but the light is extin-

guished ; a yellow deposit of sulphur is formed on the sides of the jar.

Experiment 168.—Add some litmus solution to the second jar of gas and shake up ; the colour of the litmus is changed to a port-wine tint, showing that the gas has feebly acid properties.

Experiment 169.—Prepare a jar of chlorine, invert it, with the plate on the mouth, over the third jar of sulphuretted hydrogen ; pull out the two plates and the jars open into one another ; sulphur is deposited. Remove the upper jar, and notice the characteristic fumes of hydrochloric acid.

176. Properties.—The preceding experiments illustrate several of the properties of this gas. It is colourless and has an odour of rotten eggs. Its solution in water has a corresponding taste. It is inflammable and a non-supporter of combustion. With excess of oxygen, sulphur dioxide and water are produced, according to the equation before given. When the supply of air is limited, as when the gas burns in a jar, the sulphur is in great part deposited, the hydrogen only being burned.

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur.}}{S_2} + \underset{\text{Water.}}{2H_2O}$$

The gas is condensed to a liquid by a pressure of seventeen atmospheres at ordinary temperatures.

177. Composition.—The molecule of the gas being represented by the formula SH_2, it is evident that it contains its own volume of hydrogen. Its composition may be proved by heating metallic tin in it. When cold the gas is found to have regained its original volume and to consist of hydrogen. A piece of paper dipped in a solution of lead acetate is not changed in colour by the residual gas, although it is immediately blackened by sulphuretted hydrogen. The sulphur and tin have combined to form stannous sulphide.

$$\underset{\text{Sulphuretted hydrogen.}}{SH_2} + \underset{\text{Tin.}}{Sn} = \underset{\text{Stannous sulphide.}}{SnS} + \underset{\text{Hydrogen}}{H_2}$$

The experiment may be performed in the following manner :—

Experiment 170.—First close the end of a piece of combustion tubing, eight or ten inches in length, blowing it out into a small bulb ; bend it over, about two inches from the end, to an acute angle. Place a few fragments of granulated tin in the closed end ; fill with sulphuretted hydrogen by displacement and then invert in a small trough of mercury. The mercury should stand in the tube some distance from the bottom ; some of the gas may therefore be allowed to escape by holding the tube over at an angle, its mouth being kept the whole of the time under the surface of the mercury. Clamp the tube with a holder and apply heat very carefully ; the sulphur and tin combine. Allow to cool and observe the volume. Before heating, an india-rubber ring should be slipped over the tube to mark the level of the gas.

178. Acidity of Sulphuretted Hydrogen.—The action of sulphuretted hydrogen on litmus shows that the gas possesses acid properties. These are, however, so feeble that in the case of soluble sulphides carbon dioxide is able to displace the sulphuretted hydrogen. The sulphides of all the metals are insoluble in water, with the exception of those of calcium, barium, strontium, magnesium, sodium and potassium, and a few of the very rare metals. The insolubility of the other metallic sulphides affords to the analyst a very valuable means of separating those metals from the group above mentioned. Whenever two compounds are brought together which respectively contain elements that by their union are capable of forming an insoluble compound, that compound will usually be produced ; so that, although sulphuretted hydrogen is a weak acid, it is thus able to displace stronger ones from many metals. A current of sulphuretted hydrogen passed through a solution of copper chloride precipitates copper sulphide ; thus—

$CuCl_2$	+	H_2S	=	CuS	+	$2HCl$
Copper chloride.		Sulphuretted hydrogen.		Copper sulphide.		Hydrochloric acid.

And this although hydrochloric acid is so much more powerful in its properties.

These sulphides have, in many cases, characteristic colours, by which they are immediately recognised. They possess the further advantage of being divided into two groups, one of which is soluble in dilute hydrochloric acid, the other not so.

Experiment 171.—Prepare a solution in separate test-tubes of each of the following substances :—Arsenious anhydride, copper sulphate, lead acetate, tartar emetic or antimony chloride, zinc sulphate, and ferrous sulphate. Add a few drops of hydrochloric acid to each, and pass sulphuretted hydrogen through each solution from the generating apparatus, washing the leading tube between each solution.

The following results are observed :—

$$\underset{\text{Arsenious anhydride.}}{As_2O_3} + 3SH_2 = 3H_2O + \underset{\text{Arsenious sulphide.}}{As_2S_3}, \text{ Lemon Yellow}$$

$$\underset{\text{Copper sulphate.}}{CuSO_4} + SH_2 = H_2SO_4 + \underset{\text{Copper sulphide.}}{CuS}, \text{ Black}$$

$$\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + SH_2 = \underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Lead sulphide.}}{PbS}, \text{Black}$$

$$\underset{\text{Antimony chloride.}}{2SbCl_3} + 3SH_2 = 6HCl + \underset{\text{Antimony sulphide.}}{Sb_2S_3}, \text{ Orange}$$

$ZnSO_4$ Zinc Sulphate
$FeSO_4$ Iron Sulphate } In acid solution SH_2 produces no precipitate.

Through fresh portions of zinc and iron sulphates, *without* the addition of hydrochloric acid, pass sulphuretted hydrogen :—

$$\underset{\text{Zinc sulphate.}}{ZnSO_4} + SH_2 = H_2SO_4 + \underset{\text{Zinc sulphide.}}{ZnS}, \text{ White}$$

$$\underset{\text{Iron sulphate.}}{FeSO_4} + SH_2 = H_2SO_4 + \underset{\text{Iron sulphide.}}{FeS}, \text{ Black}$$

To these two now add a few drops of hydrochloric acid ; the precipitates are immediately redissolved.

The sulphides are shown by these experiments to be well-defined salts, and a series of bodies of great importance.

Although sulphur is thus able to displace the metals from their compounds with chlorine, owing to the operation of the law previously mentioned, yet chlorine readily decomposes sulphuretted hydrogen, as shown by experiment, the action being—

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Sulphur.}}{S_2} + \underset{\text{Hydrochloric acid.}}{4HCl}$$

179. Decompositions of Sulphuretted Hydrogen.—The great affinity of hydrogen and chlorine for each other causes the decomposition of the sulphuretted hydrogen. Free oxygen has no action on the dry gas, but in the presence of water a slow oxidation takes place. Hence an aqueous solution of sulphuretted hydrogen becomes turbid on exposure to the atmosphere, through the separation of sulphur and the formation of water.

$$\underset{\text{Sulphuretted hydrogen.}}{2SH_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur.}}{S_2} + \underset{\text{Water.}}{2H_2O}$$

A curious and interesting reaction takes place between sulphuretted hydrogen and sulphur dioxide when moist; on bringing together the mouths of two jars containing these gases, they decompose each other with the separation of sulphur and formation of water. Apparently the decomposition is in part determined by the affinity of the sulphur atoms for each other, in the same way as the affinity of oxygen atoms causes the mutual decomposition of hydroxyl and silver oxide. In the above reaction an acid of sulphur known as pentathionic acid is also formed :—

$$\underset{\text{Sulphur dioxide.}}{10SO_2} + \underset{\text{Sulphuretted hydrogen.}}{10SH_2} = \underset{\text{Sulphur.}}{5S_2} + \underset{\text{Water.}}{8H_2O} + \underset{\text{Pentathionic acid.}}{2H_2S_5O_6}$$

This reaction is of interest as being that by which probably much of native sulphur has been deposited, both of these gases being emitted from volcanoes.

Under sulphur dioxide directions are given for the performance of this experiment.

Summary.

Sulphuretted hydrogen occurs free in the gases evolved from volcanoes. May be prepared by passing hydrogen into sulphur vapour; also by the action of sulphuric acid on sulphides. It burns in excess of air to sulphur dioxide and water; with less air sulphur is deposited. The sulphur dioxide produced by its burning may be recognised by its action with ammonia, and also on a mixture of potassium chromate and hydrochloric acid. Sulphuretted hydrogen is soluble in water; is colourless, and has a disgusting odour of rotten eggs; is a non-supporter of combustion. By the action of chlorine it is decomposed. A given volume of the gas contains its own volume of hydrogen; its composition is determined by heating it with metallic tin. It possesses feeble acid properties; certain sulphides possess characteristic colours by which they may be recognised.

Sulphuretted hydrogen is also decomposed by sulphur dioxide.

Laboratory Hints.

After the preparation of sulphuretted hydrogen wash out the apparatus before it is put away; otherwise a mass of crystal of iron sulphate may form. Any remaining iron sulphide should be washed, and returned, when dry, to the jar. There is sometimes some difficulty, when sulphide is taken which has been before used, in getting the action to commence; there should always be a little new sulphide added as well. The difficulty sometimes arises through the acid being too strong.

In Experiment 170 take care that the tin is not allowed to drop into the mercury. The application of heat should be continued for some time.

CHAPTER XXI.

OXIDES OF SULPHUR.

THREE oxides of sulphur are known :—

Sulphur sesquioxide, S_2O_3
Sulphur dioxide or sulphurous anhydride, SO_2
Sulphur trioxide or sulphuric anhydride, SO_3

The latter two of these only will be considered in this work.

SULPHUR DIOXIDE AND SULPHUROUS ACID.

Sulphur Dioxide.—Formula, SO_2. Molecular weight, 63·9. Density, 31·95. Specific gravity, 2·247.

Graphic formula, 

180. Occurrence.—This compound is a gas at ordinary temperatures, and is emitted in vast quantities from volcanoes. The student is already familiar with its preparation by the combustion of sulphur in oxygen.

181. Preparation.—When required for laboratory use it is prepared by the action of some deoxidising agent on sulphuric acid.

It has been already shown that zinc energetically displaces the hydrogen from sulphuric acid ; but certain other metals, as copper, silver, and mercury, are without action, except on the application of heat, when chemical action ensues, which is probably represented by the following equation :—

Cu	+	H_2SO_4	=	$CuSO_4$	+	$2H$
Copper.		Sulphuric acid.		Copper sulphate.		*Nascent* hydrogen.

At the high temperature the nascent hydrogen attacks a second molecule of sulphuric acid ; thus :—

$$\underset{\text{Nascent hydrogen.}}{2H} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

These successive steps in the reaction may be grouped together in one equation :—

$$\underset{\text{Copper.}}{Cu} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

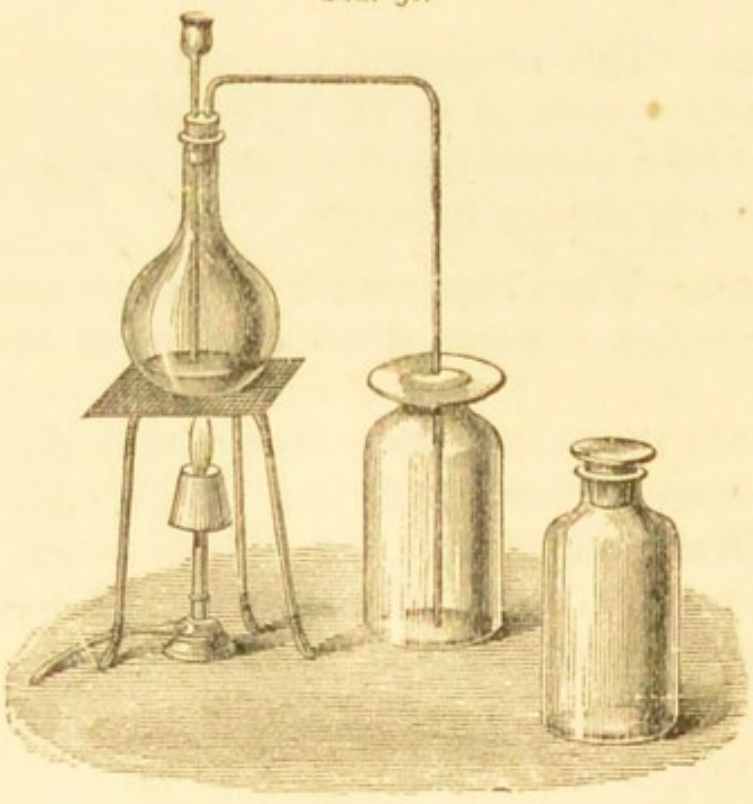
Sulphur dioxide may also be prepared from sulphuric acid by the action of charcoal ; carbon dioxide, however, is also produced :—

$$\underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Carbon.}}{C} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{2H_2O}$$

The gas being soluble in water must be collected by displacement or over mercury. For the purpose of testing the properties of the gas, prepare three jars in the following manner :—

Experiment 172.—Fit up the generating apparatus shown in Fig. 36, put in about half an ounce of copper turnings or strips, set the flask on a tripod or retort stand, pour in three ounces of strong commercial sulphuric acid, and apply heat. After a time, as the temperature increases, the liquid in the flask effervesces, and sulphur dioxide is evolved ; collect by downward displacement. To determine when the jar is full, hold a match near its mouth ; the gas extinguishes it. As soon as the action commences the flame may be lowered. The jars and plates used must be quite dry.

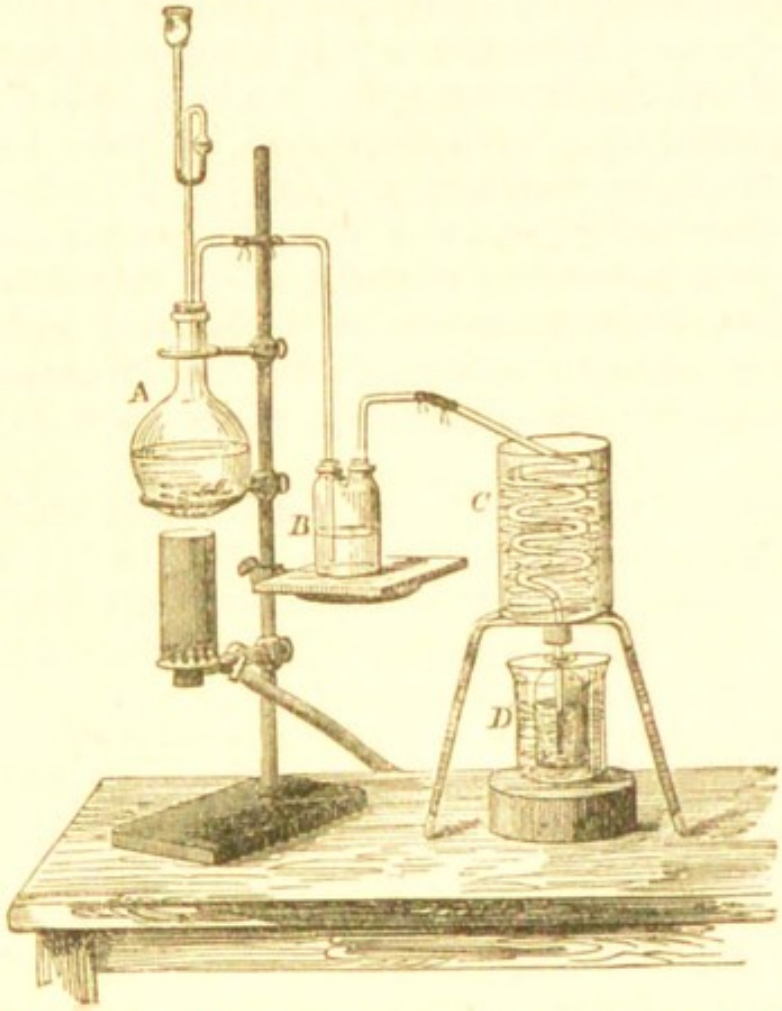
Fig. 36.



182. Properties.—At a temperature of −8° C. sulphur dioxide condenses to a colourless liquid, which freezes at −76° C.; at 15° C. the gas condenses with a pressure of $2\frac{1}{2}$ atmospheres.

Experiment 173.—Dry the gas evolved from the generating apparatus by passing it through concentrated sulphuric acid

FIG. 37.



in a small wash-bottle; next pass it through a spiral glass, or pewter worm, enclosed in a vessel containing a mixture of ice and salt. Let the end of the spiral dip into a test-tube, which is also placed in some of the ice and salt mixture; as the gas passes through the worm it is condensed, and collects in the test-tube. When a little of the liquid has accumulated, pour it on the bulb of an alcohol thermometer, around which cotton-wool has been wrapped; notice the great cold produced by the rapid evaporation. The gas may be retained in the liquid form

by hermetically sealing the tube containing it ; the upper end may be softened and drawn off by the blowpipe while the tube remains in the freezing mixture.

Fig. 37 represents a form of the apparatus : A is the generating flask, B the wash-bottle, C the condensing worm, and D the small bottle, or test-tube, in which the liquefied gas is collected.

Experiment 174.—In one of the jars of gas place a burning taper ; it is immediately extinguished, and the gas does not take fire. In the same bottle pour a little litmus solution, and shake up ; the colour changes to red, and in a little while disappears.

Experiment 175.—Open the second jar under water in the trough ; the water rushes up and fills the jar. Pass some of the gas, after washing in a very small wash-bottle containing a layer of about half an inch of water, into a little distilled water in a beaker, in the same way as sulphuretted hydrogen was obtained in solution ; notice that the gas is almost entirely dissolved, and that the liquid acquires the taste and smell of the gas.

Experiment 176.—Hold over the jet from which the gas is issuing a piece of paper dipped in a mixture of a solution of potassium chromate and hydrochloric acid ; the colour is changed from yellow to green. This is a convenient test for the presence of sulphur dioxide.

Experiment 177.—Prepare a jar of sulphuretted hydrogen, and place on it the remaining jar of sulphur dioxide ; remove the plates ; observe that sulphur is deposited. The reaction was described with an equation in the last chapter.

From experiments the student has seen that sulphur dioxide is a colourless gas with a strong pungent odour ; when diluted with air coughing and sneezing are produced by it ; in a concentrated form it causes suffocation. Water at a temperature of 15° C. dissolves 47 volumes of this gas ; the solution thus produced contains a true acid, sulphurous acid, H_2SO_3, which separates out in cubical crystals at 0° C. ; this is decomposed at a higher temperature, sulphur dioxide escapes, and water remains ; the whole of the gas may be expelled from water by boiling.

$$\underset{\text{Sulphurous anhydride.}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphurous acid.}}{H_2SO_3}$$

Experiment 178.—Add to some of the sulphurous acid previously made some barium chloride solution ; a white precipitate of barium sulphite is formed :—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + \underset{\text{Barium chloride.}}{BaCl_2} = \underset{\text{Barium sulphite.}}{BaSO_3} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

To this add a little pure dilute hydrochloric acid ; the precipitate immediately dissolves.

Place some of the solution away in a beaker or evaporating basin for a week, then add to it some barium chloride and hydrochloric acid ; the white precipitate which first formed does not probably entirely dissolve.

Like other gases which readily condense, sulphur dioxide does not implicitly follow Boyle's law (p. 29) ; the pressure being doubled, the volume contracts to less than one-half.

The gas is neither inflammable nor a supporter of combustion.

183. Bleaching Action.—The action of sulphur dioxide on litmus shows its acidity when in solution ; the further action by means of which it discharges the colour indicates that it possesses bleaching properties. As a bleaching agent it differs remarkably from chlorine ; it will be remembered that the latter decomposes water, seizing the hydrogen, and that the nascent oxygen destroys the colouring matter by change into bodies containing a larger proportion of that element.

Colouring matters which have been acted on by chlorine are entirely destroyed, and cannot be reproduced ; colours removed by sulphur dioxide are again restored either by its displacement by a stronger acid, as dilute sulphuric, or its neutralisation by combination with an alkali. Miller considers the acid to act by forming colourless compounds with the colouring matters. The action is also explained by stating that the colouring matters are reduced, the

sulphurous acid being oxidised into sulphuric ; it is difficult, however, with this assumption, to explain how the addition of either sulphuric acid or an alkali should again restore the colour, as neither of these bodies is an oxidising agent. Sulphur dioxide is used for the bleaching of articles, such as silk, straw, and wool, which would be injured by the action of chlorine.

Experiment 179.—Suspend in the upper part of a deflagrating jar a bunch of red roses, or other coloured flowers ; stand the jar on a dish, over a small spoon or iron plate containing some burning sulphur ; the sulphur dioxide, as formed, discharges the colour. Next dip the flowers in water acidulated with sulphuric acid ; the colour is restored.

In the absence of freshly gathered flowers an infusion of red roses may be employed, and some of the sulphurous acid made in a former experiment added to it.

Sulphur dioxide is used for the purpose of removing traces of chlorine from goods bleached by that agent ; sulphuric and hydrochloric acids are formed by their mutual action, and may be afterwards removed by copious washing ; more usually, however, the sodium salt of sulphurous acid is employed : this possesses the advantage that the alkaline base combines with the resulting acids and forms non-corrosive salts.

From its possessing this property, sodium sulphite is known commercially under the name of antichlor. Its action is represented in the following equation, where it is assumed that excess of the sulphite is used :—

$$\underset{\text{Sodium sulphite.}}{2Na_2SO_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Sulphur dioxide.}}{SO_2}$$

184. Composition. — As the molecule of sulphur dioxide contains two atoms of oxygen, it yields on decomposition its own volume of that gas ; or on burning sulphur in oxygen over mercury the volume of the gas remains unaltered ; from the atomic weight of sulphur being (very

nearly) double that of oxygen, the molecular weight of sulphur dioxide is also double that of oxygen.

185. Sulphurous Acid.—Sulphurous acid is dibasic, and forms two series of salts called sulphites : these are all decomposed by the action of a stronger acid, as sulphuric :—

Na_2SO_3	+	H_2SO_4	=	Na_2SO_4	+	SO_2	+	H_2O
Sodium sulphite.		Sulphuric acid.		Sodium sulphate.		Sulphur dioxide.		Water.

Summary.

Sulphur dioxide is emitted from volcanoes, is prepared by burning sulphur in air or oxygen, and by action of copper or carbon on sulphuric acid. The gas has a pungent odour, is colourless, possesses a characteristic taste, and may be condensed to a liquid by either cold or pressure. It is very soluble in water ; the solution is acid to litmus, and contains a true acid, forming a series of salts known as sulphites.

Sulphurous acid acts as a bleaching agent ; the colour, however, is restored by either the action of very dilute acid or an alkali.

Laboratory Hints.

In inserting copper strips in a flask, take care that they do not drop through the bottom ; the best plan is to hold the flask in a horizontal position and slide them in.

In heating sulphuric acid, take every precaution to prevent the cracking of the flask ; for instance, do not let the flame play direct on the glass. Never hold the hands where there is any danger, in event of a breakage, of the hot acid running on them. Should such a misfortune, by any accident, happen, *immediately* place the burned part under a copious stream of water from the tap. If sulphuric acid is spilled over the woodwork of the bench, strew over it some whiting, and when the action is over let the whole be cleaned up with sawdust.

To make a freezing mixture, pound together in a mortar two parts of ice and one of salt ; scrape this into the vessel containing the condensing worm for the condensation of sulphur dioxide. If such a condenser has to be fitted up, a deflagrating

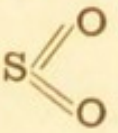
jar turned bottom upwards answers very well for the outer vessel; the mouth should be fitted with a cork, through which the end of the condensing spiral is passed. A worm made of pewter possesses the advantage of being unbreakable.

Should it be desired to preserve a sample in the liquid state, a tube of stouter glass than a test-tube must be employed; it should be drawn out at the neck before being filled, so that the final sealing may be done more quickly. Take care, however, not to draw out the neck so narrow as to prevent the tube from the end of the condenser passing in.

CHAPTER XXII.

SULPHUR TRIOXIDE AND SULPHURIC ACID.

Sulphur Trioxide.—Formula, SO_3. Molecular weight, 79·86. Density, 39·93.

Graphic formula, 

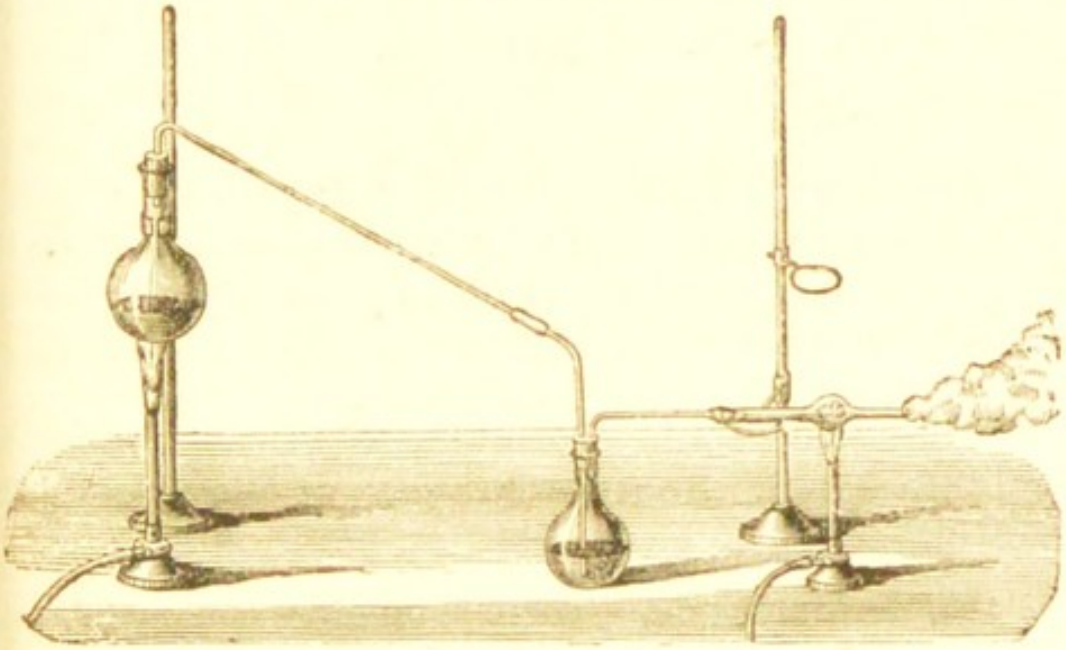
186. Preparation.—Sulphur does not readily combine with more than two atoms of oxygen; but by passing a mixture of sulphur dioxide and oxygen over ignited spongy platinum, sulphur trioxide is produced:—

$$\underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Sulphur trioxide}}{2SO_3}$$

Experiment 180.—Fit up a four-ounce flask as a wash-bottle, and one-third fill it with a saturated solution of sulphurous acid in water. Attach to the long tube in the flask an oxygen generating apparatus (either a small flask or test-tube). Blow a bulb in the centre of a piece of combustion tubing about nine inches long; draw off one end to the size of a piece of quill tubing, and fit a cork and leading tube to the other end. Take some asbestos and soak in a solution of platinum chloride;

dry it and ignite in a small crucible over the Bunsen ; the chlorine is driven off, and a finely divided coating of platinum remains on the asbestos. Introduce this into the bulb of the tube and connect up the whole by india-rubber tubing, as shown in Fig. 38. Heat the oxygen tube ; the gas, in bubbling through the sulphurous acid, disengages some sulphur dioxide, a mixture of the two emerges and passes through the bulb tube. Now heat the bulb containing the platinised asbestos ; white fumes of sulphur trioxide issue from the tube ; convey these by

FIG. 38.



means of a piece of glass tubing, attached with india-rubber, into some distilled water in a small beaker. Add to the water some pure hydrochloric acid and barium chloride ; an insoluble precipitate is formed.

Sulphur trioxide is also produced by the action of heat on Nordhausen sulphuric acid ; thus—

$$\underset{\text{Nordhausen sulphuric acid.}}{H_2S_2O_7} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sulphur trioxide.}}{SO_3}$$

187. Properties.—Sulphur trioxide, as obtained by either of the methods above given, is a white silky-looking mass, which, when purified by repeated distillations in her-

metically sealed tubes, is changed into a colourless liquid. It is devoid of all acid properties, and may be rolled between the *dry* fingers without injury. By passage through a red-hot tube, it is separated into oxygen and sulphur dioxide :—

$$\underset{\text{Sulphur trioxide.}}{2SO_3} = \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Oxygen.}}{O_2}$$

Sulphur trioxide is very deliquescent, and when dropped into water, dissolves with a hissing noise and evolution of great heat, forming sulphuric acid :—

$$\underset{\text{Sulphur trioxide, or sulphuric anhydride.}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sulphuric acid.}}{H_2SO_4}$$

When the two are once united, their separation cannot be effected by heat alone ; for a temperature sufficiently high to dissociate them also decomposes sulphur trioxide into sulphur dioxide and oxygen.

Sulphuric Acid.—Formula, H_2SO_4. Molecular weight, 97·82. Specific gravity of liquid, 1·846. Melting point, 10·5° C. Boiling point, 338°.

188. Importance.—There is no other compound, with the exception of water, which is of such importance to the chemist as sulphuric acid. The frequency of its application to various purposes in the preceding chapters will have given the student some idea of its usefulness, and have rendered him familiar with its appearance, many of its properties, and its composition. It holds an equally important position in the chemical manufactures as in the laboratory. Its preparation is the starting-point in the manufacture of hydrochloric acid, sodium carbonate, nitric acid, and many other bodies of value in the arts.

189. Preparation.—Sulphurous acid, when exposed to the atmosphere, is gradually oxidised to sulphuric acid, as was proved by an experiment described in the preceding

chapter, where directions are given for some sulphurous acid to be left in an open evaporating basin for a week. A solution of barium chloride is employed as a test for sulphuric acid, with which it forms a white precipitate, insoluble in acids :—

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Barium chloride.}}{BaCl_2} = \underset{\text{Barium sulphate.}}{BaSO_4} + \underset{\text{Hydrochoric acid.}}{2HCl}$$

The same precipitate is formed when barium chloride is added to a solution of a soluble sulphate. Barium chloride also produces a precipitate with sulphurous acid, which is, however, soluble in hydrochloric acid. In this way the two acids are distinguished from each other, and sulphuric acid detected in the other's presence.

The change of sulphurous into sulphuric acid is produced more rapidly by the aid of oxidising agents.

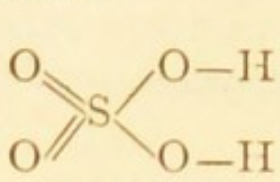
Experiment 181.—To a little sulphurous acid, free from sulphuric acid, add a few drops of pure concentrated nitric acid ; heat gently in a test-tube ; add some hydrochloric acid and barium chloride : a white precipitate of barium sulphate is formed.

The action of the nitric acid is thus represented :—

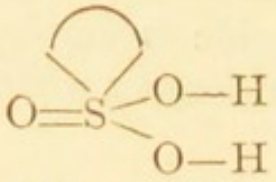
$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{2NO_2} + \underset{\text{Water.}}{H_2O}$$

190. Composition of Acids.—Sulphurous acid may be also oxidised by the action of hydroxyl. This reaction is of some theoretical importance, as many chemists view the acids as a class of bodies in which the hydrogen exists as semi-molecules of hydroxyl. Frankland, to whom we are indebted for a systematic nomenclature which indicates the constitution of bodies, writes the formula of sulphuric acid, SO_2Ho_2. Ho is here used to represent the semi-molecule of hydroxyl, the small 2 qualifying both the hydrogen and oxygen. The same formula is conveniently written $SO_2(HO)_2$. The constitution of oxy-acids is repre-

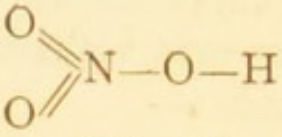
sented according to this theory by the following graphic formulæ :—



Sulphuric acid.



Sulphurous acid.



Nitric acid.

The peculiar interest of the oxidation of sulphur dioxide into sulphuric acid by hydroxyl depends on the fact that it may be regarded as an instance of direct union between the two compounds ; thus—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Hydroxyl.}}{H_2O_2} = \underset{\text{Sulphuric acid.}}{SO_2(HO)_2}$$

The reaction may also be expressed by an equation in which sulphurous acid is oxidised by the second atom of oxygen in hydroxyl :—

$$\underset{\text{Sulphurous acid.}}{H_2SO_3} + \underset{\text{Hydroxyl.}}{H_2O_2} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Water.}}{H_2O}$$

191. Direct Oxidation of Sulphur.—Sulphur itself, when moistened, is in part gradually oxidised into sulphuric acid ; by prolonged boiling with nitric acid, the whole becomes oxidised.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Nitric acid.}}{12HNO_3} = \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Nitrogen peroxide.}}{12NO_2} + \underset{\text{Water.}}{4H_2O}$$

Nitric acid has a similar action on some native sulphides.

192. Manufacture.—Sulphuric acid is always manufactured on the large scale by the oxidation of sulphur dioxide in the presence of water. The reactions involved are of great beauty and interest. The vapour of nitric acid is passed into a chamber with sulphur dioxide, air, and steam. As shown in a previous experiment, the nitric acid is deoxidised into nitrogen peroxide, with the formation of sulphuric acid. A reaction now ensues between the nitrogen peroxide and some more sulphur dioxide, more sulphuric acid is produced, and the nitrogen peroxide is reduced to

nitrogen dioxide. The student will remember that in the presence of air this colourless gas is immediately changed into the ruddy fumes of the trioxide and peroxide. Thus, higher oxides of nitrogen are again formed, and are capable of oxidising more sulphur dioxide. Sulphur dioxide does not readily combine with oxygen, but is immediately oxidised by nitrogen peroxide. The dioxide unites directly with oxygen, and so acts as a carrier of oxygen from the air to the sulphur dioxide. A small amount of nitric acid is thus capable of producing an indefinite quantity of sulphuric acid. The whole series of changes is shown in the following equations :—

$$\underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Nitrogen peroxide.}}{2NO_2}$$

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\substack{\text{Nitrogen}\\\text{peroxide.}}}{NO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{NO}$$

$$\underset{\text{Nitrogen dioxide.}}{8NO} + \underset{\text{Oxygen.}}{3O_2} = \underset{\text{Nitrogen trioxide.}}{2N_2O_3} + \underset{\text{Nitrogen peroxide.}}{4NO_2}$$

The proportions of higher oxides are not constant, but depend on the quantity of oxygen present.

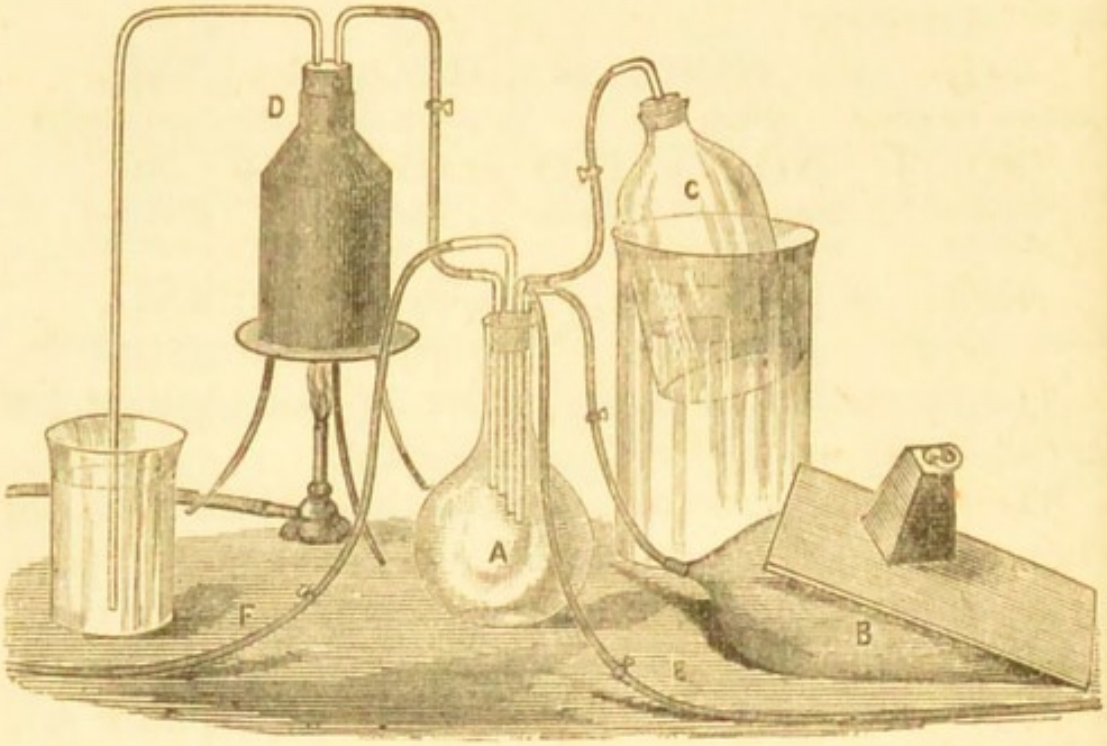
The above equations represent, in the simplest form, the action which takes place. In the absence of water a peculiar crystalline compound is produced, which may be represented by the formula $S_2O_5(NO_2)_2$. This is immediately decomposed by water, with the formation of sulphuric acid and liberation of nitrogen trioxide :—

$$\underset{\text{Crystalline compound.}}{S_2O_5(NO_2)_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sulphuric acid.}}{2H_2SO_4} + \underset{\text{Nitrogen trioxide.}}{N_2O_3}$$

Experiment 182.—In order to study the reactions above explained, fit up the following apparatus : To a dry 32-ounce flask fit a cork, through which bore five holes, and pass through each a piece of glass tubing bent at right angles, four of which reach to about the middle of the flask ; to these attach respectively, by india-rubber tubing, an apparatus for the generation of nitrogen dioxide, another evolving sulphur dioxide, a bag containing air, with a weight on the top, and a flask for the

production of steam. Through the fifth hole a tube is passed, which just enters the flask. This is provided for the escape of the waste gases ; it should be larger than the others, and have a tube leading from it into a flue or stink-cupboard. Instead of having generating flasks for the sulphur and nitrogen oxides, it is a far more convenient plan to prepare these gases previously, and store them in little gas-holders or bladders ; a dry bullock's bladder, through the neck of which a glass tube is passed, answers very well for the sulphur dioxide ; the nitric oxide may be kept in a little gas-holder over water. A screw tap

FIG. 39.



should be placed on the india-rubber tubing connecting each of these to the flask. If this form of the apparatus is used, the student's attention is not required in watching and regulating the evolution of the gases, but instead he can observe minutely the reactions taking place in the flask. The flask or other vessel in which the water is being boiled should have another outlet provided for the steam ; this may conveniently consist of a tube leading to the bottom of a beaker in which there are about four or five inches of water. When the connection between the water flask and the other is closed, the steam forces its way through the water in the beaker ; when this pipe is

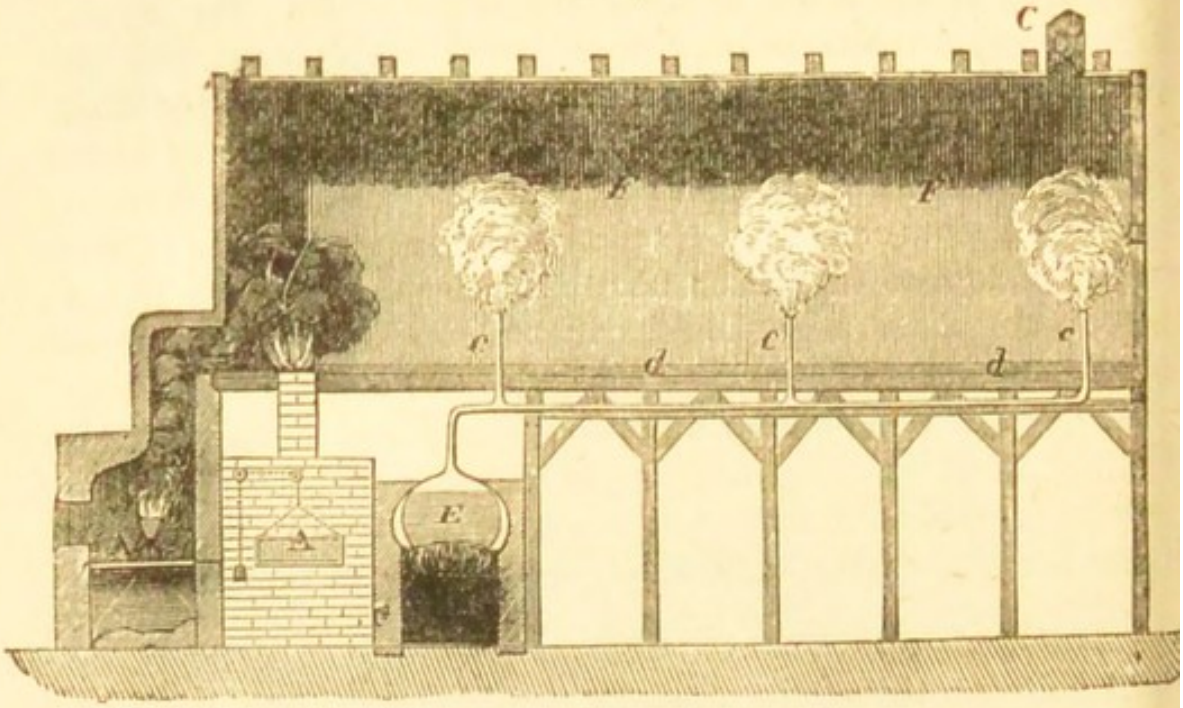
opened the steam takes the channel offering least resistance, viz. into the flask. Fig. 39 shows the whole arrangement. A is the flask in which the reaction goes on ; B is a bladder containing sulphur dioxide under a weight ; C a gas-holder containing nitric oxide ; D is the water flask with escape tube leading into beaker ; E conveys air from gas bag not shown in figure ; F is the exit tube for the waste gases. A description of the gas-holder is given in the laboratory hints for this chapter. The flask having been thoroughly dried, and everything being in readiness, allow a slow current of air, sulphur dioxide, and nitric oxide to pass into the flask ; the ruddy fumes at first formed disappear, and a crystalline deposit is observed on the sides of the flask. Now shut off the whole of these and admit steam ; the crystalline compound disappears, nitrous fumes are evolved, and sulphuric acid condenses and collects at the bottom of the flask. Then re-admit sulphur dioxide, and in the presence of steam the nitrous fumes disappear ; add air, they are again formed ; keep up a slow current of all the bodies, sulphuric acid collects at the bottom of the flask ; take out a few drops of the liquid ; test in the usual way with barium chloride and hydrochoric acid.

Place the remainder in an evaporating basin and apply heat ; at first water is given off ; finally dense suffocating fumes of sulphuric acid are evolved ; remove the flame immediately these are perceived ; a thick, oily-looking liquid remains.

In the manufacture of sulphuric acid the sulphur dioxide is usually produced by roasting sulphur ore (iron sulphide) in a furnace ; in this way a mixture of sulphur dioxide and air is formed. In Fig. 40, A, A represent these furnaces ; a pot *b* is placed in the current of heated gases : this contains a mixture of sodium nitrate and sulphuric acid, from which nitric acid is evolved. A mixture, therefore, of air, nitric acid, and sulphur dioxide is conveyed into the chamber F, F, made of timber framing lined with sheet lead. Steam is generated in the boiler E, and conveyed by jets *c*, *c*, into the chamber. The floor *d*, *d*, is covered by a layer of water, which condenses the acid. In some manufactories, instead of placing a mixture of sodium nitrate and

sulphuric acid in the pot *b*, the acid only is placed in at first, and a solution of the nitrate added in a small stream; in this way a more constant and gradual evolution of nitric acid is maintained. The acid chambers vary from 150 to 300 feet in length; they are about 12 or 15 feet high, and from 15 to 20 wide. From the waste flue C nothing but nitrogen from the air and nitric oxide should escape. The liquid which condenses at the bottom of the chamber is too dilute for most purposes, and is concentrated by evaporation in leaden pans until it contains only about one-fifth of its

FIG. 40.



weight of water; at the temperature required for the expulsion of the remaining water, the leaden pans would probably melt; the further concentration is effected either by heating in vessels of glass or of platinum.

193. Nordhausen Sulphuric Acid.—Nordhausen sulphuric acid may be looked on as a compound of a molecule of ordinary sulphuric acid with a molecule of sulphur trioxide: it is named after a town in Saxony, where it is prepared in large quantities by first drying ferrous sulphate, and at a stronger heat decomposing it. Supposing the

whole of the water were removed before the decomposition of the salt, the change might be thus represented :—

$$\underset{\text{Ferrous sulphate.}}{FeSO_4} = \underset{\text{Ferrous oxide.}}{FeO} + \underset{\text{Sulphur trioxide.}}{SO_3}$$

It is impossible, however, to first drive off the whole of the water, and a portion of the sulphur trioxide being hydrated, the remainder is dissolved :—

$$\underset{\text{Ferrous sulphate.}}{2FeSO_4} + \underset{\text{Water.}}{H_2O} = \underset{\text{Ferrous oxide.}}{2FeO} + \underset{\text{Nordhausen sulphuric acid.}}{H_2SO_4, SO_3, \text{ or } H_2S_2O_7}$$

The molecule of sulphur trioxide, in Nordhausen sulphuric acid, being only held in feeble combination, is readily driven off by heat.

194. Properties.—Sulphuric acid in the pure state is a colourless, odourless liquid of oily consistency. It has a specific gravity of 1·842, and boils at about 338° C. ; the high temperature of the boiling point renders the acid specially suitable for the preparation of the more volatile acids, as nitric acid, from their salts ; any excess of sulphuric acid and the resultant sulphate formed, being non-volatile at the temperature at which nitric acid boils, are thus easily separated.

Sulphuric acid has a very great attraction for water, with which it forms definite compounds ; the union of the two is attended with evolution of great heat.

Experiment 183.—Place not more than a cubic centimetre of water in a test-tube, and add to it the same quantity of the concentrated acid ; observe the heat developed, testing with a thermometer if one be available.

Experiment 184.—Place a small quantity of sulphuric acid in an evaporating basin, and let it remain for a week ; notice that at the end of that time the acid will have increased in volume from the absorption of moisture from the air.

From the avidity with which sulphuric acid absorbs water, it is largely used in the laboratory as a drying agent

for gases. It also attacks most organic bodies, removing from them the elements of water; the preparation of carbon monoxide from oxalic or formic acid is an example of this action. When bodies have an excess of carbon, that element is deposited in the free state, as is the case with sugar.

Experiment 185.—Prepare a concentrated solution of sugar in water and about one-eighth fill a beaker with it; add all at once twice the volume of sulphuric acid; the mixture suddenly froths up, with great heat; a charred carbonaceous mass remains.

Experiment 186.—With dilute sulphuric acid make some marks on a piece of writing paper, and dry it at a gentle heat; as the water evaporates the acid carbonises the paper.

Sulphuric acid, being a dibasic acid, forms two well-marked series of salts, the one of which is normal; the other, still containing half the hydrogen, is acid.

At a white heat the acid is decomposed into water, sulphur dioxide, and oxygen.

Summary.

Sulphur trioxide is a non-acid body produced by the union of sulphur dioxide with oxygen; the two combine when passed over red-hot spongy platinum. It has no action on litmus, but has a great affinity for water, with which it produces sulphuric acid.

Sulphuric acid is a compound of great importance: it is formed by the oxidation of sulphurous acid either by the atmosphere or oxidising agents, as nitric acid, or hydroxyl.

Oxy-acids are considered by some chemists to contain hydroxyl. In oxidation by nitric acid the nitrogen peroxide formed oxidises, a further quantity of sulphurous acid being reduced to nitric oxide, which is immediately reconverted into the higher oxide by the oxygen of the air. Sulphuric acid is manufactured by the reactions occurring between sulphur dioxide, oxygen, nitric acid, and steam. The dilute acid is concentrated by evaporation. Nordhausen sulphuric acid is prepared by heating ferrous sulphate. Sulphuric acid is a colourless, odour-

less liquid, having a great attraction for water. Being a dibasic acid it forms two series of salts called sulphates.

Laboratory Hints.

The apparatus necessary for Experiment 182 should be obtained from the general apparatus in the laboratory. The cork fitted to the large flask should be soaked in melted paraffin. The instrument makers sell bladders, which may be used for the sulphur dioxide; a bullock's bladder, however, answers equally well. To fit it up, soften the neck by soaking in water, pass a piece of glass tubing through, and bind round firmly with thin copper binding wire; the bladder must be *dry* when used, as otherwise the sulphur dioxide is dissolved. Do not fill it long before required for use, and, when done with, squeeze out any gas which remains; blow out the bladder with air and again empty; this will get rid of the sulphur dioxide; the bladder should be put away full of air. In arranging the bladder under a weighted board, take care that it is so fixed that there is no danger of the weight rolling on to the other parts of the apparatus. The air may be stored in a similar bladder, or if there be an oxy-hydrogen lime-light apparatus at hand the *oxygen* bag may be used; after the experiment *completely empty* the bag. The little gas-holder recommended for the nitric oxide is a very useful piece of apparatus in the laboratory. To prepare one take a deflagrating jar holding three pints or two quarts; fit to the top a paraffined cork, through which bore a hole and pass a bent piece of glass tube. Get a beaker or other vessel an inch or two higher than the jar, and of such a size that it easily slides up and down in it; fill this with water, and slip over the glass leading tube a piece of india-rubber tubing and a screw tap. To fill the jar, attach the gas generating apparatus to the tube; the jar as it fills rises higher; when filled, shut off the screw tap: the weight of the jar is sufficient to force the gas out of the holder as required.

CHAPTER XXIII.

BROMINE, IODINE, AND FLUORINE.

195. The Halogens.—The three elements, bromine, iodine, and fluorine, together with chlorine already described, constitute the group known as the 'halogens.' As most acids are oxy-acids, their corresponding salts must contain oxygen; but the halogens yield salts which are binary compounds by direct union with the metals. These salts, from their similarity to sea-salt, are termed 'haloid' salts, and hence the name halogens given to the elements from which, by combination with the metals, they are produced.

The relations of the members of this group to each other are very interesting, but may be studied much better after some knowledge is gained of the elements themselves.

Bromine.—Symbol, Br. Atomic weight, 79·75. Density, 79·75. Specific gravity as gas, 5·51; as liquid, 3·18. Molecular weight, Br_2, 159·5. Molecular volume, $\square$.

196. Occurrence.—Like chlorine, this element is never found free in nature, but in combination with other elements, usually either sodium, potassium, or magnesium. Balard, in 1826, discovered bromine in the mineral matter contained in sea-water; it also occurs in certain mineral deposits, particularly in the vast salt deposits of Stassfurt, in Germany.

197. Preparation.—The first step in the preparation of bromine is to separate the bromides from the chlorides with which they are associated. The solid salts are dissolved, and then concentrated by evaporation; the chlorides, being less soluble, first crystallise out and leave a mother-

liquor in which the bromides predominate. There are two reactions by which bromine may be obtained from this liquid. If chlorine be passed through the solution, bromine is liberated according to the following equation :—

$$\underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Bromine.}}{Br_2}$$

The bromine at first set free imparts a reddish-brown colour to the solution. On shaking this with ether the bromine is dissolved, and its ethereal solution rises to the surface, and may be poured off from the watery layer underneath. On this ethereal solution being treated with potassium hydrate, its red colour disappears, bromide and bromate of potassium being formed :—

$$\underset{\text{Bromine.}}{3Br_2} + \underset{\text{Potassium hydrate.}}{6KHO} = \underset{\text{Potassium bromide.}}{5KBr} + \underset{\text{Potassium bromate.}}{KBrO_3} + \underset{\text{Water.}}{3H_2O}$$

The ether may be distilled off and re-collected ; the solid residue of bromide and bromate is ignited in order to decompose the bromate, which splits up into bromide and oxygen in the same manner as does potassium chlorate. In this way potassium bromide is obtained ; the bromine may again be liberated by gently heating the bromide with manganese dioxide and sulphuric acid, when an analogous reaction occurs to that which takes place when a chloride is similarly heated :—

$$\underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Manganese dioxide.}}{MnO_2} =$$

$$\underset{\text{Hydrogen potassium sulphate.}}{2KHSO_4} + \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Bromine.}}{Br_2} + \underset{\text{Water.}}{2H_2O}$$

At times the mother-liquor, instead of being treated with chlorine, is evaporated down to dryness, and the residue mixed direct with sulphuric acid and manganese dioxide ; but in this case, as chlorides are always present in

greater or less quantity, the bromine is liable to be contaminated with chlorine.

Experiment 187.—Take some potassium bromide, dissolve it in water, and pass chlorine gas through the solution; notice that the colour deepens through the liberation of the bromine. After some time two-thirds fill a large test-tube with the solution and thoroughly cool by holding under a stream of cold water. Next add some ether, close firmly with the thumb, and shake the tube; then hold the tube still for the ether to collect at the surface, keeping the top closed all the while with the thumb until the two liquids have completely separated from each other. Notice that the ether leaves the watery solution almost colourless. (If the solution of bromine in ether is too concentrated it falls to the bottom; in this case add more ether and again shake.) Pour off the ethereal solution; and, shaking up after each addition, add potassium hydrate solution until the colour disappears. Evaporate the solution to dryness and ignite; potassium bromide remains.

Experiment 188.—Powder some potassium bromide, mix with manganese dioxide; place the mixture in a test-tube and add concentrated sulphuric acid. Heat very gently; bromine vapour is given off in abundance and collects in the upper part of the tube. Make this experiment in the stink-closet.

198. Properties.—Bromine at ordinary temperatures is a dark red liquid, so heavy that glass floats readily in it. It gives off a deep reddish-brown vapour at ordinary temperatures, with a smell resembling that of chlorine, only far more intense. Bromine freezes at $-22°$ C. and boils at $63°$ C. Water dissolves bromine; the solution possesses bleaching powers, but not to such an extent as chlorine. In this, as in its other reactions, bromine and chlorine closely resemble each other; but bromine is the less active of the two, and is displaced from its compounds by chlorine.

Bromine combines with hydrogen to form a colourless fuming gas, hydrobromic acid, HBr, very similar to hydrochloric acid. The bromides in appearance and properties closely resemble the chlorides.

Bromine vapour closely resembles nitrogen peroxide in appearance: the following tests distinguish the one from the other. On shaking with a small quantity of ether, bromine is dissolved, and imparts its characteristic tint to the ether; nitrogen peroxide does not affect the colour. If to the bottle or jar containing bromine vapour a solution of potassium hydrate be added, the colour is removed. If this solution be very slightly acidulated by the addition of dilute nitric acid, and then silver nitrate added, there is a precipitate of silver bromide. Similar treatment causes no precipitate with nitrogen peroxide.

Bromides may be readily detected by the reaction with sulphuric acid and manganese dioxide which liberates bromine in the free state.

Iodine.—Symbol I. Atomic weight, 126·53. Density, 126·53. Specific gravity as gas, 8·74; as solid, 4·95. Molecular weight, I_2, 253·06. Molecular volume,  .

199. Occurrence.—Iodine, as well as bromine and chlorine, is found in sea-water, but in much smaller quantities. There are certain varieties of sea-weed which absorb the iodides and store them up in their tissues; from these the iodine of commerce is procured.

200. Preparation.—Such sea-weeds as are sufficiently rich in iodides are dried and then burned; the ashes constitute the substance known as kelp. This kelp is next treated with sulphuric acid and manganese dioxide, when iodine is liberated, according to the equation—

$$\underset{\text{Sodium iodide.}}{2NaI} + \underset{\text{Sulphuric acid.}}{3H_2SO_4} + \underset{\text{Manganese dioxide.}}{MnO_2} =$$

$$\underset{\text{Hydrogen sodium sulphate.}}{2NaHSO_4} + \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Iodine.}}{I_2} + \underset{\text{Water.}}{2H_2O}$$

It should be observed that chlorine, bromine, and iodine are liberated from the chlorides, bromides, and iodides by a precisely similar reaction.

Experiment 189.—Mix some powdered potassium iodide with manganese dioxide and concentrated sulphuric acid in a small retort. Heat gently; purple vapours arise and condense to a blue-black solid on the neck of the retort.

201. Properties.—Iodine is at ordinary temperatures a dark coloured (blue-black) solid, which gives off small quantities of vapour of a splendid violet tint. At 115° C. iodine melts, and boils at a temperature of 200°. The violet tint of the vapour is then almost so dark as to appear black. The vapour possesses an odour resembling that of chlorine; this odour may be distinguished on smelling the substances at ordinary temperatures. Iodine is slightly soluble in water, to which it imparts a light sherry tint; it is much more soluble in solutions of potassium iodide, and also in alcohol and ether. All these solutions are brown in colour. Iodine also dissolves in carbon disulphide, to which it imparts a violet tint resembling that of its vapour.

In chemical reactions iodine closely resembles bromine and chlorine, but is less active than these elements; consequently iodine may be liberated from the iodides by the addition of either bromine or chlorine. On the other hand the oxygen compounds of iodine are much more stable than those of bromine and chlorine.

Iodine is characterised by yielding a most remarkable reaction with starch. The addition of a minute trace of free iodine colours starch solution a deep blue. The colour vanishes on boiling, but reappears as the liquid cools. Iodine when in a state of combination does not give this reaction.

Experiment 190.—Prepare some starch solution by taking a small quantity of starch and shaking up with a test-tube full of cold water. Immerse this tube in a beaker of boiling water until the starch gelatinises, stirring it meanwhile. As soon as the

thickening occurs, remove the tube and stand it in cold water until at the normal temperature.

To a small portion of the starch solution add a drop of solution of iodine in water; notice the blue coloration. Heat to boiling; note its disappearance and subsequent reappearance as the liquid cools.

To another portion of starch solution add some potassium iodide; there is no coloration. Add next a drop of aqueous solution of bromine; a blue colour at once forms as a result of the liberation of free iodine. Repeat the experiment, using chlorine water instead of bromine; the same effect is produced. Add the solutions of bromine and chlorine to separate portions of the starch solution; neither of these produces the blue coloration.

Iodine and hydrogen unite to form hydriodic acid, HI, which in general properties and behaviour resembles hydrochloric and hydrobromic acids. The iodides are very similar to the corresponding bromides and chlorides.

Fluorine.—Symbol, F. Atomic weight, 19·1.

202. Occurrence.—Fluorine occurs in nature in combination with calcium in fluor spar (calcium fluoride), CaF_2, and also in another mineral named cryolite. The teeth of animals also contain traces of fluorine.

203. Properties.—Fluorine is such an exceedingly active element that it is impossible to obtain it in the free state. Whenever liberated by any chemical reaction it immediately attacks the vessel in which it is contained. Little, therefore, is known about this element.

204. Hydrofluoric Acid, HF.—This is the most important compound of fluorine, and, like hydrochloric acid, may be prepared by the action of sulphuric acid on one of its salts, as calcium fluoride. The acid is a gas soluble in water, and most corrosive in its action. The characteristic property of hydrofluoric acid is that it attacks and dissolves glass and other compounds of silica. If glass

be covered with a thin coating of wax, and then a design scratched on the surface with a needle, hydrofluoric acid dissolves the glass where the wax has been removed, and so produces a permanent etching of the design on the surface of the glass.

Experiment 191.—Warm a piece of glass and coat it with wax by letting a little melt on the surface and draining off the excess. When cool write on this coating with the point of a needle. Mix in a small lead dish some powdered fluor spar and concentrated sulphuric acid; warm *very gently*; pungent acid fumes are evolved. Lay the glass plate with its etched face downwards on the top of the dish and let it remain for about five minutes. Remove the plate and clean from the wax; notice that the writing is permanently bitten into the glass.

In this reaction the calcium fluoride is decomposed according to the following equation :—

$$\underset{\text{Calcium fluoride.}}{CaF_2} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Calcium sulphate.}}{CaSO_4} + \underset{\text{Hydrofluoric acid.}}{2HF}$$

205. Review of the Halogens.—It will be seen that the members of this group of elements are characterised by possessing a remarkable similarity to each other. The connection between chlorine, bromine, and iodine is much closer than that with fluorine. Of these first three elements chlorine is a gas, bromine a liquid, and iodine a solid at ordinary temperatures. The density of the series increases with chlorine as the lowest and iodine as the highest. The chemical activity diminishes with the increase in density. Fluorine has a lower atomic weight than chlorine, and possesses greater chemical activity. The salts of these elements are very much alike; those of the same metal commonly crystallise in the same form.

Summary.

The group called halogens consists of chlorine, bromine, iodine, and fluorine.

Bromine is a dark red coloured liquid evolving vapours of the same colour, occurs in sea-water, and is obtained from the bromides by action of sulphuric acid and manganese peroxide. Bromine is similar in general behaviour to chlorine, but possesses less activity, and may be displaced from its compounds by chlorine.

Iodine is a dark grey solid which when warmed evolves deep violet-coloured vapours. Iodine is found in the ashes of sea-weeds, and is obtained by treatment with sulphuric acid and manganese dioxide. Iodine also resembles chlorine in chemical behaviour, but is even less active than bromine. Iodides are decomposed by either free bromine or chlorine. Iodine is characterised by imparting a deep blue colour to starch solution : it only possesses this property when in the free state.

Fluorine is so active that it is unknown in the free state : its principal compound is hydrofluoric acid, which possesses the property of dissolving glass.

Laboratory Hints.

Remember that ether is very inflammable, and that it evolves vapour with great rapidity ; the vapour mixed with air is explosive ; in consequence great care must be exercised in bringing a light near ether. Small quantities only should be used at a time. A store-bottle should be kept and a small one filled from it in a room where there are no lights burning.

As bromine vapour possesses such an overpowering smell, take care to get as little as possible of it about the room or laboratory.

In making a starch solution take care not to have it too thick ; it should be sufficiently dilute to pour as readily as oil.

Hydrofluoric acid is very corrosive ; care must therefore be taken that none of it gets on the skin.

CHAPTER XXIV.

PHOSPHORUS AND SILICON.

Phosphorus.—Symbol P. Atomic weight, 30·96. Density, 61·92. Specific gravity of ordinary variety, 1·83. Molecular weight, 123·84. Molecular volume,  .

Phosphorus is distinguished from all other elements we have so far described by there being four instead of two atoms in the molecule. The conventional symbol above given is intended to indicate not that the molecule of phosphorus is twice the normal volume, but that, with the same molecular volume as other bodies in the gaseous state, it, the molecule, contains four atoms.

206. Occurrence.—Phosphorus is not found free in nature, but occurs in many igneous rocks; thus minute crystals of minerals containing phosphorus may be discerned by the microscope in granite. These rocks, by their decomposition, produce soil which also contains phosphorus as phosphates. These are assimilated by plants and are found especially in the seeds; thus considerable quantities of phosphorus occur in wheat. In their turn animals assimilate the phosphates of vegetable food, and use them in building up certain compounds occurring in the brain and elsewhere, but more especially in the formation of bone, the mineral part of which, or bone-ash, consists largely of calcium phosphate. From this compound the phosphorus of commerce is prepared.

207. Preparation.—The first step in the preparation of phosphorus is to mix bone-ash with two-thirds of its weight of sulphuric acid diluted with water. Calcium phosphate is insoluble, but under this treatment is transformed into a soluble acid-phosphate, commonly known as

superphosphate of lime. The following equation represents the change which occurs :—

$$\underset{\text{Calcium phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Calcium hydric phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Calcium sulphate.}}{2CaSO_4}$$

The calcium sulphate is allowed to settle and then the clear solution of acid phosphate is evaporated down to the consistency of a syrup and mixed into a paste with powdered charcoal. This is dried and then heated to low redness in an earthenware retort, the stem of which dips under water.

The first result of the application of heat is that the acid or hydric-phosphate loses its water, being converted into a salt known as the metaphosphate :—

$$\underset{\text{Calcium hydric phosphate.}}{CaH_4(PO_4)_2} = \underset{\text{Calcium metaphosphate.}}{Ca(PO_3)_2} + \underset{\text{Water.}}{2H_2O}$$

The metaphosphate is at the high temperature decomposed by the charcoal ; thus :—

$$\underset{\text{Calcium metaphosphate.}}{3Ca(PO_3)_2} + \underset{\text{Carbon.}}{10C} = \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Calcium phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Carbon monoxide.}}{10CO}$$

The phosphorus thus produced distils over, and is purified by re-distillation and squeezing through wash-leather under warm water.

208. Properties.—Phosphorus is an almost colourless (slightly yellow) and transparent solid, having at ordinary temperature the consistency of bees'-wax, and may be cut with a knife. At the freezing point it becomes considerably harder and more brittle ; it then shows on being broken evidences of crystalline structure. Phosphorus melts at a temperature of 44·3° and boils at 290° C. ; the vapour is colourless. When exposed to the air phosphorus is seen to evolve small quantities of smoke, and in the dark is distinctly luminous. From this property it has received its name, which signifies light-bearer. The fumes emitted consist of phosphorus trioxide, P_2O_3, and the light is due to slow combustion of the phosphorus. This element is character-

ised by its great inflammability; at a temperature of about 44°, a very little over its melting point, it takes fire, and, as the student already knows, burns brightly with the formation of phosphorus pentoxide. Phosphorus is easily ignited by a slight amount of friction. Phosphorus is insoluble in water, slightly soluble in alcohol or ether, and readily soluble in carbon disulphide. Owing to the readiness with which it undergoes oxidation, phosphorus is kept under water, which liquid it does not decompose.

Experiment 192.—Cut some phosphorus, under water, into small fragments and carefully wipe them thoroughly dry. Add carbon disulphide to them in a test-tube; notice that the phosphorus dissolves readily and completely. Pour a few drops of the liquid on a dry crumpled newspaper; the liquid rapidly evaporates and leaves a residue of finely divided phosphorus. This oxidises so rapidly that it takes fire spontaneously and also ignites the paper.

209. Red or Amorphous Phosphorus.—In addition to the yellow variety, phosphorus occurs in another totally distinct form, known as red or amorphous phosphorus. If ordinary phosphorus be maintained at a temperature of 240° for some time, it is more or less completely changed into an opaque reddish mass, without any alteration of weight. This, on purification from the ordinary form, constitutes amorphous phosphorus. This modification differs most remarkably from the yellow kind. It is not luminous when exposed to air, does not oxidise, and so need not be kept under water. It remains solid up to a temperature beyond 250°, and does not take fire when heated in the air until 260° is reached. At this point it becomes changed into the yellow variety, and burns. If the heating be conducted in a retort filled with carbon dioxide, so as to prevent combustion, the same weight of yellow phosphorus is produced, proving most clearly that the two varieties are only allotropic modifications of one and the same element. Further, both, on being burned, produce the same weight of phosphorus pentoxide. Amorphous phosphorus is insoluble in carbon disulphide.

The change from the yellow to the red variety is much hastened by the presence of iodine in small quantities.

Experiment 193.—Place a piece of phosphorus, the size of a pea, in a long and narrow test-tube, drop on it a very small fragment of iodine ; combination at once occurs with the formation of a small quantity of phosphorus iodide. Heat gently ; the phosphorus melts and takes fire, but soon exhausts the whole of the air in the tube ; continue to warm gently for a little time and most of the phosphorus will be seen to become of a dark-red colour. Cork up the tube and allow it to cool. When quite cold pour some carbon disulphide into another tube and put away the bottle, and then from the tube pour the disulphide on to the altered phosphorus. Cork up and allow the tube to stand for some time, giving it an occasional shake. Pour off the carbon disulphide, and a residue of amorphous phosphorus remains.

Take a little commercial red phosphorus and note the absence of odour, also its non-luminosity. Heat it on a sand-bath or in an iron spoon ; note that it requires to be heated to a high temperature before it commences to burn.

Phosphoretted Hydrogen. — Formula, PH_3. Molecular weight, 33·96. Density, 16·98. Specific gravity, 1·17.

210. Preparation.—On boiling a strong solution of caustic soda or potash with phosphorus, a spontaneously inflammable gas is evolved, having the odour of putrid fish, and approximately the composition PH_3. This gas is phosphoretted hydrogen or phosphine.

Experiment 194.—Fit to an eight-ounce flask a cork and rather large delivery tube with its end leading into a pneumatic trough containing water, and arrange in a retort stand. In the flask place a few fragments of caustic potash together with some small pieces of phosphorus and a little water. Pass coal gas into the upper part of the flask, so as to completely displace the whole of the air ; then cork up tightly. Gently heat the flask ; bubbles of gas arise and displace the coal gas. In a short time, each bubble as it rises to the surface of the water in the trough bursts

into flame and generates an extremely beautiful vortex ring of smoke.

At this stage collect over the trough a jar of the gas and having tightly corked it expose for some days to the light. The inside of the jar will be found to be covered with a yellow film; and if it be opened the gas will be found to have lost its property of spontaneous inflammability. Apply a light; it burns with readiness.

The reaction by which phosphoretted hydrogen is thus produced is a somewhat complicated one, and may be thus expressed :—

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{3KHO} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Potassium}\\\text{hypophosphite.}}}{3KH_2PO_2} + \underset{\substack{\text{Phosphoretted.}\\\text{hydrogen.}}}{PH_3}$$

In addition to the phosphoretted hydrogen, PH_3, traces of another phosphide of hydrogen, P_2H_4, are formed. It is the presence of these which cause the gas to inflame spontaneously. The gas on standing loses this property, because the second phosphide, P_2H_4, suffers decomposition.

In the above method of preparing the gas, milk of lime (*i.e.* lime suspended in water) may be employed instead of caustic potash.

211. Properties. — Phosphoretted hydrogen is a colourless gas with an unpleasant odour of putrid fish. The gas is inflammable, and a non-supporter of combustion.

Phosphoric Acid.—Formula, H_3PO_4. Molecular weight, 97·84.

212. Preparation.—When phosphorus is burned in air or oxygen, phosphorus pentoxide is formed, according to an equation already familiar to the student. If the pentoxide be dissolved in water a hissing noise is produced, and phosphoric acid formed :—

$$\underset{\substack{\text{Phosphorus}\\\text{pentoxide.}}}{P_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

A method commonly employed for the preparation of

this body is to oxidise phosphorus with nitric acid, when the following reaction occurs :—

$$\underset{\text{Phosphorus.}}{P_4} + \underset{\text{Nitric acid.}}{10HNO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Phosphoric acid.}}{4H_3PO_4} + \underset{\text{Nitrogen trioxide.}}{5N_2O_3}$$

The solution on evaporation at the close of the reaction yields a viscid liquid, from which colourless crystals of phosphoric acid may be obtained.

Experiment 195.—Thoroughly dry a large bell jar and plate on which it may stand. Wipe a piece of phosphorus quite dry, and also a deflagrating spoon. Burn the phosphorus in the bell jar and allow the pentoxide to subside. Add a few drops of water, and notice the hissing noise as combination occurs.

One-third fill a beaker about six inches high with a mixture of two parts concentrated nitric acid and one of water. Cut a few fragments of phosphorus and drop them into the acid. Heat gently in a stink-cupboard ; nitrous fumes are evolved and the phosphorus is dissolved. If the action ceases before the whole of the phosphorus disappears, add a little more acid, and so dissolve the whole. At the close of the reaction evaporate down the liquid until it attains a temperature of 150° C. Phosphoric acid remains.

213. Properties.—There are not only several acids of phosphorus, but also several varieties of phosphoric acid, depending on the number of molecules of water with which a molecule of phosphoric anhydride is united. That described is the common or ortho-phosphoric acid. This acid contains three atoms of replaceable hydrogen, and so is tribasic. In the normal salts the whole three atoms are replaced by metals, but in the acid salts either one or two atoms of hydrogen may remain. The following series is illustrative of the various salts of phosphoric acid :—

H_3PO_4, Phosphoric acid.
NaH_2PO_4, Dihydric sodic phosphate.
Na_2HPO_4, Hydric disodic phosphate.
Na_3PO_4, Normal sodic phosphate.

Of these compounds the disodic phosphate is neutral to litmus, the monosodic salt has an acid, and the trisodic salt an alkaline reaction.

Silicon.—Symbol, Si. Atomic weight, 28·0. Specific gravity of crystals, 2·49.

214. Occurrence.—Next to oxygen this is the most plentiful of all the elements ; its oxide, SiO_2, occurs in the free state, as flint and quartz ; and also in combination as one of the principal constituents of most rock formations except those of coal and limestone. Silicon does not occur free in nature, and its properties as an element need not here be described.

Silicon Dioxide, Silica.—Formula, SiO_2. Molecular weight, 59·92. Specific gravity as quartz, 2·6.

215. Occurrence.—As has already been mentioned, this compound is widely distributed in nature as a rock constituent. Quartz and amethyst are examples of a crystalline variety, and agate, chalcedony, opal, and flint consist of silicas in an amorphous form mixed with more or less of the crystalline form.

216. Properties.—Quartz is, when pure, transparent and colourless : it is so hard that it scratches glass. Quartz crystals consist of hexagonal prisms capped with hexagonal pyramids. Quartz is insoluble in water and all acids, except hydrofluoric acid, by which it is readily attacked. It is not liquefied by the heat of the strongest furnaces, but may be melted into a glassy mass by the oxy-hydrogen blowpipe.

Silica is sometimes termed silicic anhydride because with water it forms acids and unites with bases to produce salts. Prolonged boiling with concentrated solutions of caustic potash or soda dissolves crystalline silica very slowly, but has a more rapid action on the amorphous varieties.

When fused with either of the alkaline carbonates an alkaline silicate is formed—

$$\underset{\text{Silica.}}{SiO_2} + \underset{\text{Potassium carbonate.}}{2K_2CO_3} = \underset{\text{Potassium silicate.}}{K_4SiO_4} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

Carbon dioxide escapes and the remaining silicate is soluble in water, and constitutes the substance known as water-glass. If hydrochloric acid be added to the solution, potassium chloride and silicic acid are formed :—

$$\underset{\text{Potassium silicate.}}{K_4SiO_4} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Potassium chloride.}}{4KCl} + \underset{\text{Silicic acid.}}{H_4SiO_4}$$

If the solution be concentrated the silicic acid separates out as a gelatinous mass, but if sufficiently dilute it remains dissolved. On the solution being placed in a drum with the bottom made of parchment paper, and this floated in its turn in a vessel of water, the potassium chloride being a crystalline body diffuses through the membrane, and a pure solution of silicic acid remains behind. In this way a solution of quartz or silica is produced. This solution may be concentrated by careful evaporation until it contains about 14 per cent. of silica ; but the solution of this degree of strength is liable to assume the gelatinous form. On further concentration the silica separates out, and on evaporation to complete dryness remains as an amorphous white powder, insoluble in water and acids.

Experiment 196.—Reduce some flint or quartz to an impalpable powder : this is most easily effected by heating to redness and plunging into cold water. The fragments then powder somewhat easily. Fuse some potassium carbonate in a platinum crucible over a good foot blowpipe flame. When quite tranquil at a bright red heat, add a small pinch of the powdered silica ; notice that effervescence occurs and that the silica is entirely dissolved. Continue the addition of silica so long as it is dissolved. Allow the crucible to cool and dissolve

out its contents with water. Add dilute hydrochloric acid until the solution has an acid reaction, then evaporate to complete dryness ; ignite gently and treat with water. Potassium chloride dissolves and insoluble silica remains.

The formula of silicic acid has been written H_4SiO_4, but there are several other modifications of the acid produced by the combination of water and silicic anyhdride in various proportions. The silicates are extremely complex in composition, frequently containing several metals and many molecules of silica, derived not merely from one but frequently two or more modifications of silicic acid.

Summary.

Phosphorus occurs as a constituent of igneous rocks ; obtained from phosphates by reduction with carbon; is inflammable; exists in two forms, which differ widely from each other in properties.

Phosphoretted hydrogen is prepared by heating phosphorus with caustic potash solution, and is an inflammable gas, with odour of putrid fish. The presence of liquid phosphoretted hydrogen causes the gaseous variety to become spontaneously inflammable.

Phosphoric acid is formed by hydration of phosphoric anhydride or by oxidation of phosphorus by nitric acid. This acid is tribasic and forms an extended series of salts.

Silicon is a widely distributed element, but does not occur free in nature ; its most important compound is silica

Silica is the only known oxide of silicon, and occurs as quartz, flint, and in other rocks. Is insoluble in acids except hydrofluoric ; dissolves when fused with alkaline carbonates to form soluble silicates, hence is viewed as the anhydride of silicic acid. From a solution of alkaline silicates, by the addition of hydrochloric acid, soluble silicic acid is formed, and may be obtained in the pure state by diffusion of the alkaline chlorides through a membrane. Silicic acid solution, on being evaporated to dryness, yields silica once more in the insoluble form

Laboratory Hints.

The student will already be sufficiently familiar with the properties of phosphorus to know that it requires extremely careful handling. In those experiments where carbon disulphide is used, be careful that the main supply bottle is kept at a distance from the phosphorus.

At times, in experiment, the phosphorus re-ignites on the top of the tube on the removal of the cork ; should it do this cork again and keep for a day or two. Or, if wished, a current of carbon dioxide may be passed down the tube until the whole of the phosphorus vapour is displaced. The carbon disulphide may then be poured in in safety.

In the preparation of phosphoretted hydrogen the coal gas is passed in in order to expel any acid, as otherwise the phosphoretted hydrogen would take fire within the flask and possibly burst it. Remember that if any air remains with the coal gas the phosphoretted hydrogen may explode the mixture, and so cause considerable damage by scattering the molten phosphorus. In the case of an inexperienced student, it would be safer to displace the air by carbon dioxide rather than by coal gas.

At the close of the experiment allow the liquid in the flask to cool until water is drawn up into it from the trough. Pull out the cork, holding it in a duster ; the gas within the flask will take fire ; therefore have in readiness a jug of cold water, with which at once fill the flask to the brim.

Platinum crucibles and dishes must be handled carefully. When heated over the blowpipe flame they should be supported in a pipeclay triangle.

PRINCIPLES OF ANALYSIS.

ABBREVIATIONS USED IN THIS SECTION.

Ppt.	for	precipitate.
Pptd.	,,	precipitated.
Sol.	,,	soluble.
Insol.	,,	insoluble.
Conc.	,,	concentrated.
O. F.	,,	oxidising flame.
R. F.	,,	reducing flame.

THE student is now in a position to proceed further in his study of practical chemistry by learning the principles of analysis and their application to the separation and recognition of unknown bodies.

There are two descriptions of analysis—**qualitative**, by which the constituents of a substance are detected, and **quantitative**, by which their actual amount is determined. The first only of these will be dealt with in this work, the study of quantitative analysis belonging to a much more advanced stage of chemistry.

The substances that a student is likely to require to analyse are either metals (including alloys), or salts. In some few cases he may meet with free acids.

The following pages contain an account of the analytical reactions of the metals and inorganic acids undermentioned, and also systematic tables for the analysis of unknown substances which may contain all or any of them:—**Silver, lead, mercury, copper, bismuth, cadmium, tin, arsenic, antimony, iron, chromium, aluminium, zinc, manganese, nickel, cobalt, barium, strontium, calcium, magnesium, potassium, sodium**, and the com-

pound radical **ammonium**; **sulphuretted hydrogen, hydrochloric, hydrobromic, hydriodic, hydrofluoric, nitric, chloric, boric, carbonic, phosphoric, silicic,** and **sulphuric acids.** The reactions of the following organic acids are also given, and tables are appended for the analysis of their salts with inorganic bases ;—**Hydrocyanic, formic, acetic, benzoic, succinic, oxalic, tartaric,** and **citric acids.**

There are two distinct methods of making the qualitative analysis of a body. The first is called the '**dry way,**' because experiments are made on the substance without its being dissolved. These experiments consist of heating it on charcoal, and in other ways observing its behaviour under certain conditions. In the second method the body is first obtained in solution, and then subjected to the reaction of different reagents. The production of a precipitate having a characteristic colour or other distinctive properties enables the analyst to recognise the substance, and also to separate it by filtration from those still remaining in solution. Each of these courses has its advantages, and usually a combination of the two is preferable to one only taken singly. In the tables given further on there are first directions for a preliminary examination by the dry way, and afterwards a wet analysis. The results of the one should confirm those of the other, and often the metals difficultly recognised by the one method give very characteristic reactions by the other.

The term **reaction** is applied to any chemical change employed in analysis. The substance applied to produce the change is called a **reagent.**

For purposes of analysis the metals are arranged in five groups, depending on the insolubility of certain of their salts. Thus :—

Group I.	Group II.	Group III.	Group IV.	Group V.
Metals whose chlorides are insoluble.[1] They may be precipitated by **Hydrochloric Acid.**	Metals whose sulphides are insoluble in dilute hydrochloric acid.[2] They may be precipitated by **Sulphuretted Hydrogen**	Group III. A.[5]—Metals whose hydrates are insoluble in excess of ammonia and ammonium chloride. They may be precipitated by **Ammonia** in the presence of **Ammonium Chloride.**	Metals whose carbonates are insoluble in an alkaline solution. They may be precipitated by **Ammonium Carbonate** in the presence of **Ammonium Chloride** and **Ammonia.**	Metals not precipitated by any group reagent.
Silver as $AgCl$. Lead as $PbCl_2$. Mercury as Hg_2Cl_2.	Mercury as HgS.[3] Lead as PbS.[4] Bismuth as Bi_2S_3. Copper as CuS. Cadmium as CdS. Tin as SnS or SnS_2. Antimony as Sb_2S_3. Arsenic as As_2S_3.	Iron as $Fe_2(HO)_6$. Aluminium as $Al_2(HO)_6$. Chromium as $Cr_2(HO)_6$.	Barium as $BaCO_3$. Strontium as $SrCO_3$. Calcium as $CaCO_3$.	Magnesium. Potassium. Sodium. Ammonium.[6]
		Group III. B.—Metals whose sulphides are insoluble in an alkaline solution. They may be precipitated by **Ammonium Sulphide** in the presence of **Ammonium Chloride and Ammonia.**		
		Zinc as ZnS. Manganese as MnS. Nickel as NiS. Cobalt as CoS.		

[1] When solubility is referred to, water is always understood as the solvent, unless some other is stated.

[2] In each group the metals of those preceding are supposed to be absent, thus the metals of Group I. also form insoluble sulphides in HCl, but in analysis would be removed previous to the precipitation of Group II.

[3] Mercury and a few other metals form two series of salts in which the metal has different active atomicities.

[4] $PbCl_2$ is somewhat soluble in cold water, and thus a small quantity of lead is always found in Group II.

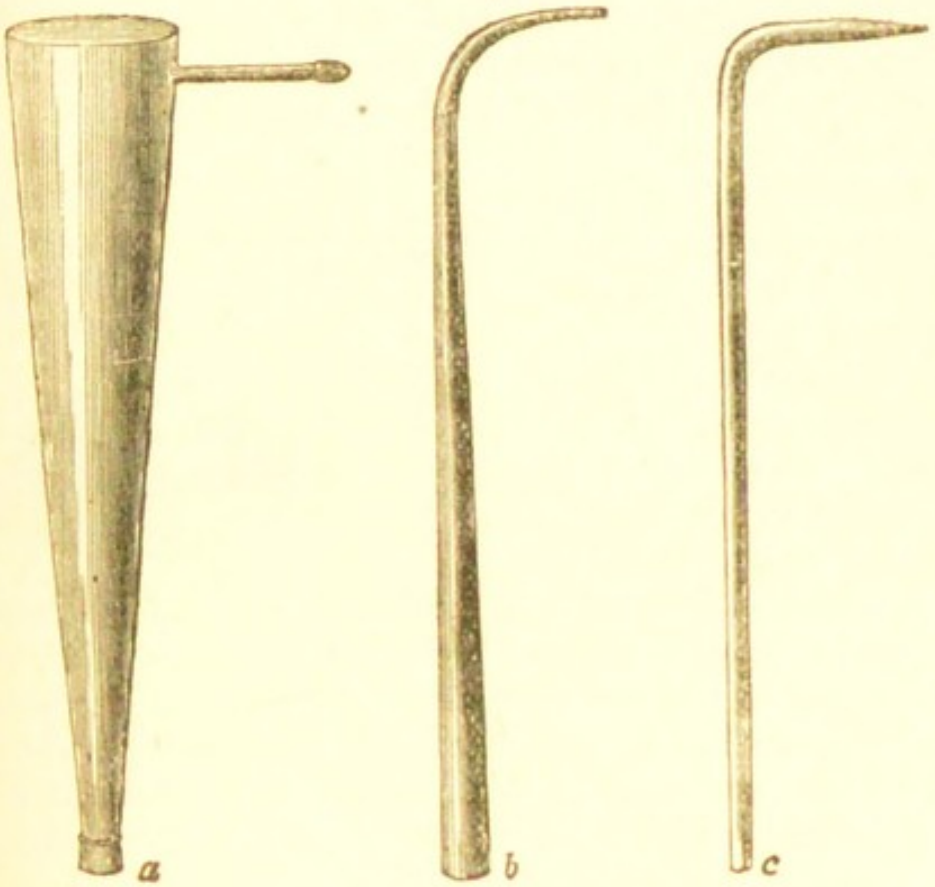
[5] The metals of Group III., A and B, are usually classed together as one group; for this reason the subdivision here adopted is referred to by letters instead of calling Group III. B, Group IV., as so doing would interfere with the usual numbers given to the groups.

[6] Ammonium is usually spoken of as a metal in analytic tables for the sake of brevity.

Operations.

Many analytic experiments require the use of methods that so far are unknown to the student. Of these the most important is the use of the blowpipe for heating purposes. There are several forms of this instrument, two of which are shown in Fig. 41, *b* and *c*, but for laboratory use the conical form devised by Black is the most convenient; it is represented in Fig. 41, *a*

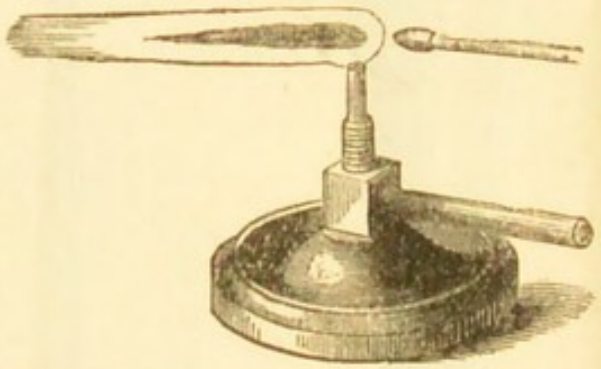
Fig. 41.



The conical tube is preferably of brass, and has a bone or ivory mouthpiece at the smaller end; the other is closed, and near it through the side of the tube a smaller one projects, to the end of which the jet is attached. The moisture of the mouth collects, while blowing, in the end of the cone instead of being blown out through the jet. In using a blowpipe the air must be forced out by the cheeks, and *not* from the lungs. A practical lesson from a teacher will do more toward teaching how this is done properly than a long description can do. Still, by attention to the following directions, the art may in most cases be

readily attained. First, with the mouth closed, inflate the cheeks with air from the lungs as full as possible; then keep on breathing through the nose with the cheeks still distended. Before long it will be found that breathing can proceed in this way, whether the cheeks be full or empty. In the next place prepare a small glass jet by drawing out a piece of fine quill tubing in the flame. While trying the experiment of breathing with the cheeks distended, introduce the end of this jet between the lips: the elasticity of the cheeks will slowly force the air out of the mouth through the jet, but this will not interfere with the act of breathing. When the mouth is nearly empty, refill it by forcing some of the air contained in the throat and lungs into it. This is the most difficult part of the whole process, but a very little practice should enable the operator to do this without ceasing to blow.

FIG. 42.

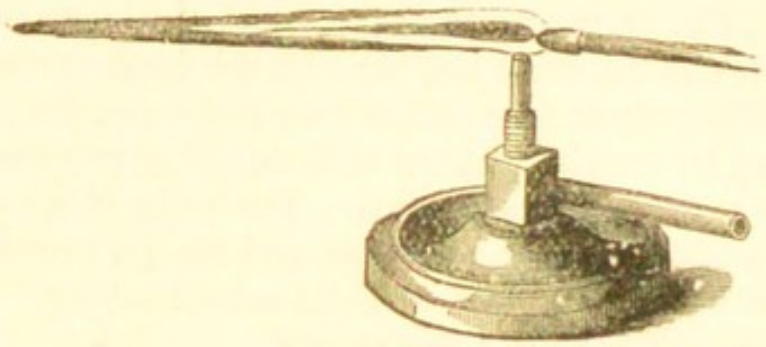


A blowpipe may be used with either a spirit or oil lamp, but in all cases where gas is obtainable it will be found most convenient. A suitable form of flame is obtained by the use of a jet to be dropped inside the tube of a Bunsen burner, or a tube with the same shaped orifice is sometimes made to screw on to the base of the Bunsen (as in Fig. 42), instead of the ordinary brass tube which is first unscrewed. With a tube of this kind the ring must be turned so as to shut off the air at the bottom of the burner.

There are two varieties of blowpipe flame, known respectively as the '**reducing**' and '**oxidising**,' from their action on oxides and metals. The reducing flame is shown in Fig. 42. To produce it, hold the jet of the blowpipe just outside the flame, and blow gently; the flame should appear of a luminous yellow tinge, through its still containing unoxidised carbon. This exerts a powerful reducing action, the carbon combining with the oxygen of many oxides when placed in it. An 'oxidising' flame (Fig. 43) is produced by placing the blowpipe jet within the flame, and blowing rather harder. The flame should be sharply defined. The point of the fine blue cone

in the middle of the flame is the region of greatest heat. Slightly beyond this there is an excess of air, and this

Fig. 43.



readily yields oxygen to any substance capable of combining with it.

Substances may be held in the blowpipe flame on a piece of *good* charcoal. This is a difficult article to obtain. Prepared charcoal blocks answer very well; those known as 'Bunring's patent' are very good. A small cavity to receive the body should be cut out with a penknife. When one experiment has been made, the face of the charcoal must be cut away until a clean surface is exposed. Other supports are sometimes used for particular experiments, as platinum wire, a thread of asbestos, or the fragment of carbon produced by charring a lucifer match.

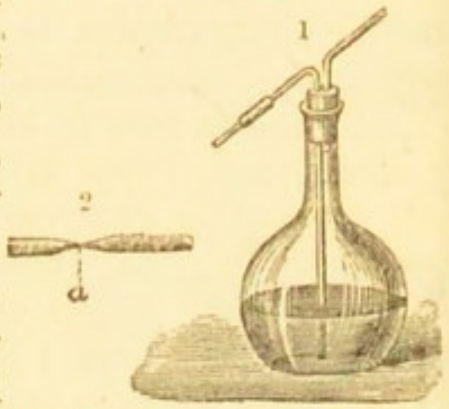
Fig. 44.



Several metallic oxides dissolve in fused borax, and produce a glass of characteristic colour. These reactions are performed most easily by obtaining a bead of borax on a loop of fine platinum wire. Fig. 44 shows a single and double loop of the actual size they should be made. To form a bead, make the wire red-hot in the Bunsen flame, and then dip it into some powdered borax. Next heat it either in the Bunsen or blowpipe flame until the borax melts down into a colourless and transparent bead. A fragment of the substance to be tested is then to be placed on the bead, which is again fused. The characteristic colour makes its appearance as the bead cools.

For washing precipitates, and to hold distilled water for general purposes, a 'wash-bottle' is required. To make this, get a 24-oz. flask, and fit a good cork to the mouth. Through this bore two holes; bend two pieces of glass tubing to the shape shown in 1, Fig. 45, the acute-angled one reacning to the bottom of the flask, and the other just through the cork. From another piece of tubing about four inches long make two jets, as shown in 2, Fig. 45, by drawing out the tube slowly after softening it in the middle over the Bunsen flame. The ends of all the tubes must be rounded with the blowpipe, and the jet attached to the wash-bottle by a small piece of india-rubber tubing. On blowing into the shorter tube a fine stream of water issues from the jet, and may be sent in any direction by bending the tube at the india-rubber joint. To obtain a larger stream, invert the bottle, and the water will run from the shorter tube.

FIG. 45.



While working at analysis, the student should bear in mind the following few directions. Test-tubes, beakers, and all other apparatus used for analysis must be **scrupulously clean.** Never put anything away dirty; a piece of apparatus that would take a minute to wash immediately after use will probably require five after lying by for a week. Give glass apparatus in general a couple of washings with tap water and then one with distilled water; allow them to drain; it is not necessary to wipe the insides of such vessels dry. Whenever water is required for purposes of solution, distilled water must be used.

REACTIONS OF THE METALS.

Each of these reactions must be carefully performed by the student: he should endeavour to remember the appearance of the precipitate or other change produced, so that if he tries the same experiment on an unknown body and gets the same result he will be able to recognise it and thus identify the substances present.

For each metal a salt is named that may be conveniently used for its reactions; they would, however, be the same with

most other salts. In a laboratory, solutions are usually kept ready made up for the use of students.

SILVER.—Silver nitrate may be used for both the dry and wet reactions.

Dry. Heated on charcoal with blowpipe in the reducing flame, a white malleable bead of silver is produced without incrustation.

A fragment the size of a shot is quite sufficient for this experiment: the salt should be first powdered for *all* blowpipe experiments.

Wet. HCl (or any soluble chloride) gives a white curdy precipitate of AgCl, which is turned violet by the action of light; the ppt. is insol. in hot H_2O, is sol. in AmHO, and re-pptd. by HNO_3.

In making the wet tests, place about half an inch of the test solution in a small test-tube, and add the re-agent, as HCl, drop by drop; observe carefully the changes produced as each drop falls into the liquid. When various solvents are to be tried on the same ppt. it must be washed between the application of each. Heavy ppts., as AgCl, may easily be washed by decantation: drain off as much of the liquid as possible and then fill up with water; shake up the tube, allow the ppt. to subside, and again decant; repeat the operation a second time, and then the ppt. will be sufficiently washed. When the ppt. does not so readily subside, it must be washed by filtration; the contents of the tube are to be poured on a filter and the liquid allowed to drain through; then fill up the filter from the wash-bottle, directing the stream at each portion of the ppt., let the washing water drain *completely* away and then refill; when the second lot of washings have passed through, the ppt. may be transferred again to a test-tube by pushing a hole through the bottom of the paper and washing it through, or the funnel may be held inverted and the ppt. washed out with a vertical stream of water from the wash-bottle. The ppt. may sometimes be taken out of the paper with the point of a penknife or a small spatula.

In every case use as small quantities of each substance as possible: large ppts. take more time to wash and render every operation of analysis tediously long.

H_2S—black ppt. of Ag_2S.

K_2CrO_4—dark red ppt. of Ag_2CrO_4.

The contents of tubes containing silver salts must not be thrown away, but should be placed in a bottle kept for the purpose.

LEAD.—Lead nitrate may be used.

Dry. Heated on charcoal with blowpipe in reducing flame —soft metallic bead, which marks paper, yellow incrustation.

Incrustations usually consist of oxide, formed by the combustion of the metallic vapour as it passes out of the reducing flame, and deposited on the cooler surrounding charcoal. Incrustations must not be confounded with the ash of the charcoal itself.

Wet. HCl—white ppt. of $PbCl_2$ somewhat sol. in cold H_2O, much more sol. in hot H_2O, from which it re-crystallises on cooling : insol. in AmHO being converted into PbHOCl.

From the solubility of $PbCl_2$ this metal cannot be entirely removed from a solution by HCl : when the solution is very dilute no ppt. is obtained.

H_2S—black ppt. of PbS insol. in dilute HCl, oxidised in part to $PbSO_4$ by HNO_3, insol. in NaHO.

K_2CrO_4—lemon yellow ppt. of $PbCrO_4$.

MERCURY, MERCUROUS SALTS.—Mercurous nitrate may be used.

Dry. Heated in tube—a sublimate of globules of metallic Hg is produced.

The nitrate is first decomposed with the liberation of nitrous fumes and production of the oxide ; and this undergoes further decomposition into Hg and O. Other salts, as Hg_2Cl_2, sublime without decomposition.

For tube reactions small test-tubes may be used : where the heat required is intense, tubes may be employed made from 'combustion' tubing (a difficultly fusible variety). Cut the tube, which should be $\frac{1}{4}$-in. bore, into lengths of about 7 inches ; draw each of these pieces in the foot blowpipe flame off into two tubes ; seal up the bottom of each, and blow a small bulb. As in tube reactions it is wished to study sublimates, it is necessary that the sides of the tube should be kept clean. With this end in view the salt should be introduced by means of a little gutter of paper. Take a piece of paper about 4 in. long and $\frac{3}{8}$ in. wide ; fold this lengthwise in the middle, put the substance on this paper and carefully push it down the tube ; then hold the tube upright, give it one or two taps and the substance will

fall to the bottom of the tube; withdraw the paper, and the sides of the tube will be found to be quite clean.

In heating these tubes, if any moisture condenses in the part near the mouth, they should be held so that it shall run *from* the hot part and not toward it.

Mixed with Na_2CO_3 or fusion mixture and heated in tube, all mercurous salts yield a sublimate of Hg globules.

The Na_2CO_3 or fusion mixture used must be perfectly dry. It is a good plan to fuse some in a platinum capsule and then powder it: keep in a well-stoppered bottle.

Wet. HCl—white ppt. of Hg_2Cl_2, blackened by the addition of AmHO.

H_2S—black ppt. of Hg_2S.

NaHO—black ppt. of Hg_2O.

$SnCl_2$—grey ppt. of metallic Hg.

MERCURIC SALTS.—Mercuric chloride may be used.

Dry. Same as for mercurous compounds.

Wet. H_2S—black ppt. of HgS insol. in HCl or HNO_3, sol. in aqua regia, insol. in NaHO.

The first trace of H_2S produces a white ppt., which changes through yellow to black. To all the sulphides of Group II. add a few drops of HCl and observe their insolubility.

NaHO—yellow ppt. of HgO.

$SnCl_2$—white ppt. of Hg_2Cl_2 changing with excess of $SnCl_2$ to grey ppt. of Hg.

COPPER.—Copper sulphate may be used.

Dry. Heated on charcoal with Na_2CO_3 and KCN in reducing flame—small malleable red beads of Cu.

The Na_2CO_3 and KCN should be in equal quantities: about five times as much of the mixture as of the copper compound should be taken: the whole quantity should not be more than would fill a cavity the size of half a pea. Careful and continuous blowing is requisite.

Heated in borax bead—in oxidising flame the bead is green while hot; blue when cold; in reducing flame, the bead is red when cold.

The red bead in R. F. is difficult to get. If the smallest scrap of metallic Sn is placed on the bead and fused with it, the reduction takes place immediately.

Heated on platinum wire in Bunsen flame—imparts to it an intense green colour.

Wet. H_2S—black ppt. of CuS insol. in dilute HCl, slightly sol. in SAm_2, insol. in NaHO.

AmHO—greenish blue ppt. sol. in very slight excess to a deep blue solution.

KCy—yellowish green ppt. of $CuCy_2$ sol. in excess; H_2S produces no ppt. in this solution.

K_4FeCy_6—brown ppt. of Cu_2FeCy_6.

BISMUTH.—Bismuth nitrate may be used.

Dry. Heated on charcoal with Na_2CO_3—brittle yellowish white metallic bead; surrounded by incrustation, dark orange while hot, lemon-yellow when cold.

Wet. H_2S—black ppt. of Bi_2S_3 insol. in dilute HCl, and in NaHO or SAm_2.

Much water added to solution—white ppt. of an oxy-salt.

This reaction takes place most readily with the chloride, $BiCl_3$; a ppt. of BiOCl is formed. From this property a salt of Bi may be dissolved in a small quantity of HCl and re-pptd., on dilution with H_2O. When this occurs in making solution of an unknown salt, the presence of Bi (or Sb, which acts similarly) may be suspected.

AmHO—white ppt. of $Bi(HO)_3$ insol. in excess.

CADMIUM.—Cadmium sulphate may be used.

Dry. Heated in tube—some salts, in particular CdBr, sublime, although difficultly.

This should be remembered, as Cd is thus sometimes mistaken for the other volatile metals.

Heated on charcoal with Na_2CO_3 in reducing flame—the metal is reduced, but is immediately oxidised and forms a brown incrustation.

Wet. H_2S—yellow ppt. of CdS, sol. in HCl unless very dilute; sol. also in dilute H_2SO_4; insol. in NaHO.

The solubility of CdS in HCl, when not sufficiently dilute, leads frequently to its being undetected in Group II.

KCy—white ppt. of $CdCy_2$ sol. in excess, from which H_2S ppts. CdS.

TIN, STANNOUS SALTS.—Stannous chloride may be used.

Dry. Heated on charcoal with Na_2CO_3 and KCy in reducing flame—a white malleable bead, which is oxidised by HNO_3 to a white compound, $Sn_5O_5(HO)_{10}$.

Traces of a tin-salt heated in R. F. in a borax bead, coloured blue by Cu—change the colour to red.

Wet. H_2S—brown ppt. of SnS, insol. in dilute HCl, sol. in NaHO, or yellow SAm_2, re-pptd. by HCl.

$HgCl_2$—white ppt. of Hg_2Cl_2; if the stannous salt be in excess, a grey ppt. of Hg is formed.

Zn granulated—spongy ppt. of metallic Sn from acid solution.

$SnCl_2$ is readily changed into $SnCl_4$ and Sn_2Cl_2O by action of O. To hinder this, granulated Sn is usually placed in a solution of $SnCl_2$.

STANNIC SALTS.

Dry. Same as for stannous compounds.

Wet. A solution of stannic chloride may be used.

H_2S—yellow ppt. of SnS_2 insol. in diiute HCl, sol. in NaHO or SAm_2, re-pptd. by HCl.

Zn—same reaction as with stannous salts.

ARSENIC, ARSENIOUS COMPOUNDS.—Arsenic trioxide may be used; for the wet tests a solution in HCl.

Dry. Heated in tube—all salts sublime.

Heated in tube open at both ends—an odour of garlic may be observed.

To make this test, take a piece of combustion tube about 4 in. long, place the substance in the middle, and apply heat; the tube must be held slightly inclined; the odour is given off at the upper end.

Heated in a small tube with Na_2CO_3 and charcoal powder (black flux)—the compound is reduced and a grey, mirror-like sublimate of metallic As is formed. Heated on charcoal very gently with the reducing flame—garlic odour is observed, and a white incrustation some distance from the assay is deposited.

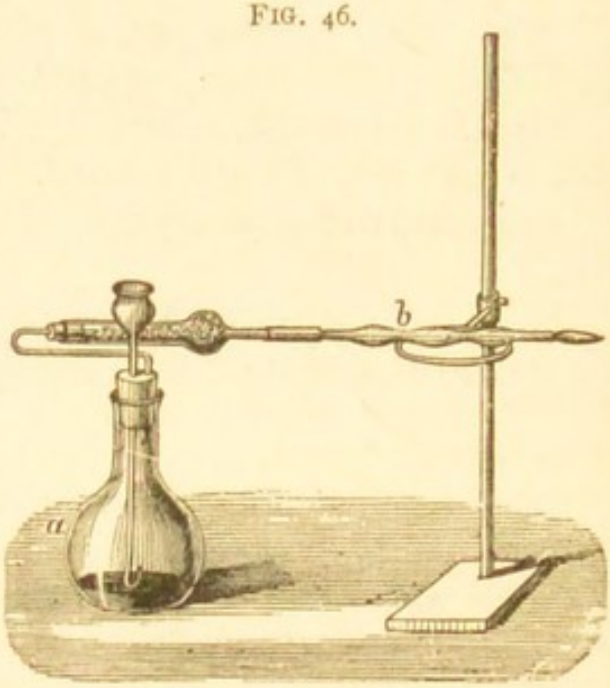
The substance heated in this way on charcoal is often called technically 'the assay.'

Wet. H_2S—yellow ppt. insol. in HCl, sol. in NaHO, and also in $AmHCO_3$.

Strips of clean Cu in solution acidulated with HCl, on gently heating—a greyish film of As_2Cu_3 is deposited, even from very dilute solutions. (Reinsch's test.)

On introducing a solution of any As compound into an apparatus in which H is being evolved, AsH_3 is formed, and may be recognised by special tests. Fit up a 4-oz. flask as a generating flask for the preparation of H from Zn and H_2SO_4 (Fig. 46), attach a $CaCl_2$ tube for drying, and to that a piece of $\frac{1}{4}$-in. combustion tubing, which has been narrowed in two or three places, as at *b*. Place in the flask some granulated Zn free from As and some water, add a very little strong pure H_2SO_4; when the H has expelled the whole of the air from the flask, heat the tube at *b*, and continue the evolution of the gas for at least five minutes; if at the end of that time there is no sign of a mirror of As beyond the heated point, it may be assumed that the reagents contain no As. Light the flame as it issues from the end of the tube, and it will be seen to burn with the usual almost colourless flame of H. Add now through the funnel a few drops of the As solution, the colour of the flame changes to a livid blue, and it is seen to give off white fumes. Depress momentarily into the flame a porcelain crucible cover—a mirror of metallic As will be formed on it: obtain two of these mirrors. A similar mirror will also be deposited within the tube, just beyond the point where the heat has been applied. Add to the mirror a drop of a solution of sodium hypochlorite (NaClO)—the mirror is immediately dissolved. (Marsh's test.)

Fig. 46.



Place in a test-tube some pure Zn and KHO, with a little water; add a very small quantity of the As solution; then cover over the top of the tube with a piece of filter paper moistened with $AgNO_3$, and heat very gently—the paper is blackened

through the decomposition of $AgNO_3$ by AsH_3. (Fleitmann's test.)

ARSENIC COMPOUNDS.—A solution of potassium arsenate (K_3AsO_4) may be used.

Dry. Same as those of arsenious compounds.

Wet. H_2S produces a ppt. from acidulated solution with extreme slowness. The ppt. consists of As_2S_3, hence the H_2S has to reduce the arsenic compound to an arsenious one. Heat the solution with H_2SO_3 until the smell of SO_2 disappears; this readily effects the reduction to the arsenious state: then add H_2S—a yellow ppt. of As_2S_3 is immediately produced.

The greatest care must be taken in all experiments on As, as its compounds are intensely poisonous; small quantities should be used, and the experiment performed either in a stink cupboard or where there is a good draught of air.

ANTIMONY.—The fused oxy-sulphide may be used for the dry reactions, and a solution of the chloride $SbCl_3$ for the wet.

Dry. Heated gently on charcoal in reducing flame with Na_2CO_3 and KCy—a brittle white metallic bead is formed; this readily oxidises with the production of a dense white incrustation.

Wet. H_2S—orange ppt. of Sb_2S_3 insol. in dilute HCl, sol. in NaHO or Am_2S, insol. in $AmHCO_3$.

Much H_2O to solution of $SbCl_3$—white ppt. of SbOCl.

Solution added to apparatus in which H is being generated from Zn and H_2SO_4, as described for As, produces SbH_3, which also deposits a mirror. The Sb mirror is darker in colour, and on the addition of NaOCl does not dissolve. (Distinction from As.)

Sb solution added to Zn and KHO, as in test for As, does not form SbH_3, and consequently there is no blackening of the filter paper moistened with $AgNO_3$.

IRON, FERROUS COMPOUNDS.—Ferrous sulphate may be used.

Dry. Heated on charcoal in reducing flame—brownish residue remains, which is attracted by a magnet.

In borax bead—in O.F. yellowish red bead, in R.F. green bead.

Wet. AmHO—white ppt. of $Fe(HO)_2$, rapidly changing in colour to green, and finally being changed into reddish brown $Fe_2(HO)_6$.

It is very difficult to procure a ferrous salt absolutely free from ferric salts, but by dissolving the crystals of $FeSO_4$ in cold H_2O they may be obtained almost free from any ferric impurity. The reduction of a trace of ferric salt may be produced by adding to the solution a drop of H_2SO_4 and a fragment of granulated Zn. The small quantity of Zn that may be dissolved does not interfere with the reactions.

Am_2S—black ppt. of FeS, sol. in dilute HCl.

Potassium Ferrocyanide (K_4FeCy_6)—white ppt. of Fe_2FeCy_6, rapidly changing to dark blue.

Potassium Ferricyanide ($K_6Fe_2Cy_{12}$)—dark blue ppt.

FERRIC COMPOUNDS. Ferric chloride (Fe_2Cl_6) may be used.

Dry. Same as those of ferrous compounds.

Wet. AmHO—reddish brown ppt. of $Fe_2(HO)_6$.

Am_2S—reduces ferric to ferrous salts and ppts. FeS with the separation of S. HCl dissolves the FeS with evolution of H_2S, when the S may be observed as a white cloud in the solution.

K_4FeCy_6—dark blue ppt. (Prussian blue).

$K_6Fe_2Cy_{12}$—no ppt., reddish brown coloration.

AmCyS—blood-red coloration.

ALUMINIUM.—Alum, $Am_2Al_2(SO_4)_4$, may be used.

Dry. Strongly ignited on charcoal, allowed to cool, moistened with cobalt nitrate solution, $Co(NO_3)_2$, and again strongly ignited—the residue assumes a blue colour.

When the quantity is very small, the reaction may be performed on a loop of Pt wire. This is specially applicable when testing a ppt. : a portion of the filter containing the ppt. may be cut out and heated on the Pt wire.

Wet. AmHO—white gelatinous ppt. of $Al_2(HO)_6$, slightly sol. in excess, readily sol. in NaHO.

The presence of AmCl in the solution prevents the solution of the ppt. by either AmHO or NaHO.

Am_2S—also ppts. $Al_2(HO)_6$, with evolution of H_2S.

CHROMIUM.—Chrome alum $K_2Cr_2(SO_4)_4$, may be used.

Dry. One part of a Cr salt mixed with about four parts of Na_2CO_3, and one of KNO_3, fused on Pt foil, produces on cooling a yellow mass containing K_2CrO_4. This on the addition of H_2O produces a yellow solution from which acetic acid and lead acetate ppt. yellow $PbCrO_4$.

Heated in borax bead in R.F.—green bead.

Wet. AmHO—green ppt. of $Cr_2(HO)_6$, slightly sol. in excess, re-pptd. by boiling, which drives off the excess of AmHO.

The presence of AmCl prevents the solution of the ppt.

Am_2S—same ppt. of $Cr_2(HO)_6$.

ZINC.—Zinc sulphate may be used.

Dry. Heated on charcoal in reducing flame—incrustation, yellow while hot, white when cold.

Strongly ignited on charcoal or Pt loop, allowed to cool, treated with $Co(NO_3)_2$, and again ignited—the residue assumes a green colour.

Wet. Am_2S—white ppt. of ZnS, sol. in dilute HCl, insol. in acetic acid, and also in NaHO.

NaHO—white ppt. of $Zn(HO)_2$, sol. in excess, from which solution $Zn(HO)_2$ is not re-pptd. by AmCl.

MANGANESE.—Manganese sulphate may be used.

Dry. Heated in borax bead—O.F. amethyst, R.F. colourless bead.

Heated on Pt foil with Na_2CO_3 and KNO_3 (same quantities as directed for Cr)—dark bluish-green mass.

Wet. Am_2S—yellow (skin-coloured) ppt. of MnS, sol. in HCl and also in acetic acid.

NaHO—white ppt. of $Mn(HO)_2$ which rapidly oxidises on exposure to air and acquires a brown tint.

The ppt. is at first sol. in AmCl, but not so after standing.

AmHO—white ppt. sol. in AmCl.

If this solution be allowed to stand, a brown ppt. of $Mn_2O_2(HO)_2$ is formed. Hence, when members of Group IIIA. are present in a mixture with Mn, a portion of the Mn is also pptd. by AmCl, AmHO.

NICKEL.—Nickel sulphate may be used.

Dry. Heated on charcoal with Na_2CO_3 in reducing flame—

greyish residue, which, when treated with water and the soluble portion removed, is slightly magnetic.

Heated in borax bead—in O.F. reddish yellow when hot, sherry colour when cold ; R.F. grey when cold.

Wet. Am_2S—black ppt. of NiS, slightly sol. in excess to yellow-brown solution, insol. in cold dilute HCl.

H_2S—no ppt. in acid solution.

Am_2CO_3—green ppt. sol. in excess to greenish-blue solution.

KCy—yellow ppt. of $NiCy_2$ sol. in excess to $(KCy)_2,NiCy_2$. This solution is unchanged by boiling and NaClO ppts., from it on heating, $Ni_2(HO)_6$ which is of a black colour.

The KCy must be free from carbonate and cyanate : the latter may be removed by fusion in a porcelain crucible with powdered charcoal. The KCy solution should be made up only when used : it must be added drop by drop until there is only just the slightest excess : the exact point may be hit by reserving a portion of the nickel solution, and adding a drop to the solution in KCy so as to produce a very slight ppt., and then filtering. A large quantity of the hypochlorite must be added, and if the Ni solution be very dilute, some little time elapses before the $Ni_2(HO)_6$ is pptd.

Bromine water may be employed instead of NaClO.

COBALT.—Cobalt nitrate may be used.

Dry. Heated in borax bead both in O.F. and R.F.—deep blue bead.

The slightest trace of Co should be taken.

Wet. Am_2S—black ppt. of CoS, insol. in excess and also in HCl.

Am_2CO_3—pink ppt. sol. in excess to red solution.

KCy—light brown ppt. of $CoCy_2$ sol. in excess to $(KCy)_2,CoCy_2$. This solution on being boiled is changed to K_3CoCy_6, in which neither NaClO, nor Br water, produces a ppt.

This affords a method of separating Ni from Co. Make a mixture of the solutions of the salts of these two metals and separate them by this method. Boil the dissolved cyanides for two or three minutes, and then cool before adding the NaClO, after which again gently warm and allow to stand.

BARIUM.—Barium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a green coloration.

Flame colorations are best seen with the chlorides.

Wet. Am_2CO_3 in presence of AmHO—white ppt. of $BaCO_3$ sol. in HCl or acetic acid.

$CaSO_4$—white ppt. of $BaSO_4$ even from very dilute solutions.

K_2CrO_4—yellow ppt. of $BaCrO_4$ from dilute solutions, sol. in HCl, but insol. in acetic acid.

STRONTIUM.—Strontium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a crimson flame coloration.

Wet. Am_2CO_3 in presence of AmHO—white ppt. of $SrCO_3$ sol. in HCl or acetic acid.

$CaSO_4$—white ppt. of $SrSO_4$, but only after standing some time, insol. in boiling saturated solution of Am_2SO_4 with AmHO.

K_2CrO_4—no ppt.

CALCIUM.—Calcium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a yellowish red flame coloration.

Wet. Am_2CO_3, with AmHO—white ppt. of $CaCO_3$ sol. in HCl or acetic acid.

H_2SO_4—from concentrated solutions ppts. $CaSO_4$; this salt is sol. in boiling Am_2SO_4.

Ammonium oxalate, $Am_2C_2O_4$—white ppt. from even very dilute solutions, sol. in HCl, but insol. in acetic or oxalic acids.

This test gives a ppt. with water from wells in chalk or limestone districts.

MAGNESIUM.—Magnesium sulphate may be used.

Dry. Strongly ignited on charcoal, allowed to cool, moistened with $Co(NO_3)_2$ and again strongly ignited—the residue assumes a rose-pink colour.

Wet. AmHO—white ppt. of $Mg(HO)_2$ sol. in AmCl.

Na_2HPO_4 in presence of AmCl and AmHO—white crystalline ppt. of $MgAmPO_4$ sol. in HCl and also acetic acid.

POTASSIUM.—Potassium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—a violet coloration, which when looked at through deep-blue glass appears of a reddish-violet colour.

Wet. $PtCl_4$ in presence of HCl—a yellow crystalline ppt. of $(KCl)_2PtCl_4$ insol. in dilute acids. The precipitation is hastened by the addition of a little of a mixture of alcohol and ether.

This reaction is best performed on a watch-glass placed on a piece of white paper or porcelain ; a drop only of each reagent should be taken.

SODIUM.—Sodium chloride may be used.

Dry. Heated on Pt wire in Bunsen flame—an intense golden yellow flame coloration. Viewed through blue glass the yellow flame is invisible.

This enables K to be detected in the presence of Na.

Wet. Almost all the sodium salts are soluble, and therefore no good wet reaction is applicable.

AMMONIUM.—Ammonium chloride may be used.

Dry. Heated in tube Am salts volatilise entirely, except the acid be fixed ; in which case NH_3 is liberated and may be recognised by its smell.

Some Am salts are decomposed by heat, as $AmNO_3$, others, as AmCl, are again deposited as a sublimate.

Wet. Heated with NaHO—ammoniacal odour.

$PtCl_4$ in presence of HCl—yellow crystalline ppt. of $(AmCl)_2PtCl_4$.

It is therefore necessary to remove Am salts by ignition previous to testing for K by $PtCl_4$.

REACTIONS OF THE ACIDS.

The acids do not admit of being so readily arranged in groups as the metals, the following classification will, however, be found to be a help in studying their reactions.

Group I.—Acids whose salts are decomposed by gently heating with dilute HCl and which evolve a characteristic gas or vapour :—**Carbonic acid** and **sulphuretted hydrogen.**

Group II.—Acids whose salts are decomposed by heating with concentrated H_2SO_4 and which evolve a characteristic gas or vapour :—**Nitric, chloric, hydrochloric, hydrobromic, hydriodic** and **hydrofluoric acids.**

Group III.—Acids whose salts evolve neither gas nor vapour on being treated with H_2SO_4 :—**Sulphuric, silicic, phosphoric,** and **boric acids.**

CARBONIC ACID, H_2CO_3.—Sodium carbonate may be used.

FIG. 47.

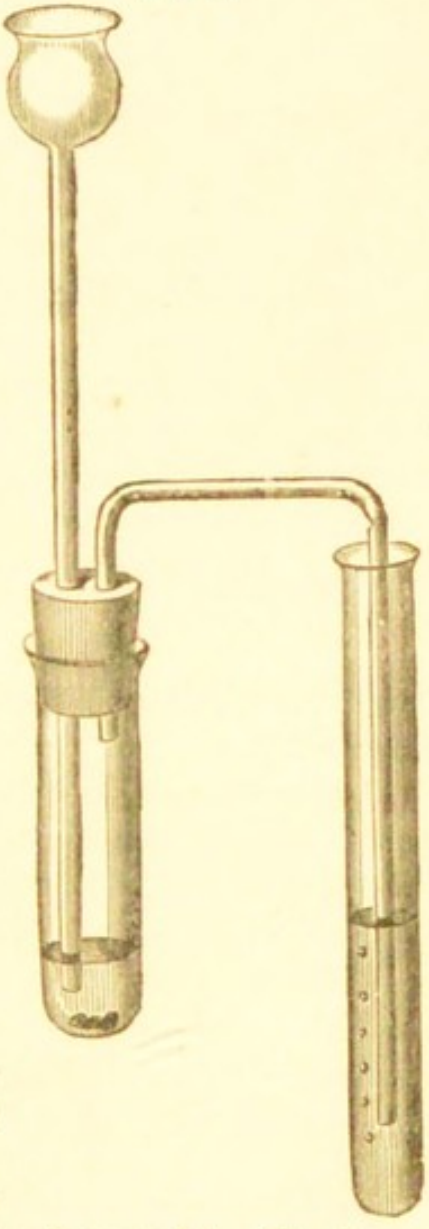


Dry. All carbonates except those of K and Na are decomposed by heat into oxides with the evolution of CO_2. $BaCO_3$ and $SrCO_3$ require a white heat.

Wet. Dilute HCl added to the powdered salt—colourless odourless gas evolved, with effervescence, that turns lime-water milky.

In this and similar tests the salt itself is to be used, and not a solution. Small quantities of CO_2 may be detected in the following manner :—Pour some $Ca(HO)_2$ in a test-tube ; put the salt in another ; add HCl, and close the mouth of the tube with the thumb ; allow gas to escape slowly ; then, when the action is over, pour the gas into the $Ca(HO)_2$ test-tube, taking care to stop before any of the liquid follows (Fig. 47). Shake up the tube containing the CO_2 and $Ca(HO)_2$: the latter is turned milky.

FIG. 48.



When small quantities have to be tested, the apparatus shown in Fig. 48 is often useful. The larger tube is fitted up with a thistle funnel and delivery tube. The whole of the gas generated may be driven into the smaller tube by blowing with an aspirator or hand-bellows (not the mouth) through the thistle

funnel. Where special accuracy is necessary the air should be first freed from CO_2 by being passed through a solution of KHO.

Another method that is serviceable for the detection of traces of CO_2 is to place a glass rod dipped in $Ca(HO)_2$ in the mouth of the tube; a film of $CaCO_3$ will be formed on it. Care must be taken, however, that the whole of the vapour of HCl has subsided, as its presence in quantity would prevent the formation of a ppt.

SULPHURETTED HYDROGEN, H_2S.—Ferrous sulphide may be used.

Dry. Certain sulphides are decomposed on being treated in a closed tube, S being deposited; this reaction is characteristic of sulphides. Others, on being heated in an open tube, are oxidised; an oxide of the metal remains, and SO_2 is evolved, which may be recognised by its smell.

Wet. HCl added to the powdered salt and gently warmed —many sulphides evolve SH_2 recognised by its odour, and property of blackening paper dipped in a solution of lead acetate.

Others, as As_2S_3, are not decomposed: these on being warmed with aqua regia are in part oxidised to sulphates; another portion of the metal forms a chloride and free S is liberated in the plastic condition. The solution must be diluted and tested for H_2SO_4 by $BaCl_2$.

FIG. 49.



NITRIC ACID, HNO_3.—Potassium nitrate may be used.

Dry. Heated in tube—all nitrates are decomposed, one of the lower oxides of nitrogen and O being evolved. N_2O_3 and NO_2 may be recognised by their smell.

Heated on charcoal—nitrates deflagrate.

Wet. Heated gently with conc. H_2SO_4—nitrates evolve HNO_3, which has a characteristic odour. On the addition of Cu turnings nitrous fumes are evolved.

$FeSO_4$ poured down the side of a test-tube containing a cold solution of a nitrate with an equal volume of conc. H_2SO_4—dark brown ring where liquids meet (Fig. 49).

To the solution of the nitrate an equal volume of the H_2SO_4 should be added, and then the tube cooled by being kept for a minute or two in

cold water; the solution of $FeSO_4$ must be added carefully so that the one liquid may float on the top of the other without immediately mixing.

CHLORIC ACID, $HClO_3$.—Potassium chlorate may be used.

Dry. Heated in tube—all chlorates are decomposed, evolving either O or a mixture of Cl and O.

Heated on charcoal—chlorates deflagrate. Chlorates may be recognised indirectly by their forming, in most instances, chlorides on ignition.

Wet. Heated gently with conc. H_2SO_4—greenish yellow explosive gas (Cl_2O_4) is evolved.

A very small quantity of both the chlorate and the acid should be taken; the quantity of $KClO_3$ should not be larger than a pea; some half-dozen drops of acid are sufficient. The mouth of the tube while being heated should be turned from the operator.

HYDROCHLORIC ACID, HCl.—Sodium chloride may be used.

Wet. Heated gently with conc. H_2SO_4—pungent fumes of HCl are evolved. The following chlorides are not readily decomposed by conc. H_2SO_4—Hg_2Cl_2, $HgCl_2$, AgCl, $PbCl_2$, $SnCl_2$ and $SnCl_4$.

Heated with conc. H_2SO_4 and MnO_2—all chlorides evolve Cl.

$AgNO_3$—white ppt. of AgCl, readily soluble in AmHO.

HYDROBROMIC ACID, HBr.—Potassium bromide may be used.

Wet. Heated gently with conc. H_2SO_4—pungent fumes of HBr, together with free Br vapour, recognised by its deep red colour and characteristic odour, are evolved.

Heated with conc. H_2SO_4 and MnO_2—Br is evolved.

Cl water—Br is liberated, and may be dissolved by CS_2, to which it imparts a deep sherry-red tint.

$AgNO_3$—light yellow ppt. of AgBr, difficultly soluble in AmHO.

HYDRIODIC ACID, HI.—Potassium iodide may be used.

Wet. Heated gently with conc. H_2SO_4—gaseous I, recognised by its violet colour, and HI fumes are evolved.

Heated with conc. H_2SO_4 and MnO_2—I is evolved.

Br water—I is liberated, and may be dissolved by CS_2, to which it imparts a characteristic violet colour.

In making this test add the Br water carefully, drop by drop, then

add the CS_2, shake up, and observe whether after standing the CS_2 is coloured.

$AgNO_3$—light yellow ppt. of AgI insol. in AmHO.

HYDROFLUORIC ACID, HF.—Calcium fluoride may be used.

Wet. Heated gently with conc. H_2SO_4—pungent acid fumes evolved, somewhat resembling those of HCl ; a glass rod moistened with water inserted in the tube becomes coated with a film of SiO_2. The glass of the tube is corroded by the HF evolved.

Heated gently in leaden capsule with H_2SO_4—a piece of glass which has been coated with wax and then some characters inscribed with the point of a needle being used as a cover, the glass is eaten away (etched) where the wax has been removed.

SULPHURIC ACID, H_2SO_4.—Potassium sulphate may be used.

Dry. Heated on charcoal with Na_2CO_3 in reducing flame—a sulphide is formed, recognised by the odour of H_2S on addition of HCl.

If the residue be placed on a silver coin, and then treated with HCl, a black stain of Ag_2S is produced.

Wet. $BaCl_2$—white ppt. of $BaSO_4$ insol. in acids.

SILICIC ACID, H_4SiO_4.—Sodium silicate may be used.

Dry. Heated in microcosmic salt bead (made in the same way as a borax bead)—silicates are decomposed, and the SiO_2 floats about undissolved in the bead while hot.

Wet. HCl—in conc. solution, gelatinous ppt. of H_4SiO_4.

If the solution be dilute, the H_4SiO_4 does not separate.

The solution being rendered distinctly acid with HCl, and evaporated to complete dryness ; then treated with a few drops of conc. HCl and H_2O and heated—an insol. residue of SiO_2 remains.

AmCl—white gelatinous ppt. of H_4SiO_4.

By fusion with Na_2CO_3 or fusion mixture insol. silicates may be decomposed, sodium or potassium silicates being formed.

PHOSPHORIC ACID, H_3PO_4.—Sodium phosphate may be used.

Wet. AmCl, AmHO, and $MgCl_2$ to alkaline phosphates (*i.e.* phosphates of K, Na, Am)—white crystalline ppt. of $MgAmPO_4$.

Am_2MoO_4 (ammonium molybdate) in presence of excess of HNO_3—yellow ppt. on heating *gently*.

To the solution tested an equal volume of conc. HNO_3 should be added, and then a volume of Am_2MoO_4 equal to that of the other two together.

All phosphates, except those of the alkalies, are insol. in H_2O; the remainder are sol. in acids, but are reprecipitated on rendering the solution alkaline. From this property of phosphates, they are, if present in a mixture, pptd. with the members of Group III. on the the addition of AmCl and AmHO. Under these circumstances the H_3PO_4 is removed before the examination of the ppt. for the ordinary members of the group is made. Directions are given in a special table for this elimination of H_3PO_4.

If H_3PO_4 is known to be absent from a substance being analysed, the special tests and methods necessary when it may possibly be present can be omitted.

BORIC ACID, H_3BO_3.—Sodium borate may be used.

Dry. Most borates contain a large quantity of water of crystallisation, and therefore swell up when heated.

Wet. Acidulated with conc. H_2SO_4 and alcohol (methylated spirits) added—the mixture on being inflamed burns with a green flame.

The reaction may be performed in a small evaporating basin.

Cu and Ba salts have green flame colorations, and in their presence the following modification of this reaction should be used.

Fit a two-oz. flask with a cork, through which a glass jet is passed. Put the borate with H_2SO_4 and alcohol in the flask, replace the cork, and apply heat. Set fire to the vapour as it issues from the jet—it burns with a green flame coloration.

Cu and Ba do not affect the flame when produced in this manner.

ORGANIC ACIDS.

HYDROCYANIC ACID, HCN or HCy.[1]—Potassium cyanide may be used.

Dry. Cyanides of the heavy metals, as $HgCy_2$, are decomposed by heat, with the evolution of Cy, which burns with a purple flame.

[1] Cyanogen—CN is such an important compound radical that it has received the special symbol 'Cy.'

Cyanides evolve their N as NH_3 when heated with soda-lime.

KCy and NaCy are not decomposed by ignition, but in the presence of air are rapidly converted into KCyO and NaCyO (cyanates). Owing to the avidity with which they combine with O they are valuable reducing agents.

Wet. Heated with HCl—all cyanides evolve HCy, having a characteristic odour of bitter almonds. Hold a watch-glass, on the bottom of which a drop of SAm_2 has been placed, in the gas thus evolved from a cyanide—AmCyS is formed; allow the excess of SAm_2 to evaporate, and wash the AmCyS into a test-tube, add a single drop of Fe_2Cl_6—reddish coloration.

$AgNO_3$—white ppt. of AgCy readily sol. in AmHO.

OXALIC ACID, $H_2C_2O_4$.—Ammonium oxalate may be used.

Dry. Oxalic acid sublimes on being heated, forming dense white fumes; the sublimate crystallises in long needles, generally radiating from a common centre. Oxalates are decomposed into carbonates or oxides with evolution of CO and CO_2.

Wet. Heated with conc. H_2SO_4—CO and CO_2 are evolved; the mixture does not blacken.

$CaCl_2$ or $CaSO_4$, from ammoniacal or acetic acid solution—white ppt. of CaC_2O_4, readily soluble in HCl or HNO_3. The ppt. on being evaporated to dryness and raised to a dull red heat is converted into $CaCO_3$, which effervesces on the addition of HCl.

FORMIC ACID, $HCHO_2$.—Sodium formate ($NaCHO_2$) may be used.

Dry. Formates, on being heated, split up into carbonates, oxides, or metals, with evolution of H_2, CO, and CO_2, and separation of C.

Wet. On addition of conc. H_2SO_4—characteristic smell of $HCHO_2$; on heating CO is evolved without blackening or evolution of CO_2.

$HgCl_2$ or $Hg_2(NO_3)_2$—grey ppt. of Hg, CO_2 being evolved.

Fe_2Cl_6—in neutral solution, a deep red coloration; addition of HCl changes the colour to yellow. On boiling, the solution becomes colourless, with separation of the iron as a basic formate.

ACETIC ACID, $HC_2H_3O_2$.—Sodium acetate may be used.

Dry. Acetates are decomposed on the application of heat; an inflammable liquid termed acetone, having a characteristic odour, is evolved. The metal remains as either carbonate or oxide, or in the metallic state mixed with C.

Acetates, heated with a small quantity of As_2O_3 evolve cacodyl, having a most disgusting odour.

Wet. Heated with H_2SO_4—characteristic smell of acetic acid is evolved. On heating with conc. H_2SO_4 and a single drop of alcohol (not methylated spirit), acetic ether, having a characteristic and pleasant smell, is yielded.

Fe_2Cl_6—reaction similar to that with formates.

BENZOIC ACID, $HC_7H_5O_2$.—Ammonium benzoate may be used.

Dry. Heated in a tube, benzoic acid sublimes and re-condenses in acicular crystals, an incense-like odour is evolved; heated on platinum foil the acid burns with a bright smoky flame.

Wet. Heated with conc. H_2SO_4—benzoates produce neither blackening nor evolution of SO_2.

Fe_2Cl_6—in neutral solution a yellowish ppt. of ferric benzoate, soluble in excess.

$CaCl_2$ and alcohol—no ppt.

SUCCINIC ACID, $H_2C_4H_4O_4$.—Ammonium succinate may be used.

Dry. Heated in a tube, the acid sublimes and re-condenses as long and very delicate needles, fumes are evolved which produce violent coughing; heated on platinum foil, the acid burns with a blue smokeless flame.

Wet. Heated with conc. H_2SO_4—no reaction.

F_2Cl_6—in neutral solutions a brownish-red ppt. which darkens in colour on adding AmHO.

$CaCl_2$ and alcohol—white ppt.

TARTARIC ACID, $H_2C_4H_4O_6$.—Sodium potassium tartrate (Rochelle salt) may be used.

Dry. Heated in a tube, the acid and tartrates are decomposed with separation of C and evolution of odour of burnt sugar.

Wet. Heated with conc. H_2SO_4—SO_2, CO_2 and CO are evolved, and C separates and blackens the mixture.

KCl—in solution acidulated with acetic acid—white crystalline ppt. of $HKC_4H_4O_6$.

$CaCl_2$—white ppt. of calcium tartrate, sol. in acids, cold NaHO and ammonic salts, but insol. in AmHO.

CITRIC ACID, $H_3C_6H_5O_7$.—Citric acid may be used.

Dry. Heated in a tube, pungent acid fumes are evolved, and C remains.

Wet. Heated with conc. H_2SO_4—CO and CO_2 are evolved. After *prolonged* heating the mixture blackens, and SO_2 is given off.

$CaCl_2$ added to solution exactly neutralised with NaHO—no ppt. in the cold (except on long standing), on boiling—white ppt. of calcium citrate.

DIRECTIONS FOR THE ANALYSIS OF UNKNOWN INORGANIC SUBSTANCES.

Observe the appearance of the substance. Note particularly whether it be metallic, as if so, no acids need be searched for. Powder the substance finely, and keep in a clean watch glass, or if deliquescent, in a corked test-tube.

Should the substance be a liquid, test whether acid or alkaline to litmus paper. Evaporate a portion to dryness, and use the residue for the dry examination. If the solution is neutral to litmus paper, leaves no residue on evaporation, and is odourless and tasteless, it consists of pure water only. (Ether, alcohol, &c., would also leave no residue, but would be at once distinguished by their smell.)

Perform the experiments in the order in which they are given, as in the later ones it is presumed that the information from the earlier ones is in the possession of the student. Want of attention to this rule is a fruitful source of error with young students.

An account must be kept of each experiment as performed; a specimen of the results of analysis of a body as they should be written out is given on page 297.

Preliminary Examination by the Dry Way.

I. Heat a little of the powdered substance in a test-tube or piece of small combustion tubing closed at one end, and a small bulb blown.

Result.	Deduction. Presence of—
NH_3 is evolved	**Am** salts
Nitrous fumes evolved	**Nitrates** of the heavy metals
A sublimate is formed.[1]	
White	**Am** salts, $HgCl_2$, Hg_2Cl_2, As_2O_3, **CdBr**. At a red heat Sb_2O_3.
Reddish-brown drops	**Sulphur.**
Yellow	As_2S_3, HgI_2. The latter turns red on being rubbed.
Black	**HgS**; turns red on being rubbed.
	In case of white sublimate. Test for Am by heating a little of the original substance with solution of NaHO—NH_3 evolved. **Am is present.**
	Heat some of the original substance in a small tube with five times its weight of fusion mixture—solid metallic sublimate—**As.** Sublimate of liquid globules—**Hg.**
Solid metallic sublimate	**As.**
Sublimate of liquid globules	**Hg.**

[1] If there be no sublimate or other principal reaction the confirmatory tests, &c., under the heading of 'Deduction' are to be omitted.

II. Heat some of the substance on charcoal with the blowpipe in oxidising flame.

Result.	Deduction. Presence of—
The substance deflagrates	**Nitrates, Chlorates.**
An infusible residue remains.	
White	**ZnO, Al_2O_3, SiO_2, BaO, SrO, CaO, MgO**, &c. Moisten the white residue, when cold, with $Co(NO_3)_2$, and ignite strongly. Blue mass—**Al_2O_3.** Pink mass—**MgO.** Green mass—**ZnO.**
Residue coloured . . .	**CuO, MnO, NiO, CoO, Fe_2O_3, Cr_2O_3.** Heat a portion of the substance in borax bead— O.F. green while hot, blue when cold—**Cu.** O.F. amethyst bead, R.F. colourless—**Mn.** O.F. sherry-red—**Ni.** In both flames, dark blue bead—**Co.** O.F. pale yellow, R.F. olive-green bead—**Fe.** In both flames, green bead—**Cr.** Test specially for **Mn** and **Cr** by heating with fusion mixture and KNO_3 on Pt foil.

III. HEAT THE SUBSTANCE WITH FUSION MIXTURE IN THE REDUCING FLAME.

RESULT.	DEDUCTION. Presence of—
An incrustation is formed without metallic bead.	
White, with garlic odour.	**As** compounds.
Yellow while hot, white when cold.	**Zn.**
Reddish brown, deposited some distance from assay.	**Cd.**
A metallic bead is formed.	**Ag, Pb, Cu, Bi, Sn, Sb.**
The bead is white, malleable and not coated with oxide.	**Ag** ; dissolves readily in HNO_3.
Soft bluish-white malleable bead which marks paper. Incrustation yellow while hot, white when cold.	**Pb.**
Small red malleable beads with black coating of oxide.	**Cu.**
Brittle yellowish white bead ; with dark orange incrustation while hot, light yellow when cold.	**Bi.**
Soft malleable yellowish white bead ; with incrustation yellow when hot, white when cold.	**Sn** ; does not dissolve in HNO_3, but is changed into white $Sn_5O_5(HO)_{10}$.
Brittle white bead, with dense white fumes, which form a white incrustation.	**Sb.**

IV. DIP A CLEAN Pt WIRE, MOISTENED WITH HCl, INTO SOME OF THE SUBSTANCE, AND HEAT IN THE BUNSEN FLAME.

RESULT.	DEDUCTION. Presence of—
Green flame coloration.	**Cu, Ba, H_3BO_3**; with Cu bluish-green
Crimson	**Sr.**
Yellowish red	**Ca.**
Golden yellow	**Na.**
Violet	**K.** In the presence of Na test flame coloration for K, with blue glass.

This preliminary examination must on no account be omitted. Many reactions other than those mentioned in the table will occur, but those only are introduced which are characteristic of the different elements and compounds. When the substance under examination is a mixture of several salts, the reactions of the one may hide those of the others. The student, therefore, must not in every instance assume that an element is absent because he does not get its particular reaction.

The following are the most important and characteristic reactions of the preliminary examination :—

Experiment I. The presence or absence of salts of Am, Hg, and As.

The presence of nitrates of the heavy metals.

Experiment II. The presence or absence of nitrates and chlorates.

The presence or absence of Mn, Co, and Cr.

Experiment III. Confirmation of the presence of As.

The presence of Zn, Cd, Bi and Sb.

The borax bead and incrustation reactions of some metals are particularly liable to be obscured by the others—thus Co masks all other bead reactions; and one incrustation may hide another. By watching carefully, two incrustations may often be detected, as one metal may be more easily reduced than another, and so form an incrustation first, which may afterwards be overlaid.

Experiment IV. The presence or absence of Sr, Na, and K.

When more than one of the metals which colour a flame are present, alternate flashes of each may sometimes be seen.

If the substance be metallic, the presence or absence of Hg and As may be learned from Experiment I. Nos. II. and IV. may be omitted. In No. III. heat a fragment of the metal and observe if any characteristic incrustation be observed.

Examination in the Wet Way.

If the substance be solid, proceed to make a solution, remembering that the substance must first be finely powdered.

I. If the substance is metallic, add dilute HNO_3; and then, if necessary, the concentrated acid; heat gently. The substance either entirely dissolves, or leaves a white residue of $Sn_5O_5(HO)_{10}$ or Sb_2O_5.

Wash the residue and boil with a concentrated solution of tartaric acid; Sb_2O_5 is soluble, test the solution by H_2S for Sb. Test the insoluble residue for Sn by reaction on charcoal.

Evaporate the solution in HNO_3 until the nitrates begin to crystallise out; then add water, and again evaporate down. By this treatment the free acid is driven off. The solution may then be examined in the ordinary way.

II. If the substance is non-metallic, test its solubility in the following reagents in the order given :—

1. H_2O. Heat a small portion of the substance with H_2O in a test-tube; if it be soluble, pass on to analysis. If it dissolve on boiling and re-ppts. on cooling, or is insoluble, pass on to trying. HCl.

2. HCl. First heat a small portion gently with the dilute acid; if not readily dissolved, try concentrated HCl, and boil for some time if necessary; this will dissolve out almost all that is soluble. Filter off the solution.

3. HNO_3. If the substance contains either Hg, Ag, or Pb, use HNO_3 as a solvent instead of HCl. As oxides of Sn or Sb would be insoluble in HNO_3 wash the residue and treat with HCl; mix the two solutions together; any ppt. formed will belong to Group I.

4. Aqua regia. Digest any insoluble residue from 2 or 3 with aqua regia; dilute and filter. Note whether globules of plastic S separate out; in which case a sulphide is present. Evaporate down the acid solutions until almost free from acid before proceeding to analysis; HNO_3 in particular should be carefully driven off.

$PbCl_2$ is sol. in hot H_2O and acids, and crystallises out as the liquid cools.

If a ppt. is produced on diluting the acid solution, it probably consists of an oxy-compound of Bi or Sb (as BiOCl). It readily dissolves on the addition of a little more acid. The dry examination will have proved the presence or absence of these metals.

III. A residue insoluble in acids remains. The number of such substances is but few; the following are the most important :—

SiO_2, and most silicates, Ag and Pb chlorides; Pb, Ba, Sr, and Ca sulphates; native and ignited compounds of Al_2O_3, Fe_2O_3, Cr_2O_3, SnO_2, and some native fluorides.

Take about three grammes of fusion mixture and melt it in a platinum capsule over the foot-blowpipe flame; raise to a bright red heat. Take about half a gramme of the very finely-powdered substance and add it in small quantities at a time to the liquid fusion mixture; on each addition an effervescence follows; wait until all action is over before adding more. When the whole has been introduced and thus decomposed, allow it to cool. The blowpipe heat must be maintained during the whole of this operation.

Should there be any reducible metal present, a porcelain crucible must be used instead of platinum; but in this case traces of SiO_2 and Al_2O_3 will be found from the crucible.

By fusion in this way the metal is obtained either as carbonate, oxide, or in the free state. The acid will have formed a potassium or sodium salt with the fusion mixture. When cold, boil up with water. The aqueous solution must be tested for acids. Filter off, and wash the residue thoroughly; dissolve in HCl, and examine the solution for the base. Should there still be any insoluble residue, the substance has not been entirely decomposed by the fusion mixture.

It is impossible by this method to determine whether or not any alkalies are present in the insoluble substance. To examine for alkalies, proceed in the following manner :—

Take not more than 0·5 grammes of the substance; mix with 0·5 grammes of pure AmCl and 4 grammes of pure precipitated $CaCO_3$; mix thoroughly, and heat in a platinum crucible with a small Bunsen flame. The crucible should be placed obliquely, and the heat applied to the upper part of the crucible first, working toward the bottom. The heat should then be increased, and finally the mass ignited strongly for half an hour with the foot-blowpipe. Extract with successive small quantities of hot H_2O and filter : the filtrate contains the alkalies, as chlorides, and also $CaCl_2$. Remove the Ca by ammonium oxalate and examine the filtrate for Na and K in the usual manner.

The solutions obtained by decomposing an insoluble residue by fusion mixture must be examined separately from the aqueous or acid solutions.

Proceed to examine a portion of the solution obtained by Table A.

Table A, for the separation of the bases into Groups.

To the original solution add HCl until it no longer produces a precipitate.

The ppt. may contain

AgCl, white.
$PbCl_2$, ,,
Hg_2Cl_2, ,,

Filter and wash thoroughly with *cold* H_2O.

Group I.

Examine by Table B.

Dilute the filtrate, and pass SH_2 gas until the solution smells strongly of the gas. Heat gently.

The ppt. may contain

HgS, black.
PbS, ,,
Bi_2S_3, ,,
CuS, ,,
CdS, yellow.
SnS, brown.
SnS_2, yellow.
Sb_2S_3 orange.
Sb_2S_5, ,,
As_2S_3, yellow.

Filter and wash.

Group II.

Examine by Table C.

Boil the filtrate till free from SH_2. Test a small portion for H_3PO_4 by HNO_3 and Am_2MoO_4. To another small portion add AmCl and AmHO; if there is no ppt. add these reagents to the main portion of the filtrate, and at once proceed to pass SH_2 gas or add SAm_2. But if there be a ppt. add to the main portion of the filtrate a few drops of conc. HNO_3 and evaporate to complete dryness; add a little conc. HCl and then heat with H_2O; the substance either dissolves completely or leaves a residue of SiO_2, which must be filtered off. Two cases now present themselves—**1, H_3PO_4 is absent; 2, H_3PO_4 is present.**

To the remainder of the solution, in absence of SiO_2, or to the filtrate from SiO_2 when present, add AmCl and AmHO in slight excess, and immediately boil until it no longer smells of NH_3.

1, H_3PO_4 is absent.

The ppt. may contain

$Fe_2(HO)_6$, reddish brown.
$Cr_2(HO)_6$, green.
$Al_2(HO)_6$, white.

Filter immediately and wash.

Group III. A.

Examine by Table D.

2, H_3PO_4 is present.

The ppt. may contain

$Fe_2(HO)_6$, reddish brown.
$Cr_2(HO)_6$, green.
$Al_2(HO)_6$, white,

and also the **phosphates** of all or any of the following metals—**Fe, Cr, Al, Zn, Mn, Ni, Co, Ba, Sr, Ca,** and **Mg.**

Filter immediately and wash.

Group III. A with H_3PO_4.

Examine by Table E.

To the filtrate add SH_2 gas or SAm_2 in slight excess. Heat gently.

The ppt. may contain

ZnS, white.
MnS, tawny yellow.
NiS, black.
CoS, ,,

Filter and wash.

Group III. B.

Examine by Table F.

To the filtrate add AmHO and Am_2CO_3. Heat gently and allow to stand for a few minutes.

The ppt. may contain

$BaCO_3$, white.
$SrCO_3$, ,,
$CaCO_3$, ,,

Filter and wash.

Group IV.

Examine by Table G.

The solution may contain

Mg
K
Na

Group V.

Examine by Table H.

Notes on Table A.

The separation into groups is based on the insolubility of the chlorides and other salts formed by the addition of various reagents; they are then removed by filtration, each ppt. being thoroughly washed.

Before proceeding to add the following group reagent, be sure that the preceding one has been added in excess. If the ppt. subsides readily, leaving a clear solution on the top, a drop of the reagent should be carefully added; if the liquid remains clear, go on to the next group; if a trace of ppt. forms, more of the reagent must be added, until a drop no longer produces a ppt. In some cases it will be necessary to filter a portion of the solution and make this test on the filtrate. An excess of SH_2 and AmHO may be recognised by their odour.

In addition to the metals of Group I., HCl may ppt., from an alkaline solution, As_2S_3, Sb_2S_3, SnS, and also H_4SiO_4 (gelatinous ppt.) Note the colour of the ppt. $BaCl_2$ may also be pptd. from a saturated solution of a baric salt, but is dissolved readily on the addition of a little H_2O.

SH_2 in the presence of oxidising agents produces a ppt. of S in the second group; it may be recognised by its being white and remaining suspended in the liquid. It does not interfere with the reaction of the metals, and may therefore be neglected.

The solution must not be too acid, as CdS is not pptd. in the presence of a large excess of HCl.

AmCl and AmHO ppt. not only the metals of Group III. A, but also phosphates of the metals of Groups III. and IV., and H_4SiO_4, if present. A small portion only of the filtrate of Group II. is first tested; should there be a ppt., it is necessary to test for and remove the H_4SiO_4, if present. (Except in very few cases, SiO_2 will not be found when the substance has completely dissolved in H_2O.) The presence of H_3PO_4 requires special steps to be taken for its removal. The filtrate is boiled with HNO_3 in order to oxidise any ferrous salts present.

The ppt. in Group III. A must be filtered and washed immediately, because Mn, if present, is after a time oxidised into $Mn_2O_2(HO)_2$, and is then found in the ppt. If Mn be present in the substance, traces are always pptd. with the metals of Group III. A; these, however, may be neglected.

NiS is somewhat soluble in SAm_2, to which it imparts a yellowish-brown tint. Under these circumstances, after filtering off the ppt., evaporate the filtrate nearly to dryness, add H_2O, again filter, and test

the ppt. specially for Ni by the borax bead reaction. Add Group IV. reagents to this second filtrate.

Special care must be taken not to boil Group IV. solution, to which the reagents have been added, as thereby $CaCO_3$ is in part reconverted into $CaCl_2$, and passes over into the fifth group.

Table B, for the examination of Group I. precipitate.

<table>
<tr><td colspan="3">Transfer the ppt. to a test-tube, add water, boil and filter while hot. Wash the ppt. with boiling water.</td></tr>
<tr><td colspan="2">Residue.—Add AmHO, and filter.</td><td rowspan="2">Solution.—Add K_2CrO_4 —yellow ppt. of $PbCrO_4$.

Confirmed by dry reaction.

Pb is present.</td></tr>
<tr><td>Residue is blackened, and consists of NH_2Hg_2Cl.

Confirmed by dry reactions.

Hg is present as a mercurous salt.</td><td>Solution.—Add HNO_3 —a white curdy ppt. of AgCl, turning purple on exposure to light.

Confirmed by dry reaction.

Ag is present.</td></tr>
</table>

The separation of the metals of this group depends on solubility of $PbCl_2$ in hot H_2O; the solubility of AgCl in AmHO, and the insolubility of Hg_2Cl_2 in that reagent.

The absence of the reactions given may be taken as evidence of the absence of the particular metals. Thus, if the ppt. left no residue on being boiled with water, AgCl and Hg_2Cl_2 cannot be present; or if the water dissolved out nothing, $PbCl_2$ must be absent.

If a portion of the $PbCl_2$ solution be set aside to cool, $PbCl_2$ will crystallise out.

Table C, for the examination of Group II. precipitate.

Thoroughly wash the ppt. with water, to which a few drops of SH_2 solution have been added, transfer the ppt. to a test tube, digest with NaHO and filter.

Residue may contain **HgS, PbS, Bi_2S_3, CuS,** and **CdS**. Note the colour, if yellow CdS only is present. If dark coloured, wash, boil with conc. HNO_3, dilute and filter.

Solution may contain the sulphides of **Sb, Sn,** and **As**. Re-ppt. by adding HCl in slight excess; filter, wash and digest with one or two fragments of *solid* ammonium carbonate (sesquicarbonate), and filter.

Residue is black, and consists of HgS.

Confirmed by dry reaction.

Hg is present as a mercuric salt.

Solution.—Add H_2SO_4 and equal volume of alcohol (methylated spirit); filter.

Precipitate consists of $PbSO_4$.

Confirm by dissolving the ppt. in boiling ammonium acetate, and adding K_2CrO_4—yellow ppt. of $PbCrO_4$.

Pb is present.

Filtrate.—Boil off alcohol, add AmHO in excess, boil and filter.

Precipitate consists of $Bi(HO)_3$.

Confirm by dissolving in the smallest possible quantity of HCl, and then adding H_2O—white ppt. of BiOCl.

Bi is present.

Filtrate—if blue, Cu is present, if not Cu is absent. If Cu is present, add solution of KCy drop by drop until the blue colour just disappears. Add SH_2 solution.

Precipitate is yellow, and consists of CdS.

Confirmed by dry reaction.

Cd is present.

Filtrate will contain $CuCy_2$ if Cu is present.

Confirm by acidulating with HCl, boiling off HCy, and adding K_4FeCy_6—brown ppt. of Cu_2FeCy_6.

Cu is present.

Residue may contain Sb_2S_3 and SnS or SnS_2. Dissolve in boiling conc. HCl, dilute with H_2O, introduce a piece of Pt foil and a fragment of Zn.

Solution may contain As_2S_3. Acidulate with HCl — bright yellow ppt. of As_2S_3 is re-pptd.

Confirmed by dry reactions. (Fleitmann's and Marsh's tests may be used as further confirmatory tests if thought desirable.)

As is present.

Sb produces a black stain on the Pt: dissolve this off with HNO_3, evaporate down and add SH_2—orange ppt. of Sb_2S_3.

Confirmed by dry reaction on charcoal. (May be further confirmed by Marsh's test.)

Sb is present.

Sn is deposited on the Zn: dissolve by boiling with conc. HCl with the aid of a piece of Pt foil introduced. Dilute with H_2O and add $HgCl_2$—white ppt. of Hg_2Cl_2 or grey ppt. of Hg.

Sn is present.

The separation of the metals of this group depends (1st) on the solubility of the sulphides of Sb, As, and Sn in NaHo, while the others are insoluble. The As_2S_3 is soluble in hydric ammonic carbonate (solution of the solid carbonate, $AmHCO_3$), and is thus separated from the sulphides of Sn and Sb. These are then dissolved in HCl; on Pt and Zn being introduced, a voltaic action is set up, and this causes the deposition of the Sb on the Pt; the Sn is deposited on the Zn; both are then recognised by confirmatory tests.

The sulphides insoluble in NaHO are soluble in HNO_3, with the exception of HgS. This reaction therefore enables us to separate this sulphide. Any traces of Pb are removed by precipitation with H_2SO_4 and alcohol (most sulphates are less soluble in alcohol and H_2O than H_2O alone). $Bi(HO)_3$ is insoluble in excess of AmHO; $Cu(HO)_2$ and $Cd(HO)_2$ are soluble. The blue colour of the ammoniacal solution of $Cu(HO)_2$ is a sure test of the presence of Cu. Cu and Cd are both pptd. by KCy, and are both soluble in excess; from this solution SH_2 ppts. CdS, but not CuS; in this way the last two are separated.

S_2Am_2 may be used instead of NaHO for the separation of the sulphides of As, &c. If the presence of HgS is suspected, it is preferable to use S_2Am_2, as HgS is somewhat soluble in NaHO. If NaHO or S_2Am_2 leaves a yellow residue, it can only consist of CdS. To be sure that it is not confounded with S, dissolve in HCl, and filter; add AmHO and SH_2—CdS is re-pptd. In the absence of the other sulphides, treatment with HNO_3, &c., is of course unnecessary. HNO_3 ppts. S from SH_2; a white ppt., therefore, on treating the mixed sulphides with this reagent may be neglected.

If, from the absence of any blue coloration on the addition of AmHO for the separation of Bi, Cu is known not to be present, proceed at once to test for Cd by adding AmHO in slight excess and SH_2, when Cd will be pptd. as CdS if present.

A careful preliminary examination should reveal with certainty the presence or absence of As, and Sb ought also to be detected if present. This knowledge is of material help in the examination of the ppt. containing As_2S_3, &c. In the known absence of As, treatment with $AmHCO_3$ is unnecessary.

When directions are given to 'digest' a ppt., put the test-tube containing it into a beaker of boiling water. This prevents the temperature of the substance to be digested actually reaching the boiling point.

Table D, for the examination of Group III. A precipitate in the absence of Phosphoric Acid.

Note the colour of the ppt.: if white, $Al_2(HO)_6$ only is present; if coloured green or reddish brown, Cr or Fe is present. Dissolve the ppt. in dilute HCl, add NaHO in excess, boil and filter.

RESIDUE.—Dry and test for Cr by fusing on Pt foil with fusion mixture and KNO_3. Dissolve in hot H_2O, and filter.		SOLUTION may contain Al: acidulate with HCl, and add a slight excess of AmHO—white gelatinous ppt. of $Al_2(HO)_6$. **Al is present.**
RESIDUE.—Dissolve in HCl, and test by K_4FeCy_6—a dark blue ppt. **Fe is present.**	SOLUTION is of a yellow colour through the formation of K_2CrO_4. Confirm by adding $HC_2H_3O_2$ (acetic acid) and lead acetate—yellow ppt. of $PbCrO_4$. Confirmed also by borax bead reaction. **Cr is present.**	

The separation and detection of the metals of this group depends on the solubility of $Al_2(HO)_6$ in NaHO; the formation of a chromate by fusion of Cr compounds with fusion mixture and KNO_3, while Fe remains in the residue.

To determine whether the Fe is present in the substance as a ferrous or ferric salt, test the original solution in H_2O or HCl by $K_6Fe_2Cy_{12}$ and AmCyS.

Should the group ppt. contain any Mn, the solution after fusion with fusion mixture and KNO_3 will be coloured purple by permanganate. This, although obscuring the yellow colour of the fused mass and its solution, will not interfere with the precipitation of $PbCrO_4$.

It is difficult to obtain NaHO free from alumina. In cases where the detection of Al is very important, NaHO prepared from Na should be used. The student should test the NaHO for Al, and thus he will be able to judge whether his ppt. in this group is more than that afforded by the reagents alone.

Table E, for the examination of Group III. A precipitate in the presence of Phosphoric Acid.

Dissolve the ppt. in slight excess of HCl. Test specially for Fe in small portion by K_4FeCy_6. Add AmHO to the main portion drop by drop until the solution is nearly neutral (this is known by a drop producing a slight ppt. which only just dissolves on shaking the solution); add ammonium acetate: if the liquid does not redden, add a single drop of dilute Fe_2Cl_6 solution, or sufficient to produce a slight red coloration. Boil and filter.

PRECIPITATE contains all the H_3PO_4 in combination with Fe, or Al and Cr if present. Wash, boil with excess of pure NaHO, and filter.

RESIDUE. — Dry a portion and fuse on Pt foil with fusion mixture and KNO_3. Dissolve in H_2O, filter if necessary, and add acetic acid and lead acetate to the filtrate — yellow ppt. of $PbCrO_4$.

Cr is present.

SOLUTION. — Acidulate with HCl, add AmHO — white gelatinous ppt. of $Al_2(PO_4)_2$.

Confirm by igniting the ppt. on charcoal and treating with $Co(NO_3)_2$ — blue coloured mass.

Al is present.

FILTRATE may contain any of the metals of Groups III. B and IV. Proceed, as directed in general table A, to add the several reagents for these groups.

Ammonium acetate ppts. the phosphates of Al, Fe, and Cr, if present. Should these be absent, Fe_2Cl_6 is added in order to decompose the phosphates of Groups III. B and IV., chlorides of these metals being formed and $Fe_2(PO_4)_2$ pptd. The Fe_2Cl_6 must be added cautiously, as the phosphate is soluble in excess of Fe_2Cl_6. The slightest excess produces a red coloration, owing to the formation of iron acetate. On boiling, the whole of the iron is pptd. Fe_2Cl_6 being here used as a reagent, Fe must be specially tested for.

The detection of Al depends on the solubility of $Al_2(PO_4)_2$ in NaHO.

Table F, for the examination of Group III. B precipitate.

Should the filtrate from this ppt. be dark in colour, proceed according to note on Table A. This coloration is a valuable indication of the presence of Ni. Wash the ppt. with water to which a little SH_2 has been added. Shake up with cold dilute HCl, and filter.

Residue may contain CoS and NiS.		Solution.—Boil off SH_2 (filter if necessary), add excess of NaHO, heat and filter.	
Co will have been detected by the deep-blue coloration of the borax bead in dry reaction. Confirm by repeating this test with a trace of the residue—blue coloration. **Co is present.**	Ni will have been indicated by solubility of NiS. In the presence of Co, dissolve the residue by boiling with conc. HCl and a small fragment of $KClO_3$, boil until the chlorous odour disappears, nearly neutralise with Na_2CO_3, add KCy drop by drop until the ppt. first formed is just redissolved, boil briskly, then add large quantity of NaClO solution or Br water, and warm gently—black ppt. of $Ni_2(HO)_6$. Confirm by testing the ppt. for Ni in borax bead. **Ni is present.**	Precipitate is white, and consists of $Mn(HO)_2$ but rapidly turns brown. Confirm by fusion on Pt foil with fusion mixture and KNO_3—blue residue. **Mn is present.**	Filtrate.—Add SH_2—white ppt. of ZnS. Confirm by igniting the ppt. on charcoal and then heating with $Co(NO_3)_2$—green mass. **Zn is present.**

The separation of the metals of this group depends, first on the insolubility of CoS and NiS in cold dilute HCl. In the presence of Co, which is detected in the preliminary examination by the borax bead reaction, Ni is separated by ppting. the metals as cyanides, and then dissolving the ppt. in excess of KCy: from this solution NaClO ppts. $Ni_2(HO)_6$ but not Co.

The separation of Mn and Zn depends on the solubility of $Zn(HO)_2$ and insolubility of $Mn(HO)_2$ in an excess of NaHO.

Should the group ppt. be light in colour NiS and CoS are absent; if no Co reaction has been obtained in the dry examination, a black ppt. can only be NiS; separation by KCy and NaClO is then unnecessary. It is well, however, to make sure of the absence of Co by testing the group ppt. by the borax bead reaction.

Table G, for the examination of Group IV. precipitate.

Wash the ppt., dissolve in the smallest possible quantity of acetic acid. Test a small portion of this solution for Ba by adding K_2CrO_4: if absent, test another small portion for Sr by flame coloration on Pt wire, and also by adding $CaSO_4$ to a portion and allowing it to stand for some minutes; if Ba and Sr are absent, the ppt. must be $CaCO_3$. Confirm by largely diluting a portion of the solution with H_2O and adding ammonium oxalate—white ppt. of calcium oxalate. In the presence of Ba, add K_2CrO_4 in slight excess to the main portion of the acetic acid solution, and filter.

PRECIPITATE is yellow, and consists of $BaCrO_4$. Wash and confirm by flame coloration — green. **Ba is present.**	FILTRATE.—Add dilute H_2SO_4, filter and wash. Digest the ppt. for some time with AmHO and a saturated solution of Am_2SO_4. Filter.	
	RESIDUE consists of $SrSO_4$. Confirm by moistening with HCl and testing flame coloration —crimson. **Sr is present.**	SOLUTION.—Dilute largely and add ammonium oxalate—white ppt. of calcium oxalate. **Ca is present.**

The separation depends on the insolubility of $BaCrO_4$ in acetic acid, and the solubility of $CaSO_4$ and the insolubility of $SrSO_4$ in Am_2SO_4.

$BaCrO_4$ is very difficult to filter; the best plan is to use for this purpose a 'Swedish' filter paper, as this make has much finer texture.

In making flame tests, the yellowish red Ca coloration must not be confounded with the rich crimson of Sr.

Table H, for the examination of Group V. solution.

To a portion of the solution add Na_2HPO_4 and shake well—a white crystalline ppt. of $MgAmPO_4$—Mg is present. Mg, if present, must be removed as follows :—Evaporate the solution to dryness, and ignite to expel Am salts, add a few crystals of pure oxalic acid and one or two drops of water, evaporate solution and again ignite ; add water and filter ; evaporate the filtrate or the main portion of the group to dryness ; if there is no residue K and Na are absent.[1] Dissolve the residue in a very little H_2O with one or two drops of HCl, and test a portion for K by $PtCl_4$ and a few drops of alcohol in a watch glass.

PRECIPITATE is yellow and crystalline, and consists of $(KCl)_2PtCl_4$. Confirm by flame coloration on Pt wire—violet. **K is present.**	REMAINDER OF SOLUTION IN H_2O. Test for Na by flame coloration —golden yellow. [Na may be confirmed by filtering off the ppt. of $(KCl)_2PtCl_4$, removing excess of $PtCl_4$ (known by yellow colour of solution), by adding a grain of pure sugar, evaporating to dryness and igniting. The residue is then treated with H_2O, filtered, and the filtrate evaporated to dryness; if Na were present, there will be a residue of NaCl.] **Na is present.**

The separation depends on the insolubility of $MgAmPO_4$ for the detection of Mg, which is then removed by driving off Am salts, and converting the bases into carbonates by ignition with oxalic acid, $MgCO_3$ being insoluble in H_2O and alkaline carbonates. The K is detected by its reaction with $PtCl_4$. Na is rarely separated out, the golden flame coloration being usually relied on.

If it is desired in Group V. to detect the bases of the group without separating them, the following simpler method may be adopted :—

Evaporate the solution to dryness and ignite so as to expel

[1] Should H_3PO_4 be present, in the absence of Mg and Groups III. and IV., it would form a residue here ; under such circumstances, therefore, a residue is no proof of the presence of K and Na. H_3PO_4 will have been tested for between Groups II. and III. ; if present, and it be desired to separate out Na, the H_3PO_4 must be removed by the addition of AmHO, ammonium acetate and dilute Fe_2Cl_6 solution as directed in Table E. The separation may then be proceeded with by adding HCl and $PtCl_4$.

Am ; if there be no residue all members of the group are absent. Dissolve the residue in H_2O and

Test a portion of the solution for **Mg** by adding AmCl, AmHO, and Na_2HPO_4.

Test a second portion for **K** by adding HCl and $PtCl_4$: confirm by flame coloration.

Test for Na by flame coloration.

The presence of H_3PO_4 does not interfere with the reactions of K and Na.

Examination for Acids.

Knowing the bases present, refer to the table of solubilities, page 304, as, if the substance were soluble in H_2O, certain acids must be absent : thus a substance soluble in H_2O or HCl and containing Ba cannot also contain H_2SO_4.

The presence or absence of **nitric**, **chloric**, **silicic**, and **phosphoric** acids will have been determined when examining for bases.

Preliminary Examination.

Treat a little of the Powdered Substance in a Test-Tube with Dilute HCl—warm gently.[1]

Result.	Deduction. Presence of—
Colourless, odourless gas evolved, which turns lime-water milky.	**CO_2** from carbonates.
A gas evolved, having the odour of rotten eggs, which blackens lead-paper.	**SH_2** from certain sulphides.

[1] When told to warm gently, the heat must not be sufficiently intense to drive off fumes of the acid reagent being used.

TREAT ANOTHER PORTION OF THE POWDERED SUBSTANCE WITH CONCENTRATED H_2SO_4—WARM GENTLY.

RESULT.	DEDUCTION.
CO_2 and SH_2 as on treatment with HCl.	
Nitrous fumes evolved and odour of HNO_3.[1]	**HNO_3**, also indicated by deflagration on charcoal. Confirm by adding to aqueous solution of the substance mixed with H_2SO_4, $FeSO_4$.
Greenish-yellow explosive gas evolved.	Cl_2O_4 from **chlorates**, also indicated by deflagration on charcoal.
Pungent acid fumes evolved.	**HCl, HF.** Add a little MnO_2, Cl is evolved from **HCl**. The glass is corroded. Introduce into the mouth of the tube a glass rod moistened with a drop of H_2O, film of SiO_2—from **HF**. Confirm by etching on glass.
Acid fumes and reddish-brown vapours evolved, condensing into minute drops on the sides of the tube.	**HBr.**
Acid fumes and violet vapours evolved.	**HI.** Confirm by cooling the tube and then adding CS_2—violet coloration through I being dissolved.

Examination in the Wet Way.

The acids do not admit of such ready and complete classification as the bases, therefore in many instances special tests for certain acids are absolutely necessary.

[1] In the presence of an iodide, or bromide, this reaction of HNO_3 is very likely to be overlooked ; if there have been any indications of a nitrate given by the preliminary examination for the bases, test specially by H_2SO_4 and $FeSO_4$.

In preparing solutions for acids care must be taken to avoid the not uncommon error of dissolving the substance in the very acid to be tested for. For this reason separate portions of solution are prepared in different acids for the different tests.

The preliminary examination will have furnished the most characteristic tests for **CO_2**, **HF**, and **HNO_3** ; these and the acids detected in the examination for bases need not, therefore, be further tested for.

Test systematically for other acids as follows :—

H_2SO_4.—Treat a portion of the original substance with H_2O and a little dilute HCl ; heat very gently, and filter from any insoluble residue if necessary. Test the filtrate or solution by adding $BaCl_2$, and heating—white ppt. of $BaSO_4$. **H_2SO_4 is present.**

Sulphides not decomposed by dilute HCl.—The presence of these will have been indicated by treatment with aqua regia, which liberates plastic S. The aqua regia solution also gives a H_2SO_4 reaction from the oxidation of the S. To test for these sulphides in the presence of sulphates, treat the substance with successive quantities of boiling water until these washings, after being acidulated with HCl, no longer afford a ppt. with $BaCl_2$; then treat the residue with aqua regia and test the solution for H_2SO_4 by $BaCl_2$—white ppt. of $BaSO_4$. **H_2SO_4, produced by oxidation of sulphides, is present.**

HCl, HBr, HI.—Treat a portion of the original substance with H_2O and a little dilute HNO_3, heat very gently, and filter from any insoluble residue if necessary. To the solution or filtrate add $AgNO_3$—

White curdy ppt. of AgCl sol. in AmHO. **HCl is present.** Confirmed by preliminary examination.

Pale yellow ppt. of AgBr slightly sol. in AmHO. **HBr is present.** Confirmed by preliminary examination.

Yellowish-white ppt. of AgI almost insol. in AmHO. **HI is present.** Confirmed by preliminary examination.

Separation of HCl, HBr, and HI.—Wash the pptd. silver salts with water ; heat a small portion in a test-tube with conc. H_2SO_4. AgI is decomposed by this treatment with liberation of free I, which may be recognised by its colour in the tube. AgCl and AgBr are not acted on by H_2SO_4. In this way the presence or absence of iodides is determined.

An Iodide being present.—Prepare the following reagent. Mix

together some solution of $CuSO_4$ and strong H_2SO_3, and heat gently. In this way cuprous sulphate, Cu_2SO_4, is formed. Add to the original HNO_3 solution of the substance some of this Cu_2SO_4 and warm gently, cuprous iodide, Cu_2I_2, is pptd.; heat with this reagent until no more ppt. is formed, thus showing that the whole of the iodide has been removed. Next proceed in the following manner.

Iodides being absent.—Render the solution alkaline by adding pure KHO, and evaporate to dryness. Mix the residue with about four times its weight of powdered potassium bichromate, $K_2Cr_2O_7$, and transfer to a small retort. Add some concentrated H_2SO_4, and place the stem of the retort in a test-tube containing distilled water. (Care must be taken that no trace of the mixture gets into the stem of the retort). Heat very gently; if bromides be present, reddish-brown vapour of bromine is liberated and is carried over into the test-tube. If chlorides be present, a volatile compound of chlorine with chromium and oxygen, termed chlorochromic acid, CrO_2Cl_2, is formed and distils over also as a reddish-brown vapour. Distil as long as any coloured vapour is evolved.

Test the water for bromine by adding CS_2 and shaking up—brown coloration of the CS_2 shows that **bromides are present.**

Decant the water from the CS_2 and add to it excess of AmHO, acetic acid in excess, and then lead acetate solution—a yellow ppt. of lead chromate shows that CrO_2Cl_2 has distilled over, and consequently that **chlorides are present.**

$HClO_3$.—This acid is in most cases sufficiently recognised in the preliminary examination; its presence may further be confirmed by ignition of the substance and testing for HCl. If chlorides be present, first remove these by precipitation with $AgNO_3$, filter, evaporate to dryness, and ignite the residue; dissolve in H_2O with a little HNO_3 and test by adding $AgNO_3$—white ppt. of AgCl. **$HClO_3$ is present** in original substance.

H_3BO_3.—Mix a portion of the substance with conc. H_2SO_4 and alcohol, and set fire to the mixture. If Cu or Ba be present, perform the reaction in a flask, inflaming the vapour—green flame coloration. **H_3BO_3 is present.**

Having thus made a complete analysis of the substance, the various bases and acids found should be entered at the foot of the account of the analysis in the student's note-book.

Appended are the results of an analysis as they should be written. Remember that each experiment should be entered as performed.

Example showing how analytic results should be written.

SUBSTANCE GIVEN FOR ANALYSIS—a light grey powder.

Heated a little of the substance in a dry tube.

RESULT.	DEDUCTION. Presence of—
White sublimate, dark-coloured. residue.	Am, Hg, As. Tested specially for Am by heating a portion with NaHO—no ammoniacal odour—Am is absent. Heated another portion of the original substance with fusion mixture—liquid metallic sublimate Hg.

Heated a portion of the substance on charcoal before the blowpipe in oxidising flame.

Dark-coloured residue.	CuO, &c. Heated in borax bead in OF.—Amethyst bead, Mn. Tested specially for Mn by heating with fusion mixture and KNO_3 on Pt foil—bluish-green mass—Mn.

Heated a portion of the substance with fusion mixture in the reducing flame.

No special reaction.	Zn, &c., absent.

Heated a portion of the substance, moistened with HCl, in the Bunsen flame.

No reaction	Cu, &c., absent.

Tested the solubility of the substance, first with H_2O, partly soluble; second with dilute HCl. Dissolved readily with effervescence.

To portion of solution added HCl—				
No ppt.	Diluted solution and passed H_2S—			
	Black ppt. filtered and washed.	Boiled filtrate till free from H_2S. Tested portion for H_3PO_4—absent. Added to small portion AmCl and AmHO—no ppt. Added these reagents and H_2S to the main portion—		
		Tawny yellow ppt. filtered and washed.	To filtrate added AmHO and Am_2CO_3.	
			No ppt.	Reserved solution for tests for Group V.

Examination of Group II. ppt.

Washed, transferred to a test-tube, and digested with NaHO—					
Residue.—Washed, boiled with conc. HNO_3, diluted and filtered.					Solution — acidulated with HCl—
Residue is black, and consists of HgS. Confirmed by dry reaction in preliminary. Hg is present as a mercuric salt.	Solution, added H_2SO_4 and alcohol—				No ppt. As, Sb and Sn are absent.
	No ppt. Pb is absent.	Boiled off alcohol and added AmHO in excess—			
		No ppt. Bi is absent.	Solution is not blue, added SH_2 solution.		
			No ppt. Cd is absent.	No blue coloration. Cu is absent.	

Examination of Group III. B ppt.

The ppt. being light-coloured, Ni and Co are absent; washed, added excess of NaHO, heated and filtered—	
White ppt., which rapidly turned brown. Confirmed by preliminary reactions. Mn is present.	Filtrate—added SH_2—No ppt. Zn is absent.

Examination of solution for Group V.

To a portion added Na_2HPO_4, and shook violently—	
No ppt. Mg is absent.	Evaporated the main portion of the Group solution to dryness and ignited—no residue. K and Na are absent.

Examination for Acids.

Added HCl to a portion of the substance in a test-tube.

Result.	Deduction.
Colourless, odourless gas evolved, which turned lime-water milky	CO_2 from a carbonate.

Added conc. H_2SO_4 to another portion of the substance, and heated.

At a comparatively high temperature, a slight quantity of acid fumes evolved.	HCl. Added a little MnO_2, Cl was evolved—from HCl.

Special Tests in the Wet Way.

For

H_2SO_4.—Added $BaCl_2$ to portion of HCl solution—no ppt. H_2SO_4 is absent.

HCl.—Added H_2O and HNO_3 to portion of original substance, and then added $AgNO_3$—white curdy ppt. of AgCl, readily soluble in AmHO. HCl is present.

H_3BO_3.—Mixed a portion of the substance with conc. H_2SO_4 and alcohol, and set fire to the mixture—no green flame coloration. H_3BO_3 is absent.

Results of Analysis, Found—

Bases—HgO, MnO.
Acids—CO_2, HCl.

Directions for the Analysis of unknown Substances containing Organic Acids in combination with Inorganic Bases.

The methods employed for the analysis of these substances are in the main similar to those used in the case of inorganic compounds ; somewhat greater care is, however, necessary in discriminating between the various acids.

Preliminary Examination for Base.—This is to be conducted in the same manner as with inorganic salts, except that the reactions of the various inorganic acids given in the table for the preliminary examination need not be looked for ; but instead the following ADDITIONAL reactions in a dry tube may occur :—

Heat a portion of the Powdered Substance in a Dry Tube.

Result.	Deduction. Presence of—
Gas evolved, which burns with a peach-blossom-coloured flame.	Cy, from certain **cyanides.**
Acetone is evolved.	From **acetates.**
Crystalline sublimate is formed, and incense-like odour evolved.	**Benzoic acid.**
Crystalline sublimate is formed, and fumes which cause violent coughing.	**Succinic acid.**
Crystalline sublimate is formed, and abundance of white fumes.	**Oxalic acid.**
CO is evolved.	From **formates** and **oxalates.**
Odour of burnt sugar evolved, and carbonaceous residue.	**Tartaric acid.**
Pungent acid fumes, and carbonaceous residue (also slight odour of burnt sugar.)	**Citric acid.**

In the examination for bases in the wet way, proceed as directed in the tables as far as the separation of Group II., then, after boiling the filtrate till free from SH, add a little conc. HNO_3, evaporate to complete dryness, and ignite the residue,

which should be kept at a red-heat until any C present is burned away.[1] When cool, add a little conc. HCl, dissolve in H_2O, and add AmCl and AmHO ; proceed for the rest of the table as with an inorganic compound. The organic acids are destroyed at this stage of the analysis by ignition, because the presence of some of them prevents the precipitation of the members of Group III. A. Ignition is not advisable before commencing the analysis, as thereby Hg and As salts would be expelled.

Examination for Acids.

The preliminary examination must be made with very great care, as a systematic separation of the organic acids is in many instances only performed with difficulty.

Preliminary Examination.

Heat a portion of the Substance in a Test-tube with conc. H_2SO_4.

Result.	Deduction. Presence of—
Gas evolved having odour of bitter almonds.	**HCy.** Confirm by allowing the gas to act on a drop of SAm_2 on a watch-glass, and subsequently testing by Fe_2Cl_6 (see page 274).
Odour of formic acid	**Formic acid.**
Smell of vinegar	**Acetic Acid.** Confirm by adding single drop of alcohol and observing smell of acetic ether.
CO and CO_2 evolved (gases which respectively are inflammable, and turn lime-water milky).	**Oxalic acid.**
CO, CO_2 and SO_2 evolved with blackening of the mixture.	**Tartaric acid.**
CO and CO_2 evolved, but mixture does not blacken until after some time, when SO_2 is also evolved.	**Citric acid.**

[1] In the absence of a ppt. with HCl and SH_2, time may be saved by igniting a portion of the original substance instead of evaporating to dryness.

The preliminary tests for organic acids depend largely on the sense of smell; the reactions should therefore be carefully made on the known substances until the various odours can be recognised with certainty. When more than one acid is present the difficulty is increased, but even then the different acids may often be detected. Apply to the nose several times during the experiment, as the reactions of the whole of the acids do not occur at the same temperature, and thus they may frequently be detected in succession. Many persons are unable to smell HCy; when such is the case, special tests must be made for the detection of that acid.

Separation in the Wet Way.

If sulphuric acid give a reaction in the preliminary examination, introduce a portion of the substance in a small retort, add dilute H_2SO_4, and distil: acetic and formic acids, if present, will be found in the distillate; to a portion of this add $Hg_2(NO_3)_2$ and beat gently—grey ppt. of metallic Hg. **Formic acid is present.**

To test for the remaining acids, prepare a solution in the following manner:—If the metals of Groups I. and II. be present, remove them by their respective group reagents, boil off SH_2, and filter; add slight excess of Na_2CO_3 to filtrate, and boil for five minutes, filter off any ppt. and test filtrate for acids. In the absence of Groups I. and II. proceed at once to adding Na_2CO_3; if the only bases present are Na_2O and K_2O, the subsequent tests may be made directly on the original solution.

Acidulate a portion of the solution thus prepared by HNO_3, add $AgNO_3$ in slight excess: a white ppt. is formed consisting of AgCl (from the HCl used in separating Group I.), and AgCy if HCy be present. Wash, dry and ignite the ppt.: AgCy, if present, is decomposed with separation of metallic Ag (AgCl remains unaltered). Dissolve in HNO_3, filter, and add HCl—white ppt. of AgCl. **HCy is present in substance.**

In the known absence of HCl, the ppt. with $AgNO_3$ can only be AgCy. Care must be taken that in igniting the ppt. no reducing action takes place—thus none of the filter must be present.

Neutralise the main portion of the solution if alkaline (from the addition of Na_2CO_3) by adding dilute HNO_3 drop by drop,

and boiling, until a slightly acid reaction is obtained on testing with litmus; then exactly neutralise by adding a drop (or two) of dilute NaHO. Neutralise if acid (from original substance containing a free organic acid), by adding NaHO drop by drop until without action on litmus-paper.

Table for the separation of Organic Acids.

<table>
<tr><td colspan="4">To the neutral solution add large excess of $CaCl_2$, shake up, allow to stand for twenty minutes, and filter.</td></tr>
<tr><td colspan="2">PRECIPITATE.—Wash, add cold NaHO, and filter.</td><td colspan="2">FILTRATE.—Boil for some minutes.</td></tr>
<tr><td>RESIDUE consists of calcium oxalate.

Confirm by gentle ignition, $CaCO_3$ is produced and effervescence on addition of HCl.

Oxalic acid is present.</td><td>SOLUTION.—Boil, calcium tartrate, if present, is re-pptd.

Confirmed by reactions in preliminary examination.

Tartaric acid is present.</td><td>PRECIPITATE consists of calcium citrate.

Confirm by dissolving in HCl and re-ppting. by AmHO; also by preliminary reactions.

Citric acid is present.</td><td>FILTRATE.—Add three times the volume of alcohol, and filter.

PRECIPITATE consists of calcium succinate.

Confirmed by reaction when heated in dry tube.

Succinic acid is present.</td><td>FILTRATE.—Boil off alcohol; add neutral solution of Fe_2Cl_6—pale yellow ppt.

Benzoic acid is present.</td></tr>
</table>

It is necessary before testing for the organic acids to remove the heavy metals, as they interfere with certain of the reactions; ammonia, if present, is also expelled (by boiling with Na_2CO_3) for the same reason.

The NaHO, used for the separation of oxalic and tartaric acids, must be free from carbonate. To effect this, add some lime to the NaHO solution, shake up, allow to subside, and draw off the clear solution, as wanted, with a small pipette. Keep the bottle closely stoppered and shake up from time to time.

The Fe_2Cl_6 used for the precipitation of ferric benzoate must contain no free acid; to effect this, add a drop of AmHO, so as to produce a slight ppt., and filter. The separation of the organic acids must throughout be conducted with great care.

I. Table of Solubilities.—(See Page 293.)

(Thorpe and Muir.)

This table is so arranged that the *bases* are placed at the heads of the columns, the *acids* with which they may be combined at the side.

The figures refer to the various *menstrua* in which the salts are soluble. Thus:

I. means soluble in water.
II. means soluble in acids, but insoluble in water.
III. means insoluble in both water and acids.

The solubilities of the more commonly occurring salts are indicated by large letters I. II. III., while those which are of less frequent occurrence have small letters placed after them—1, 2, or 3.

Some substances belong to more than one class—this is indicated thus: 1-2 means a substance difficultly soluble in water, but soluble in acids. 1-3 means a substance soluble with difficulty in water, the solubility of which is not increased by the addition of acids.

2-3 means a substance insoluble in water, and but slightly soluble in acids. The solubilities of the more commonly occurring double salts are given in a separate table. In this table a few of the simple and compound Cyanides are also enumerated.

A small number attached to the figure indicating the solubility of a substance, thus II_6, means that further information is given in the notes to the table.

Acids and Halogens, &c.	Group I.			Group II. Div. 1				Group II. Div. 2 (See Acids)				
	PbO II.	Ag_2O 2	Hg_2O II.	HgO II.	Bi_2O_3 2	CuO $II._2$	CdO 2	As_2O_3 I.–II.	As_2O_5 II.	SnO 2	SnO_2 2–3	Sb_2O_3 2_3
S . .	2	2_3	$II._4$	$II._4$	2	2	2	$II._3$	$II._5$	2_6	2_6	2_7
Cl . .	I.–III.	III.	II.–III.	I.	I.	I.	1	—	—	I.	1	I.
I . .	II.	3	II.	—	—	—	1	—	—	2	1	—
SO_4. .	II.–III.	I.–III.	1–2	I.	1	I.	I.	—	—	1	—	—
NO_3 .	I.	1	I.	I.	$I._9$	I.	I.	—	—	—	—	—
PO_4. .	2	2	2	2	—	2	2	—	—	—	—	—
CO_2 .	II.	2	2	2	2	II.	2	—	—	—	—	—
BO_3 .	2	1	—	2	2	2	1–2	—	—	—	2	—
C_2O_4 .	II.	2	2	2	2	2	2	—	—	—	2	1–2
ClO_3 .	1	1	1–2	1	—	1	1	—	—	—	—	1
As_2O_3 .	2	2	2	2	2	2	—	—	—	—	—	2
As_2O_5 .	2	2	2	2	—	II.	—	—	—	—	—	2
$C_2H_3O_2$.	I.	1	1–2	1	1	I^{11}	1	—	—	1	1	1
$C_4H_4O_6$.	2	2	1–2	2	2	1	1–2	—	—	1–2	—	I.
CHO_2 .	1	1	1	—	1	1	1	—	—	2	—	—
$C_6H_5O_7$.	2	2	2	—	—	1	1	—	—	—	—	—

Bases (continued).

Acids and Halogens, &c.	Group III.				Group IV.				Group V.				Group VI.		
	FeO II.	Fe_2O_3 II.	Cr_2O_3 II.–III.	Al_2O_3 II.	CoO II.	NiO II.	ZnO II.	MnO II.	BaO I.	SrO I.	CaO I.–II.	MgO II.	$(NH_4)_2O$ I.	Na_2O I.	K_2O I.
S . .	II.	II.	—	—	$II._8$	$II._8$	II.	II.	I.	I.	I.–II.	2	I.	I.	I.
Cl . .	I.	I.	I.	1	I.	I.	1	I.	I.	I.	I.	1	I.	I.	I.
I . .	1	1	—	—	—	—	1	1	1	1	1	1	1	1	I.
SO_4 .	I.	I.	I.	I.	1	I.	I.	I.	III.	III.	I.–III.	I.	I.	I.	I.
NO_3 .	1	1	1	1	I.	1	1	I.	1	1	1	1	I.	I.	I.
PO_4 .	2	II.	2	2	2	2	2	2	2	2	II.	2	I.	I.	I.
CO_2 .	2	—	—	—	2	—	II.	II.	II.	II.	II.	II.	I.	I.	I.
BO_3 .	2	2	2	2	2	2	2	2	2	2	2	2	1	1	I.
C_2O_4 .	1–2	2	1	2	2	2	2	2	2	2	II.	2	I.	I.	I.
ClO_3 .	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
As_2O_3 .	2	2	1	2	2	2	3	2	2	2	2	2	I.	1	1
As_2O_5 .	2	—	—	—	2	2	—	—	2	1	2	—	I.	1	1
$C_2H_3O_2$.	1	I.	1	1	1	1	1	—	I.	1	1	1	I.	I.	I.
$C_4H_6O_6$.	1–2	I.	1	1	1	—	2	1–2	2	2	II.	1–2	I.	I.	I.
CHO_2 .	1	1	—	1–2	1–2	1	1	1	1	1	1	1	1	1	1
$C_6H_5O_7$.	1	1	1	1–2	—	2	2	1	2	1	2	1	1	1	1

Table of Solubilities.—No. 2.

Cyanide of Potassium	I.
Ferrocyanide ,, ...	I.
Ferricyanide ,, ...	I.
Ferrocyanide of Zinc and Potassium	II.
Prussian blue	III.

DOUBLE SALTS.

Potassium-aluminium sulphate	I.
Aluminium-ammonium sulphate	I.
Potassium-ammonium tartrate	I.
,, *Sodium* ,, ...	I.
,, *Ferric* ,, ...	I.
,, *Antimony* ,, ...	I.
Sodium-ammonium phosphate	I.
Ammonium-copper chloride	I.
,, *Mercury* ,, ...	II.
Platinum-ammonium ,, ...	1–3.
,, *Potassium* ,, ...	1–3.

Notes to Table of Solubilities.

1. *Hydrochloric acid* converts *minium* into chloride insoluble in excess of the reagent. Nitric acid dissolves it partially, but converts some of it into insoluble brown lead peroxide.

2. *Antimonious oxide*, soluble in hydrochloric, but insoluble in nitric acid.

3. *Silver sulphide*, soluble only in nitric acid.

4. *Mercurous and mercuric sulphides*, soluble only in aqua regia.

5. *Arsenic sulphides*, decomposed slightly by boiling strong hydrochloric acid, but decomposed and dissolved by nitric acid.

6. *Tin sulphides* are decomposed and dissolved by hydrochloric acid, nitric acid converts them into insoluble hydrates.

7. *Antimonious sulphide*, dissolves in strong hydrochloric acid.

8. *Nickel and cobalt sulphides*, much more easily decomposed and dissolved by nitric than by hydrochloric acid.

9. *Basic bismuth nitrate*, soluble in acids.

10. *Basic lead acetate*, partially soluble in water, completely so in acids.

List of Reagents.

Sodium Hydrate, NaHO. Dissolve one part of the pure sticks or lumps in ten parts of water.

Sodium Phosphate, Na_2HPO_4. One part to ten of water.

Sodium Carbonate, Na_2CO_3. One part to five of water.

Potassium Ferrocyanide, K_4FeCy_6. One part to twelve of water.

Potassium Cyanide, KCy. One part to eight of water. (Solution made only when required.)

Ammonium Oxalate, $Am_2C_2O_4$. One part to twenty-four of water.

Ammonium Chloride, AmCl. One part to six of water.

Ammonium Carbonate, Am_2CO_3. One part to five of water, and one part of strong ammonia.

Ammonium Sulphide, Am_2S. Three parts of concentrated hydric ammonic sulphide, two of strong ammonia, and fifty of water.

Ammonium Hydrate, AmHO. One part of concentrated solution to three of water.

Ammonium Sulphate, Am_2SO_4. Make a saturated solution.

Barium Chloride, $BaCl_2$. One part to ten of water.

Ferric Chloride, Fe_2Cl_6. One part to ten of water.

Calcium Chloride, $CaCl_2$. One part to five of water.

Silver Nitrate, $AgNO_3$. One part to twenty of water.

Lead Acetate, $Pb.(C_2H_3O_2)_2$. One part to ten of water.

Cobalt Nitrate, $Co(NO_3)_2$. One part to ten of water.

Acetic Acid, $HC_2H_3O_2$. One part of the glacial acid to two of water.

Sulphuric Acid (dilute), H_2SO_4. One part of the concentrated acid to five of water.

Nitric Acid (dilute), HNO_3. One part of the concentrated acid to three of water.

Hydrochloric Acid (dilute), HCl. One part of the concentrated acid to three of water.

Sulphuretted Hydrogen solution, H_2S. Pass the washed gas into water until saturated.

Borax.
Fusion Mixture. } Used in the solid state

Sodium Hypochlorite, NaClO. Dissolve six parts of bleaching powder ($CaOCl_2$) in seven parts of water; add twelve parts of crystallised sodium carbonate, dissolved in the smallest possible quantity of water: shake up, allow to subside, and filter off the clear liquid, which is a solution of NaClO.

Potassium Ferricyanide, $K_6Fe_2Cy_{12}$. One part to twelve of water. (Solution made only when required.)

Potassium Chromate, K_2CrO_4. One part to eight of water.

Potassium Iodide, KI. One part to twenty of water.

Potassium Nitrate, KNO_3. Used in the solid state.

Ammonium Sulphocyanide, AmCyS. One part to ten of water.

Ammonium Acetate, $AmC_2H_3O_2$. One of concentrated solution to one of water.

Ammonium Molybdate, Am_2MoO_4. Dissolve 150 grammes of the salt in one litre of water, and pour into one litre of dilute nitric acid (one of acid to one of water). The acid must not be poured into the solution of the salt.

Mercuric Chloride, $HgCl_2$. One part to sixteen of water.

Platinum Chloride, $PtCl_4$. One part to ten of water.

Magnesium Sulphate, $MgSO_4$. One part to ten of water.

Stannous Chloride, $SnCl_2$. Dissolve by boiling with a little concentrated hydrochloric acid; to one part of the salt add four parts of water. Keep some granulated tin in the bottle.

Calcic Sulphate, $CaSO_4$. Shake up the salt with water, and decant the saturated solution.

Ferrous Sulphate, $FeSO_4$. One part to ten of water. (Solution made only when required.)

Tartaric Acid, $H_2C_4H_4O_6$. One part to three of water. (Solution made only when required.)

Concentrated Sulphuric, Nitric, and Hydrochloric Acids.

Sulphurous Acid Solution, H_2SO_3. Pass the washed gas into water until saturated.

Lime Water, $Ca(HO)_2$. Place some quicklime into a bottle, add water, shake up, allow to subside, and decant the clear solution.

Barium Hydrate, $Ba(HO)_2$. One part to twenty of water, shake up, allow to subside, and decant the clear solution.

Hydrogen Potassium Sulphate, $KHSO_4$. Used in solid state.

Starch. Shake up one of starch to about twenty of cold water, boil, and allow to cool. (Solution made only when required.)

Microcosmic Salt, $NaHAmPO_4$. Used in solid state.

Methylated Spirit. Use the commercial spirit.

Alcohol. Use the '*Sp. Vini. Rect.*' of the chemist.

QUESTIONS AND EXERCISES

WITH which are incorporated the whole of the Inorganic Chemistry questions set during the years 1886-92 inclusive, both by the Science and Art Department in the Elementary Stage, and the London University in the Matriculation Examination.

The questions are arranged, so far as practicable, in the order of the text.

1. Define 'chemistry,' 'element,' 'compound,' 'mixture.'

2. Describe any experiments you have witnessed which serve to illustrate the difference between mixture and chemical combination.

N.B.—You are desired not to attempt the description of experiments which you have not seen.

London University Matriculation, 1892.

3. Describe an experiment you have actually seen performed which affords an example of chemical action.

Science and Art, 1890.

4. Describe an experiment to illustrate the indestructibility of matter in the case of a burning candle. Give a drawing of the apparatus you would use. *S. and A.*, 1878.

5. It is stated that matter is indestructible; describe any experiments which confirm the truth of this statement.

S. and A., 1881.

6. In what ways do a mixture of copper and sulphur differ after being heated from their condition previous to the application of heat?

7. Describe the relation which exists between chemical action and other forces, especially *heat*.

8. Explain the meaning of the terms 'analysis' and 'synthesis,' and give two cases of each in illustration.

S. and A., 1886.

9. How can you show that the volume of a gas is changed by temperature and pressure?

S. and A., 1890.

10. What are the effects respectively of 'gravitation,' 'cohesion,' and 'chemical action' on matter?

11. In what way does chemical attraction differ from the other natural forces? Mention some experiments which illustrate this difference.

12. A wooden lath is suspended horizontally by means of a thread. A dry glass rod or tube is now briskly rubbed with warm silk, and then brought near to one end of the suspended lath: what occurs? *S. and A.*, 1876.

13. What happens when a glass rod moistened with concentrated sulphuric acid is brought very near to a small heap of a mixture of sugar and potassic chlorate, but so as not to touch the heap? *S. and A.*, 1876.

14. Mention and describe the different modes of chemical action. Give at least one experimental illustration of each.

15. What takes place when solution of mercuric chloride is added to solution of potassic iodide? *S. and A.*, 1875.

16. A white powder is shaken up with distilled water: how would you ascertain whether any of it dissolves?

S. and A., Pract., 1880.

17. A glassful of dirty water is given to you. Describe with sketch the plan you would adopt, first, for rendering the water clear, and secondly, for ascertaining whether the clear water contains any dissolved solid matter.

S. and A., 1880.

18. How would you prepare pure water and common salt from sea-water? *L. U. M.*, 1892.

19. Explain the meaning of the terms 'sublimation,' 'volatile,' 'fixed,' and 'ignition.'

20. Give a short account of the metric system of weights and measures.

21. Express in English weights and measures 500 grams, 500 cubic centimetres, 500 millimetres.

Find the weight in grams of 350 c.c. of sulphuric acid of density 1·8. *S. and A.*, 1891.

22. Define the gram and the litre. How many grams are contained in 1·725 kilogram?

Find the weight of a block of sulphur 50 c.c. in volume and of relative density 2·05. *S. and A.*, 1892.

23. What do you understand by the *temperature* of a body, and how is it measured?

24. Describe the Fahrenheit and Centigrade scales. Convert 200° and −10° C. into Fahrenheit, and 60° and −40° F. into Centigrade degrees.

$$\frac{200^\circ \text{ C.} \times 9}{5} + 32 = 360 + 32 = 392^\circ \text{ F.}$$

$$\frac{(60^\circ \text{ F.} - 32) \times 5}{9} = \frac{28 \times 5}{9} = 15{\cdot}5^\circ \text{ C.}$$

25. Define *quantity of heat*, and explain wherein it differs from temperature.

26. What is meant by *absolute temperature?* State the laws governing the relation of the volume of a gas to its pressure and temperature.

27. Classify the chief elementary substances into metals and non-metals, and into positive and negative elements. *S. and A.*, 1875.

28. By what properties is a metal distinguished from a non-metal? Arrange the following elements under the above heads: Cl, K, P, S, N, Na, As, H, Fe. *S. and A.*, 1879.

29. Mention the elements which at ordinary temperatures are respectively gases and liquids. State the approximate composition of the earth's crust.

30. Explain carefully what is meant by 'symbol,' 'formula, and 'chemical equation.'

31. What is understood by the terms 'atom,' 'combining proportion,' 'combining weight,' and 'atomic weight'?

32. Explain the meaning in chemistry of the word 'molecule.' Write in words the meaning of each of the following symbols: H, O, O_2, O_3, $3H_2$, NH_3. *L. U. M.*, 1891.

33. What do you understand by the density of a gas? The volume of a given weight of a gas has to be calculated at the standard temperature and pressure: what does this mean? *S. and A.*, 1888.

34. Give an account of the discovery of oxygen.

35. You have given to you some *red precipitate* (mercuric oxide): state (1) whether you consider this substance to be a

simple or a compound body; (2) whether it undergoes any chemical change when submitted to the action of heat; and if so, (3) what is the nature of the change, and how it can be expressed symbolically. *S. and A.*, 1874.

36. How would you prove by experiment that mercuric oxide is a compound and not an elementary substance? Sketch and describe the apparatus you would use for this purpose. *S. and A.*, 1880.

37. I heat potassic chlorate in a flask until effervescence commences: what chemical change takes place? I then drop into the flask some peroxide of manganese: what happens? *S. and A.*, 1879.

38. What are the resulting products when hydrogen, carbon, sulphur, and phosphorus are burnt in oxygen? Express the reactions by equations. *S. and A.*, 1874.

39. I heat, as strongly as possible, a fragment of each of the following substances in a glass tube through which a current of air is passing: sulphur, phosphorus, charcoal. What chemical changes take place? *S. and A.*, 1876.

40. What are the principal properties of oxygen?

41. Why does a candle burn more brightly in oxygen than in air? *S. and A.*, 1892.

Nitrogen, with which oxygen is mixed in air, is a very inert gas, which does not support combustion.

42. What takes place when electric sparks are passed through dry oxygen? *S. and A.*, 1877.

43. Some moist phosphorus is placed in a jar filled with atmospheric air, and a slip of paper which has been dipped into water containing starch and potassic iodide is suspended in the jar: state what occurs. *S. and A.*, 1875.

44. What do you understand by an allotropic form of oxygen? How is this substance distinguished from ordinary oxygen? *S. and A.*, 1881.

45. What is meant by the term 'allotropic modification'? Give examples of some allotropic modifications of non-metallic elements. *S. and A.*, 1890.

46. Describe two methods of obtaining hydrogen from water. What weight of hydrogen is contained in 250 grams of water? *S. and A.*, 1890.

The molecule of water, H_2O, weighs 18, and consists of 2 atoms of hydrogen, together weighing 2, and 1 atom of oxygen, weighing 16. The 250 grams contain hydrogen in the same proportion.

47. Sketch the apparatus you have seen used for preparing hydrogen (1) by the action of sodium on water, (2) by that of zinc on sulphuric acid. *S. and A., Pract.*, 1881.

48. Translate into words the following equation :—

$$2OH_2 + K_2 = 2OKH + H_2.$$ *S. and A.*, 1879.

The reaction is similar to that with Na.

49. Into a boiling solution of caustic soda I drop some fragments of granulated zinc : what chemical change, if any, takes place? *S. and A.*, 1876.

50. Describe the chemical change which takes place when steam is passed over red-hot iron filings.

51. Describe exactly how you would show the formation of water from burning hydrogen, and sketch the apparatus. *S. and A., Pract.*, 1880.

52. What are the principal properties of hydrogen?

53. Describe the process of gaseous diffusion, and state the law governing its rate.

54. Give examples of oxidising and reducing agents.

55. Wherein does nascent hydrogen differ in its chemical behaviour from that element in its free state?

56. How would you prove the presence of solid and gaseous impurities in water?

57. By what simple experiments could you distinguish three samples of water, one of which may be rain-water, another water from a well, and the third sea-water? How may the presence of air dissolved in water be demonstrated? *L. U. M.*, 1891.

On evaporation on platinum foil, rain-water would leave practically no residue, with well-water the residue would be perceptible, while sea-water would leave a considerable mass of saline matter.

58. Describe some of the most characteristic physical and chemical properties of water, and state exactly how you would demonstrate them without the use of very special or elaborate apparatus. *L. U. M.*, 1890.

59. Describe carefully the changes produced by raising the temperature of a piece of ice from − 10° to 150° C.

60. Explain the terms 'crystal,' 'dimorphous,' 'amorphous,' and 'water of crystallisation.'

61. Describe an experiment for proving that water is a compound body, and state precisely the conclusions to which the experiment leads you. *S. and A.*, 1877.

62. A mixture of five volumes of hydrogen and three volumes of oxygen are exploded by an electric spark: will any gas remain? If so, how much, and how will you ascertain what it is? *S. and A.*, 1879.

63. Describe an experiment by means of which you would prove the relation which exists between the volume of hydrogen and oxygen, and of the steam produced by their combination.

64. What is the composition of water by weight, and how may it be experimentally determined?

65. Describe two processes for the preparation of chlorine. Give an equation and a sketch of the apparatus in each case. *S. and A.*, 1878.

66. By what experiments could you prove that chlorine is a constituent of (1) common salt, and (2) potassium chlorate? *S. and A.*, 1891.

This is demonstrated in the case of common salt, NaCl, by its being evolved from that body by the action of manganese dioxide and sulphuric acid. The student already knows that potassium chlorate, $KClO_3$, is reduced to the chloride, KCl, by heat. The chlorate of potassium can be made to yield chlorine by the similar reaction to that with sodium chloride.

67. Three pint bottles of chlorine are given to you: describe the experiments you would make with them in order to show clearly the characteristic properties of this body. *S. and A.*, 1880.

68. Hydrogen burns in chlorine: how would you make this experiment? Give a sketch. *S. and A., Pract.*, 1881.

69. Chlorine water exposed to light loses its colour: how do you account for this?

70. What happens when steam is passed through a red-hot porcelain tube, and when a mixture of steam and chlorine is passed through the same tube? *S. and A.*, 1877.

71. How does chlorine act as a bleaching agent? How is it prepared from salt, and what are its properties? *S. and A.*, 1890.

72. Name the materials and sketch the apparatus required for the production of dry hydrochloric acid. Explain by means of an equation the chemical change in which the acid is produced. *L. U. M.*, 1888.

73. How would you prepare pure and dry hydrogen chloride, and prove by experiment that it contains half its volume of hydrogen and half its volume of chlorine? *S. and A.*, 1891.

74. Describe the apparatus you would use, and the precise manner in which you would set to work, to prepare from common salt such a solution as is sold under the names 'spirit of salt,' 'muriatic acid,' or 'hydrochloric acid.'

L. U. M., 1891.

75. What are the principal properties of hydrochloric acid?

76. How could you prove that chlorine is a constituent of common salt and of hydrochloric acid? Calculate the percentage composition of these two substances.

S. and A., 1888.

77. Describe fully experiments showing (1) the analysis of hydrochloric acid, and (2) the synthesis of hydrochloric acid.

S. and A., 1889.

78. Describe the methods you would employ to verify the facts implied by the formula HCl. *L. U. M.*, 1886.

79. Three bottles are given you: in one is hydrochloric acid gas, in another chlorine, and in the third is ozone: by what properties and experiments would you recognise and identify each gas? *S. and A.*, 1886.

80. Describe clearly why the formula H_2O has been given to water.

81. Describe and explain any two simple experiments which serve to illustrate the law of definite proportions.

L. U. M., 1888.

82. What do you understand by the term 'chemical action'? Explain how the recognition of the fact that chemical action always takes place between definite proportions of matter led to the establishment of Dalton's atomic theory.

S. and A., 1892.

83. Calculate the percentage composition of potassium chlorate (chlorate of potash). (K = 39; Cl = 35·37; O = 16.)

S. and A., 1878.

84. What weight of oxygen gas could be obtained by the

complete decomposition of 100 grams of pure potassium chlorate? If the chlorate used contained 10 per cent. of its weight of potassium chloride, what would be the difference in the amount of oxygen obtained? *S. and A.*, 1891.

As potassium chloride yields no oxygen, the second part of this question resolves itself into a calculation of the difference in the amount of oxygen obtained from 90 grams of chlorate as compared with 100 grams of that salt.

85. What is the percentage composition of water?
S. and A., 1875.

The formula of water is H_2O; the molecular weight = 2 + 16 = 18.
Therefore 18 parts of water contain 2 parts of H.
" " " 16 " O.
As 18 : 100 :: 2 : 11·11 per cent. of H.
" 18 : 100 :: 16 : 88·88 " O.

86. What is the percentage composition of hydrochloric acid? *S. and A.*, 1874.

87. Calculate the percentages of carbon, hydrogen, and oxygen in a compound of the formula $C_{12}H_{22}O_{11}$. (C = 12; O = 16.) *L. U. M.*, 1890.

88. Determine the percentage composition of the following substances: potassium nitrate, sulphuric acid, zinc sulphate, and ammonium nitrate.

89. What is the chemical formula of a body having the following percentage composition?—

S . . .	32·65
O . . .	65·31
H . . .	2·04
	100·00

S. and A., 1876.

Dividing each number by the atomic weight of the element—

$$\frac{32{\cdot}65}{32} = 1{\cdot}02 \text{ of S.}$$

$$\frac{65{\cdot}31}{16} = 4{\cdot}08 \text{ of O.}$$

$$\frac{2{\cdot}04}{1} = 2{\cdot}04 \text{ of H.}$$

Determining the lowest series of whole numbers having the same ratio—

$$\frac{1{\cdot}02}{1{\cdot}02} = 1 \text{ of S}; \quad \frac{4{\cdot}08}{1{\cdot}02} = 4 \text{ of O}; \quad \frac{2{\cdot}04}{2{\cdot}04} = 2 \text{ of H}.$$

The formula is H_2SO_4.

90. A body on analysis gave the following results ; what is its formula?—

C . . .	14·29
O . . .	57·14
H . . .	1·19
Na . . .	27·38
	100·00

91. Calculate the formula for a body which has the following percentage composition : oxygen, 38·1 ; hydrogen, 0·8 ; phosphorus, 24·6 ; sodium, 36·5.

92. Air contains 23 per cent. of its weight of oxygen : how many grams of phosphorus are needed to burn out the whole of the oxygen in 100 grams of air when the highest oxide of phosphorus is formed? (P = 31.) *S. and A.*, 1878.

From the question, there are 23 grams of O in 100 grams of air. The chemical action when P burns in O is represented in the following equation— :

$$2P + 5O = P_2O_5.$$
$$31 \times 2 = 62 \quad 16 \times 5 = 80 \quad 62 + 80 = 142.$$

To burn out 80 by weight of O, 62 of P are required ; then—

As 80 : 23 :: 62 : 17·8 grams of P required to burn out 23 grams of O.

93. If 112 litres of hydrogen weigh 10 grams, what is the weight in grams of the same volume of chlorine, and of the same volume of hydrochloric acid gas? *S. and A.*, 1880.

The density of every gas is half its molecular weight ; the densities, therefore, of hydrogen, chlorine, and hydrochloric acid are—

$$\text{Hydrogen } \frac{2}{2} = 1$$

$$\text{Chlorine } \frac{71}{2} = 35{\cdot}5$$

$$\text{Hydrochloric acid } \frac{36{\cdot}5}{2} = 18{\cdot}25$$

The weight of 112 litres of chlorine is therefore—

10 grams × 35·5 = 355 grams ;

and of hydrochloric acid, 10 × 18·25 = 182·5 grams.

94. How many grams of oxygen and how many of hydrogen are required in order to prepare 500 grams of water? How many litres will the hydrogen measure if each gram measures 11·2 litres? How many litres will the oxygen measure, its density being 16 times as great as that of hydrogen?

$$\underset{2}{H_2} + \underset{16}{O} = \underbrace{H_2O}_{18}$$

As 18 : 500 :: 2 : 55·55 grams of hydrogen.
As 18 : 500 :: 16 : 444·44 grams of oxygen.
55·55 × 11·2 = 622·16 litres of hydrogen.

$$\frac{444{\cdot}44 \times 11{\cdot}2}{16} = 311{\cdot}10 \text{ litres of oxygen.}$$

Note.—The volume of oxygen is here calculated from the data given in the question, but the simpler and more natural method is to determine it direct from that of hydrogen. A molecular equation shows that two volumes of hydrogen unite with one of oxygen to form water; consequently, the volume of oxygen must be half that of hydrogen—

$$\frac{622{\cdot}16}{2} = 311{\cdot}08 \text{ litres of oxygen.}$$

Having determined the actual volume of any one gas taking part in any chemical change, the relative volumes of any others should be deduced from the molecular equation. (The slight discrepancy between the two results, as shown above, is due to decimals not being absolutely exact fractions.)

95. Hydrogen is passed over red-hot copper oxide (CuO): how much metallic copper is produced in forming 9 grams of water, and what is the volume of hydrogen at normal temperature and pressure which has been used? *S. and A.*, 1886.

96. Ten grams of hydrochloric acid (HCl) act on zinc, and the same weight acts on calcium carbonate: what bulk of gas, measured at the normal temperature and pressure, is produced in each case?

The following equations represent the chemical changes:—

$$\underbrace{2HCl}_{73} + \underset{65}{Zn} = \underbrace{ZnCl_2}_{136} + \underset{2}{H_2}.$$

$$\underbrace{2HCl}_{73} + \underbrace{CaCO_3}_{100} = \underbrace{CaCl_2}_{111} + \underbrace{H_2O}_{18} + \underbrace{CO_2}_{44}.$$

As 73 : 10 :: 2 : 0·274 gram of hydrogen evolved.
As 1 : 0·274 :: 11·2 : 3·068 litres of hydrogen evolved.

An inspection of the equations shows that two molecules of hydrochloric acid cause respectively the evolution of one molecule of hydrogen (H_2), and one molecule of carbon dioxide (CO_2); the volume of

the two gases must consequently be the same, and 3·068 litres of carbon dioxide are evolved.

97. How many litres of oxygen gas measured at 10° C. and 755 mm. can be obtained from 1 kilogram of potassium chlorate? (1 litre of oxygen at 0° and 760 mm. = 1·43 gram.) *S. and A.*, 1887.

98. What weight of oxygen is required to burn 16 grams of hydrogen to water, and what bulk of steam at standard temperature and pressure would this amount of water produce? *S. and A.*, 1889.

99. How many cubic centimetres of oxygen and of hydrogen are obtainable from 10 grams of water? *S. and A.*, 1888.

100. Calculate the volume of chlorine gas, measured at 10° C. and 760 mm., obtainable by heating 1 gram of pure MnO_2 with excess of hydrochloric acid. (Mn = 55; O = 16; Cl = 35·5.) *L. U. M.*, 1888.

101. Explain what is meant by the terms, 'combining proportion by weight and by volume.' Give examples. *L. U. M.*, 1887.

102. Write out the various names by which the following compounds are known: Fe_2O_3, CuO, Cu_2O, BaO, Fe_3O_4, NaHO, SO_3, SO_2, H_2SO_4, H_2SO_3, Na_2SO_3, K_2SO_4, $KHSO_4$.

103. What are the characteristic properties of an acid and of a base? Explain the effect of mixing sulphuric acid and caustic soda. *S. and A.*, 1881.

104. Name and give the formula of a salt, and describe how you would prepare it. *S. and A.*, 1888.

105. You are required to neutralise two quantities of 50 grams each of sulphuric acid diluted with water, the one with caustic soda, the other with sodium carbonate: describe how you would do this, and how you would ascertain that neutralisation had been effected. What difference would be noticeable between the two operations, and what quantity of product would be obtained in each case? (Na = 23.) *L. U. M.*, 1892.

The chemical actions are represented by the two following equations:—

H_2SO_4	+	2NaHO	=	Na_2SO_4	+	$2H_2O$.
Sulphuric acid.		Sodium hydrate (Caustic soda).		Sodium sulphate.		Water.

$$\underset{\text{Sulphuric acid.}}{H_2SO_4} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}.$$

For a description of the second reaction, the student is referred to the chapter on the oxides of carbon.

The dilute acid should have a drop of litmus solution added, and then the caustic soda added either in the solid state or preferably in solution, until the red tint of the litmus changed to the intermediate port-wine colour due to neutrality of the mixture. When adding the carbonate, effervescence will be caused by the escape of carbon dioxide gas; the solution should in this case be kept at a boiling temperature, so as to expel the gas, as otherwise it (the carbon dioxide) obscures the colour reaction with litmus. An inspection of the equations shows that the quantity of the resultant sulphate is the same in both cases.

106. Express in words the meaning of the following equation: $OKH + HCl = KCl + OH_2$. *S. and A.*, 1878.

107. Explain the following terms: 'analysis,' 'synthesis,' 'mixture,' 'compound,' 'acid,' 'neutral,' 'alkaline.' *S. and A.*, 1892.

108. Explain what is implied by the following terminations: *-ous*, *-ic*, *-ite*, *-ate*, and *-ide*, and give examples of their use. *S. and A.*, 1887.

109. What do you understand by atomicity, and how is it measured?

110. State why carbon is termed a tetrad element and oxygen a diad element. *S. and A.*, 1880.

111. Give the atomicity of each element in the following compounds: $HCl - (OH)_2 - NH_3 - CO_2 - SO_2$ and SH_2. *S. and A.*, 1877.

$(OH)_2 = H_2O_2$.

112. Indicate by graphic notation the atomicity of the following elements: nitrogen, sulphur, carbon, chlorine, oxygen, boron, silicon, bromine, phosphorus, zinc, and calcium. *S. and A.*, 1879.

113. Why must NO be written as the formula of nitric oxide? and in what way is it an exception to the general rule which governs the active atomicity of elements in a compound? State that rule.

114. Define the terms 'monobasic' and 'dibasic' as applied to acids. Knowing the atomicity of the various metals, write the formulæ of the following salts: silver nitrate, gold chloride, copper nitrate, zinc sulphate, lead chloride, silver sulphate.

115. Give some account of the different varieties of carbon, and mention the uses to which they are applied.

S. and A., 1891.

116. By what experiments can it be shown that charcoal, graphite, and diamond consist essentially of the same material?

S. and A., 1892.

117. What is coke, and how is it made? Explain the difference noticeable in the burning of coke and the burning of coal. Why does coke leave more ashes than the coal from which it is made? *L. U. M.*, 1892.

The student should bear in mind that coal contains not only carbon, but also hydrogen. On being heated the coal evolves hydrocarbons in the vaporous condition, and therefore burns with luminous flame (see Chapters XIV. and XV.). As 100 grams of coal produce a much less weight of coke, which coke contains the whole of the ash of the original coal, it is evident that the coke must contain the higher percentage of ash.

118. If air contains 21 per cent. by volume of oxygen, how many litres of it at standard temperature and pressure are required to burn completely 18 grams of carbon, and what would be the volume of the product formed? (Weight of 11·2 litres of O = 16 grams.) *S. and A.*, 1886.

119. Classify the following substances as elements and compounds: chalk, graphite, water, sulphur, iron, ammonia, oil of vitriol, chlorine, diamond, ozone. *S. and A.*, 1887.

120. State which of the following substances are elements and which are compounds, and express their chemical composition by symbols or formulæ: ozone, ammonia, water, lime, diamond, nitric acid, sulphur, graphite, marble, nitre.

S. and A., 1891.

121. Express in words the meaning of the following equation: $Ca(HO)_2 + CO_2 = CO(CaO_2) + OH_2$.

S. and A., 1874.

121A. Quicklime is slaked with water, diffused through more water, and filtered. When carbonic anhydride gas is passed through the filtered liquid, it becomes very turbid: what is the composition of the substance which causes the turbidity? Give an equation. *S. and A.*, 1879.

122. You are required to prove that carbon dioxide (carbonic acid gas) is formed when wood is burnt: describe and sketch the apparatus you would use. *S. and A., Pract.*, 1881.

123. Describe the preparation of carbon dioxide, and give a sketch of its properties.

124. A piece of marble is placed in dilute hydrochloric acid. Explain why it disappears, and state the change which the marble and the acid undergo. *S. and A.*, 1889.

125. Express the following changes by equations :—

(*a*) The action of hydrogen chloride solution on chalk.

(*b*) The action of diluted sulphuric acid on iron.

(*c*) The action between caustic soda and sulphuric acid.

(*d*) The action of chlorine on water at a high temperature. *L. U. M.*, 1890.

126. Describe experiments with carbon dioxide to show (*a*) its density ; (*b*) its solubility in water ; (*c*) its action on lime-water. *S. and A.*, 1892.

127. Why is carbon dioxide frequently called carbonic acid? Describe (with sketch) the apparatus you would make use of to prepare this gas in a dry state. *L. U. M.*, 1892.

128. Describe experiments by which you are led to believe that coal-gas contains hydrogen, that common salt contains chlorine, and that white marble contains carbon. *L. U. M.*, 1892.

129. Calculate the weight of pure marble that must be treated with hydrochloric acid in order to afford 100 c.c. of carbon dioxide measured at 0° C. and 760 mm. (Ca = 40 ; C = 12.) *L. U. M.*, 1887.

130. Ten grams of hydrochloric acid (HCl) act on zinc, and the same weight acts on calcium carbonate : what bulk of gas, measured at the normal temperature and pressure, is produced in each case? *S. and A.*, 1886.

131. You boil common well-water for a few minutes, and observe the separation of a white precipitate : how do you explain the formation of the precipitate? How would you test your explanation by experiment?

132. What do you understand by the terms 'hard' and 'soft' as applied to water? Explain the difference between permanent and temporary hardness. *L. U. M.*, 1889.

133. The hard water of our chalk districts is rendered soft by the addition of lime-water : explain fully why lime-water is able to produce this result.

134. How are the two oxides of carbon prepared, and by what tests may they be recognised? *S. and A.*, 1887.

135. How is carbon monoxide prepared? Describe and explain the tests by which you would recognise it. *L. U. M.*, 1888.

136. State any facts known commonly which suggest that the air is concerned in the changes which attend the combustion of coal in an ordinary fire. Describe any experiments you have witnessed which afford proof that such is the case. *L. U. M.*, 1891.

137. Explain the blue flame seen upon a blacksmith's fire. What effects, if any, would be produced by blowing steam, together with air, into the fire? *L. U. M.*, 1890.

Carbon monoxide is formed from the oxygen of the air when blown through a red-hot mass of coke. Steam under similar circumstances is decomposed with the production of carbon monoxide and free hydrogen.

$$\underset{\text{Water.}}{H_2O} + \underset{\text{Carbon.}}{C} = \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Hydrogen.}}{H_2}.$$

138. How do coal and coke differ from each other in composition? What are the products obtained when (*a*) air and (*b*) steam are separately passed over red-hot coke? *L. U. M.*, 1888.

139. Represent by equation, and otherwise describe, what happens when oxalic acid is heated with strong sulphuric acid. *S. and A.*, 1879.

140. Oxalic acid is heated with sulphuric acid: how would you experimentally prove that the gases evolved are carbonic anhydride (CO_2) and carbonic oxide (CO)? *S. and A., Pract.*, 1880.

141. Describe the properties of carbon monoxide (carbonic oxide). Under what conditions is it formed as a product of combustion, and why is it important to ensure the removal of the products of combustion by a proper ventilating pipe when gas is burnt for heating purposes? *L. U. M.*, 1891.

142. Lime-water is shaken up in a jar filled with carbonic oxide: what occurs? The carbonic oxide is then inflamed, and the lime-water once more shaken up with the contents of the jar: what now takes place? *S. and A.*, 1875.

143. Describe two experiments to show the properties of (1) carbon monoxide, and (2) carbon dioxide. How would you convert the carbon dioxide into the monoxide, and what relation

would the volume of the monoxide formed bear to that of the dioxide from which it was made? *S. and A.*, 1890.

144. 100 c.c. of air are passed over red-hot charcoal: how would you ascertain if the air was altered in volume or had experienced any alteration in properties? *S. and A.*, 1887.

The exact measurement in an experiment of this kind is somewhat difficult, as both before and after the passage over charcoal the temperature and pressure of the gas require to be observed and allowed for. The best form of apparatus would consist of a tall cylinder graduated in c.c. for holding the air at the commencement of the experiment. This should be fitted with a cork carrying a thistle funnel leading to the bottom of the vessel, and a delivery tube. The leading tube is attached to a tube containing charcoal heated red hot in a tube-furnace. The outlet end of this tube is conveyed into a pneumatic trough containing mercury, in which is inserted another graduated cylinder arranged for the collection of the gas. Mercury is now poured through the thistle funnel of the first flask until the air just commences to escape into the reception cylinder. The height of the mercury in each cylinder is then measured, and mercury is slowly poured into the first one until 100 c.c. of air have been forced through the tube. The volume in the second cylinder should now be read, less the amount of air it contained at the commencement of the experiment. The difference in temperature may be neglected unless extreme accuracy is required, as both quantities of air speedily acquire the temperature of the room; otherwise a thermometer must be introduced into each vessel and a correction made for temperature. In order to make a correction for the pressure to which each lot of air is subject, measure first the height in millimetres which the column of mercury stands in the tube of the thistle funnel above the level of the liquid in the jar itself. Suppose this height is 50 mm., and assuming the barometer to be standing at 760 mm., then the air in the flask is under a pressure of $760 + 50 = 810$ mm.; from this its volume at normal pressure is easily calculated. The readiest plan with the air in the reception jar is to depress the jar in the mercury until the level of the mercury in the jar is the same as that in the trough; the air is then under barometric pressure. The volume is then read, and that before the action of charcoal may be compared with that after.

As one molecule of oxygen produces two molecules of carbon monoxide, and there are about 21 c.c. of oxygen in 100 c.c. of air, there will be an increase in volume of about 21 c.c. as the result of the passage over red-hot charcoal.

145. How may it be shown that the gases named carbon monoxide and carbon dioxide contain different proportions per cent. by weight of carbon? *L. U. M.*, 1891.

The proportion by weight of carbon in the dioxide is determined by passing oxygen over a weighed quantity of red-hot carbon, and weighing the resultant carbon dioxide. The carbon is introduced into a tube heated in a furnace, having its exit end packed with fragments

of copper oxide, CuO; on passing oxygen, combustion ensues, and any monoxide produced is converted into the dioxide during its passage over the copper oxide. The escaping gas is led into a weighed tube containing fragments of caustic potash, KHO, by which it is absorbed. The difference in weight of this tube before and after the experiment gives the weight of carbon dioxide produced.

On exploding carbon monoxide with excess of oxygen in a eudiometer, and subsequently absorbing the resultant dioxide by caustic potash, the composition of the gas may be ascertained. It will be found that two volumes of the monoxide combine with one of oxygen and produce two volumes of the dioxide. From these data the weight may be indirectly determined. A direct determination of weight may be made by passing a known volume of the monoxide (knowing its density) over red-hot carbon monoxide, absorbing the dioxide produced with caustic potash, and then weighing.

146. By what experiments can you show that in carbonic oxide the proportion of carbon to oxygen is twice as great as in carbon dioxide? *S. and A.*, 1892.

147. Ten grams of oxalic acid are heated with sulphuric acid: what weight of carbon monoxide is evolved? If the resultant mixed gases be passed through a tube containing red-hot charcoal, so as to effect the complete conversion of the carbon dioxide into carbon monoxide, what weight of carbon monoxide will be produced?

148. How many volumes of carbon dioxide (carbonic acid gas) will be formed when a mixture of four volumes of carbon monoxide (carbon oxide gas) and four volumes of oxygen is burnt? State what volume of oxygen, if any, remains uncombined. *S. and A.*, 1881.

149. One volume of carbon monoxide (carbonic oxide) gas is mixed with two volumes of oxygen, and an electric spark passed through the mixture: what volume of carbon dioxide gas (carbonic anhydride) is formed, and what volume of oxygen left? *S. and A.*, 1877.

150. How is marsh-gas prepared, and what are its general properties?

151. How is olefiant gas prepared? Mention the distinguishing characteristics of this compound. By what means could you convince yourself that this gas contains twice as much carbon as an equal bulk of marsh-gas does?

152. Describe the preparation and properties of olefiant gas. How is it proved that its molecule contains two atoms of carbon? *L. U. M.*, 1887.

153. How is olefiant gas made? What volume of it would be equal in weight to 10 litres of marsh-gas? *L. U. M.*, 1889.

154. How may it be proved that any given volume of ethylene (olefiant gas) contains twice as much carbon as an equal volume of marsh-gas, but the same amount of hydrogen? *L. U. M.*, 1892.

155. Explain exactly what is implied by the formula C_2H_4. *L. U. M.*, 1885.

156. How much pure air ought to be mixed with 100 measures of fire-damp (marsh-gas) in a coal-mine in order to supply material for the complete combustion of marsh-gas during explosion?

The combustion of marsh-gas is represented by the following equation:—

$$CH_4 + 2O_2 = CO_2 + 2H_2O.$$

One volume of marsh-gas requires two volumes of oxygen; therefore 100 measures will require 200 measures of pure oxygen.

Air contains 21 per cent. by volume of oxygen; therefore—

As 21 : 200 : : 100 : 952 volumes of pure air.

157. How much oxygen do you require for the complete combustion of 10 c.c. of marsh-gas? How many cubic centimetres of each product of combustion would be formed?

158. A gaseous mixture consisting of 100 volumes of carbon monoxide and 150 volumes of oxygen is confined over mercury; an electric spark is passed through the mixture, and a ball of caustic potash is then brought into the gas: describe the chemical changes which occur, and state what volume (if any) of gas remains at the end of the operation. (Caustic potash possesses the property of absorbing carbon dioxide gas.)

159. To burn 16 grams of acetylene, how many cubic centimetres of oxygen will be required, and what will be the volume of the products of combustion?

160. State what volume of oxygen will be required for the combustion of 250 c.c. of each of the following gases; state also the volume of the products of combustion in each case: hydrogen, carbon monoxide, marsh-gas, acetylene, ethylene, ammonia, and sulphuretted hydrogen.

161. How many volumes of air are required for the complete combustion (*a*) of one volume of marsh-gas, and (*b*) of one volume of olefiant gas? Specify the composition by volume of the products in each case. *L. U. M.*, 1886.

162. Ten measures of ethylene are mixed with 50 measures of oxygen, and the mixture is fired by an electric spark: what volume of gas remains after the explosion? of what does this gas consist? and how would you demonstrate the proportions of the constituents present in this residual gas? *L. U. M.*, 1890.

163. On heating water for a bath in a large copper vessel by means of one of the so-called air-gas burners now frequently used, it is noticed that liquid appears on the outer surface of the vessel above the flame: what simple experiments could you make in order to show that this liquid consists of nearly pure water? How is the appearance of water in such a case to be accounted for? *L. U. M.*, 1890.

164. Both water and carbon dioxide are formed when coal-gas burns: describe, and show by sketch, how you would prove this to be the case. *S. and A.*, 1886.

165. Define 'combustion,' and state clearly what you understand by that term.

166. Define the terms 'combustible' and 'supporter of combustion:' describe an experiment to show that they are purely relative.

167. How may oxygen be caused to burn in either hydrogen or coal-gas? Explain the terms 'complete combustion' and 'incomplete combustion.' *L. U. M.*, 1892.

Incomplete combustion may occur when there is a deficiency of oxygen; thus when carbon is burned to the monoxide, there is an example of incomplete combustion.

168. Give some account of the nature and composition of ordinary fuel. State fully the chemical changes which occur in the combustion of coal. *L. U. M.*, 1887.

169. If 100 parts by weight of air contain 23 of oxygen and 77 of nitrogen, how many tons of air would be needed to burn one ton of coal, consisting of?—

Carbon	90·55
Hydrogen	4·14
Nitrogen	1·26
Oxygen	2·35
Ash	1·70
	100·00

Assume that, on burning, the carbon is wholly converted into

carbon dioxide, and the hydrogen into water; that the nitrogen is evolved as such, and that the ash is already fully oxidised.
L. U. M., 1885.

The quantity of oxygen present in the coal must be deducted from the amount found necessary to burn the carbon and the hydrogen.

170. A certain metallurgical operation absorbs one million units of heat: how many grams of each of the following substances respectively would require to be burned in oxygen to furnish the necessary quantity of heat: hydrogen, carbon, carbon monoxide, olefiant gas, and alcohol?

171. Why does olefiant gas burn with a brighter flame than hydrogen?

172. Describe the structure of the flame of a common candle, and explain why carbon is set free by the combustion in the interior, but not on the surface of the flame.

173. Give some account of the structure of flame, and explain the principle of the Davy lamp. *L. U. M.*, 1889.

The Davy lamp is used by the miner as a source of light where there is danger of the atmosphere containing an inflammable mixture of gases. It consists essentially of an ordinary oil-lamp completely enveloped in a casing of fine wire gauze; such gauze prevents the passage of flame through it. This may be readily tested by depressing a piece of fine gauze over a Bunsen flame; the flame does not pass through the gauze, but the gas above it burns on a light being applied. If the gas below be extinguished, and then again turned on, the gas may be kindled *above* the gauze, and the flame will not descend through. It will be readily understood that the gauze envelope of the Davy lamp operates in a similar manner. The effect is due to the rapid cooling effect produced by the conductive power of the gauze; by this means the temperature of the burning gases is reduced below that necessary for combustion.

174. Explain fully why the flame of a common gas-light is brighter than the flame from a Bunsen burner. What special advantages does the latter possess?

175. If you place the chimney glass over the flame of a reading-lamp the flame increases in brightness: why does it do so? If you blow a current of air into the flame of an ordinary candle, the flame appears less bright than it did before the introduction of the air: explain why this is the case.

176. Describe two processes for the preparation of nitrogen, one suitable for the production of small and the other of large quantities of the gas. *L. U. M.*, 1889.

177. Write an account of the principal properties of nitrogen.

What effect is produced by passing a series of electric sparks through a mixture of nitrogen and oxygen?

178. How would you distinguish the following gases from one another: chlorine, oxygen, nitrogen, carbon monoxide, marsh-gas, olefiant gas? *L. U. M.*, 1888.

179. What is the composition of the atmosphere, and how may it be determined (1) by volume, (2) by weight?

180. By what experiments can you prove that the air contains four-fifths of its volume of nitrogen? *S. and A.*, 1887.

181. Name the principal gases in the air. How is their amount determined? *S. and A.*, 1888.

182. Explain as fully as you can why air is said to be a mixture of two elements, and hydrochloric acid a chemical combination of two elements. *S. and A.*, 1890.

183. How can you prove that the constituents of the atmosphere are merely mechanically mixed and not chemically combined? *L. U. M.*, 1887.

184. Why is the flame of a taper extinguished in nitrogen gas, and why does it continue to burn in air? *S. and A.*, 1887.

185. Describe three experiments, the best you can think of: one is to prove that the air contains oxygen, another that it contains carbon dioxide, and the third that it contains aqueous vapour. *S. and A.*, 1881.

186. In what respects does the air in a crowded room differ from fresh air? *S. and A.*, 1889.

187. Describe an experiment illustrating the action of plants in sunlight on carbon dioxide. *L. U. M.*, 1886.

188. What volume of water vapour results from the explosion of a mixture of two volumes of hydrogen and one volume of oxygen? Explain how the fact that one volume of oxygen unites with two volumes of hydrogen to form water may be made use of in order to determine the amount of oxygen in the air. *L. U. M.*, 1887.

189. Fifty measures of air were mixed with 30 measures of hydrogen gas, and fired by an electric spark; after cooling, 48·8 measures of gas remained: what volume of oxygen was present in the air examined? *L. U. M.*, 1888.

190. Calculate the weight of 10 litres of air (measured at 0° C. and 760 mm.) containing 21 per cent of oxygen and 79 per cent. of nitrogen. *L. U. M.*, 1888.

191. Describe the mode of preparation of ammonia gas. What are its principal properties, and how may its composition be determined? *S. and A.*, 1892.

192. How is ammonia prepared? Describe the means by which you would demonstrate the volumetric composition of the gas. *L. U. M.*, 1889.

193. What takes place when a lighted taper is immersed in gaseous ammonia? *S. and A.*, 1874.

194. Ammonia gas is led into solution of hydrochloric acid: what is produced? Give an equation. The resulting liquid is evaporated to dryness in a porcelain crucible, which is afterwards heated to redness: what will remain in the crucible? *S. and A.*, 1879.

195. Write equations showing the action of hydrochloric acid on (*a*) caustic soda (sodium hydrate); (*b*) sodium carbonate; and (*c*) ammonia gas. Name the several products. *L. U. M.*, 1888.

196. What volume of oxygen is required for the complete combustion of one volume of each of the following gases: hydrogen, carbon monoxide, ammonia, and marsh-gas? *L. U. M.*, 1887.

197. How can you demonstrate that ammonia is composed of nitrogen and hydrogen? *S. and A.*, 1886.

198. What is the percentage composition of ammonic chloride? *S. and A.*, 1876.

199. By what experiments could you show that hydrogen was a constituent of hydrochloric acid, sulphuric acid, and ammonia? *S. and A.*, 1889.

200. Express in words what is implied in the following equations:—

(*a*) $Zn + H_2SO_4 = ZnSO_4 + H_2$.

(*b*) $CaCO_3 = CaO + CO_2$.

(*c*) $2NH_4Cl + CaO = 2NH_3 + H_2O + CaCl_2$.

S. and A., 1888.

201. Complete the following equations:—

$$MnO_2 + 4HCl =$$
$$2NH_4Cl + CaO =$$
$$Zn + H_2SO_4 =$$
$$Zn + 2HCl =$$
$$NH_4NO_3 + H_2SO_4 =$$
$$NH_3 + HNO_3 =$$

S. and A., 1891.

202. Give an account of the various methods by which a gas might be liquefied, illustrating your description by the examples of ammonia, oxygen, and carbon dioxide.

L. U. M., 1886.

Cailletet liquefied oxygen by first highly compressing the gas, cooling it to as low a temperature as possible, and then allowing it to suddenly expand. The sudden absorption of heat reduced the temperature so low that the gaseous oxygen condensed to a liquid.

203. Define a compound radical, and give an example.

S. and A., 1875.

204. How is nitric acid usually prepared? What are its properties, and by what reactions can it be distinguished from hydrochloric acid and sulphuric acid? *S. and A.*, 1890.

205. Prove by chemical equations that more nitric acid can be obtained from sodium nitrate than from an equal weight of potassium nitrate. *S. and A.*, 1891.

206. Explain in words all that is expressed by the following equation :—

$$2KNO_3 + H_2SO_4 = 2K_2SO_4 + 2HNO_3.$$

S. and A., 1881.

207. How many pounds of nitric acid can be obtained from 150 pounds of nitre (potassium nitrate), and how many grains of sulphuric acid will be needed? *S. and A.*, 1879.

208. I put some gold-leaf into a jar of nitric acid and into one of liquid hydrochloric acid: what takes place? I mix the contents of the two jars: what then occurs?

S. and A., 1876.

209. How would you distinguish hydrochloric acid from nitric acid? Give the formulæ of the two acids, and describe the preparation of a salt of each acid. *S. and A.*, 1887.

210. What weight of pure nitric acid would contain 100 grams of oxygen; and what weight of pure hydrochloric acid would contain 100 litres of chlorine at the standard temperature and pressure? *S. and A.*, 1889.

211. A solution of nitric acid of specific gravity 1·46 contains 80 per cent. of HNO_3: what weight of this solution is theoretically required to dissolve 10 grams of copper oxide?

212. What changes take place when zinc dissolves in dilute nitric acid? *S. and A.*, 1876.

213. Carbonate of ammonia and nitric acid are given to

you : how would you prepare nitrous oxide from these? Draw a sketch of the apparatus you would use, and give an equation showing the decomposition which takes place in making the gas. *S. and A.*, 1879.

214. How is pure nitrous oxide made? By what characters or tests can it be distinguished from oxygen and from nitric oxide respectively? *S. and A.*, 1891.

215. How is the compound N_2O prepared? Explain the process and state the means you would adopt to determine its composition and molecular weight. *L. U. M.*, 1885.

216. Describe the preparation of nitrous oxide gas. A mixture of equal volumes of nitrogen and oxygen has nearly the same effect upon flame as nitrous oxide : how would you distinguish by experiment the mixture from the compound? *L. U. M.*, 1891.

217. A lighted taper burns brilliantly when plunged into a jar of gas. What gases are capable of producing such effect, and how would you determine what gas was present in any particular case? *S. and A.*, 1890.

218. Why are the nitrogen and oxygen in nitrous oxide said to be in a state of combination, and why in air are they said to be in a state of mixture? *S. and A.*, 1888.

219. How could you obtain nitrogen from (1) ammonia, (2) nitrous oxide, and (3) air? *S. and A.*, 1889.

220. What are the principal properties of nitrogen monoxide? Feebly burning sulphur is extinguished when plunged into this gas, while, if brightly burning, it continues to do so with increased brilliancy : state clearly the reason for this.

221. Ten grams of nitric acid are neutralised by ammonia : what weight of nitrogen monoxide may be obtained from the ammonium nitrate thus produced?

222. Calculate the weight of ammonium nitrate which must be decomposed in order to afford one litre of nitrous oxide gas, measured at 15° C. and under 740 mm. pressure. *L. U. M.*, 1886.

223. How would you prepare nitrous and nitric oxides? Give equations for the reactions, and state how you would recognise these bodies. *S. and A.*, 1886.

224. How are the two lowest oxides of nitrogen (nitrous and nitric oxides) prepared? By what properties are they

distinguished? How could you prove the volumetric composition of the two oxides? *L. U. M.*, 1886.

225. State what is observable when saltpetre is distilled with sulphuric acid, and also when a portion of the product is poured on to some copper in a test-tube. *L. U. M.*, 1892.

226. Describe the effect, if any, noticeable when nitric oxide gas is mixed with dry oxygen, with oxygen confined over water, and with nitrous oxide respectively. Afterwards explain the changes by equations. *L. U. M.*, 1892.

227. By what properties would you recognise nitric oxide? Compare its power of supporting combustion with that of nitrogen monoxide.

228. Two bottles are placed before you, each containing a colourless gas. On removing the stoppers, colourless steamy fumes escape from the one (*a*), and orange-red vapour from the other (*b*). What might each of these gases be, and how would you further test it in order to identify it with certainty?

L. U. M., 1890.

229. I want 6 grams of nitric oxide: how much copper and nitric acid shall I require for its production?

230. Nitric acid is poured upon copper, hydrochloric acid upon chalk, and sulphuric acid into water. What are the chemical changes which occur in each case, and the appearances which accompany each reaction? *S. and A.*, 1890.

231. Express in the form of equations the action of—

(1) Heat upon mercuric oxide.
(2) Sulphuric acid upon common salt.
(3) Hydrochloric acid upon marble.
(4) Nitric acid upon copper.
(5) Steam upon red-hot iron. *S. and A.*, 1887.

232. Give an account of the mode of preparation and properties of nitrous acid. *L. U. M.*, 1887.

233. What sulphur compounds occur in nature? Describe the chief properties of sulphur, and state how it may be converted into its various allotropic modifications. *S. and A.*, 1888.

234. How is sulphur commonly obtained? Give an account of the action of heat on sulphur. *L. U. M.*, 1888.

235. By what tests could you prove that a substance which was stated to be sulphur actually was that element?

S. and A., 1889.

236. What is meant by the term 'allotropy'? Describe the various allotropic modifications of sulphur, oxygen, and carbon. *S. and A.*, 1887.

237. Explain what is meant by 'chemical combination in definite and in multiple proportions.' Give illustrations from carbon or sulphur compounds. *S. and A.*, 1886.

238. Describe an experiment by which you can show that when a piece of charcoal or sulphur is burnt in the air the substance of the charcoal or sulphur is not destroyed, but only changes its form. *S. and A.*, 1891.

239. With what bodies will sulphur, chlorine, and carbon dioxide combine? Give the formulæ for the compounds formed. *S. and A.*, 1888.

240. Some purchased milk of sulphur is suspected to be adulterated with plaster of Paris (calcium sulphate). How could you test it, and by a simple process ascertain the amount of the impurity?, *L. U. M.*, 1890.

241. What is the action of heat upon the following substances?—

(1) Ammonium nitrate.
(2) Ozone.
(3) Sulphur.
(4) Charcoal in presence of (*a*) oxygen ; (*b*) carbon dioxide.

S. and A., 1890.

242. Sketch and describe apparatus used in demonstrating the following facts : (*a*) water is produced by the union of pure oxygen and hydrogen ; (*b*) sulphur burned in oxygen does not alter the volume of the gas. *L. U. M.*, 1890.

243. What volume of atmospheric air (measured at 15° C. and 750 mm.) is required for the complete combustion of one gram of sulphur? (S = 32.) *L. U. M.*, 1889.

244. What weight of sulphur would you expect to obtain from 10 tons of sulphur ore (ferric sulphide)? Allow what you consider a fair percentage for loss.

245. Describe exactly the preparation of sulphuretted hydrogen, and point out the chief properties of the gas.

L. U. M., 1889.

246. Describe how sulphuretted hydrogen is prepared. By what experiments would you show its properties and demonstrate its composition? *S. and A.*, 1886.

247. How is sulphuretted hydrogen prepared? What are its properties, and what is formed when it burns in air?
S. and A., 1888.

248. How is sulphuretted hydrogen made? Describe its chief properties, and state how you could prove that it contained its own volume of hydrogen? *S. and A.*, 1889.

249. How is sulphuretted hydrogen prepared? Write equations expressing the changes which take place when the gas is (*a*) mixed with chlorine; (*b*) heated with tin; and (*c*) led through an aqueous solution of sulphurous acid. *L. U. M.*, 1887.

For (*c*) refer to the chapter on sulphur dioxide and sulphurous acid.

250. Sulphuretted hydrogen is passed into solutions of the following substances in different test-tubes: arsenious anhydride, lead acetate, zinc sulphate, antimony chloride, and ferrous sulphate: what is the result in each instance?

251. How could you prove that sulphur was a constituent of sulphuretted hydrogen? What weight of sulphur is contained in 100 grams of sulphuretted hydrogen? *S. and A.*, 1890.

252. Required one litre of sulphuretted hydrogen gas at 0° C. and 760 mm. pressure; calculate the weight of iron sulphide necessary for its production. Trace the chemical changes which take place when the gas is led into (*a*) aqueous solution of chlorine, and (*b*) solution of ammonia. *L. U. M.*, 1885.

253. Calculate the weight of 100 litres of hydrogen sulphide, measured at 27° C. and 740 mm. (S = 32.) *L. U. M.*, 1892.

254. Express in the form of equations the action of—
(1) Heat upon ammonium nitrate.
(2) Hydrogen upon (*a*) cold, (*b*) hot copper oxide.
(3) Sulphuric acid upon ferrous sulphide.
(4) Hydrochloric acid upon chalk.
(5) Sulphuric acid upon nitre. *S. and A.*, 1888.

255. Classify the following substances as solids, liquids, and gases: ozone, nitric acid, graphite, nitric oxide, ammonia, nitre, sal ammoniac, hydrogen chloride, sodium chloride, nitrous oxide, calcium carbonate, ferrous sulphide. *S. and A.*, 1892.

256. Describe and explain, with equations, the methods of preparing sulphur dioxide from (*a*) sulphur, (*b*) sulphuric acid, (*c*) a sulphite. *L. U. M.*, 1889.

257. How is sulphur dioxide made? How can you prove that it contains its own volume of oxygen? *S. and A.*, 1886.

258. Describe the modes of origin and properties of sulphur dioxide. How could you demonstrate the volumetric composition of the gas? *L. U. M.*, 1886.

259. What bodies are formed when sulphur burns in (*a*) air, (*b*) hydrogen? Express the changes which occur by means of chemical equations, and describe the characteristic properties of the products. *L. U. M.*, 1886.

260. What are the principal uses of sulphur dioxide?

261. Name any bodies formed by the action of sulphuric acid, concentrated and dilute, hot and cold, upon the following substances: sodium chloride, zinc, copper, nitre, and oxalic acid. Give equations in each case. *L. U. M.*, 1886.

262. Arrange the following gases in the order of their solubility in water: oxygen, carbon dioxide, hydrogen, nitric oxide, nitrous oxide, sulphur dioxide, chlorine, sulphuretted hydrogen, ammonia. *S. and A.*, 1891.

263. What is a chemical equation? Give in the form of chemical equations the action of—

(1) Sulphuric acid upon common salt.
(2) Sulphuric acid upon copper when heated.
(3) Sulphuric acid upon an aqueous solution of ammonia.

S. and A., 1889.

264. Complete the following equations:—

$$Cu_3 + 8HNO_3 =$$
$$2NH_4Cl + CaH_2O_2 =$$
$$Cu + 2H_2SO_4 =$$
$$C + 2H_2SO_4 =$$

S. and A., 1890.

265. Complete the following equations:—

$$FeS + H_2SO_4 =$$
$$Cu + 2H_2SO_4 =$$
$$Zn + H_2SO_4 =$$
$$Na_2CO_3 + H_2SO_4 =$$
$$Na_2SO_3 + H_2SO_4 =$$
$$NaCl + H_2SO_4 =$$

S. and A., 1892.

266. How would you prepare sulphur trioxide, and what are its properties? Give a sketch of the apparatus.

267. How could you convert sulphur dioxide into sulphuric acid, and sulphuric acid into sulphur dioxide?

S. and A., 1887.

268. How can sulphurous acid be converted into sulphuric

acid, and how can sulphuric acid be converted into sulphurous acid? How could you distinguish a sulphite from a sulphate?
S. and A., 1889.

269. What are the principal properties and uses of sulphuric acid?

270. 1 lb. of sulphur may combine with 1 lb. of oxygen or with 1½ lb. of oxygen: what compound is formed in each case? If no other compounds of sulphur and oxygen are known, how does the existence of these two only illustrate the law of multiple proportions? *S. and. A.*, 1891.

271. What are the properties common to acids? In what respects does sulphurous acid differ from sulphuric acid?
S. and A., 1892.

272. What volume of sulphur dioxide is formed by burning 10,000 litres of hydrogen sulphide, and how many kilograms of sulphuric acid, H_2SO_4, are theoretically producible therefrom? (S = 32; O = 16.) *L. U. M.*, 1891.

273. Calculate the weight of sulphur required to afford 100 tons of sulphuric acid. Briefly explain the method by which sulphuric acid is made. (S = 32.) *L. U. M.*, 1888.

274. How much zinc must be dissolved in dilute sulphuric acid in order to produce 40 lbs. of crystallised zinc sulphate ($ZnSO_4, 7H_2O$)? *S. and A.*, 1892.

275. Name the substances having the following formulæ: $H_2S, NH_3, CO, H_2CO_3, NO, NO_2, SO_3, O_3$. *S. and A.*, 1889.

276. Give the formulæ for three carbonates, three sulphates, three sulphites, and three nitrates. *S. and A.*, 1886.

277. How is bromine prepared? In what forms does it commonly occur in nature? Give some account of the chief properties of bromine and of the tests by which it may be recognised. *L. U. M.*, 1887.

278. Two bottles are given you; one contains vapour of bromine, and the other vapour of nitric peroxide (NO_2): how would you ascertain which of the two contains bromine?

279. Complete the following equations:—

(*a*) $HNO_3 + NH_3 =$

(*b*) $2HCl + Na_2CO_3 =$

(*c*) $2NaBr + Cl_2 =$

(*d*) $NaNO_3 + NaHSO_4 =$

(*e*) $Na_2SO_3 + H_2SO_4 =$ *L. U. M.*, 1891.

280. Explain what occurs when a current of chlorine is passed through a solution of potassium iodide. How would you prove a brown liquid to be an aqueous solution of iodine?

281. Two aqueous solutions are given you; one contains free bromine only, the other free iodine only: describe how you would prove the presence of the bromine in the one solution, and of the iodine in the other.

282. Two solids are given to you, one of which may be graphite, the other iodine: describe in detail the physical and chemical experiments you would make in order to identify these two substances. *L. U. M.*, 1890.

283. Describe exactly how you would use a solution of iodine for the detection of starch. If the solution of iodine be first rendered alkaline by the addition of caustic potash, will it still answer the purpose? if not, why not?

284. Describe the action of heat upon (*a*) iodine, (*b*) nitric acid, (*c*) ammonia solution. *L. U. M.*, 1890.

285. Specify the common sources of the elements chlorine, bromine, and iodine; explain, with the aid of equations, the methods adopted for their liberation, and state how you would distinguish between aqueous solutions of each of the free elements. *L. U. M.*, 1885.

286. Chlorine, bromine, and iodine are said to be members of one family of elements; make a comparison of their properties and of their chief compounds so as to show why they are so described. *L. U. M.*, 1892.

287. How is hydrofluoric acid prepared, and what is its action on glass?

288. What volume of chlorine at normal temperature and pressure would be required?—

(*a*) To combine with 10 litres of olefiant gas.

(*b*) To decompose 10 litres of sulphuretted hydrogen, liberating the sulphur;

(*c*) To decompose 10 grams of potassium iodide. (K = 39.) *L. U. M.*, 1889.

289. If hydrogen sulphide is passed into a mixture of iodine and water, sulphur is deposited and hydrogen iodide formed; the iodine may be in turn displaced from combination by bromine, and the bromine by chlorine: what weight of each of these elements would be required to displace the sulphur

contained in 100 grams of hydrogen sulphide? (S = 32; I = 127; Br = 80; Cl = 35·5.) *L. U. M.*, 1891.

290. By what tests or chemical reactions could you distinguish carbonate of lime from fluor-spar? *L. U. M.*, 1886.

291. What is the action of sulphuric acid on the following substances: limestone, copper, zinc, fluor-spar, and common salt? Represent the reactions by equations, and very briefly describe the chief properties of the products. *L. U. M.*, 1885.

292. Trace the phosphorus of commerce back to its original and ultimate source.

293. How is phosphorus prepared? Describe the two chief varieties of phosphorus, and state how they may be converted one into the other. *L. U. M.*, 1889.

294. Describe the characteristic properties of common and of red phosphorus; and state the conditions under which the white is turned into the red, and the red into the white variety. *L. U. M.*, 1891.

295. By what experiments would you distinguish ordinary phosphorus from amorphous phosphorus, graphite from iodine, chlorine from ozone, carbon dioxide from nitrogen? *S. and A.*, 1888.

296. Explain the chemical action which takes place when phosphorus and caustic potash solution are boiled together. What are the properties of the gas evolved? How do you account for ordinary phosphoretted hydrogen losing its property of spontaneous inflammability when kept for some time at a low temperature?

297. How is phosphoretted hydrogen prepared? Describe its chief properties. What is formed when it burns in the air? In what respects does it resemble ammonia? *L. U. M.*, 1887.

Phosphoretted hydrogen resembles ammonia in the constitution of its formula; it forms one or two compounds analogous in composition to those produced by the combination of ammonia with acids. Of these, phosphonium iodide is an example. Its similarity to the corresponding ammonia compound is shown in the following equations:—

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Ammonium iodide.}}{NH_4I.}$$

$$\underset{\text{Phosphoretted hydrogen.}}{PH_3} + \underset{\text{Hydriodic acid.}}{HI} = \underset{\text{Phosphonium iodide.}}{PH_4I.}$$

298. How is phosphoretted hydrogen gas prepared? Give an account of its properties, and calculate the volume of air required for the complete combustion of one litre of the gas.
L. U. M., 1886.

299. Which of the following gases burn in air, and in which will the flame of a taper be extinguished: carbon dioxide, nitrous oxide, nitric oxide, carbonic oxide, sulphuretted hydrogen, marsh-gas, hydrogen, oxygen, nitrogen, sulphur dioxide, ammonia, hydrochloric acid, and phosphoretted hydrogen?
L. U. M., 1887.

300. Write the formula of common phosphoric acid. Describe and explain its usual mode of preparation, and the tests by which it can be identified. *L. U. M.*, 1888.

301. Give some examples, with formulæ, of 'acids,' 'bases,' and 'salts,' and point out the distinctive characters of each group of substances. Cite evidence as to the basicity of common phosphoric acid. *L. U. M.*, 1889.

302. Give a short account of the forms of silica met with in nature, and point out the chief characters by which crystallised silica and diamond can be distinguished. *L. U. M.*, 1886.

Diamond is combustible, while silica is non-inflammable.

303. Describe how you would render silica soluble in aqueous hydrochloric acid, and how the soluble modification of this substance can be converted into the insoluble form.

304. Flint is said to be a compound of silica; the aqueous solution of this substance, although it has no sour taste, is said to contain silicic acid: why is it so called?

305. How would you propose to distinguish between fragments of the following substances: (*a*) graphite, (*b*) iodine, (*c*) diamond, (*d*) silica (quartz)? *L. U. M.*, 1889.

306. The oxides formed by burning carbon, sulphur, and phosphorus in oxygen, and the material of which flint and quartz consist, are all regarded as members of one class of compounds: what properties have those substances in common which have led to their being thus regarded? *L. U. M.*, 1891.

307. Describe carefully any two simple chemical experiments (not referred to in the preceding questions) which you have either made yourself or seen performed. State the object of the experiments, their results, and what you learned from them. *L. U. M.*, 1890.

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